Effect of pressure on the thermodynamics of rare earth compounds
the use of pressure for magnetic cooling

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EFFECT OF PRESSURE ON THE THERMODYNAMICS OF RARE EARTH COMPOUNDS: THE USE OF PRESSURE FOR MAGNETIC COOLING

A dissertation submitted to the SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH for the degree of Doctor of Natural Sciences presented by THIERRY STRÄSSION presented by THIERRY STRÄSSLLE Dipl. Phys. ETH Zurich born 05.06.1972 citizen of Kirchberg SG accepted on the recommendation of Prof. A. Furrer, examiner Prof. K.A. Müller, co-examiner Prof. B. Batlogg, co-examiner

2002
Effect of Pressure on the Thermodynamics of Rare Earth Compounds:

the Use of Pressure for Magnetic Cooling

Dissertation

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Abstract

A new method for the adiabatic cooling by application of pressure has been recently proposed by Müller et al. [1]. The present thesis thoroughly investigates this method. It represents the first comprehensive work in this field.

As well as any other (magnetic) adiabatic cooling technique, the cooling results from a change in the magnetic entropy of the system under investigation. As opposed to the well known method of adiabatic demagnetization (for paramagnets) or to the magnetocaloric effect (for ferro- and antiferromagnets), the entropy change does not result from the application of an external magnetic field, but from the application of external pressure.

The original idea of realizing the entropy change by a pressure-induced structural phase transition [1] has been extended by other mechanisms equally resulting in a change of magnetic entropy. These include: pressure-induced magnetic phase transitions, pressure-induced changes in the degree of $4f - sd$ hybridization in Kondo systems, pressure-induced valence transitions and pressure-induced spin-fluctuations. The above mechanisms have all been verified experimentally with an experimental setup allowing for the direct observation of the cooling effect. For the modelling of the effect, microscopic properties of the respective system were used, which have been determined by neutron diffraction, inelastic neutron scattering and measurement of the specific heat and the magnetic susceptibility.

Rare-earth compound are among the most interesting systems for the study of the above mentioned effect. In these compounds the magnetic entropy is governed by the crystal-field splitting of the rare earth ion, which for the ground-state $J$ multiplet is of the order of a few 10 K. The large value of total angular moment $J$ allows for comparatively large entropy changes. The systems studied within this work include: CeSb, Ce$_{1-x}$La$_x$Sb, HoAs, Ce$_3$Pd$_{20}$Ge$_6$ and EuNi$_2$(Si,Ge)$_2$. Measurements on a single crystal sample of CeSb revealed a directly observed cooling of -2 K upon a release of 0.52 GPa uniaxial pressure at $\sim$ 20 K. The cooling is a result from a pressure-induced magnetic phase transition. In HoAs the observed cooling effect also results from a pressure-induced magnetic phase transition. An additional contribution to the effect is caused by the structural distortion of the system under uniaxial pressure (-0.35 K per 0.3 GPa uniaxial pressure release at $\sim$ 6 K). In the Kondo compound Ce$_3$Pd$_{20}$Ge$_6$ a combination of decreased $4f$-conduction electron hybridization and structural distortion upon pressure is found responsible for the observed cooling (-0.75 K per 0.3 GPa uniaxial pressure release at $\sim$ 4 K). Finally the pressure-induced valence transition in EuNi$_2$(Si,Ge)$_2$ revealed an observed cooling of -0.52 K upon 0.48 GPa hydrostatic pressure release at $\sim$ 60 K.
While the release of uniaxial pressure may be realized to a fair amount quasi-adiabatically, the realization of adiabatic conditions under hydrostatic pressure becomes considerably more difficult.

The studies on the above compounds revealed values for the entropy change induced by moderate pressure (a few kbar), which are well comparable with those resulting from the magnetocaloric effect induced by large magnetic fields (a few Tesla). Quantitative comparison of the directly observed adiabatic temperature changes with the model calculations yielded differences, which could well be explained in terms of the non-adiabaticity of the experimental setup. Aim of the present study was to verify experimentally the proposed technique of magnetic cooling by use of pressure and to extend the class of potential refrigerating materials. The variety of underlying mechanisms resulting in a cooling effect may be regarded as a specific quality of this very technique.

The above mentioned compounds are all well studied and characterized at ambient pressure. Nevertheless corresponding experimental data at elevated pressure is rare and must often be extrapolated from data at ambient conditions. The applied extrapolation schemes do commonly not account for all the parameters affected by pressure. For instance, the application of pressure is often reduced to mere geometric factors neglecting the electronic and magnetic properties of the solid.

Hence the second part of the thesis is devoted to the interplay between the structure and the electronic or magnetic properties of solids. Elastic and inelastic neutron scattering under pressure proved to be a powerful experimental technique in this respect. The investigated systems include NdAl$_3$, RAl$_x$Ga$_{1-x}$ (R=rare earth) and Cs(Mn,Mg)Br$_3$. The effect of pressure on the crystal-field splitting of NdAl$_3$ has shown that even at moderate pressures (a few kbar) the observed changes may indeed not be explained by mere geometric factors anymore. On the other hand in RAl$_x$Ga$_{1-x}$ the realized structure is found to be dictated by the electronic properties, while in Cs(Mn,Mg)Br$_3$ the magnetism directly influences the local structure of the compound via the mechanism of exchange-striction.

Zusammenfassung


Wie in anderen (magnetischen) adiabatischen Kühlmethoden, rührt die Kühlung von einer Änderung der magnetischen Entropie des zur Kühlung verwendeten Systems her. Im Gegensatz zur wohlbekannten Kühlung durch adiabatische Demagnetisierung (in Paramagneten) oder zum magnetokalorischen Effekt (in Ferro- oder Antiferromagneten), wird die Entropieänderung nicht durch Anlegen eines äußeren magnetischen Feldes, sondern durch Anlegen von Druck erzwungen.


Seltenerdverbindungen haben sich für eine druckinduzierte magnetische Kühlung als besonders geeignet herausgestellt. In diesen Verbindungen wird die magnetische Entropie durch die Kristallfeldaufspaltung des Seltenerdions bestimmt. Diese beträgt für das Grundzustandsmultiplett des Seltenerdions einige 10 meV. Die grossen Gesamtdrehimpulse $J$ dieser Ionen führt zu vergleichsweise grossen Entropieänderungen. Die untersuchten Systeme beinhalten: CeSb, Ce$_{1-x}$La$_x$Sb, HoAs, Ce$_3$Pd$_{20}$Ge$_6$ und EuNi$_2$(Si,Ge)$_2$. Messungen an CeSb Einkristallen zeigten eine direk beobachtbare Kühlung von -2 K beim Entspannen von 0.52 GPa uniaxialen Druck bei ~ 20 K. Die Kühlung rührt von einem druckinduzierten magnetischen Phasenübergang her. Der in HoAs beobachtete Kühleffekt ist ebenfalls Folge eines druckinduzierten magnetischen Phasenübergangs. Darüberhinaus wird hier der Effekt auch von einer druckinduzierten strukturellen Verzerrung hervorgerufen (-0.35 K per -0.3 GPa uniaxialen Druck bei ~ 6 K). Im Kondosystem Ce$_3$Pd$_{20}$Ge$_6$ geht die Kühlung einher mit einer Reduktion der $4f - sd$ Hybridisierung und einer strukturellen Verzerrung des Systems unter Druck (-0.75 K per -0.3 GPa uniaxialen Druck bei ~ 4 K). Schliesslich wurde für den druckinduzierten Valenzübergang in
EuNi$_2$(Si,Ge)$_2$ eine Kühlung von -0.52 K per -0.48 GPa bei ~ 60 K beobachtet.

Während uniaxialer Druck in genügender Weise unter quasi-adiabatischen Bedingungen entfernt werden kann, stellt das adiabatische Lösen von hydrostatischen Druck ein sichtlich schwierigeres Problem dar.


Im zweiten Teil der vorliegenden Arbeit wird daher das Wechselspiel zwischen Struktur und elektronischen oder magnetischen Eigenschaften in Festkörpern untersucht. Die elastische und inelastische Neutronenstreuung unter Druck hat sich dabei als eine sehr wertvolle Untersuchungsmethode herausgestellt. Die untersuchten Systeme beinhalten NdAl$_3$, RAl$_x$Ga$_{1-x}$ (R=Seltenerdion) und Cs(Mn,Mg)Br$_3$. In der Tat hat die Untersuchung der Kristallfeldaufspaltung in NdAl$_3$ bereits bei vergleichsweise niedrigem Druck (einige kbar) gezeigt, dass die veränderte Kristallfeldaufspaltung nicht bloss durch geometrische Effekte erklärt werden kann. Andererseits scheinen in RAl$_x$Ga$_{1-x}$ elektronische Eigenschaften für das Auftreten bestimmter Kristallstrukturen verantwortlich zu sein. In Cs(Mn,Mg)Br$_3$ schliesslich konnte der direkte Einfluss magnetischer Eigenschaften auf die lokale Struktur des Systems beobachtet werden.

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Chapter 1

Introduction
- what it is all about

Ever since Warburg (1881) first observed the heat evolution in iron upon the application of a magnetic field, the so-called magnetocaloric effect (MCE) attracted science. The effect is a consequence of the variation in the total entropy of a solid by the magnetic field. It was first Debye (1926) and Giauque (1927) who proposed the principle of adiabatic cooling or more specifically the technique of adiabatic demagnetization. In the first stage, an external magnetic field is applied isothermally (the system is in contact with a heat sink), thus reducing the magnetic entropy\(^1\) of the system. In the second stage, the magnetic field is removed adiabatically (the system is isolated from the heat sink). In order to keep the entropy unchanged, the system is forced to lower the temperature.\(^2\)

Progress in the theoretical as well as the experimental characterization of the magnetothermal properties of materials has renewed the interest in the investigation of the MCE for two reasons: (i) the MCE can yield information on magnetic phase transitions not obtainable by other experimental techniques, (ii) its potential for the implementation of magnetic cooling machines (magnetic refrigerators) [1]. These days, magnetic refrigeration proved to be one of the most efficient cooling techniques in a wide range of temperatures. For the time before the rise of \(^3\)He dilution cryostats, adiabatic demagnetization represented the only technique allowing temperatures below 4.2 K down to the milli Kelvin range (Giauque (1927)). Nowadays, magnetic cooling at room temperature and even higher has been demonstrated for a wide class of rare-earth compounds [2, 3]. Up to now, all magnetic refrigerators suffer the drawback of needing large magnetic fields of a few Tesla in order to achieve cooling effects in the Kelvin range.

Despite the fact that adiabatic cooling has to be associated by no means with an entropy change induced by an external magnetic field, its implementation by vari-

\(^1\)A definition of the magnetic entropy and of other contributions to the total entropy of a solid is given in section 2.4.
\(^2\)The term adiabatic demagnetization is generally used in context with the application of a magnetic field on a paramagnet, whereas for the MCE the field is applied on a ferro- or antiferromagnet. Both effects result in magnetic cooling and are referred in a wider context to as adiabatic cooling techniques (compare Fig.2.7).
Figure 1.1: Principle of adiabatic cooling: due to an external influence the entropy of the system gets changed ($S_i \rightarrow S_f$).

An example for the principle of adiabatic cooling in general and more specifically for the BCE is illustrated schematically in Figure 1.1. The system is assumed initially in a state $i$ of large CEF splitting with low degeneracy of its lowest CEF levels. Therefore the magnetic entropy will increase only slowly with temperature (solid line, Fig. 1.1). The application or removal of external pressure can bring the system via a pressure-induced structural phase transition into a state $f$ of small CEF splitting and high degeneracy of its CEF energy levels. In state $f$ the system happens to have a higher entropy than in state $i$ at the same temperature (dashed line, Fig. 1.1). Thus if the transition $i \rightarrow f$ is performed adiabatically the system must cool down by $\Delta T$ in order to remain its entropy unchanged (adiabatic). Even though no magnetic ordering in this system is present, the effect is solely a consequence of the variation in the magnetic entropy. Hence the BCE leads to what may be called pressure-induced magnetic cooling.

The present thesis project aimed to provide a detailed understanding of this new cooling technique, which before has been verified experimentally on a single compound only [4]. The use of an external applied pressure instead of an external magnetic field as the thermodynamic variable driving the entropy change and hence cooling, may open new technical applications. The large magnetic fields of a

---

3The crystal field (crystalline electric field) is introduced in section 2.4.4.
few Tesla needed for the efficient cooling by the MCE must be considered the main drawback of magnetic refrigeration these days which hinders its broad, technical application in everyday life. On the other hand the application of a few kbar pressure on a solid is comparatively easy to achieve even outside of the laboratory. This becomes especially true for the application of uniaxial pressure generated, e.g. by use of piezo actuators. In what follows the technical problems associated with an efficient realization of the MCE or BCE are though not tackled with priority. The main focus is set on the exploration of suitable refrigerating materials and the modelling of the observed cooling effects on the basis of microscopic parameters. In this connection other pressure-induced mechanisms were found which equally well result in an effective change of the magnetic entropy, as for instance pressure-induced magnetic phase transitions [5]. Many rare-earth compounds show pronounced pressure-dependences in their magnetism and thus may be suitable candidates for the BCE. In the ordered state a large splitting of the CEF levels due to the internal magnetic field occurs (Zeeman effect). Thus cooling can be realized by a transition from the ordered state $i$ (with low entropy) into the disordered state $f$ (with high entropy) in the very same way as in the structurally driven case. Other mechanisms leading to a BCE have also been considered throughout this work, these include: effects of pressure on Kondo systems, pressure-induced valence transitions and pressure-dependent spin-fluctuations.

In either case detailed knowledge about the microscopic properties of the material is indispensable for the explanation of the BCE and in the search for best-suited BCE materials. Elastic and inelastic neutron scattering together with macroscopic measurements of the specific heat and the magnetization proved to be the experimental techniques of choice in order to study the BCE. The effect itself can be directly measured in a simple experimental setup as shown in Figure 1.2.

---

4In this sense the magnetically driven BCE can also be considered as an internal MCE using the molecular field of the solid instead of an external magnetic field.
To the knowledge of the author the present thesis represents the first compilation of experimental work dedicated to the BCE and pressure-induced magnetic cooling. The chapters are organized as follows: In the first chapter a short introduction to the basic thermodynamic theory necessary for the understanding of the BCE is given. The notation is followed in as close as possible analogy to the MCE. Special issues valid for rare-earth compounds are addressed. The second chapter explains the experimental methods used in the course of this work. Special importance is paid to methods that may not be common to the reader, these include the setup for the measurement of the BCE and high pressure techniques. Experimental results of the barocaloric effect are summarized in the third chapter. Eventually the fourth chapter resumes neutron scattering experiments under pressure on compounds which were considered as potential refrigerating materials or which constituted systems well suited to test the extrapolation schemes carried out in chapter three.
Chapter 2

Thermodynamic Theory

In what follows the thermodynamics of adiabatic cooling are recalled and issues specific for the barocaloric effect are discussed with a focus on the microscopic properties causing this effect. Comprehensive introductory reviews about the magnetocaloric effect and about the crystal field in rare-earth compounds can be found in [1] and [6], respectively. Some theoretical aspects specific to measured systems introduced later in the experimental part of this work are given at the respective places of chapters 4 and 5. These include the resonance-level model for the description of the magnetic entropy in Kondo lattice compounds, and the theory of exchange-striction for dimer systems. Models involving measurement techniques of the BCE are given in section 3.1.

2.1 General thermodynamics of adiabatic cooling

All adiabatic cooling techniques (i.e. adiabatic demagnetization, MCE and BCE) are based on the same thermodynamic principle and hence suffer the same general thermodynamic restrictions. They make use of the fact that the total entropy $S$ of a system is a thermodynamic state function and thus depends on three external thermodynamic variables, namely besides temperature $T$ on pressure $p$ and magnetic field $H$

$$S = S(T, p, H)$$

(2.1)

with

$$dS(T, p, H) = \left(\frac{\partial S}{\partial T}\right)_{p, H} dT + \left(\frac{\partial S}{\partial p}\right)_{T, H} dp + \left(\frac{\partial S}{\partial H}\right)_{T, p} dH.$$  

(2.2)

Apparently, varying only one of the external variables\(^1\) $p$ or $H$, denoted as the control variable $X$, and keeping the temperature $T$ and the other variable $K$ ($H$ or $p$) constant, leads to a change in entropy (2.2) (Fig. 2.1, step 1 $\rightarrow$ 2)

$$\Delta S(T, X, K)_{X_1 \rightarrow X_2} = S(T, X_2, K) - S(T, X_1, K)$$

(2.3)

$$= \int_{X_1}^{X_2} \left(\frac{\partial S(T, X, K)}{\partial X}\right)_{T, K} dX.$$  

(2.4)

The extensive quantity $\Delta S$ upon isothermal\(^2\) change of $H$ is often given the name

\(^1\) $p$ for the BCE, $H$ for the MCE and adiabatic demagnetization

\(^2\)
Figure 2.1: A schematic of adiabatic cooling. The adiabatic temperature change \( \Delta T_{ad} \) strongly depends on the slope of the \( S(T, p, H) \) function (isothermal entropy change \( \Delta S_{X_1 \rightarrow X_2} \) kept constant).

extensive MCE, hence in the general case we may call \( \Delta S \) the extensive caloric effect.

Subsequent adiabatic\(^3\) change of \( X \) from \( X_2 \) back to \( X_1 \) leads to a change in temperature \( \Delta T_{ad} \) as the total entropy must be conserved (Fig. 2.1, step 2 → 3)

\[
S(T, X_2, K) = S(T + \Delta T_{ad}, X_1, K).
\]

(2.5)

Accordingly the intensive quantity \( \Delta T_{ad} \) is given the name intensive caloric effect. Recalling the second law of thermodynamics

\[
\left( \frac{dS(T, X, K)}{dT} \right)_{X,K} = \left( \frac{C(T, X, K)}{T} \right)_{X,K}
\]

(2.6)

with \( C \) denoting the total heat capacity of the system, \( \Delta T_{ad} \) may be written (2.4)

\[
\Delta T_{ad}(T, X, K)_{X_2 \rightarrow X_1} = \int_{X_2}^{X_1} \left( \frac{T}{C(T, X, K)} \frac{\partial S(T, X, K)}{\partial X} \right)_{T,K} dX.
\]

(2.7)

The intensive and the extensive caloric effect are coupled via the adiabatic equation (2.5)

\[
S(T, X_2, K) = S(T + \Delta T_{ad}, X_1, K) = S(T, X_1, K) + \left( \frac{\partial S(T, X, K)}{\partial T} \right)_{X,K} \Delta T_{ad} + O(\Delta T_{ad}^2)
\]

(2.8)

(2.9)

For \( \Delta T_{ad} \) follows in 1st order (i.e. assuming \( S \propto T \))

\[
\Delta T_{ad} = \frac{\Delta S(T, X, K)_{X_1 \rightarrow X_2}}{\partial S(T, X, K)/\partial T}
\]

(2.10)
and with \( C = T \frac{\partial S}{\partial T} \) (2.6)

\[
\Delta T_{ad} = \Delta S(T, X, K)_{X_1 \rightarrow X_2} \frac{T}{C(T, X, K)}.
\]  

(2.11)

The same result is obtained by linearization of (2.7) (i.e. assuming \( C \equiv \text{const} \)). These strong assumptions are hardly justified in any real system, nevertheless (2.11) has some important consequences valid for the non-linear cases too:

- \( \Delta T_{ad} \propto \Delta S_{X_1 \rightarrow X_2} \); large intensive caloric effects require large extensive caloric effects
- \( \Delta T_{ad} \propto T/C \); the intensive caloric effect is large for either very low \( T \) as \( C \rightarrow 0 \) (\( T \rightarrow 0 \)) or for high \( T \) as \( C \rightarrow \text{const} \) (\( T \) high enough).

The fact \( \Delta T_{ad} \propto 1/C \) is also depicted in Figure 2.1. While \( \Delta S \) is the same for both illustrated cases, the large slope in case B reduces \( \Delta T_{ad} \) considerably. These considerations are valid for all adiabatic cooling techniques. For more quantitative conclusions the specific relation of the entropy on the control variable \( X \) (i.e. \( \frac{\partial S}{\partial X} \) in (2.4)) must be considered.

### 2.2 Magnetocaloric effect and adiabatic demagnetization

In the magnetocaloric effect and in the adiabatic demagnetization, the external magnetic field \( H \) acts as the control variable \( X \) and the isothermal entropy change is related to the change in bulk magnetization \( M \). Hence the extensive (2.4) and the intensive (2.7) MCE can be written in \( M(T, p, H) \) using the Maxwell relation\(^4\) [1, 7]

\[
\left( \frac{\partial S}{\partial H} \right)_{T,p} = \left( \frac{\partial M}{\partial T} \right)_{p,H}
\]

(2.12)

resulting in

\[
\Delta S(T, p, H)_{H_1 \rightarrow H_2} = \int_{H_1}^{H_2} \left( \frac{\partial M(T, p, H)}{\partial T} \right)_{p,H} dH
\]

(2.13)

\[
\Delta T_{ad}(T, p, H)_{H_2 \rightarrow H_1} = \int_{H_2}^{H_1} \frac{T}{C(T, p, H)} \left( \frac{\partial M(T, p, H)}{\partial T} \right)_{p,H} dH.
\]

(2.14)

In practice the lack of analytical forms for \( M(T, p, H) \) and \( C(T, p, H) \) makes an analytical integration of these equations for the MCE (which involves a magnetic phase transition) impossible. In the case of adiabatic demagnetization, analytical forms for both the magnetization and the heat capacity for paramagnets at low temperatures exist and analytical expressions for \( \Delta S \) and \( \Delta T_{ad} \) can be worked out [8].

\(^4\)This Maxwell relation results from the differential of the Gibbs potential \( dG = -SdT + M dH \) \((dG = -SdT + V dp \text{ with } V \rightarrow -M, p \rightarrow H)\) and the relation \( \left( \frac{\partial v}{\partial y} \right)_x = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} = \left( \frac{\partial u}{\partial x} \right)_y \) valid for the exact differential \( df \) of \( f(x, y) \) with \( df = u(x, y) dx + v(x, y) dy \) and \( u(x, y) = \left( \frac{\partial f}{\partial x} \right)_y, v(x, y) = \left( \frac{\partial f}{\partial y} \right)_x \) \([G \rightarrow f]\).
For the MCE on the other hand, numerical integration of (2.13) and (2.14) requires very precise experimental data of the magnetization and the heat capacity in function of both, temperature and magnetic field. Hence the numerical evaluation of (2.13) and (2.14), although completely defining the MCE, may result in an accumulation of errors as large as 20-30 % [9]. Another often applied approach for an indirect determination of the MCE is based on the second law of thermodynamics (2.6) [1]

\[ S(T, p, H) = \int_0^T dS(T, p, H) = \int_0^T \frac{C(T, p, H)}{T} dT \]  

(2.15)

and

\[ \Delta S_{H_1 \rightarrow H_2} = \int_0^T \frac{C(T, p, H_1) - C(T, p, H_2)}{T} dT. \]  

(2.16)

The intensive MCE \( \Delta T_{ad} \) may be then calculated numerically from \( S(T, p, H_1) \) and \( S(T, p, H_2) \) by use of the adiabatic equation (2.5). Note however, that this approach requires heat capacity measurements down to the lowest temperatures and similarly may result in large accumulated errors [9, 3].

Nevertheless the calculation of the extensive MCE via the \((H, T)\)-dependence of the magnetization or via the \((H, T)\)-dependence of the heat capacity has proven to be a valuable first check for materials expected to show a MCE. The procedure is fast and standard setups for the measurement of \( C \) and \( M \) may be used. With to the ongoing discussion as to what extent indirect measurements of the MCE are valid [10, 11], the direct measurement of the MCE has gained in importance and recently much more literature on direct measurements is available ([12, 13, 14], [1] and references therein). This tendency is partly influenced by the discovery of materials showing the so called giant MCE [15, 16, 17]. These materials involve first order magnetic transitions (which in turn are strongly coupled to simultaneous structural phase transitions) resulting in huge \( \Delta S \). Note that for any first order transition the entropy becomes discontinuous and the Maxwell relation \( \partial S/\partial M = \partial H/\partial T \) must no longer be used. In these cases the indirect determination of the MCE is restricted to the integration of \( C \) (2.16) and the complicated nature of the phase transition often does not allow the analysis of the MCE on the basis of general macroscopic thermodynamics [18].

### 2.3 Barocaloric effect and elastic heating/cooling

In the barocaloric effect and in elastic heating/cooling the entropy change \( \Delta S \) is caused by external pressure \( p \) being the control variable \( X \). In principle the Maxwell relation analogous to (2.12) may be applied\(^5\), i.e.

\[ \left( \frac{\partial S}{\partial p} \right)_{T,H} = - \left( \frac{\partial V}{\partial T} \right)_{p,H} \]  

(2.17)

\(^5\)This Maxwell relation is deduced in the same way as for (2.12), i.e. by means of the differential of the Gibbs potential.
\[ \Delta S(T, p, H)_{p_1 \rightarrow p_2} = - \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial T} \right)_{p, H} dp \tag{2.18} \]

\[ \Delta T_{ad}(T, p, H)_{p_2 \rightarrow p_1} = - \int_{p_2}^{p_1} \left( \frac{T}{C(T, p, H)} \frac{\partial V(T, p, H)}{\partial T} \right)_{p, H} dp. \tag{2.19} \]

From these equations the change of volume appears as the source for the BCE (in analogy to the change of bulk magnetization in the MCE). It is noteworthy to address a few important remarks at this point. Although (2.18) and (2.19) explicitly include the thermal expansion coefficient \( \alpha = 1/V(\partial V/\partial T) \) they may equally well include magnetic terms in an utterly implicit manner. The exact incorporation of these terms depends on the nature of the pressure effect and requires a microscopic description of the thermodynamics involved. Additionally, in contrast to (magnetic) transitions induced by external magnetic fields (e.g. metamagnetic transitions), pressure-induced transitions often involve a change in structure of the system under investigation. Note that structural phase transitions are often of first order and thus the use of the Maxwell relations is strictly not allowed. The continuation of the formalism of macroscopic thermodynamics on general grounds must be given an end already at this point, except for the special case of elastic heating, which will be addressed in section 2.4.2. In this case pressure does not alter the magnetic properties of the system and the problem can be handled analytically. It thus may be regarded as the analogue to adiabatic demagnetization.

The important fact, that the application of pressure may well influence the magnetic properties of the system implies a somewhat more difficult macroscopic thermodynamic description which shall not be discussed here. On the other hand the very same fact allows the BCE to alter exactly the same quantity of a solid as an external field does in the MCE, namely the magnetic entropy. Thus the next sections will discuss the microscopic thermodynamics involved in the BCE on the basis of the total entropy of the respective system. Once the entropy \( S(T, p, H) \) may be modeled the extensive as well as the intensive BCE can be calculated (2.16),(2.5). In finishing the discussion about macroscopic thermodynamics it must not be forgotten, that (2.15) and (2.16) remain valid for the BCE too. As in the case of the MCE these equations allow in principle the indirect determination of the BCE given that accurate data on the specific heat under pressure is available (see 3.3.1).

### 2.4 Entropy and its pressure dependence

In order to discuss how pressure affects the thermodynamics of a solid the entropy must be split into terms of different origin. In a magnetic solid with localized moments the total entropy is the sum of the lattice \( S_L \), electronic \( S_E \) and magnetic \( S_M \) entropy:

\[ S = S_L + S_E + S_M \tag{2.20} \]

All three contributions are functions of both temperature and pressure. The magnetic entropy is generally also a function of the magnetic field. The electronic contribution \( S_E \) is not directly affected by the magnetic field, however in 4f magnetism \( S_E \) and \( S_M \) may be coupled via 4f-conduction electron hybridization, so that they
cannot be strictly separated anymore. In 3d magnetism the separation between $S_M$ and $S_E$ is inherently not straightforward. In solids with a coupling between the magnetic and the chemical lattice, $S_L$ may show also a dependence on magnetic fields. Before discussing the three contributions separately two definitions for the entropy are recalled.

### 2.4.1 Two definitions for the entropy

**Communication theory**

$M$ events are considered with the respective probabilities $p_1,\ldots,p_M$ ($\sum_m p_m = 1$). The degree of *non-predictivity, uncertainty* or *choice* is an intuitive concept which can be assigned a number called the *statistical entropy* [19]:

$$S(p_1,\ldots,p_M) = -k \sum_{m=1}^{M} p_m \ln p_m$$

(2.21)

where $k$ is a multiplicative factor. The statistical entropy is maximal for $M$ equiprobable events $S(1/M,\ldots,1/M) = k \ln M$.

**Statistical mechanics**

Considering a system with Hamiltonian $\mathcal{H}$ the canonical partition function $Z$ and free energy $F$ at temperature $T$ is defined as [20]

$$Z(T,\mathcal{H}) = \text{tr}(e^{-\mathcal{H}/kT}),$$

(2.22)

$$F(T,\mathcal{H}) = -kT \ln Z$$

(2.23)

with $k$ the Boltzmann factor. The entropy is then given by

$$S = - \left( \frac{\partial F}{\partial T} \right)_{p,\mathcal{H}}.$$  

(2.24)

For a Hamiltonian resulting in a set of discrete energy levels $E_i$ both definitions become equivalent and maximal entropy is found for a fully degenerate ground-state.

### 2.4.2 Lattice entropy

The lattice entropy results from the occupation of vibrational states of the lattice by phonons. The associated internal energy is

$$U_L = \int_0^\infty dE \rho(E)n(E)E$$

(2.25)

with $\rho(E)$ the phonon density of states and $n(E)$ the Bose-Einstein distribution

$$n(E) = (e^{E/kT} - 1)^{-1}.$$  

(2.26)

The lattice specific heat and entropy are derived from $C = \partial U/\partial T$ and $S = \int C/TdT$ (2.6). In the Debye approximation

$$\rho(E) = \begin{cases} 
\propto E^2, & E \leq k\Theta_D \\
0, & E > k\Theta_D 
\end{cases}$$

(2.27)
the specific heat $C_L$ is then

$$C_L(T) = 9Nk \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \to \frac{12\pi^4}{5} Nk \left( \frac{T}{\Theta_D} \right)^3 \text{ for } T \ll \Theta_D$$

(2.28)

with $N$ the total number of atoms in the system and $\Theta_D$ the Debye temperature. Thus at low temperatures the lattice specific heat and entropy $S = \int C/TdT$ are often modelled by a simple $T^3$-law

$$C_L = \beta T^3$$

(2.29)

$$S_L = \frac{\beta}{3} T^3.$$  

(2.30)

The application of pressure generally leads to an increase in the stiffness of the lattice and the phonon density of states is shifted to higher energies (see inset of Fig. 2.2). In the Debye approximation this shift results in a scaling of $\Theta_D$ with volume $V$

$$\Theta_D(V) = \Theta_D(V_0) \left( \frac{V_0}{V} \right)^\Gamma$$

(2.31)

with $\Gamma$ the (phononic) Gr"uneisen parameter defined by this relation.\(^6\) The shift of the phonon spectrum to higher energies results in a decrease of the lattice entropy as “the phonons may now choose on fewer states” (2.21). Pressure hence generally results in a decrease of lattice entropy if applied isothermally and in an increase of temperature i.e. heating if applied adiabatically.

The elastic heating may also be calculated in the framework of macroscopic thermodynamics starting from (2.19)

$$\Delta T_{ad} = \int_{p_1}^{p_2} \left( \frac{T}{C(T,p,H)} \frac{\partial V}{\partial T} \right)_{p,H} dp = \int_{p_2}^{p_1} \left( \frac{T}{C(T,p,H)} \alpha V \right)_{p,H} dp$$

(2.32)

using the thermal expansion coefficient $\alpha = 1/V (\partial V/\partial T)$. The Gr"uneisen parameter may be introduced via the relation $(\alpha BV = \Gamma C)_{V,H}$ with $B$ the isothermal bulk modulus. Assuming $(C)_V \approx (C)_p$ and $\Gamma$, $B$ constant with pressure one finds

$$\Delta T_{ad} = \int_{p_2}^{p_1} \frac{\Gamma}{B} dp \approx T \frac{\Gamma}{B} \Delta p.$$  

(2.33)

Figure 2.2 compares the elastic heating of copper ($\Theta_D = 316$ K, $d\Theta_D/dp = 3.2$ K/GPa [21]) derived from the Debye model (2.28) and derived from the macroscopic approximation (2.33). The difference results from the strong assumptions made by both models: the Debye model assumes $\rho_L \approx E^2$; the macroscopic model assumes $(C)_p = (C)_V$ and linearizes twice. Nevertheless the calculations demonstrate the order of magnitude of elastic heating that can be expected under hydrostatic application of pressure (i.e. typically $\Delta T_{ad}/\Delta p < 20$ mK/0.1GPa for $T \leq 20$ K).

\(^6\)In a more general approach every vibrational mode $\eta$ can be assigned a separate Gr"uneisen parameter $\Gamma_\eta$. 

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2.4.3 Electronic entropy

The electronic heat capacity of a solid may be discussed within the theory of free electrons. The Pauli exclusion principle requires that only those electrons for which corresponding free states are available, can be thermally excited, i.e. only electrons within an energy range \( E_F - kT \ldots E_F \) and \( E_F \ldots E_F + kT \). They contribute to an internal energy of

\[
U_E = \int_0^{E_F} D(E)(1 - f(E))(E_F - E)dE + \int_{E_F}^{\infty} D(E)f(E)(E - E_F)dE
\]  

(2.34)

with \( E_F \) the Fermi energy, \( D(E) \) the electron density of states and \( f(E) \) the Fermi-Dirac distribution. The corresponding heat capacity follows from \( \partial U_E/\partial T \) [22]:

\[
C_E = \frac{\partial U_E}{\partial T} \approx \frac{1}{3} \pi^2 D(E_F)kT = \gamma T, \quad (kT \ll E_F).
\]  

(2.35)

Hence for the entropy \( S = \int C/TdT \) one can write (2.6)

\[
S_E = \gamma T.
\]  

(2.36)

In practice \( \gamma \) often does not agree well with the value calculated by the free electron model. Departures origin from band effects, interactions with phonons and interactions with other itinerant or localized electrons and may be expressed by an effective mass \( m \equiv m_{\text{free}}\gamma/\gamma_{\text{free}} \). Compounds with considerably enhanced effective mass are called heavy-fermion compounds (\( \gamma \gtrsim 100 \text{ mJ/K}^2\text{mol} \)). In this context lanthanide and actinide ions with an almost empty or almost full \( f \)-shell play a special role. Here the conduction electrons may interact, i.e. hybridize, very strongly with the \( f \)-electrons leading to an increase of \( \gamma \) by as much as three orders of magnitude.
This effect is referred to as the Kondo effect, corresponding compounds are called Kondo lattice compounds. Most prominent ions for the Kondo effect are Ce, Yb and U, but also in Pr strong hybridization is often observed.

In the frame of the free electron model pressure results in a decrease of $D(E_F)$ and hence in a lower $C_E$ as the reciprocal lattice gets mechanically dilated.\(^7\) On the other hand one generally observes an increase of the hybridization in Kondo compounds and hence larger $\gamma$ values with the application of hydrostatic pressure (see [23] and section 4.5).\(^8\)

### 2.4.4 Magnetic entropy in rare-earth compounds - the crystal field

The crystal-field (CEF) interaction is the manifestation of the quantum mechanical Stark effect on a single ion caused by the electric field of neighboring ligand ions. While for $3d$ ions this interaction turns out to be larger than the spin-orbit coupling, it is found to be smaller for $4f$ ions. Hence for $4f$ ions the CEF interaction can be treated as a perturbation on the $2J + 1$-fold degenerate energy states $|J\rangle$ with total angular momentum $J$ combined from the spin and the orbital momentum. For metallic rare-earth compounds the CEF interaction results in a total splitting of the ground-state $J$-multiplet of typically a few 10 K.\(^9\) Hence the CEF is the dominating factor defining the magnetic and thermodynamic properties in rare-earth compounds at low temperatures (in paramagnetic state).

In what follows the CEF is treated as a perturbation within the ground-state $J$-multiplet only. Admixtures from excited $J$-multiplets are neglected. This approximation is valid for most metallic compounds, where generally the CEF splitting of the ground-state $J$-multiplet is found small compared to the distance to the first excited $J$-multiplet, which accounts to more than 2700 K (except for Sm\(^{3+}\) and Eu\(^{3+}\)). The corresponding formalism is referred to as the Stevens notation.

#### Description of the crystal field

The energy of an ion with unfilled $4f$-shell in a crystal field is given by the Hamiltonian

\[
\hat{H}_{CEF} = e \sum_i V(\mathbf{r}_i) \quad (2.37)
\]

with $V$ the electrostatic potential of its surrounding charge distribution $\rho(\mathbf{r})$ and $i$ running over all $4f$ electrons. At the rare-earth site the CEF potential fulfills $\Delta V = 0$ and hence may be written as a multipole series

\[
V(\mathbf{r}) = \sum_{n,m} c_n^m r^n Y_n^m(\theta, \phi) \quad (2.38)
\]

in the spherical harmonics $Y_n^m$.\(^{10}\) Stevens [24] demonstrated that the polynomial terms in the cartesian coordinates $\mathbf{r}_i$ can be replaced by polynomial terms $\hat{O}_n^m$ in $\mathbf{k}$-space.

---

\(^7\)direct $a \downarrow \Rightarrow$ reciprocal $k \uparrow \Rightarrow D(E_F) \downarrow \Rightarrow \gamma \downarrow$

\(^8\)Also note that a $4f$-conduction electron hybridization generally leads to a decrease of the magnetic entropy discussed in the next section.

\(^9\)1 meV = 11.6 K

\(^{10}\)with $l_{4f} \leq 3$ follows $n \leq 6$
\( J^z, J^- \) and \( J^+ \) retaining all transformation properties and acting on the unfilled 4f-shell as a whole. The Hamiltonian (2.37) can thus be written as

\[
\hat{H}_{CEF} = \sum_{n,m} A^m_n \langle r^n \rangle \chi_n \hat{O}^m_n = \sum_{n,m} B^m_n \hat{O}^m_n
\]  

(2.39)

with \( \hat{O}^m_n \) and \( \chi_n \) the Stevens operators and coefficients respectively [25], \( \langle r^n \rangle \) the average of the \( n \)'th radial moment of the 4f electron [26] and \( A^m_n (B^m_n) \in \mathbb{C} \) the CEF parameters reflecting the charge distribution \( \rho(r) \), i.e. the CEF potential \( V(r) \).

The point symmetry at the respective rare-earth ion limits the terms appearing in (2.39) [27]. E.g. for cubic and hexagonal\(^{11}\) symmetry one finds

\[
\hat{H}_{CEF}^\text{cub} = B^0_4 \left( \hat{O}^0_4 + 5\hat{O}^4_4 \right) + B^0_6 \left( \hat{O}^0_6 - 21\hat{O}^4_6 \right),
\]

(2.40)

\[
\hat{H}_{CEF}^\text{hex} = B^0_2 \hat{O}^0_2 + B^0_4 \hat{O}^0_4 + B^0_6 \hat{O}^0_6 + |B^6_6| \hat{O}^6_6.
\]

(2.41)

The diagonalization of \( \hat{H}_{CEF} \) is now straight forward and yields \( 2J + 1 \) energy eigenstates \( |n\rangle \) which can be assigned to irreducible representations of the respective point group.

**Crystal-field entropy**

The splitting of the ground-state \( J \)-multiplet into \( 2J + 1 \) energy levels, i.e. into the energy eigenvalues \( E_i \) of (2.39), causes an entropy according to (2.21) and (2.24)

\[
S_{CEF} = -Nk \sum_i p_i \ln p_i , \quad p_i = \frac{1}{Z} e^{-E_i/kT}, \quad Z = \sum_i e^{-E_i/kT}
\]

(2.42)

with \( Z \) the partition function, \( N \) the total number of rare-earth ions in the system and \( p_i \) the thermal population factors of the energy levels. The associated free energy and heat capacity are

\[
F_{CEF} = -NkT \ln Z,
\]

(2.43)

\[
C_{CEF} = T \frac{\partial S_{CEF}}{\partial T} = Nk \left[ \sum_i \left( \frac{E_i}{kT} \right)^2 p_i - \left( \sum_i \frac{E_i}{kT} p_i \right)^2 \right].
\]

(2.44)

The CEF contribution to the total heat capacity causes an anomaly known as the Schottky anomaly which is absent in compounds with non-magnetic rare-earth ions since they have no effective splitting from the CEF as \( J = 0 \) (Fig. 2.3). Hence for rare-earth compounds \( S_{CEF} \) can be associated with the magnetic entropy \( S_M \).

It follows from (2.42) that \( S_{CEF} \) grows with the number of thermally activated energy levels. For a singlet ground-state system \( S_{CEF} \) vanishes at absolute zero, \( S_{CEF} \to 0 (T \to 0) \). However for a system with an \( m \)-fold degenerate ground-state one finds \( S_{CEF} \to Nk \ln m \neq 0 (T \to 0) \) in apparent disagreement with the third law of thermodynamics. Especially for all rare-earth ions with an odd number of 4f electrons (Kramers ions), the time-reversal invariance of \( \hat{H}_{CEF} \) requires at least twofold degenerate energy levels with \( S_{CEF} \to \geq Nk \ln 2 (T \to 0) \) (Kramers

\(^{11}\)point groups \( D_{6h}, D_{1h}, C_{6v}, D_6, C_{6h}, C_{3h}, C_6 \) only [27]
Figure 2.3: The CEF splitting in PrAl$_3$ ($J_{Pr} = 4$) causes a pronounced Schottky anomaly in the specific heat, whereas LaAl$_3$ ($J_{La} = 0$) shows no CEF splitting and hence no $S_{mag}$ (data taken from Mahoney [28]).

degeneracy [29]). In these cases $S \to 0$ ($T \to 0$) is retained by further symmetry breaking perturbations on $\mathcal{H}$ with $T \to 0$ preventing a truly degenerate ground-state. The most prominent of these mechanisms include: magnetic ordering of the rare-earth ion sublattice, magnetic ordering of the nuclear spins or a Jahn-Teller distortion.

**Point-charge model and its extensions**

In principle the CEF parameters can be calculated on the basis of the charge distribution $\rho(r)$. In the point-charge model (PCM) $\rho(r)$ is defined by the positions $R_i$ and effective charges $q_i$ of the neighboring ligand ions [6]

$$\rho(r) = \sum_i q_i \delta(R_i - r).$$

Generally the CEF parameters can then be expressed by

$$B_n^m = a_n^m \gamma_n^m \langle r^n \rangle \chi_n$$

(2.46)

with reduced CEF parameters $a_n^m$ reflecting the charge distribution independent of geometry and rare-earth and geometric coordination factors $\gamma_n^m$ calculated by the PCM. However the computation of the CEF parameters from microscopic theory turns out to be a difficult task and the application of the above model is of limited success even in the case of rare-earth salts [6]. Morisson [30] has introduced an extension of the original PCM, which corrects the free Hartree-Fock 4$f$–radial-moments $\langle r^n \rangle \to \langle r^n \rangle / \tau^n$ for the situation of ions embedded in solids and which takes into account the shielding due to the outer $5s^2$ and $5p^6$ shells of the rare-earth
ion by scaling $B_n^m \rightarrow (1 - \sigma_n)B_n^m$. $\tau$ and $\sigma_n$ are phenomenological parameters of the rare-earth ion tabulated in [30]. Equation (2.46) reads then

$$B_n^m = a_n^m \gamma_n^m \left( \frac{1 - \sigma_n}{\tau_n} \right) \chi_n.$$  \hspace{1cm} (2.47)

The application of these corrections in the case of insulators leads to a much better agreement with the experimental observation of the CEF parameter. However in the case of metals the conduction electrons further screen the CEF potential. In the Thomas-Fermi theory of screening (strictly valid in the free-electron approximation only) this effect is implemented by substituting the Coulomb potential by a screened Coulomb potential (i.e. the Yukawa potential) with a screening factor $k_0$ proportional to the square root of the density of states at the Fermi level $D(E_F)$ [31, 32]. Even with these extensions the PCM generally fails to predict the parameters quantitatively for metallic compounds. However it has been proven to be helpful in accounting for general tendencies and dependencies of the CEF parameters upon a change in chemical structure or upon the substitution of ions [33]. For metals with strong screening it is valid to consider the electric potential caused by the nearest neighbors of the rare-earth only. Within this limit the effect of the conduction electrons can be discussed equally well by either introducing a screening parameter $k_0$ or by reducing the effective charge of the ligand and thus decreasing the reduced CEF parameters $a_n^m$. E.g. in cubic symmetry with lattice constant $a$ one finds [34]

$$\tilde{a}_n(k_0) = a_n(0) \left( 1 - \frac{k_0^2 a^2}{\eta_n} \right) ; \quad \eta_4 = 14, \eta_6 = 22$$  \hspace{1cm} (2.48)

with $a_n(0)$ the unscreened reduced CEF parameter. In considering only the nearest neighbors of one kind analytical forms of $B_n^m$ can be found for the cubic [6] and hexagonal [35] case. As $B_n^m$ represents the $n$'th moment of the CEF potential one generally finds

$$B_n^m \propto d^{-(n+1)}$$  \hspace{1cm} (2.49)

with $d$ the interatomic distance between the $4f$- and the ligand charges. It becomes obvious from (2.49) that the estimation of the $B_n^m$ parameters is least reliable as this parameter probes the charge distribution over a considerably larger region than $B_2^m$ and $B_6^m$.

In the context of barocaloric cooling the extended point-charge model has been found to be useful with respect to estimating trends in the change of the $B_n^m$ caused by a pressure-induced change in geometry (i.e. distortion or structural phase transition): in the first step based on the initial geometry, microscopic parameters, e.g. $q_i$, $k_0$, $\sigma$ and $\tau$, are found to parametrize the observed CEF splitting at $p = 0$. Then in the second step these parameters are fixed and the CEF is recalculated using the geometric parameters $R_i$ for $p > 0$. It remains to be noted that this procedure does not account for any change in the electronic properties of the system (e.g. screening of the charges), which however is also expected to occur under pressure (sections 2.4.3 and 5.2).

### Bilinear exchange and interaction with magnetic fields

So far interactions of the rare-earth ion with an external magnetic field or with the molecular field in case of spontaneous magnetization have not been considered.
These interactions lead to further splitting of the energy levels due to the Zeeman effect and result in a decrease of the magnetic entropy (2.42). Assuming isotropic bilinear exchange and spontaneous magnetic order of the rare-earth sublattice only, the magnetic interaction can be written within the mean-field approximation [36, 37]:

\[ \hat{H}_{\text{mag}} = -g_J \mu_B (\mathbf{H}_{\text{ex}} + \mathbf{H}_{\text{mf}}) \cdot \mathbf{J} + O(M^2) \] (2.50)

where \( g_J \) stands for the Landé factor of the respective rare-earth ion and \( \mathbf{H}_{\text{ex}} \) and \( \mathbf{H}_{\text{mf}} \) denote an external magnetic field and the molecular field, respectively.\(^{12}\) The latter must obey the self-consistency equation

\[ \mathbf{H}_{\text{mf}} = \lambda \mathbf{M} = g_J \mu_B \lambda \langle \mathbf{J} \rangle \] (2.51)

with \( \lambda \) the mean-field parameter and \( \mathbf{M} \) the magnetic moment of the rare-earth ion. The mean-field parameter is related to the magnetic susceptibility \( \chi \) of the system via

\[ \chi = \frac{\chi_0}{1 - \lambda \chi_0}, \] (2.52)

where \( \chi_0(T) = \chi_0(T, B_{\text{mn}}) \) denotes the single-ion susceptibility defined by the CEF ([36, 37] and section 3.2.2). At the ordering temperature \( T^* \), the magnetic susceptibility \( \chi \) diverges, so that \( \lambda \) must fulfill

\[ \lambda = \chi_0^{-1}(T^*, B_{\text{mn}}). \] (2.53)

Figure 2.4 illustrates the Zeeman splitting resulting from diagonalization of \( \hat{H} = \hat{H}_{\text{CEF}} + \hat{H}_{\text{mag}} \) in function of the effective molecular field \( \mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{ex}} + \mathbf{H}_{\text{mf}} \) acting on the Ce\(^{3+} \) ion in CeSb together with the magnetic entropy \( S_M \). Apparently, Zeeman splitting can lead to a drastic reduction in \( S_M \), especially for systems with spontaneous magnetization as the associated molecular fields are often found to be bigger than conventionally applicable by external magnetic fields.

**Biquadratic exchange**

In analogy to the two-ion bilinear exchange discussed in the previous section, higher-degree pair interaction, i.e. interactions in higher powers of the spins

\[ J_{ij}^{(n)} (\mathbf{S}_i \cdot \mathbf{S}_j)^n, \quad n \geq 2 \] (2.54)

may also be relevant in some systems.\(^{13}\) In rare-earth compounds quadrupolar terms \( (n = 2) \) may origin from indirect Coulomb interactions and exchange interactions where conduction electrons with \( d \)-character are dominant or from the coupling between the quadrupoles of the 4\( f \)-shell and the lattice [36]. The latter case is associated with a magnetoelastic interaction and the corresponding macroscopic lattice distortions are described by a cooperative Jahn-Teller distortion. The incorporation of quadrupolar exchange can have a large impact on the thermodynamics of the system. In addition to spontaneous magnetization, i.e. an ordering of the dipolar

\(^{12}\)The non-operator term \( O(M^2) \) in (2.50) is often omitted as it only causes a shift in absolute energy. However it becomes important, if different magnetic models are compared to one another.

\(^{13}\)For convenience the general spin operator is denoted by \( \mathbf{S} \) whereas \( \mathbf{J} = \mathbf{L} \pm \mathbf{S} \) is used for the combined total angular moment.
Figure 2.4: Left: Zeeman splitting in CeSb ($J = 5/2$) for an effective magnetic field along the cubic axis. Right: magnetic entropy at $T = 5$ K in function of the magnetic field. The molecular field $H_{mf}$ for this compound corresponds to about 160 kOe = 16 T ($T_N = 16.1$ K). The upturn in $S_{mag}$ above 170 kOe results from the convergence of the second with the third excited energy level.

moment, an ordering of the quadrupolar moment also evolves. The different multipole moments are found to affect each another resulting in a kinematic coupling between the two order parameters. Levy [38] has illustrated the effect of biquadratic exchange on a simple spin-one system considering the Hamiltonian

$$\hat{H} = -J \sum_{\langle i,j \rangle} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \alpha (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)^2)$$

(2.55)

with $\alpha$ denoting the ratio between biquadratic and bilinear exchange and taking only nearest neighbor interactions into account. The phase diagram resulting from a mean-field approximation with $J > 0$, i.e. ferromagnetic alignment of the spins, is shown in Figure 2.5. Regions with both quadrupolar and dipolar moment and regions with only quadrupolar moment are found. The most striking feature concerns the presence of first order transitions for $\alpha > 2/3$. Note that within the mean-field approximation first order transitions are absent in systems with bilinear exchange only.

Biquadratic exchange is also found to trigger first order transitions in more complicated systems. Here the CEF interaction often plays a crucial role in silent features of the coupling between dipolar and quadrupolar moment. The operator equivalence method used by Stevens for the description of the CEF may be used for biquadratic exchange too. The resulting mean-field Hamiltonian for isotropic biquadratic exchange is then given by [36, 38]

$$\hat{H}_Q = -\lambda_Q \left( \langle \hat{O}_2^2 \rangle \hat{O}_2^2 + 3 \langle \hat{O}_2^0 \rangle \hat{O}_2^2 \right)$$

(2.56)
Figure 2.5: Phase diagram for a spin-one system described by (2.55). Thin and thick lines denote continuous and first order transitions. \( \langle M \rangle \) and \( \langle Q \rangle \) stand for the dipolar and quadrupolar moment, respectively (after Levy [38]).

with \( \lambda_Q \) the quadrupolar mean-field parameter and with the Stevens operators

\[
\hat{O}^0_2 = 3\langle \hat{J}^z \rangle^2 - \hat{J}(\hat{J} + 1),
\]

(2.57)

\[
\hat{O}^2_2 = \frac{1}{2}\left[\langle \hat{J}^+ \rangle^2 + \langle \hat{J}^- \rangle^2 \right].
\]

(2.58)

2.5 Implementations of the barocaloric effect

Effects of pressure on the different parts of the total entropy have been discussed in the previous sections. The effect on the lattice entropy is the most familiar one. However one may not want to call it a barocaloric effect and instead reserve the term barocaloric in the context with a pressure-induced change of the magnetic entropy.

In this sense the caloric effect caused by a pressure-induced change of the electronic entropy must not be called a BCE too. However, as the change of the Sommerfeld parameter \( \gamma \) (2.36) often involves a change in the magnetic entropy (e.g. by a pressure-induced enhancement or suppression of spin-fluctuations) the effect may well be called barocaloric.

Concerning the magnetic entropy and specifically the CEF entropy in the case of rare-earth compounds, it turns out that the very same is influenced by a diversity of factors introduced in the previous sections. These include

- the specific type of rare-earth ion,
- the point-symmetry at the rare-earth site,
- the charges of the ligands and the rare-earth ion\(^{14}\),
- screening of the charges and 4f-hybridization due to conduction electrons,

\(^{14}\)In most cases the rare-earth ion is trivalent.
• Zeeman splitting due to an internal or an external magnetic field.

On most of these factors pressure has a direct influence. The corresponding pressure effects open various mechanisms of how the BCE may be implemented. In what follows these mechanisms are summarized. Some of them have been observed experimentally and references to the corresponding sections of chapter 4 are given.

**(point-symmetry of the rare-earth site)** The point-symmetry of the rare-earth ion site may be directly changed by a pressure-induced structural phase transition or a pressure-induced distortion of the actual structure. This type of BCE may be called *structurally driven* BCE. In general the high-symmetrical state shows higher magnetic entropy than the low-symmetrical state. Representatives of this type of BCE are the rare-earth nickelate Pr$_{1-x}$La$_x$NiO$_3$ (chapter 4), RAl$_x$Ga$_{2-x}$ (section 5.1) and to some respect HoAs (section 4.3) and Ce$_3$Pd$_{20}$Ge$_6$ (section 4.5).

**(Zeeman splitting)** Large internal magnetic fields may be provided by the molecular field in the magnetically ordered state. The change from the paramagnetic (high entropy) to the magnetically ordered state (low entropy) may be accomplished by a pressure-induced magnetic phase transition. Many rare-earth compounds show pronounced shifts of the ordering temperature by pressure. Magnetically critical systems may be triggered between the magnetic and non-magnetic state with moderate pressure. The effect is referred to as *magnetically driven* BCE, representatives are the BCE in CeSb (section 4.1) and HoAs (section 4.3).

**(screening and hybridization by conduction electrons)** Pressure is known to affect the degree of 4f-conduction electron hybridization in many of the heavy-fermion systems. The gain in electronic entropy (see section 2.4.3) is thereby coupled to a loss in magnetic entropy as the CEF gets smeared out (see section 4.5 on Ce$_3$Pd$_{20}$Ge$_6$ for the resonance level model).

**(type of rare-earth ion)** Although the rare-earth ion type cannot be physically replaced by the application of pressure, a pressure-induced valence transition may well result in a similar effect. E.g. pressure may drive a divalent Eu$^{2+}$ ion, which behaves like a trivalent Gd$^{3+}$ ion ($J = 7/2$), to a trivalent Eu$^{3+}$ ($J = 0 \rightarrow S_M \equiv 0$). The associated change in the CEF and hence magnetic entropy can be dramatic. Thereby the difference in ionic radius between corresponding valence states makes valence transitions prominent for large pressure dependences. The associated effect may be called *valence driven* BCE.

In cases involving phase transitions it becomes important to further distinguish two categories of systems.

1. Systems *non-critical in p*, where the respective phase transition takes place primarily in function of temperature and where the phase transition temperature $T^*$ is only found to be shifted by pressure. For every pressure, corresponding temperatures for either phase can be found. In these systems a change of pressure from $p_1$ to $p_2$ only results in a pressure-induced phase transition for

---

15 $R$=rare earth
temperatures within the interval $T^*(p_1) \leq T \leq T^*(p_2)$. For many systems at low temperatures it is this constraint, and not the size of the extensive BCE $\Delta S$ nor the slope in $S(T)$, which limits the intensive BCE $\Delta T_{ad}$ (compare conclusions from (2.11) and Fig. 4.12). The corresponding $(p, T)$-phase diagram and $S(T)$-curves are illustrated in the upper part of Figure 2.6.

2. Systems critical in $p$. In this case only one phase is found for certain pressures irrelevant of temperature. Here the pressure-induced transition is not limited to a certain temperature interval (or limited to one side only) and $\Delta S$ and the slope of $S(T)$ are the dominating factors limiting $\Delta T_{ad}$ (2.11) (Fig. 2.6, lower part).

Hence systems critical in $p$ are preferred for a large BCE. Unfortunately critical systems are not nature’s favorites and are a lot less frequent than non-critical ones.

In the case of non-critical systems, the pressure dependence of the transition...
temperature $dT^*/dp$ becomes a crucial factor. The equation of Clausius-Clapeyron for first order transitions
\[
\frac{dT^*}{dp} = \frac{\Delta S}{\Delta V}
\]
(2.59)
and Ehrenfest’s equations for continuous transitions
\[
\frac{dT^*}{dp} = \frac{VT\Delta \alpha}{\Delta C}, \quad \frac{dT^*}{dp} = \frac{\Delta \alpha}{\Delta \kappa}
\]
(2.60)
relate the pressure dependence of the transition temperature with discontinuities in macroscopic thermodynamic quantities ($\kappa$ stands for the isothermal compressibility). In principle the two equations allow to calculate $dT^*/dp$ given that all necessary parameters are known accurately enough. At this point however, it is important to apply (2.59), (2.60) in the proper thermodynamic context and to remember the remarks already addressed in section 2.3. Both equations are correct in the paramagnetic state only, where any effect from a change in the magnetism of the system can be ignored. The Clausius-Clapeyron\textsuperscript{16} and Ehrenfest’s equations\textsuperscript{17} are based on the comparison of differences in the Gibbs free energy $G$ and their slopes, respectively at constant magnetization $M$. However $G$ is a thermodynamic state function and thus generally depends on $M$ too:
\[
dG = -SdT + Vdp + HdM + \ldots
\]
(2.61)
Strictly, both equations can only be applied for the structurally driven BCE and the valence driven BCE and only if the corresponding phase transitions take place within the paramagnetic state ($dM = 0$, $H_{eff} = 0$).

The diversity in mechanisms leading to a BCE may be regarded as a specific feature of this kind of caloric effect that makes the BCE worthwhile to be studied not only from an applicative but also from a fundamental point of view.

All adiabatic cooling techniques and underlying mechanisms discussed in this chapter are schematically summarized in Figure 2.7.

\textsuperscript{16}Clausius-Clapeyron: $dG_1 = -S_1dT + V_1dp \equiv dG_2 = -S_2dT + V_2dp \rightarrow dT/dp$

\textsuperscript{17}Ehrenfest: $\frac{\partial}{\partial T}dG_1 \equiv \frac{\partial}{\partial T}dG_2 \rightarrow dT/dp, \quad \frac{\partial}{\partial p}dG_1 \equiv \frac{\partial}{\partial p}dG_2 \rightarrow dT/dp$
### Figure 2.7: Classification of adiabatic cooling techniques discussed in this chapter.

<table>
<thead>
<tr>
<th>thermodynamic principle</th>
<th>control variable</th>
<th>entropy affected</th>
<th>mechanism</th>
<th>classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic field</td>
<td>SM</td>
<td>change of spin alignment</td>
<td>adiabatic demagnetization in paramagnetic salts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SM</td>
<td>shift/enhancement/suppression of magnetic transition</td>
<td>MCE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SM+SL</td>
<td>same as above + coupling of magnetic and chemical sublattice</td>
<td>giant MCE</td>
<td></td>
</tr>
<tr>
<td>adiabatic cooling</td>
<td>SL</td>
<td>shift of phonon spectrum</td>
<td>elastic heating/cooling</td>
<td></td>
</tr>
<tr>
<td>pressure</td>
<td>SM</td>
<td>shift/enhancement/suppression of structural transition</td>
<td>structurally driven BCE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SM</td>
<td>shift/enhancement/suppression of magnetic transition</td>
<td>magnetically driven BCE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SM</td>
<td>shift/enhancement/suppression of valence transition</td>
<td>valence driven BCE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SM+SE</td>
<td>change of 4f-cond.\textsuperscript{e} hybridization in heavy-fermion systems</td>
<td>BCE in heavy-fermion systems</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>enhancement/suppression of spin-fluctuations</td>
<td>BCE not based on SM</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3

Experimental Techniques

This chapter discusses the experimental techniques, setups and data analysis tools used throughout this work. Emphasis is given to issues which may not be common to the reader, these include the setups for the BCE experiments and the high-pressure techniques applied to neutron scattering methods and to macroscopic measurements. For an introduction to more general aspects of neutron scattering methods or macroscopic measurements the reader is referred to the extensive literature available. The reader may feel free to continue reading chapter 4 about the experimental results while using this chapter as a convenient reference.

3.1 Setups for the barocaloric measurements

Two different setups for the measurement of the BCE on single crystals (uniaxial pressure) and on powder samples (hydrostatic pressure) have been developed. The two setups do not only differ in mechanical aspects but also in the thermometry applied.

3.1.1 Thermometry

Aside a carefully designed mechanical apparatus to apply pressure, a fast and accurate thermometry to observe the BCE is of utmost importance. The demands on the thermometry can be summarized as follows:

- The sensor must be as small as possible to account for the typical sample dimensions and to allow for a prompt response.
- Hydrostatic pressure must have as little as possible influence on the sensor.
- The sensitivity of the sensor must be large enough to guarantee good relative accuracy.
- To account for the dynamic nature of the measurement, the temperature must be tracked at high repetition rates.

Among all the different temperature sensors, thermocouples have some superior features. They are an excellent choice to meet the two first requirements. Thermocouples are known to be only a little dependent on external hydrostatic pressure.
Figure 3.1: The two basic setups for the thermometry used for the measurement of the BCE. Left: direct circuit suitable for relative T measurements; thermal instabilities at the voltage measuring point $P$ result in noise. Right: reference circuit allows absolute T measurements with no noise from thermal instabilities at $P$.

[39], whilst sensors based on changes in the electrical resistivity cannot be used for hydrostatic pressure experiments at all.\footnote{The inverse diameter of the wire is directly proportional to the resistivity and subject to change with pressure.} For a comprehensive introduction to the theory and the applications of thermocouples see e.g. [40].

Thermocouples consists of two wires of two different metals connected to a junction at one end. The latter may be spot-welded to very small dimensions and hence allows fast response times. Thanks to the Seebeck effect a voltage in function of the temperature difference between the junction and the measuring point $P$ occurs (Fig. 3.1, left). The sensitivity $S(T) \equiv \Delta V/\Delta T$, known as the Seebeck coefficient, is a polynomial function in $T$. For most types of thermocouples corresponding tables with Seebeck coefficients can be found in literature [39]. It is important to state that with thermocouples principally only temperature differences can be measured. Hence in the direct circuit (Fig. 3.1, left) thermal instabilities at the voltage measuring point $P$ result in noise and hinder an accurate measurement even in the case of a relative temperature measurement. Hence on the right side of Figure 3.1 an asymmetric reference junction is added to the primary thermocouple (reference circuit). Intermediate temperatures along the thermocouple do not matter. Therefore the resulting voltage is a direct (absolute) measure for the temperature difference between the sample and the reference independent of temperature variations at $P$.

An inherent disadvantage of thermocouples is their relative small and hard to measure signals (typically a few 10 $\mu$V/K) and their loss in sensitivity with decreasing temperature. Fortunately, a wide variety of different thermocouples for different applications are known, with some of them suitable at the lowest temperatures too [39]. Among the most commonly used thermocouples are the Chromel-Alumel couples\footnote{also referred to as type-K thermocouples} with a useful working range between ca. 20 K and 1400 K. Although this type can hardly be used for temperatures below 20 K, two-core thermocouples with a protective ceramic tube are available from stock. Mechanically these thermocouples...
easily sustain high hydrostatic pressure (even in non-liquid environments). The smallest available standard diameter is 0.5 mm.

At low temperatures Au/Fe-Chromel thermocouples\(^3\) are one of the best choices. They allow the measurement down into the sub-K ranges. Unfortunately these thermocouples are not manufactured with protective tubes and hence they can be used for the uniaxial BCE setup only.

For all the measurements presented in this work the voltage signal of the thermocouple(s) had to be amplified before being fed into a commercial HP multimeter. A linear, analog amplifier with a 37x and 9700x gain factor has been used for this purpose. The data of the multimeter is either instantly logged by a computer at a rate of 20 meas/sec. or firstly stored in the internal memory of the multimeter at rates of up to 300 meas/sec. and later read out by the computer. The voltages were then converted to temperatures by means of calibration against the cryostat temperature sensors (for the reference circuit) or according to published Seebeck tables (for the direct circuit).

### 3.1.2 Force transmitting system

All BCE measurements have been carried out in a standard ILL He-cryostat equipped with a specially designed force transmitting system. This system consists of an adapted cryostat insert shown in Figure 3.2. Technical details are given in [41]. Pressure is produced with a hydraulic (oil) hand-pump and converted to uniaxial force by a hydraulic cylinder mounted on top of the cryostat insert. The uniaxial force is then transmitted via a hollow plunger onto a piston and the sample (uniaxial setup) or onto the piston of a pressure cell (hydrostatic setup). The geometry and the dimensions of the plunger are chosen in order to minimize effects of thermal expansion and misalignment of the acting force. Sealing rings at the top of the plunger ensure a proper sealing of the sample chamber while adding only a little extra friction to the plunger.

The hydrostatic pressure \(p_h\) of the oil is measured with a manometer. Assuming little frictional losses of the system the force \(F\) of the plunger is given by the effective area \(A_h\) of the hydraulic cylinder via

\[
F = A_h \cdot p_h. \quad (3.1)
\]

The system is designed to transmit forces up to about \(F^{\text{max}} = 10\ \text{kN}\). With \(A_h = 640 \ \text{mm}^2\) this corresponds to a hydrostatic pressure in the hand-pump of about \(p^{\text{max}}_h = 150 \ \text{bar}\).\(^4\) The friction force of the plunger system accounts to less than 20 N and may hence be neglected.

Originally the system was designed for neutron diffraction studies under uniaxial pressure. Thus the hydrostatic pressure may be kept to a less than 10 % loss over a period of 24 h thanks to two extra valves positioned between the manometer and the hydraulic cylinder and between the manometer and the hand pump, respectively. A further bypass-valve installed in the hand pump allows for the fast release of the oil pressure. The force of the plunger was found to be released within less than 0.01 s as determined by measurements of the BCE and the elastic heating of

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\(^3\)Au-(0.02-0.03)at.Fe vs Ni-10Cr

\(^4\)1 bar \(\equiv 10^5\) Pa; 1 GPa \(\equiv 100\ \text{kg/mm}^2\).
samples at room temperature with the two extra valves fully opened. An additional Cernox thermometer is attached at the very bottom of the device in order to compare the temperature of the sample against the temperature of the heat exchanger. Within the experimental accuracy no difference between the two sensors was observed. Hence an effective heat flow from the end of the plunger through the sample can be ruled out for a constant heat exchanger temperature of the cryostat.

3.1.3 Uniaxial setup

The setup for the measurement of the BCE under uniaxial pressure is described in this section. The samples studied under uniaxial pressure include: CeSb, Ce$_{0.85}$(La,Y)$_{0.15}$Sb, HoAs, YbAs and Ce$_3$Pd$_{20}$Ge$_6$. Figure 3.3 depict this setup. The single crystal is placed on a socket. The uniaxial force of the force transmitting system is directed via an additional piston onto the sample. Piston and socket are made of zirconia. Polycrystalline stabilized zirconia (ZrO$_2$) is characterized by very small thermal conductivity. The heat flow from the sample to the piston and to the socket is hence minimized insuring quasi-adiabatic conditions for the measurement of the intensive BCE. The effective uniaxial pressure $p_s$ acting on the sample is given
by (3.1)

\[ p_s = \frac{F}{A_s} = p_h \frac{A_h}{A_s} \]  

(3.2)

with \( A_s \) being the sample area. Measuring single crystal samples of a typical dimension such as 3·3·3 mm\(^3\), the maximum applicable pressure is generally restricted by the mechanical limits of the single crystal and not by the force transmitting system.

Maximal pressures can only be applied along symmetry directions of a crystal. Hence only crystals with nice, clean cleavage planes can be used. Smallest defects in the structure of the crystal, e.g. cracks, steps, twins, etc., drastically reduce the mechanical limit of the crystal and lead to early sample breakage. Shear stresses originating from a misalignment of the acting force must also be avoided. In order to further minimize the risk of breaking the sample due to microscopic imperfections of the sample surface, dust particles, etc., a thin Teflon disk (0.1 mm) is placed between the sample and the socket and between the sample and the piston. In the course of this work thin foil of tin (0.02 mm) has been proven to work equally well. Experiments without the use of these soft spacers have shown that these are essential and should also be used for neutron diffraction experiments despite their contribution to the background intensity.

The thermometry for the uniaxial setup turns out to be a lot simpler than for the hydrostatic setup. The thermocouple is glued directly onto one of the free surfaces of the crystal. GE Insulating Varnish from General Electrics proved to be best suited for this purpose. This glue shows good thermal conductivity and keeps being sticky down to the lowest temperatures. For all experiments carried out with this setup the thermocouple voltage was measured by using the reference circuit (section 3.1.1).

### 3.1.4 Hydrostatic setup

The hydrostatic setup was used for the BCE measurements on polycrystalline bulk samples of CeSb and EuNi\(_2\)(Si\(_{0.15}\)Ge\(_{0.85}\))\(_2\). The basic ideas for the design of this setup are borrowed from experience with hydrostatic clamp pressure cells as used...
for neutron scattering measurements under pressure described later in section 3.2.1. However the need to change pressure *in situ* at low temperatures requires some special measures.

The hydrostatic setup is depicted in Figure 3.4. The sample is placed in a pressure matrix, which is bottom loaded into the pressure cell and fixed with a screw. All parts are made of stainless steel as this setup is primarily designed for use at low temperatures where the thermal conduction of stainless steel becomes fairly poor. The sample is placed within a solid pressure transmitting medium and has no contact with the walls of the pressure matrix. A Teflon cap and a copper-beryllium (Cu/Be) ring ensure the sealing of the pressure cell and stop the piston getting blocked by the pressure transmitting medium. Indeed the piston was never found to be blocked after the experiments and could be removed by bare hands. In order to minimize friction between the (solid) pressure transmitting medium and the walls of the pressure matrix, a thin foil of Pb (0.02 mm) is placed between the two. The temperature is measured inside the sample. For this purpose a small hole of 0.52 mm is drilled into the sample. A Chromel-Alumel thermocouple (0.5 mm diam) with a protective tube is used to track the temperature. Good thermal contact with the sample is ensured by some Apiezon grease put between the sensor and the sample. The thermocouple is fed out via holes through the pressure matrix (0.52 mm diam) and the pressure cell (0.6 mm diam) and fixed with Araldit glue onto the pressure matrix. Inspection of the thermocouple after the experiment has found that it was remained in the correct position at all times. The temperature was measured using the direct circuit for the thermometry with the voltage measuring point at the outside of the massive pressure cell (section 3.1.1).
The reason a solid pressure transmitting medium was used was due to prior experience that at high-pressures almost all known liquid media are already frozen at moderate temperatures. In fact Fluorinert, which is one of the most often used pressure transmitting media\textsuperscript{5}, is known to become solid at room temperature for $p \gtrsim 1$ GPa and freezes at around 150 K for $p = 0$ into an amorphous glass. Hence the use of a 'liquid' pressure transmitting medium would bring in many additional unknowns, which may all affect the BCE signal of the sample. On the other hand, the $p - T$ phase diagrams of solid pressure media are generally known and present less 'surprises'. Solids are comparatively harder than liquids and correspondingly result in less elastic heating/cooling superimposed on the BCE of the sample. The preparation and sealing of the pressure cell can be done in a much more controlled manner. On the other hand they contribute to less hydrostatic conditions for the sample and therefore a considerably broad pressure distribution cannot be ruled out. At low temperature a solid medium also results in more friction with the sample and the walls, which is superimposed on the BCE from the sample.

Lead constitutes a solid pressure transmitting medium which already has been used successfully for neutron scattering experiments under hydrostatic pressure [42]. Lead is comparatively soft and thus transmits pressure well. In these experiments pressure was applied at room temperature and clamped before the pressure cell was cooled to base temperature. To the knowledge of the author, lead has not been used as a pressure medium in conjunction with an \textit{in situ} change of the pressure at low temperatures before. Hence preliminary experiments have been carried out on a pressure matrix filled only with lead. The elastic cooling of lead was tracked in function of temperature. As can be seen from Figure 3.5 the elastic cooling vanishes at around 60 K which was later found to coincide with the \textit{ductile-brittle} transition of lead. Like most other metals, lead becomes mechanical brittle if the temperature is low enough and thereafter cannot transmit the pressure anymore.

\textsuperscript{5}Fluorinert contains no hydrogen and hence is especially well suited for neutron scattering measurements (see section 3.2).
For this reason a pressure medium other than a metal must be used. An analogous test experiment on sodium chloride has shown the elastic cooling to decrease about linearly with decreasing temperature as expected (see section 2.4.2) and hence has confirmed the applicability of \textit{in situ} pressure changes at cryogenic temperatures. After both experiments on CeSb and EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$, inspection of the pressure matrix has shown that the sodium chloride has become non-porous and has flown nicely around the sample.

### 3.1.5 Relaxation models

In all the measurements the observed intensive BCE $\Delta T$ is followed by a relaxation back to the initial temperature due to heat flow between the sample and the environment, i.e., due to the non-adiabaticity of the system. In experiments performed at high measurement rates it is further observed that the temperature does not drop down instantaneously but continuously. The analysis of these two relaxations reveals parameters specific for the sample and the setup. At this point it is noteworthy to mention that a temperature measurement of any dynamical process\(^6\) always yields the temperature of the sensor as the measured variable but not necessarily the temperature to be probed for. Nevertheless the knowledge of the sensor temperature evolution in function of time allows for the reconstruction of the true sample temperature.

In the two following models the change in the \textit{sample} temperature $\Delta T$ (caused by the BCE) is assumed to occur instantaneously with the release of pressure. In comparison with the two time constants of the two observed relaxations, this assumption turns out to be well justified for all the studied BCE systems (see also section 3.1.2).

#### $\tau$-model

The relaxation of the temperature after the release of pressure back to the initial temperature $T_0$ can be described by an exponential decay with corresponding time constant $\tau$. An exponential decay of the sample temperature $T_1$ arises assuming the sample (1) to stay in contact with the environment (0) via an effective thermal conductivity $\eta_{10}$ and by treating the environment as a heat sink\(^7\) (Fig. 3.6, left). Note that the sensor and the sample temperature are not distinguished in this model. The change in heat of the sample is then given by

$$\dot{Q}_1(t) = \eta_{10}(T_0 - T_1(t)).$$

(3.3)

Introducing the heat capacity of the sample $C_1 \equiv \delta Q_1/\delta T_1$ one finds for the sample temperature

$$\dot{T}_1(t) = \frac{\eta_{10}}{C_1}(T_0 - T_1(t))$$

(3.4)

and for $T_1(0) = T_0 + \Delta T$ the solution

$$T_1(t) = T_0 + \Delta T e^{-t/\tau}$$

(3.5)

\(^6\) dynamical process $\leftrightarrow$ process not in thermal equilibrium

\(^7\) $Q_0 \to \infty$, $T_0 \equiv \text{const.}$
where

\[ \tau = \frac{C_1}{\eta_{10}} \]  

(3.6)

denotes the characterizing time constant which reflects the non-adiabaticity of the system. Equation (3.6) explains the observed bump of \( \tau(T) \) in the measurement of \( \text{Ce}_{0.85}(\text{La}, \text{Y})_{0.15}\text{Sb} \) (section 4.2, Fig. 4.13): in the vicinity of the magnetic phase transition the heat capacity \( C_1(T) \) varies a lot more than the conductivity \( \eta_{10}(T) \), so that \( \tau(T) \) effectively reflects the heat capacity of the sample. In fact, the method of inducing a temperature change to the sample with a subsequent analysis of the relaxation over a defined thermal conductivity is known as the relaxation method and is the most commonly applied experimental technique for the determination of the heat capacity (section 3.3). In this sense the BCE represents a very integral determination of the specific heat, as \( \Delta T \) is provided by the sample itself and not for instance by a Joule heater. Note that \( \eta_{10} \) is a combined property of the sample, spacers, piston, socket and exchange gas of the sample chamber and hence difficult to estimate from primary material constants.

2\( \tau \)-model

A closer look at the measured data reveals small deviations from a pure exponential decay for the sensor temperature, which actually constitutes the observable of this dynamic process. In addition, at high measurement rates the minimum of the sensor temperature is found to be delayed with respect to the pressure release. The 2\( \tau \)-model accounts for these observations and has the sample (1) also staying in contact with the sensor (2) via an effective thermal conductivity \( \eta_{12} \) (Fig. 3.6). The sensor itself is assumed to be thermally isolated from the environment (0). In analogy to (3.3) and (3.4) the temperature of the sample (1) and the sensor (2) obey

\[ \dot{T}_1(t) = \frac{1}{C_1} \left[ \eta_{12}(T_2(t) - T_1(t)) + \eta_{10}(T_0 - T_1(t)) \right] \]  

(3.7)

\[ \dot{T}_2(t) = \frac{1}{C_2} \left[ \eta_{12}(T_1(t) - T_2(t)) \right]. \]  

(3.8)
Figure 3.7: Temperature evolutions of the sample $T_1$ and the sensor $T_2$ after (3.9) and (3.10). The first row of figures (1a-c) illustrates the dependence on medium ($a_{21} = 8 \text{ s}^{-1}$), small ($a_{21} = 30 \text{ s}^{-1}$) and large ($a_{21} = 2 \text{ s}^{-1}$) heat load of the sensor ($a_{10} = 0.5 \text{ s}^{-1}$, $a_{12} = 1 \text{ s}^{-1}$, $\Delta T = -1 \text{ K}$). The second row (2a-c) shows the analogous evolutions with better thermal isolation between the sample and the environment (i.e. under improved adiabatic conditions, $a_{21}$ and $a_{12}$ same as above, $a_{10} = 0.1 \text{ s}^{-1}$).

Note that only $T_2$ can be measured directly.

The parameter $a_{21}$ can be associated with the heat load of the sensor. Figure 3.7 shows the evolution of $T_1$ and $T_2$ for different values of $a_{21}$. Obviously a large heat load of the sensor results in a substantial difference between the minimum of the sample temperature $T_1$ and the minimum of the sensor temperature $T_2$. Also note that this difference is linked to the non-adiabaticity of the setup, i.e. to $\eta_{10}$. For a well isolated\(^8\) sample the heat load of the sensor influences the system less (second row in Fig. 3.7). Therefore the least difference between the minima in $T_1$ and $T_2$ is found for small mass ratio and good thermal contact between the sensor and the sample and for a minimal non-adiabaticity of the system.

The effect of the sensor heat load constitutes an important correction to keep in mind when the size of the observed data is to be compared against model calculations of the BCE. At this point it is stressed that in all measurements the, what is called *directly observed* BCE, is denoting the minimum in the measured sensor temperature $T_2$ and not the *true* BCE of the sample $\Delta T$.

\(^{8}\rightarrow \eta_{10} \text{ small}\)
For the measurements on Ce$_3$Pd$_{20}$Ge$_6$ (section 4.5) the true BCE $\Delta T$, i.e. the temperature of the sample $T_1(t)$, has been reconstructed from the directly observed effect by fitting the observed data $T_2(t)$ with (3.10). However the least-squares procedure has proven to be numerically unstable due to a strong correlation between $a_{12}$, $a_{21}$ and $\Delta T$. In order to reduce the number of free model parameters, the relaxation of the sample temperature $T_1$ has been assumed to decay exponentially. The heat flow from the sample to the sensor and to the environment is then combined and characterized by an effective thermal conductivity $\tilde{\eta}_{10}$. The two differential equations (3.7) and (3.8) then reduce to

$$\dot{T}_1(t) = \frac{\tilde{\eta}_{10}}{C_1} [T_0 - T_1(t)]$$

(3.11)

$$\dot{T}_2(t) = \frac{\eta_{21}}{C_2} [T_1(t) - T_2(t)].$$

(3.12)

with solutions $(T_1(0) = T_0 + \Delta T, T_2(0) = T_0)$

$$T_1(t) = T_0 + \Delta T e^{-t/\tau_1}$$

(3.13)

$$T_2(t) = T_0 + \Delta T \frac{\tau_1}{\tau_1 - \tau_2} \left[ e^{-t/\tau_1} - e^{-t/\tau_2} \right]$$

(3.14)

where the two relaxation constants are $\tau_1 = C_1/\tilde{\eta}_{10}$ and $\tau_2 = C_2/\eta_{12}$.

The resulting curves $T_1(t)$ and $T_2(t)$ are essentially indistinguishable from (3.9) and (3.10) within the parameter range of interest ($\tau_2 \ll \tau_1$). The fitting of the experimental data on (3.14) can now be done without numerical difficulties and yields the true BCE $\Delta T$ as well as the evolution of the sample temperature $T_1(t)$ (3.13).

3.1.6 Comments on the adiabaticity of the setups

In all uniaxial measurements the directly observed intensive BCE is found to be smaller by a factor of 2...3 compared to the expected (calculated) true intensive BCE. One reason for this has been discussed in the previous section with its roots in the non-adiabatic conditions for the sample, i.e. in the heat flow between the sample and its environment. The problem can also be discussed within a stationary picture as schematically shown in Figure 3.8. Heat flow $\Delta Q$ out or into the sample can always be associated to an entropy change $\Delta S = \Delta Q/T$. Hence a fully isothermal application (or release) of pressure corresponds to $A \rightarrow B_{\text{isoth}}$ in Figure 3.8; while a fully adiabatic process corresponds to $A \rightarrow B_{\text{adiab}}$. In practice the measurement of the intensive BCE $\Delta T$ cannot be performed fully adiabatically (which becomes obvious from the relaxations observed) and must be related to the two limits of a fully adiabatic and fully isothermal process, i.e. described by the line $A \rightarrow B^*$ in Figure 3.8. Depending on the slopes of the two entropy curves $S_0(T)$ and $S_1(T)$ at $p = 0$ and $p > 0$, respectively, small non-adiabatic contributions may already be sufficient to cause a severe reduction of the intensive BCE $\Delta T$ (compare Figure).

In this stationary picture the non-adiabaticity can be quantified by the ratio between the isothermal $\Delta S$ and adiabatic component $\Delta T$

$$\frac{\Delta_{\text{isoth}}}{\Delta_{\text{adiab}}} = \frac{\Delta S}{\Delta T} = \tan \alpha = \frac{\eta}{1 - \eta}$$

(3.15)

The other three fitting parameters $T_0$, $\eta_{10}$ and the origin of the time-scale were fitted without any problems.
where $\eta = \Delta S / (\Delta S + \Delta T)$ serves as a measure for the non-adiabaticity. The directly observed intensive BCE $\Delta T$ is then given by the intersection of $S_0(T)$ and the line $AB^*$ with slope $-\alpha = -\eta / (1 - \eta)$

$$S_0(T) \cap \left[ S_1(T_A) - \frac{\eta}{1 - \eta} (T - T_A) \right] \rightarrow T_{B^*}$$

and $\Delta T = T_{B^*} - T_A$.

In the case of measurements performed under uniaxial pressure with the samples relatively well thermally isolated, the dynamic corrections described in the previous section turn out to account well for the true BCE. However for the measurements performed under hydrostatic pressure, the non-adiabaticity becomes a severely limiting factor reducing the observed $\Delta T$ by as much as one order of magnitude! In these cases the comparison between the expected true BCE and the directly observed BCE may yield an estimation for the non-adiabaticity parameter $\eta$ (see section 4.6 on EuNi$_2$(Si,Ge)$_2$).

### 3.2 Neutron scattering

The peculiar quality of the neutron being an uncharged particle results in large penetration depths into matter. As a consequence the neutron probes the bulk properties and allows measurements under extreme sample conditions as these require special sample containment like cryostats, furnaces, magnets, pressure cells, etc. A well defined beam path (collimation), adapted energy of the neutron and carefully chosen components can reduce the disturbing influence of the sample containments to a minimum and ensure an affordable cost in data quality.

Together with another property, namely its intrinsic magnetic moment, the neutron makes the ideal probe to study the microscopic properties of many of the BCE systems. These include$^{11}$: (i) chemical structures and structural phase transitions

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$^{10}$\(\eta = 0 \leftrightarrow 100\% \text{ adiabatic}, \quad \eta = 1 \leftrightarrow 100\% \text{ isothermal}\)

$^{11}$ND : neutron diffraction, INS : inelastic neutron scattering
(ii) magnetic structures and magnetic phase transitions [ND], (iii) excitations of the lattice → phonon dispersion [INS], (iv) magnetic excitations → CEF energy levels, magnon dispersion [INS] – at ambient and elevated pressure.

3.2.1 Neutron diffraction (ND)

All neutron powder diffraction measurements, except the anvil pressure-cell study on NdAl$_x$Ga$_{1-x}$ (section 5.1), were carried out on angular-dispersive multidetector diffractometers. If not otherwise stated the data is evaluated in terms of a Rietveld analysis with the program Fullprof. The experiments were carried out on the diffractometers DMC (SINQ), HRPT (SINQ) and D2B (ILL, France). The measurements on NdAl$_x$Ga$_{1-x}$ (section 5.1) using anvil-pressure cells were carried out on the TOF$^{12}$ multidetector powder diffractometer IN12 (Dubna, Russia). The single-crystal diffraction measurements on Ce$_{0.85}$(La,Y)$_{0.15}$Sb (section 4.2) were carried out on TriCS (SINQ).

For details about the instruments or general aspects of the neutron diffraction technique the reader is referred to the corresponding literature [43, 44, 45, 46, 47, 48, 49]. In what follows issues specific to neutron diffraction under high pressure are discussed.

Zero-matrix clamp pressure-cells

The technical difficulties encountered when applying hydrostatic pressures increase very quickly with the sample size and hence explain the success of anvil pressure cells ever since they have been first proposed. However the relatively small interaction between the neutron and the nuclei or between the neutron and the magnetic moments of the sample requires large sample volumes of preferably a few cm$^3$ on most of the diffractometers currently in use. Although special instrumental measures like beam focussing, wavelength limitations, extensive background reduction and TOF techniques may improve the relative intensity considerably, these measures often limit the functionality of the instrument and hence are normally not applied on multi-purpose powder diffractometers.

_Clamp pressure cells_ (or _piston-cylinder cells_) account for this situation and allow pressure of up to about 2 GPa with sample volumes of about 1 cm$^3$. The concept of this type of pressure cell is depicted in Figure 3.9. The cell consists of a hollow cylinder with a inner-outer diameter ratio less than 1 : 3. A general rule of thumb valid for most metals states that any larger ratio results in elastic deformation of the cylinder and hence in a saturation of pressure much before the mechanical limit of the material is reached. Two inner pistons apply the pressure onto the pressure transmitting medium and the sample. The symmetric arrangement, i.e. the use of two pistons, is not mandatory but helps the pressure to be applied more uniformly and eases the later removal of the sample. When the cell is loaded the force is transmitted onto the inner piston(s) with the help of auxiliary pistons. The force is gradually increased while screw parts fix the inner pistons so as to keep the pressure on after the release of the loading force. The auxiliary pistons are then removed and the cell can be mounted on the instrument or placed into a cryostat.

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$^{12}$TOF: time-of-flight
Figure 3.9: Schematic illustration of how a clamp pressure cell is loaded (body (1), inner pistons (2), screw parts (3) and auxiliary pistons (4)).

Thanks to the special property of the neutron allowing for negative coherent scattering lengths in some of the elements, alloys can be composed with effectively vanishing coherent scattering length. The most often used so called zero-matrix alloy is Ti-Zr.\textsuperscript{13} Pressure cells built of this material only contribute to incoherent (flat) background in the diffraction pattern but not to Bragg peaks. The drawback of this material is (i) the relatively large absorption and (ii) the mechanical limit, which restricts the maximum pressure to about 1.2 GPa. Additional mechanical support of the zero-matrix components with non-zero-matrix material, like e.g. hardened steel, allows to extend the maximum pressure to about 2.0 GPa.

The two zero-matrix pressure cells used in our laboratory are a non-supported cell for pressures up to 0.9 GPa at 7.5 mm diam ($V \approx 0.9$ cm$^3$) and a supported cell up to 1.7 GPa at 9.1 mm diam ($V \approx 0.3$ cm$^3$). The two cells are shown in Figure 3.10.

The preparation of these two cells consists of the following steps:

1. A cylinder of thin lead foil is prepared and placed within the body of the cell. This foil reduces the friction between the powder sample and the walls of the cell considerably and reduces the corrosion of the cell with the calibrant (see below). The cylinder is closed at the bottom end.

2. The lead cylinder is filled with the sample-calibrant mixture (see below). Small amounts of Fluorinert FC-77 are added.\textsuperscript{14} The powder should be wet but not

\textsuperscript{13}coherent scattering lengths: $b_c$(Ti) = $-3.438(2)$ fm, $b_c$(Zr) = $+7.16(3)$ fm [50].

\textsuperscript{14}Fluorinert is a perfluorinated liquid (perfluorcarbon: chains of singly bonded carbon atoms terminated with fluorine atoms) containing no hydrogen and hence is widely used as a pressure medium in neutron scattering experiments.
necessarily swimming in the liquid. At this point it is important that the powder is already well compressed in order to minimize void volume. Finally the top of the lead cylinder is folded shut.

3. Two rings of non-hardened Cu/Be (or alternatively fabricated from a soft steel) are placed at the top and the bottom of the lead package in order to seal the cell properly. It is important that neither the sample nor the lead can move between the walls of the cell and the inner pistons and cause the latter to get blocked. Teflon caps like used for the hydrostatic BCE setup (section 3.1.4) are not used here. Teflon has a large thermal expansion coefficient and hence results in substantial pressure loss after cooling of the cell. Furthermore Teflon was found to cause Bragg peaks in the diffraction patterns, presumably originating from Teflon which has flown inwards to the sample.

4. The cleaned inner pistons are then inserted in the cell and once more checked to ensure that they cannot hit the neutron beam.

5. Finally the cell is loaded on a hydraulic press in several steps from both sides of the cell. The pistons are found to move a lot within the first effective 0.1 GPa of applied pressure eliminating the remaining void volume of the sample. Hence it is important to compress the sample well while preparing the cell. Typical loads are 40 kN (0.9 GPa) and 110 kN (1.7 GPa), respectively.

Due to the friction of the sample with the walls of the cell and due to thermal shrinkage of the sample when cooling, the effective pressure on the sample is typically about 10 % less at base temperature, than what one would expect from the load.
force. The actual size of the pressure loss depends on the sample. Hence the pressure
must be measured at base temperature. For this purpose the sample is mixed with a
pressure calibrant which shows a known pressure dependence of its lattice constants.
Typical calibrants are NaCl or CsCl. These calibrants are soft and hence lead to
a large shift in their Bragg peaks. Calibration tables for both salts can be found
in literature [51, 52, 53, 54]. Note, that all tables use the lattice constant at room
temperature and ambient pressure as the reference point. They hence already include
thermal expansion of the calibrant. Also note, that some of the tables are based on
semi-empirical models. To the knowledge of the author, the table for NaCl published
by Skelton et al. [51] is the most reliable one based on synchrotron measurements.
Considering the relatively small volume changes under pressure it is very important
to actually measure the reference point (i.e. \( p = 0, T = RT \)) at the very same
diffractometer. Typical amounts of the calibrant account for about 20-30 % vol.
Thanks to the comparative softness of the two salts, they also serve as pressure transmitters.

**Beyond 2 GPa - anvil pressure cells**

Anvil pressure techniques must be applied in order to perform diffraction experi-
ments beyond 2 GPa pressure. The principle of an anvil pressure cell is shown in
Figure 3.11. Spherical holes at the end of two anvils form the sample space. To con-
fine the sample laterally a metallic ring (gasket) is placed between the two anvils.
This concept allows the application of extremely high pressure with a modest force
load of the cell (typically a few 10 kN). The major drawback of this technique is the
small sample volume of typically less than a few mm\(^3\). The anvils are commonly
chosen from single-crystalline sapphire (for pressure up to 7 . . . 10 GPa depending on
the diameter of the spherical holes) or from diamond (for pressure beyond \( \approx 7 \) GPa).
The support of the anvils is fabricated of stainless steel or Cu/Be. The force is ap-
plied by screws. The diffraction is best performed in axial geometry with a fixed
scattering angle for energy dispersive instruments (TOF) or in axial transmission
geometry for angular dispersive synchrotron X-ray diffraction measurements. Both
configurations allow an effective collimation of the gasket material. The few single-
crystal Bragg peaks from the anvils can be conveniently excluded from the data. The
optical transparency of sapphires and diamonds allows the pressure to be measured
by means of optical methods. For this purpose several tiny ruby chips are placed
on top of the sample. The pressure-induced shift of the R-fluorescence line of ruby
is well known up to the highest applicable pressure and serves as a standard for
pressure determination above 1 GPa [55].

A variant of this type of cell is represented by the family of toroidal cells with the
Paris-Edinburgh pressure cell being the most prominent member used for neutron
scattering and synchrotron experiments [56]. In these cells the toroidal gasket is
centered by means of two concentric grooves in the anvils forming a torus. The
Paris-Edinburgh cell allows for sample volumes of \( \sim 100 \text{ mm}^3 \) (for 10 GPa). Its
anvils are made of tungsten carbide or sintered diamond. Other toroidal cells for
macroscopic measurements or high-pressure synthesis have been built with sample
volumes of up to \( \sim 1000 \text{ cm}^3 \) (!). A hydraulic press is generally needed to load the
cells because of the large load forces. The pressure in the Paris-Edinburgh cell can
be changed **in situ**.

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The room temperature measurements on \( \text{NdAl}_x\text{Ga}_{1-x} \) presented in section 5.1 were carried out using sapphire-anvil pressure cells with fixed 90° scattering angle on the TOF powder diffractometer DN12 in Dubna, Russia. The diameter of the anvil holes were 2 mm which allowed pressures up to about 5 GPa. Typical beam exposure times were 16 h. The gasket was composed from soft aluminum and harder zero-matrix material. Pressure was measured via the fluorescence of ruby chips.

### 3.2.2 Neutron spectroscopy

With neutron spectroscopic methods structural as well as magnetic excitations of the sample can be directly probed. In the context of the BCE the determination of the CEF splitting scheme represents the most important issue to be tackled by means of inelastic neutrons. As opposed to other experimental methods inelastic neutron scattering (INS) directly reveals the energy differences and strengths of transitions between the CEF levels.

The spectroscopic studies presented in this work were carried out on the cold-triple axis spectrometers DrüchaL (SINQ) and IN12 (ILL, France) and on the TOF spectrometer FOCUS (SINQ). All the measurements were done in neutron energy loss configuration. For details about these instruments as well as on general topics about inelastic neutron scattering the reader is referred to the corresponding literature [47, 57].

### Crystal fields

For a powder sample with \( N \) non-interacting rare-earth ions the neutron cross-section for the CEF transition \( |n\rangle \rightarrow |m\rangle \) in the dipole approximation is given by [58]

\[
\frac{d^2\sigma}{d\Omega d\omega} = N \left( \frac{\gamma e^2}{m_e c^2} \right) \frac{k_1}{k_0} e^{-2W(\vec{Q})} F^2(\vec{Q}) \times
\]

\[
\times \; p_n \left| \langle m|\hat{J}_\perp|n\rangle \right|^2 \delta (E_n - E_m + \hbar\omega) \quad (3.17)
\]

where \( k_0, k_1 \) denote the wave numbers for the incoming and scattered neutron, respectively, \( \hbar\omega \) the energy transfer of the neutron, \( W(\vec{Q}) \) the Debye-Waller factor, \( F(\vec{Q}) \) the magnetic form factor, \( p_n = p_n(T) \) the Boltzmann factor for state \( |n\rangle \) and \( \hat{J}_\perp \) the operator of the total angular momentum’s component perpendicular to the
scattering vector $\vec{Q}$. All remaining symbols have their usual meaning. Hence an INS measurement reveals the energy differences $E_n - E_m$ between different CEF states and the relative strengths $\propto |\langle m|\hat{J}_\perp|n\rangle|^2$ of the respective transitions. Note that not necessarily all transitions $|m\rangle \rightarrow |n\rangle$ are observable by the neutron.

In order to account for all the information of the INS measurement (energies and intensities of the transitions), the observed spectrum is preferably analyzed in terms of a profile fit. For this purpose the expected spectrum is calculated in function of the CEF parameters by means of (3.17) and convoluted with the resolution of the instrument. Intrinsic broadening of the transitions due to e.g. chemical inhomogeneities or life-time effects can be further allowed for by substituting the $\delta$-functions in (3.17) with Gaussians or Lorentzians, respectively. The resulting calculated spectrum is then fitted against the observed spectrum yielding scaling, CEF and other sample- and instrument-dependent parameters.

A look on the number of CEF parameters allowed by the respective point-symmetry of the rare-earth ion [27] shows the difficulties one may encounter with compounds of low symmetry. While reliable parametrizations for the cubic, tetragonal and hexagonal cases can be found with some modest effort, the orthorhombic case is often only solvable under the assumptions of some constraints between the CEF parameters (e.g. relations based on the extended point-charge model or extrapolations from known CEF sets). For the monoclinic and triclinic cases, the parametrization of the CEF must be considered almost impossible.

Confidence in the physically correct parametrization can be gained by a variety of additional measures: (i) The simultaneous fit of spectra taken at different temperatures provides additional information about the absolute energy position of the levels via their thermal population. (ii) The parameters can be put in relation to CEF parameters of other isostructural compounds by means of extrapolation methods, e.g. the (extended) point-charge model (section 2.4.4). (iii) The compound can be measured in the magnetically ordered state, where the corresponding energy levels and transition matrix elements $\langle m|\hat{J}_\perp|n\rangle$ are given in mean-field approximation by $\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{mag}}$, (2.39) and (2.50). The saturated magnetic moment resulting from the mean-field calculation can then also be compared to values obtained from neutron diffraction or macroscopic measurements. (iv) The calculated single-ion susceptibility and Schottky (2.44) anomaly can be compared with macroscopic measurements of the DC magnetization and the specific heat, respectively.

A further difficulty may arise by the presence of phonon excitations erroneously interpreted as CEF excitations. The separation between the two excitations however becomes obvious with the study of their respective dependence upon temperature and magnitude of scattering vector $Q$.\(^{17}\)

\[
\chi_0^\alpha = \frac{g^2 \mu_B^2}{k_B T} \left[ \sum_{n,m} p_n |\langle m|\hat{J}_\alpha|n\rangle|^2 - \sum_{n,m} p_n |\langle m|\hat{J}_\alpha|n\rangle|^2 \right] + 2g^2 \mu_B^2 \sum_{n,m} p_n \frac{|\langle m|\hat{J}_\alpha^n|n\rangle|^2}{E_m - E_n}
\]

The summation $\sum$ is carried out only over states $|m\rangle$ and $|n\rangle$ with $E_m = E_n$, whereas $\hat{\sum}$ includes all other states [37].

\(^{15}\)Boltzmann distributed for CEF states, Bose-Einstein distributed for phonons

\(^{16}\)\(\propto F^2(Q)\) for CEF states, \(\propto Q^2\) for phonons

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A clamp pressure cell for the TOF spectrometer FOCUS

In order to perform INS measurements under pressure, a clamp cell has been developed and tested in collaboration with the High Pressure Institute of the Russian Academy of Sciences in Troitsk, Russia. A picture of the cell is shown in Figure 3.12. The cell is an ordinary clamp type pressure cell as described earlier in section 3.2.1. A few peculiarities however distinguish it from the zero-matrix pressure cells. The inelastic signal of an INS measurement is significantly smaller compared to the elastic signal, e.g. of a neutron diffraction measurement. Even under ambient pressure an INS measurement may take as long as several days. Hence for successful INS experiments under pressure, the absorption due to the cell must be minimized while allowing for largest possible sample volumes. The geometry of a TOF spectrometer requires further consideration about the geometry of the cell in order to minimize (i) corrections of the data due to anisotropic absorption of the cell and (ii) the presence of spurious inelastic intensity originating from elastic neutrons multiply scattered on the sample and the cell.

The developed cell matches these requirements. The axial-symmetric cell of 70 mm outer and 7 mm inner diameter is built of a hardened aluminum type and allows a sample volume of 2500 mm$^3$ at a maximum pressure of 1 GPa. Aluminum has little absorption for the neutron$^{18}$, however it represents also a rather soft basic

$^{18}$absorption cross sections for 2200 m/s neutrons: $\sigma_a(Al) = 0.231(3) \text{ barn}$, compared to $\sigma_a(Ti) = 6.09(13) \text{ barn}$, $\sigma_a(Zr) = 0.185(3) \text{ barn}$ [50].
material. To strengthen the structure, the cell is built with an inner core tube of 1.5 mm thickness made of stainless steel (or zero-matrix alloy) and the screw thread is tapped in a hardened steel insert. The loss due to absorption and elastic scattering by the cell is estimated to a factor of about 6 for an incoming neutron wavelength of $\lambda_i = 2.09$ Å. Clean spectra without inelastic features originating from the cell are obtained for $\lambda_i$ above and below the Bragg limit of aluminum (e.g. measured for $\lambda_i = 2.09, 4.3, 5.0$ Å).

The cell is filled in the same way as for the zero-matrix clamp cells. In addition to the INS measurement the shift in the lattice parameter of the pressure calibrant must be measured on a powder diffractometer before or after the experiment. Experience with the clamp cells has shown that the pressure in the cell is retained for several days and is not affected by multiple thermal cycling.

3.3 Macroscopic measurements

The presented measurements of the specific heat, DC magnetization and AC susceptibility were carried out on the Quantum Design PPMS of our laboratory.\(^\text{19}\) This system allows measurements in the temperature range of 1.8 K and 400 K with magnetic fields of up to 9 T. The specific heat is measured with the relaxation method with typical sample masses of 2...20 mg. The DC magnetization is measured with the extraction method. Samples for DC magnetization or AC susceptibility measurements are limited to a maximum diameter of 7.5 mm.

3.3.1 Macroscopic measurements under pressure

Specific heat

In principle the measurement of the specific heat $c_p$ under pressure would allow the indirect determination of the extensive and intensive BCE via $S = \int C/T dT$ according to (2.16) and (2.5), i.e. in the very same way as done for the MCE by variation of the magnetic field. Unfortunately the relaxation method is the least suited approach for this purpose. The mass of even the smallest clamp pressure cell would not yield reasonable relaxation times for temperatures higher than about $T > 50$ K. Other difficulties arise from the unfavorable ratio between sample mass and mass of the pressure cell. While a clamp cell for measurements under uniaxial pressure might be feasible, the measurement of $c_p$ under hydrostatic pressure is definitely out of scope when using the relaxation method (at least on a quantitative level). Hence the development of a $c_p$ pressure cell for our PPMS system was not further studied throughout this work.

It is noteworthy that, generally, the measurement of $c_p$ under pressure remains a task of considerable difficulty and is by far not commonly applied. There are two experimental approaches especially well suited for the measurement of $c_p$ under pressure. In the adiabatic method a defined quantity of heat is transmitted to the otherwise thermally isolated sample. The resulting increase of sample temperature is thence a direct measure of the specific heat. The thermometry as well as the heater can be built within the pressure cell. Quasi-adiabatic conditions are guaranteed.

\(^{19}\)PPMS: physical property measurement system
by encapsulating the sample, heater and thermometry with a thermally insulating material and by choosing large dimensions for all components. The AC method represents another approach well suited for small samples. Sinusoidal modulated heat is transferred to the sample. The resulting sample temperature is then tracked and compared against the signal from the heater. It can be shown that the imaginary part of the sample response is related to $c_p/T$. The AC method can be miniaturized and used in combination with the anvil pressure technique for small enough samples [59]. Finally it must be noted that none of the two approaches reveals quantitative values for $c_p$ under pressure as the contributions in $c_p$ from the pressure cell, heater, thermometry and pressure transmitting medium are utterly non-trivial to be distinguished. Hence the indirect determination of the BCE via the measurement of $C(T,p)$ is of no practical importance.

**DC magnetization and AC susceptibility**

The realization of a pressure cell for the measurement of magnetic properties is comparatively easy to achieve: (i) the pressure cell and the pressure transmitting medium may be chosen from non-magnetic material and hence do not contribute to the observable and (ii) no wires must enter the pressure cell. Commonly clamp cells are used. The design of the pressure cell developed throughout this work is shown in Figure 3.13. All parts of the cell are made of hardened copper-beryllium (Cu/Be). The cell is loaded with an auxiliary piston made of hardened steel which transmits the force to the inner piston. Subsequently a screw part fixes the inner piston and the auxiliary piston can be removed. The sample itself is placed in a thin capsule of lead (thickness 0.2 mm) filled with Fluorinert FC-77 allowing for
Figure 3.14: DC magnetization of CeSb under hydrostatic pressure measured with the pressure cell described in the text (numbers denote the sequence of the measurements, $H_{DC} = 1$ kOe).

The use of the lead capsule eases the preparation of the cell and ensures good sealing. Alternatively, Sn or Al capsules can be used for measurements below 7.16 K.\textsuperscript{20}

Figure 3.14 shows the DC magnetization of CeSb measured with this type of pressure cell up to $p = 1$ GPa. The shifts of the magnetic transitions agree well with previous studies\textsuperscript{61} (see section 4.1). The cell is designed for a maximum pressure of about $p = 1.1$ GPa. In order to achieve higher pressure other material than Cu/Be must be used (e.g. Ni\textsubscript{57}Cr\textsubscript{39.5}Al\textsubscript{3.5} alloy\textsuperscript{21}).

\textsuperscript{20}Be aware of the Meissner effect!

\textsuperscript{21}also known as Russian Alloy
Chapter 4

Experimental observation of the barocaloric effect

This chapter presents the direct measurements of the BCE carried out throughout this work. The observed cooling effects all result from a pressure-induced change of magnetic entropy, the reasons for this however vary.

The rare-earth nickelate Pr$_x$La$_{1-x}$NiO$_3$ represents the first compound studied for the occurrence of a BCE. It is also this compound for which the concept of cooling by adiabatic pressure application was first proposed by Müller et al. [4]. The results on Pr$_x$La$_{1-x}$NiO$_3$ are summarized briefly here.

First observation of a BCE in Pr$_x$La$_{1-x}$NiO$_3$

Pr$_x$La$_{1-x}$NiO$_3$ is a perovskite system and undergoes a temperature-induced structural phase transition from orthorhombic $Pbnm$ ($T < T_{SPT}$) to rhombohedral $R3c$ ($T > T_{SPT}$) space-group.\(^1\) The transition temperature $T_{SPT}$ may be tuned seamlessly by the Pr content $x$, and is found to shift to a lower temperature by the application of hydrostatic pressure.\(^2\) Hence pressure-induced phase transitions $Pbnm \rightarrow R3c$ may be realized over a temperature range up to 700 K at modest pressures (see [4] and references therein). The CEF in orthorhombic and rhombohedral symmetry differ considerably [63] (Fig. 4.1) and allow for a pure structurally driven BCE.

BCE measurements have been carried out on Pr$_x$La$_{1-x}$NiO$_3$ above room temperature on $x = 0.66$ [4] and at low temperatures on $x = 0.5, 0.4$ [5]. All measurements were carried out on bare powders with little precautions to minimize friction effects at low temperatures. The BCE at temperatures above room temperature have yielded an effective cooling of a few 0.1 K for $p = 0.5$ GPa in Pr$_{0.66}$La$_{0.34}$NiO$_3$ at $T = 350$ K in competition to elastic heating [4] (note that the cooling by the BCE takes place while pressure is applied). For lower temperatures, where elastic contributions become less of a problem, the BCE has been found in competition to friction effects $\propto 1/C$, which are an inherent problem of powder samples (compare sections 4.1.5 and 4.4).

\(^1\)Note that this transition is of first order.  
\(^2\)\(T_{SPT}(x = 1) \approx 700\) K, \(dT_{SPT}/dx \approx 1000\) K, \(dT_{SPT}/dp(x = 0.5) \approx -50\) K/GPa [4], \(dT_{SPT}/dp(x = 0.4) \approx -23(2)\) K/GPa [62]
Unfortunately, Pr$_x$La$_{1-x}$NiO$_3$ can only be synthesized under high oxygen pressure. Up to now, only powder samples are available. The BCE in Pr$_x$La$_{1-x}$NiO$_3$ has not been further studied throughout this work.

**Wish list for the ideal BCE compound**

Based on theory and experimental experiences, the ideal BCE compound should have the following properties:

- large entropy change $\Delta S$, i.e. highly degenerate $\leftrightarrow$ highly non-degenerate CEF
- large pressure effect on the corresponding mechanism causing the change in entropy
- cooling by the BCE should happen with the release of pressure, so that the effect is not in competition with elastic heating
- 1st order and critical transition in $p$
- single crystal or sintered material to minimize heating by friction at low $T$
- minimal non-magnetic entropy $S_N$, i.e. the carrier of the entropy should be well represented in the chemical formula (all non-magnetic ions just add up to $S_N$)
- wide temperature range the effect may be induced in
- resistance to mechanical and thermal cycling
- good thermal conductivity for potential technical applications

Unfortunately there is only limited literature available about pressure-induced structural and magnetic phase transitions. A comprehensive review of pressure-induced phase transitions including results from geophysics can be found in [64].
It remains to be stated that in solid state physics, systems with large effects for pressures less than 1 GPa constitute an exception owing to favorable circumstances (making them all the more worth to have a closer look at!).
4.1 CeSb

CeSb shows a purely magnetically driven BCE upon application of uniaxial pressure. The experimentally observed intensive BCE of $\Delta T_{ad} = -2$ K per $\Delta p = -0.52$ GPa pressure release is found to be largest of all the studied systems. The BCE may be modelled with a simple mean-field calculation taking into account CEF, bilinear and biquadratic interactions. Part of what follows has been published in [65, 66, 67].

4.1.1 Introduction

The monopnictide CeSb crystallizes in the cubic NaCl structure (space group $Fm\bar{3}m$, $a = 6.412$ Å). Despite its simple chemical structure CeSb shows one of the most complex magnetic phase diagrams ever found. Below $T_N \approx 16$ K antiferromagnetic ordering occurs in various magnetic phases with different stackings of ferromagnetic (001) planes with up (+) or down (-) spins along [001] and paramagnetic planes (0). The stacking sequences are characterized by a magnetic ordering wave vector $q_0 = (2\pi/a) \cdot (0, 0, q_0)$. The first magnetic phase found below $T_N$ with stacking sequence $+-0$, i.e. $q_0 = 2/3$, is followed by at least 14 more experimentally observed magnetic phases before the system eventually realizes the AF-IA phase with $++--$ sequence for $T < 8$ K. All of these magnetic phase transitions are found to be of first order (Fig. 4.2 at $p = 0$).

The origin of this complex phase diagram resulted in a thorough study of the magnetic properties of CeSb. Boehm and Bak [68] proposed a simple mean-field model taking into account competing bilinear interactions between first- and second-nearest neighbor planes. The so-called ANNNI$^3$ model successfully explains the observed sequence of magnetic phases and postulates that infinite more phases will occur, which often are cited as the Devil’s stairs. The respective temperature ranges of some of these phases may well be tiny enough, so that they cannot be accessed experimentally. The crystal-field splitting of CeSb has been studied by Heer et al. [69]. The CEF is found to be unexpectedly small with a $\Gamma_7$ doublet ground-state and an excited $\Gamma_8$ quartet at $\Delta_{CF} = 37(1)$ K. The magnetic interactions have been studied by Hälg et al. [70] by means of inelastic neutron scattering in the AF-IA phase. Strong intra-plane and much weaker inter-plane magnetic exchange are found leading to a distinct magnetic anisotropy. In the AF-IA phase the bilinear exchange shows a maximum for $q_0 = 1$ which in principle would favor the AF-I structure. Similar results have been found by diffuse critical neutron scattering studies [71] which reveal pronounced AF-I fluctuations above $T_N$ like the system wants to realize the very same phase. However at ambient pressure the AF-I phase is not found to be realized in CeSb at any temperature. Accordingly the occurrence of AF-I fluctuations has been explained by a competition of bilinear and higher-degree exchange. Indeed dilution studies [72] in Ce$_x$(La,Y)$_{1-x}$Sb have shown the coexistence of two different kinds of spin fluctuations associated with the AF-I and a modulated structure, respectively. For $x = 0.9$ a continuous phase transition into a modulated structure is observed. Eventually for $x < 0.8$ AF-I fluctuations dominate. However strong fluctuations suppress the development of magnetic long-range order into the AF-I phase (down to $T = 1.9$ K). The magnetic phase diagram in function

\footnote{anisotropic next-nearest neighbor interaction model}
of $x$ can be explained in terms of a mean-field theory including biquadratic terms in the corresponding Hamiltonian and shows that bilinear ordering favors the AF-I phase, while quadrupolar ordering favors the modulated phases. Uniaxial pressure experiments \cite{73} on CeSb finally confirmed a critical end-point with an appearance of the AF-I phase at $T = 18.1(2)$ K and $p = 0.20(3)$ GPa (Fig. 4.2). Under hydrostatic pressure the magnetic phase-diagram has been studied by Chattopadhyay \cite{61} by means of neutron diffraction and measurement of the magnetization. The respective phase diagram shows a striking analogy to the phase diagram under uniaxial pressure. A critical end-point at $T = 18$ K and $p = 0.25$ GPa is determined. For pressures $p > 1$ GPa the paramagnetic planes vanish completely. Finally the phase diagram of CeSb under an external magnetic field has been experimentally determined by Chattopadhyay and others (\cite{61} and references therein) and has been explained by Kasuya et al. \cite{74} in terms of an extended ANNNI model including higher-degree interactions. Considerable interest in the theoretical aspects of CeSb has emerged. The origin of paramagnetic planes has been explained in terms of Kondo states \cite{74}. The $p$-$f$ model introduced by Takahashi and Kasuya \cite{75} and Cooper \cite{76} accounts for the mixing mechanism between the $4f$ states and holes in the valence bands. This model is able to explain many of the unusual magnetic properties of the Ce monopnictides CeSb and CeBi, e.g. their pressure effects and effects upon dilution with Te \cite{77} both acting on the number of valence holes.

From all studies on CeSb it is found that a subtle balance between the crystal-field, valence hole concentration, bilinear and higher-degree exchange interaction
results in a manifold of magnetic states with free energies close to the ground-state energy. Hence the system shows a very rich magnetic phase diagram characterized by large frustration and pronounced dependence upon chemical substitution, external magnetic fields and external pressure, etc. (Fig. 4.3).

4.1.2 Principle of the magnetically driven BCE in CeSb

In view of the almost degenerate manifold of magnetic states below \(T_N\) the magnetic entropy \(S_M\) may be considered almost indistinguishable for all the magnetic phases in accordance with \(c_p\) measurements (Fig. 4.3). Hence the phase-diagram may be simplified by only discriminating between a magnetically ordered and the paramagnetic state (Fig. 4.4, top). Due to the first order character of the transition the entropy curves at \(p = 0\) and \(p > 0\) are expected to show a discontinuity at the respective ordering temperatures \(T_N(p)\) (Fig. 4.4, middle). Adiabatic cooling may now be implemented in two stages, with the system being initially in the paramagnetic state at point A:

A→B Uniaxial pressure is applied isothermally\(^4\) driving the system from the paramagnetic into the ordered state (Fig. 4.4, top). Thereby the magnetic entropy is reduced and heat \(Q = -T\Delta S\) is transferred from the system to the heat sink (Fig. 4.4, middle).

B→C The applied pressure is released adiabatically\(^5\). In order to keep the entropy constant the system must cool down (2.5).

The phase-diagram and the entropy curves imply that

\(^4\)i.e. the system in thermal contact with the heat sink.
\(^5\)i.e. the system thermally isolated from its environment.
Figure 4.4: Schematics for the magnetically driven BCE in CeSb: $p - T$ phase diagram (top), associated entropy curves (middle) and expected intensive BCE (bottom). Points $A$, $B$, $C$ denote the two stages of adiabatic cooling: isothermal application of pressure $A \rightarrow B$ with extensive BCE $\Delta S_M$ and adiabatic release of pressure $B \rightarrow C$ with intensive BCE $\Delta T_{ad}$. 
1. for temperatures higher than $T_N(p > 0)$ or lower than $T_N(p = 0)$ no cooling effect can be achieved and

2. the final temperature $T_C$ cannot fall below $T_N(p = 0)$.

Hence one expects for the temperature dependence of the intensive BCE a triangular shape as depicted in the bottom part of Figure 4.4 with a maximum $-\Delta T = T_N(p > 0) - T_N(p = 0)$ given the extensive BCE $\Delta S_M$ is large enough (2.11).

4.1.3 Direct observation of the intensive BCE

The BCE measurements on CeSb have been carried out on a single crystal of $2.7 \cdot 2.3 \cdot 2.1 \text{ mm}^3$ volume with the experimental setup described in section 3.1.3. The temperature of the sample was tracked by a Chromel/Alumel thermocouple at a rate of 2 meas/sec. Figure 4.5 shows a representative measurement of the intensive BCE for a pressure release of $\Delta p = -0.52 \text{ GPa} \parallel [001]$. With the release of pressure the sensor temperature falls sharply down and relaxes back to the temperature of the environment. The pressure is applied much slower than released nevertheless an inverse BCE can be observed (Fig. 4.5). The temperature dependence of the BCE has been sampled for different pressures and nicely exemplifies the triangular shape expected from the $p-T$ phase diagram (Fig. 4.6). The linear growth of the maximal BCE with pressure indicates that the intensive BCE is limited by the shift in $T_N$ with pressure rather than by the size of the extensive BCE $\Delta S_M$ (see section 2.5). No attempt was made to correct the observed $\Delta T$ for the dynamics of the thermometry as described in section 3.1.5. The poor sample rate of the temperature does not allow for an accurate determination of the corresponding relaxation time-constants.
4.1.4 Model for the BCE in CeSb

The observed BCE may be modelled by introducing a crude mean-field calculation neglecting the exact nature of the magnetic ordering: 

$$\mathcal{H} = B_0^4 \left[ \hat{O}_4^0 + 5\hat{O}_4^4 \right] - \lambda_D \langle \hat{J}^z \rangle \hat{J}^z - \lambda_Q \langle \hat{O}_2^0 \rangle \hat{O}_2^0$$

(4.1)

with $B_0^4$ the CEF parameter$^6$, $\lambda_D$ and $\lambda_Q$ the dipolar and quadrupolar mean-field parameters.$^7$ Self-consistent diagonalization of (4.1) leads to the six energy levels defining the magnetic entropy $S_M$ with (2.21). The total entropy at low temperatures is then given by (2.30,2.36)

$$S = S_M + \frac{\beta}{3} T^3 + \gamma T.$$ 

(4.2)

Figure 4.7 shows the modelled entropy curves at ambient and elevated pressure together with the resulting intensive BCE (2.5). The parameters used for this calculation are listed in Table 4.1. The CEF parameter $B_0^4$ is taken from [69] and assumed to be independent of pressure. The mean-field parameters $\lambda_D$ and $\lambda_Q$ at ambient pressure are chosen to match (i) $T_N(p = 0)$, (ii) $S(T)$ at $p = 0$ resulting from integration of the measured $c_p$ data (gray line, Fig. 4.7), (iii) the magnetic moment of Ce$^{3+}$ as measured by neutron diffraction [78]. $\gamma$ is taken from [74], $\beta$ 

$^6B_0^6 = 0$ for Ce$^{3+}$

$^7\langle \hat{O}_2^2 \rangle = 0$ as the spins align parallel to the quantization axis $z$ (2.58).
Figure 4.7: Calculated entropy curves and resulting intensive BCE in CeSb. The gray line in the upper curve represents the total entropy $S$ from integration (2.13) of experimental $c_p$ values (Fig. 4.3).

<table>
<thead>
<tr>
<th>$p$ [GPa]</th>
<th>$B_0^1 \cdot 10^2$ [meV]</th>
<th>$\lambda_D$ [$\mu$eV]</th>
<th>$\lambda_Q$ [$\mu$eV]</th>
<th>$\beta \cdot 10^3$ [R/K$^2$]</th>
<th>$\gamma \cdot 10^6$ [R/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.89</td>
<td>524</td>
<td>37.0</td>
<td>2.4</td>
<td>1.35</td>
</tr>
<tr>
<td>$\approx 0.26$</td>
<td>0.89</td>
<td>690</td>
<td>30.5</td>
<td>2.4</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters for the model of the BCE in CeSb (Fig. 4.7).

is extrapolated from the Debye temperature of other monopnictides [79, 80]. Both values are assumed to be pressure-independent. The two mean-field parameters for $p > 0$ are adjusted to reproduce the pressure-dependence of the ordering temperature $dT_N/dp = 8$ K/GPa [73] and a pressure-independent magnetic entropy $S_M$ for $T < T_N(p = 0)$. The latter criterion comes from the fact, that (i) the magnetic phases below $T_N$ are energetically almost indistinguishable and (ii) no cooling effect below $T_N(p = 0)$ can be observed experimentally (i.e. $S_A = S_B$). The calculated BCE satisfies the experiment except for a factor 2.5 for the magnitude of the BCE. As mentioned above, the linear growth of the maximal signal with pressure implies that the intensive BCE is not restricted by the extensive BCE. Hence the value of the maximal $\Delta T$ is expected to be about the difference of the two ordering temperatures $T_N(p = 0)$ and $T_N(p > 0)$. Subsequent BCE experiments on Ce$_3$Pd$_{20}$Ge$_6$ have revealed that corrections due to the heat load of the temperature sensor and due to the thermal conductivity between sample and its environment are well necessary. These correction factors arising from the dynamics of the thermometry may well be as large as 3 (see 3.1.5). The formalism of this correction is discussed in section 3.1.5 but is not applied for these measurements. The pressure-dependence

---

With $\beta$ independent of pressure, elastic heating is neglected (section 2.4.2).
of the mean-field parameters $\lambda_D$ and $\lambda_Q$ shown in table 4.1 are in accordance with the $p-T$ phase diagram. Especially the tendency of $\lambda_Q$ to become smaller with pressure is consistent with a weakening of the quadrupolar order eventually driving the system at the critical end-point into the AF-I phase.

Finally it is worthwhile to address two comments on the pressure dependence of the (paramagnetic) CEF in CeSb, which is completely neglected in the above model. Uniaxial pressure is expected to distort the crystal. Correspondingly the CEF cannot be described by a Hamiltonian for cubic symmetry anymore. The tetragonal distortion results in an additional small term $\propto B_2^0 \hat{O}_2^0$ in (4.1). As a consequence the quartet at 37 K gets split into two doublets. Note however, that any change in symmetry cannot split the CEF levels in more than doublet states, as Ce$^{3+}$ is a Kramers ion ($J = 5/2$), thus the ground-state remains unchanged. The splitting of the quartet will have a negligible influence on the magnetic entropy $S_M$ due to its low thermal population at $T < 20$ K. Similarly, a pressure dependence on $B_4^0$ will only shift the quartet slightly keeping $S_M$ almost constant for $T < 20$ K. Hence at low temperatures the change of $S_M$ results almost entirely from the Zeeman effect on the ground-state doublet of CeSb and the above made approximations neglecting the pressure-effect on the CEF are well justified.

4.1.5 BCE under hydrostatic pressure

In preparation for the measurements on EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ (section 4.6) the hydrostatic setup as described in section 3.1.4 had been tested on a bulk sample of CeSb. In doing so, the BCE was found to be reduced by more than one order of magnitude compared to the uniaxial measurements and the calculations.

In Figure 4.8 a selection of measurements is shown, demonstrating the problems encountered with this setup. At temperatures $T < T_N(p = 0)$ one observes considerable heating caused by friction. For temperatures $T_N(p = 0) < T < T_N(p > 0)$ an effective cooling from the BCE is observed superimposed on friction. Finally for $T > T_N(p > 0)$ the BCE vanishes and the heating due to friction becomes dominant again. The hydrostatic measurements on CeSb are summarized in Figure 4.9. Note that for the effect of friction $\Delta T_f$ one expects roughly a temperature dependence $\sim 1/C(T)$ (see section 4.4). Hence the effect of friction $\Delta T_f$ is damped down near the vicinity of the phase transition of CeSb, i.e., for the temperature range in which the BCE can be observed. The effective cooling $\Delta T$, defined by the measured minimum temperature, is shown in the middle of Figure 4.9 for a pressure release of $p = 0.23(2)$ GPa. A maximal cooling of 0.15 K is observed. Keeping in mind the analogy in the phase diagram for uniaxial ($dT_N/dp = 8$ K/GPa [73]) and hydrostatic pressure ($dT_N/dp = 7$ K/GPa [61]) one may well expect a maximal cooling of the order of $\Delta T \approx 1$ K with respect to the uniaxial measurements. Furthermore taking into account the discrepancy between the measured and calculated uniaxial $\Delta T$ by a factor 2...3, one may estimate the intensive BCE $\Delta T$ reduced by a factor 14...21 due to the non-adiabaticity of the setup (compare sections 3.1.6 and 4.6). Note that despite the severe lack in the adiabaticity of this setup one may feel confident in the pressure applied to the sample: the analysis of both the critical temperature and the critical pressure for the BCE to vanish completely, agrees with $dT_N/dp = 7$ K/GPa.
4.2 The diluted system Ce\(_{x}(\text{La}, \text{Y})_{1-x}\) Sb

Measurements on the Ce\(_{0.85}(\text{La}, \text{Y})_{0.15}\) Sb system have been undertaken in order to lower the working temperature of the BCE (Fig. 4.10). The magnetic Ce ion is substituted by non-magnetic La and Y ions so that the lattice constant remains unchanged and to avoid internal strain in the compound. The observed BCE is found to be considerably smaller than for CeSb. Dilution with non-magnetic ions decreases the extensive BCE \(\Delta S\), which then most likely acts as the limiting factor for the intensive BCE in Ce\(_{0.85}(\text{La}, \text{Y})_{0.15}\) Sb. During the study of the Ce\(_{x}(\text{La}, \text{Y})_{1-x}\) Sb system as a possible candidate for the BCE, other interesting magnetic properties of this system were uncovered, which are summarized in a separate section. Part of what follows has been published in [66, 67].

4.2.1 The BCE in Ce\(_{0.85}(\text{La}, \text{Y})_{0.15}\) Sb

Figure 4.11 shows the intensive BCE of Ce\(_{0.85}(\text{La}, \text{Y})_{0.15}\) Sb measured on a single crystal of volume 1.66 \(\cdot\) 2.43 \(\cdot\) 2.60 mm\(^3\) with the uniaxial-setup introduced in section 3.1.3. The temperature was logged with an Au/Fe-Chromel thermocouple at a rate of 20 meas/sec. None of the presented values are corrected for the dynamics of the thermometry (section 3.1.5). The intensive BCE shows a saturation at \(p = 0.36\) GPa for which only two data points could be measured before the sample was crushed. The shift of the sharp right flank of \(-\Delta T(T)\) illustrates the shift in \(T_N\) with pressure. From the BCE measurements one finds \(dT_N/dp = 12(2)\) K/GPa assuming...
Figure 4.9: BCE measurements on CeSb under hydrostatic pressure. Top and middle: friction effect and observed cooling after a pressure release of \( p = 0.23 \text{ GPa} \) (defined by the maximum and minimum in \( T(t) \), respectively) [the lines are guides for the eyes]. Bottom: upper limits for the BCE to occur determined by varying pressure (temperature) at constant temperature (pressure), the line denotes a slope 7 K/GPa as expected from the phase diagram of CeSb under hydrostatic pressure.

linear dependence. Surprisingly, a cooling effect at temperatures below the ordering temperature at ambient pressure \( T_N(p = 0) = 8.0(1) \text{ K} \) is observed.

The saturation of the effect with pressure is indicative of an intensive BCE \( \Delta T_{ad} \) which is limited by the extensive BCE \( \Delta S_M \) rather than by the shift of \( T_N \) with pressure (Fig. 4.12). The weakened \( \Delta S_M \) seems to result from the dilution with nonmagnetic ions as well as from the continuous order character of the phase transition. The cooling observed within the ordered phase, i.e. for \( T < T_N(p = 0) \) indicates a reduction of the magnetic entropy with pressure down to the lowest temperatures, which could have its origin in a pressure-induced strengthening of the magnetic order. Indeed neutron diffraction and macroscopic measurements presented in the next section support this picture.
Figure 4.10: The chemical phase diagram of $\text{Ce}_x(\text{La},\text{Y})_{1-x}\text{Sb}$ established by macroscopic measurements ($c_p$, $\chi$) and neutron diffraction ($\mu$) [78] shows the characteristics of a dilute magnetic alloy with long-range order (LRO) and a spin-cluster (SG) region ($T_N$: Néel temperature, $T_f$: spin freezing temperature). The inset shows the general (schematic) $T - x$ phase diagram for a dilute magnetic alloy taken from Mydosh [81].

Figure 4.11: Observed BCE in $\text{Ce}_{0.85}(\text{La},\text{Y})_{0.15}\text{Sb}$ without corrections for the dynamics of the thermometry (inset: representative evolution of the sample temperature upon pressure release).
Figure 4.12: Schematics for the limiting factor of the intensive BCE in magnetically driven systems non-critical in \( p \). Left: The extensive BCE \( \Delta S_M \) is large enough, so that the intensive BCE \( \Delta T_{ad} \) is only limited by the shift in \( T_N \) (max[\( \Delta T_{ad} \)] = \( \Delta T_N \), e.g. in CeSb). Right: \( \Delta T_{ad} \) is restricted by the magnitude of \( \Delta S_M \) (max[\( \Delta T_{ad} \)] < \( \Delta T_N \), e.g. in Ce\(_{0.85}(\text{La,Y})_{0.15}\)Sb).

Figure 4.13: The relaxation rates \( \tau \) of the BCE in Ce\(_{0.85}(\text{La,Y})_{0.15}\)Sb are pressure-independent and nicely reflect the heat capacity of the sample as expected from the 1\( \tau \)-model.

The improved data acquisition rate allows for the evaluation of the relaxation rate \( \tau \) originating from the thermal coupling between the sample and its environment. Measurements at different exchange gas pressures within the cryostat have shown that the relaxation is not dominated by the coupling via the exchange gas but rather by the direct coupling with the socket and the piston.\(^9\) The observed relaxation rates are shown in Figure 4.13. They show no pressure-dependence and reflect directly the heat-capacity of the sample as expected from the 1\( \tau \)-model (section 3.1.5, Eq. (3.5)).

\(^9\)The data acquisition rate did not allow for the evaluation of the fast relaxation \( \tau_2 \). Consequently, the measurements are discussed within the 1\( \tau \)-model introduced in section 3.1.5.
4.2.2 Spin-cluster behavior in Ce$_x$(La,Y)$_{1-x}$Sb for $x \leq 0.85$

Additional macroscopic measurements as well as neutron diffraction measurements have shown signatures of a spin-cluster state developing for $x < 0.85$. The left of Figure 4.14 shows the specific heat divided by temperature for $x = 1.0, 0.85$ and 0.7. Aside a shift of the peak in $c_p$, the $x = 0.85$ sample shows a pronounced linear term in $c_p$ ($\gamma \approx 450$ mJ/K$^2$mol). The large $\gamma$ value may be indicative of spin-glass behavior. Indeed measurements of the DC magnetization show a difference in the field-cooled and zero-field-cooled cases implying a frustrated magnetic ground-state (right side of Fig. 4.14).\(^\text{10}\) AC magnetization measurements on $x = 0.7$ and $x = 0.85$ show a cusp in the real and imaginary part of the susceptibility $\chi$. Figure 4.15 shows this AC cusp at different frequencies of the AC field for the $x = 0.7$ sample. The cusp is found to shift with increasing frequency to higher temperatures. Similar results are found for the $x = 0.85$ sample. An AC cusp with such frequency dependence is indicative of spin-glass or spin-cluster behavior [81].\(^\text{11}\) The temperature for the AC cusp to occur is referred to as the spin freezing temperature $T_f$. The observed frequency dependence of the AC cusp can be fitted by an activated behavior, as shown by the plot of $1/T_f$ vs log($f$) (inset of Fig. 4.15). The relative fractional change in $T_f$ per decade change in the frequency is found $\Delta T_f / (T_f \Delta \log_{10} f) = 0.018(2)$. This value is comparable to values found for other spin-glass and spin-cluster systems [81]. Another feature indicative for spin-cluster behavior can be found in the time dependence of the thermoremanent static susceptibility (Fig. 4.16). The sample is first cooled within a DC field $H_{fc}$ down to a temperature $T_0 < T_f$. Subsequently the field is switched off and the static susceptibility is measured at constant temperature $T_0$. For a spin glass the

\(^{10}\) In CeSb the observed frustration is accompanied with a modest $\gamma$.

\(^{11}\) The terms spin glass and spin clusters are used in the context of highly diluted paramagnetic systems and systems with magnetic short range order, respectively.
Figure 4.15: Frequency dependence of the AC cusp in Ce$_{0.7}$(La,Y)$_{0.3}$Sb (amplitude of AC field $h = 5$ Oe).

Figure 4.16: Log-Log plot of the thermoremanent static susceptibility $\chi_{DC} \equiv M_{DC}/H$ vs time in Ce$_{0.7}$(La,Y)$_{0.3}$Sb after field-cooling in a DC field $H_{fc}$ ((a): $H_{fc} = 200$ Oe, $T_0 = 3$ K, (b): $H_{fc} = 200$ Oe, $T_0 = 2$ K, (c): $H_{fc} = 50$ Oe, $T_0 = 3$ K, (d): $H_{fc} = 50$ Oe, $T_0 = 2$ K).

magnetization is expected to decay according to a power law [82]. Figure 4.16 illustrates that the spins show a slower dynamic at $T_0 = 2$ K than at $T_0 = 3$ K and that the decay rate is an inherent property of the system independent of the magnitude of the cooling field. Last but not least, the observed dependence of $T_N$ and $T_f$ upon the degree of dilution shows characteristics typical for systems developing a spin-glass or spin-cluster state (Fig. 4.10) [81]. The classification of Ce$_x$(La,Y)$_{1-x}$Sb ($x \leq 0.85$) being a spin-cluster system is well in accordance with the observation of short-range order accompanied by large spin fluctuations as pointed out by Hälg [72].

In order to investigate the influence of uniaxial pressure on the magnetism of
these diluted systems, neutron diffraction experiments have been carried out on the single-crystal diffractometer TriCS (SINQ). The same sample setup as for the measurement of the BCE has been used, except that the socket and piston have been made of vanadium and carefully shielded with cadmium. The geometrical setting allowed for the measurement of scans along \([11q_0]\) which are shown in Figure 4.17 for three different pressures \(|[001]\) at \(T = 2\) K. No indications for a magnetic ordering into the AF-IA or AF-I state could be observed, instead the sample orders in a modulated structure characterized by \(q_0\). Pressure is found to increase the magnetic peak substantially at modest pressures and to shift the modulation to slightly lower \(q_0\). This finding is in accordance with the observation that the \(x = 0.85\) sample is on the border between long-range and short-range order. Uniaxial pressure increases the magnetic exchange and eventually allows the system to develop long-range order. On the other hand, the applied uniaxial pressure is not found to suppress quadrupolar ordering strong enough to allow AF-I order. Hence the pressure-induced strengthening of the magnetic ordering observed in this experiment may well explain the observed BCE at \(T \ll T_N\) in Ce\(_{0.85}\)(La,Y)\(_{0.15}\)Sb (Fig.4.11). The temperature evolution of the \([11q_0]\) peak at different pressures allows the determination of \(dT_N/dp = 12.4 \pm 1.2\) K/GPa which is in good agreement with the value estimated from the BCE measurements \((dT_N/dp = 12(2)\) K). The pressure-dependence of \(T_N\) is hence found to be somewhat larger than for CeSb \((8\) K/GPa).
4.3 HoAs

In the rare-earth monopnictide HoAs a combination of magnetically and structurally driven BCE has been found for the first time. The latter results from the tetragonal distortion induced by uniaxial pressure. The experimental data could be explained in terms of mean-field calculations and the extended point-charge model for the distorted CEF. Part of what follows has been published in [83].

4.3.1 Introduction

HoAs crystallizes in the cubic rock-salt structure $Fm\bar{3}m$ \((a = 5.771 \text{ Å})\) and orders below $T_N = 4.3(1) \text{ K}$ in the antiferromagnetic type-II structure with the moments aligned along the cube edges [84, 85]. Like for most of the rare-earth monopnictides pressure is expected to increase $T_N$ [86]. To the knowledge of the author the CEF splitting of HoAs has not yet been investigated by inelastic neutron scattering (INS). As the CEF is crucial for the understanding of the BCE, INS measurements of the CEF have been carried out, which will be briefly presented in the next section before the BCE is discussed.

4.3.2 Inelastic neutron scattering measurements of the CEF

The INS measurements of the CEF in HoAs have been performed on Drüechal (SINQ) and on IN12 (ILL, France). Measurements on a single crystal \((3 \cdot 4.4 \cdot 4.8 \text{ mm}^3)\) were carried out in the paramagnetic state at $T = 10 \text{ K}$ and in the ordered state at $T = 1.5 \text{ K}$ with fixed analyzer energy. Higher order contamination was suppressed by a cooled Be filter after the sample.

In the paramagnetic state two unresolved broad shoulders at $\pm 0.2$ and $\pm 0.4 \text{ meV}$ appear with a further peak near $10 \text{ meV}$ (Fig. 4.18). Between 1 and $6 \text{ meV}$ no inelastic scattering could be observed. In the ordered state inelastic intensity is observed at $0.8\ldots1.4 \text{ meV}$ and at $1.8 \text{ meV}$. In all these experiments no dispersion of the peaks was found within the experimental accuracy.

The observed data were analyzed by a least-squares fitting procedure (solid line in Fig. 4.18) assuming a Hamiltonian resulting (from the cubic CEF interaction and the molecular field (quantized along [001]) \((2.40,2.41)\):

$$
\mathcal{H} = B_4 (\hat{O}_2^4 + 5\hat{O}_4^4) + B_6 (\hat{O}_6^6 - 21\hat{O}_6^4) - \lambda_D \langle \hat{J}_z \rangle \hat{J}_z - \lambda_Q \langle \hat{O}_2^6 \rangle \hat{O}_2^0
$$

The resulting CEF and molecular-field parameters are listed in Table 4.2. The CEF parameters found for the paramagnetic data set \((T = 10 \text{ K})\) are in good agreement with the values extrapolated from HoP [79] using (2.49): $B_4^{\text{extrap}} = -2.79 \cdot 10^{-4} \text{ meV}$ and $B_6^{\text{extrap}} = -3.7 \cdot 10^{-7} \text{ meV}$. Deviations are explained by different degrees of screening of the CEF by the conduction electrons in the two compounds. The lowest six CEF states are calculated to be a $\Gamma_3^{(2)}$ ground-state doublet, a $\Gamma_4^{(2)}$ triplet at $0.20 \text{ meV}$ and a $\Gamma_1$ singlet at $0.63 \text{ meV}$ (Fig. 4.20); higher levels are at $9.8$, $10.1$, $12.8$ and $13.1 \text{ meV}$. In the magnetically ordered state \((T = 1.5 \text{ K})\) the observed intensity around $1.8 \text{ meV}$ can only be explained by the presence of a quadrupolar field, as the matrix element for this transition would be too weak if only dipolar interaction was
considered. Nevertheless the large $B_6$ found for this data set is questionable and all further calculations are based on the first CEF set; i.e. $B_4 = -3.02 \cdot 10^{-4}$ meV and $B_6 = -3.87 \cdot 10^{-7}$ meV.

### 4.3.3 Barocaloric Effect

For the measurement of the BCE a cubic crystal of 3 mm side length was placed in the uniaxial pressure device described in section 3.1.3. The temperature was tracked with an Au/Fe-Chromel thermocouple at 20 meas/sec. Figure 4.19 shows the uncorrected\textsuperscript{12} BCE as a function of initial temperature for a pressure release up to 0.3 GPa. The maximal cooling $-\Delta T$ increases almost linearly with pressure and is shifted to higher temperatures $T$. At higher pressures a pronounced shoulder at the high temperature side appears up to around 18 K.

### 4.3.4 Discussion

From measurements on CeSb it is known that the peak position of the BCE can be assigned to the Néel temperature $T_N(p > 0)$ (see previous two sections). Thus for HoAs a pressure dependence of $dT_N/dp \approx 7.6$ K/GPa can be estimated from Figure 4.19. The broad shoulder at the high temperature side cannot be explained by a magnetically driven BCE, i.e. by phase transition from the ordered to the disordered state, as the sample remains in the disordered state at any given time.

\textsuperscript{12}uncorrected with respect to the dynamics of the thermometry (see section 3.1.5)

---

Figure 4.18: Energy spectra of HoAs in the paramagnetic and ordered state (fit with parameters from Table 4.2).
Figure 4.19: Measured BCE together with a model calculation (CEF parameters from Table 4.2 (1st set), $T_N = 5.9, 6.7$ K, $\lambda_D = 19.3, 20.5$μeV, $\lambda_Q \equiv 20$ neV for the 0.2 and 0.3 GPa data set, respectively).

Table 4.2: CEF parameters of HoAs: non-distorted ($t = 0$) values from INS measurements, distorted values ($t > 0$) from extended point-charge model (values in brackets from Eq. (4.7)) [all values in meV].

<table>
<thead>
<tr>
<th></th>
<th>INS $T = 10$ K</th>
<th>INS $T = 1.5$ K</th>
<th>calc. $t = -0.2%$</th>
<th>calc. $t = -0.3%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0^0 \cdot 10^4$</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$B_0^0 \cdot 10^4$</td>
<td></td>
<td>$-3.02(5)$</td>
<td>$-3.03(5)$</td>
<td></td>
</tr>
<tr>
<td>$B_4^0 \cdot 10^3$</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$B_4^0 \cdot 10^7$</td>
<td></td>
<td>$-3.87(30)$</td>
<td>$-4.66(30)$</td>
<td></td>
</tr>
<tr>
<td>$B_6^0 \cdot 10^6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_D \cdot 10^3$</td>
<td>$8.0(1)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_Q \cdot 10^5$</td>
<td>$3.9(1)$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However the application of uniaxial pressure $p$ along [001] leads to a tetragonal distortion. The change in symmetry from $Fm\bar{3}m$ to $I4/mmm$ alters the splitting of the CEF levels and thus influences the magnetic entropy.\(^{13}\)

\(^{13}\)Note that in the case of CeSb, the tetragonal distortion does not influence the BCE, as the ground state remains a Kramers doublet and only the excited quartet at 37 K gets split into two doublets, which however has minor influence upon the entropy at low temperatures.
Influence of the structural distortion on the magnetic entropy

The distortion upon uniaxial pressure is quantified by

\[ t \equiv \frac{c-a}{a} = \Delta \left( \frac{c}{a} \right) \]

with \( a \) and \( c \) being the lattice parameters. It can be calculated within the theory of elasticity. Generally, the dilatation \( \epsilon \) is given by the tensor product of the elastic constants \((c_{ij})^{-1}\) and the strain \( \sigma \)

\[ \epsilon = (c_{ij})^{-1} \cdot \sigma \]

which in the case of cubic symmetry and uniaxial pressure along the \( c \) axis reads

\[
\begin{pmatrix}
  c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\
  c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\
  c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\
  0 & 0 & 0 & c_{44} & 0 & 0 \\
  0 & 0 & 0 & 0 & c_{44} & 0 \\
  0 & 0 & 0 & 0 & 0 & c_{44}
\end{pmatrix}^{-1}
\begin{pmatrix}
  0 \\
  0 \\
  -p \\
  0 \\
  0 \\
  0
\end{pmatrix}
= \begin{pmatrix}
  \frac{c_{12}}{\%} \\
  \frac{c_{12}}{\%} \\
  \frac{-(c_{11}+c_{12})}{\%} \\
  0 \\
  0 \\
  0
\end{pmatrix} \cdot p
\]

where \( \% \equiv c_1^2 + c_{11}c_{12} - 2c_{12}^2 \). In the limit of small tetragonal distortion (i.e. almost cubic symmetry) the change in \( c/a \) is hence

\[ \Delta \frac{c}{a} = 1 - \frac{1 + \epsilon_3}{1 + \epsilon_1} \approx - \frac{c_{11} + 2c_{12}}{\%} \cdot p \]

(mixed terms in \( p \) and \( c_{ij} \) are neglected as \( p \ll c_{ij} \)). With \( c_{ij} \) values found from literature for other monopnictides (ErSb, PrSb, YbAs) \[87\] one finds \( t \approx -0.8 \) %/GPa.\(^{16}\)

The structurally induced changes of the CEF can now be estimated based on the non-distorted CEF. In tetragonal symmetry five independent CEF parameters have to be considered because \( B_0^2 \) now differs from zero and the relations \( B_4^4 = 5B_0^4 \) and \( B_6^4 = -21B_0^6 \) \[2.40\] no longer hold. The five CEF parameters can be estimated based on the extended point-charge model introduced in section 2.4.4. In the first step, the model was used to parametrize the observed non-distorted CEF. The only free parameter accounts for the screening parameter \( k_0 \), while the charges of the ions were kept fixed at \( \pm 3 e^- \). The calculation was performed over a neighborhood of \( d = 15 \) Å. In the second step, the model was fed the positions of the ions in the tetragonal distorted structure and \( k_0 \) fixed to the value from the \( p = 0 \) parametrization.\(^{17}\) Within \( t < 1\% \) the resulting CEF parameters show a linear dependence upon \( t \) and may serve as an estimation for the CEF under uniaxial pressure. The corresponding values are listed in Table 4.2. The strongest impact on the CEF is from the non-zero \( B_0^2 \) which is responsible for the additional splitting of the CEF states, while the increase in the \( B_0^6 \) parameter predominantly affects the scaling of the CEF. The level scheme of the six lowest energy states at \( t = 0 \) and \( t = -0.3 \% \) is depicted on the right side of Figure 4.20. The ground-state doublet \( \Gamma_3^{(2)} \) is split into two separate singlet states and the triplet state \( \Gamma_4^{(2)} \) into a singlet and a doublet. The resulting magnetic entropy (Eq. 2.42) is significantly reduced and hence explains the BCE above the Néel point (Fig. 4.20 and inset).

\(^{14}\)\( \epsilon \) and \( \sigma \) are tensors of rank 2, \((c_{ij})^{-1}\) is a tensor of rank 4.

\(^{15}\)Hydrostatic pressure \( \rightarrow \sigma = (-p, -p, -p, 0, 0, 0) \).

\(^{16}\)\( c_{11} = 12.4 \cdot 10^{10} \) Pa, \( c_{12} = 1.4 \cdot 10^{10} \) Pa, \( c_{44} = 2.0 \cdot 10^{10} \) Pa.

\(^{17}\)In doing so the effect of the pressure is limited to a change in geometry only and all its effects on the electronic properties are neglected.
The intensive BCE \( -\Delta T \) may now be calculated by solving the adiabatic equation (2.5) for the total entropy \( S = S_M + S_L + S_E \) including phononic and electronic contributions. The phononic part is modelled by the Debye function (2.28) using \( \Theta_D = 230 \) K extrapolated from non-magnetic LaAs and LuAs [88]. The electronic contribution is assumed to be linear at low temperatures with \( S_e = \gamma \cdot T \) and \( \gamma \approx 10 \) mJ/K\(^2\)mol ([74, 88]). Both contributions are only weakly pressure dependent and elastic heating may well be neglected in this temperature range (sections 2.4.2 and 4.4). The solid line in Figure 4.19 shows the best fit, which well explains the shape of the BCE - except close to the magnetic phase transition temperature, where fluctuation phenomena must be considered too. As in the case of CeSb the observed values of the BCE are considerably smaller than the calculated ones (i.e. in Fig. 4.19 the calculation has been downscaled by 0.25 to fit the observed data). Note that the present data acquisition rate did not allow for the correction of the dynamics of the measurement (section 3.1.5).
Figure 4.21: Contour plots of the structurally driven BCE in function of $B_2^0$ and temperature for increasing tetragonal distortion $t$, i.e., pressure ($B_m^4$ and $B_m^6$ from Eq. (4.7), contour level spacings are 0.5 K). The experimental observation of the BCE is only in agreement with negative $B_2^0$. The extended point-charge model also yields $B_2^0 < 0$.

Another interesting point has emerged from the comparison between the CEF parameters for $t < 0$ predicted by the point-charge model and the experimentally observed BCE. The exact splitting of the six lowest energy levels is governed by $B_2^0$ while all other CEF parameters play a minor role. As these states constitute the thermally active levels their respective positions are crucial for the temperature dependence of the magnetic entropy and hence they "shape" the BCE above $T_N$. On the other hand one of the obvious weaknesses of the point-charge model is the difficulty in accurately predicting $B_2^0$ as this parameter probes the charge distribution over a large neighborhood $\propto r^{-(2+1)}$ (section 2.4.4). While for the above problem the perturbation from cubic symmetry is very small, the quantitative prediction of the $B_2^0$ parameter must be considered a tough task for the general case by means of the point-charge model (even for the sign of $B_2^0$). The close relation between $B_2^0$ and the (structurally driven) BCE may serve though to cross-check the predictions of the point-charge model as shown in the following. On the basis of a point-charge model, which takes only nearest neighbors into account, an analytical expression for the CEF Hamiltonian of a slightly tetragonal distorted, cubic system can be found [89, 90]:

$$\hat{H}(C_{4h}) = B_2^0 \hat{O}_2^0 + B_4^0 \left[ (1 - \frac{10}{3} t) \hat{O}_4^0 + 5 \hat{O}_4^1 \right] + B_6^0 \left[ (1 - \frac{28}{3} t) \hat{O}_6^0 - 21 \hat{O}_6^1 \right]$$  (4.7)

with $B_2^0 \neq 0$. The resulting values for $B_4^0$ and $B_6^0$ are included in Table 4.2 (values in brackets). The value of $B_2^0$ remains undetermined by this model. With the observed structurally driven BCE in HoAs one may though interfere the size and the sign of this parameter. Figure 4.21 depicts contour plots of the calculated, structurally driven part of the BCE for different degrees of distortion $t = 0, -0.2$ and $-1.0\%$ in function of $B_2^0$ and temperature. The values for the other CEF parameters are
taken from (4.7). Only a negative $B_{2}^{0}$ leads to an increase of the BCE with increasing distortion, while a positive value yields a weakening of the BCE. Therefore from the observed structurally driven BCE in HoAs one may conclude that the tetragonal distortion $t < 0$ leads to a negative $B_{2}^{0}$ in HoAs, which is in complete agreement with the calculations on basis of the extended point-charge model.
4.4 The missing BCE in YbAs

The monopnictide YbAs is another interesting candidate for the BCE. The cubic $Fm\bar{3}m$ compound orders below $T_N = 0.5$ K in the antiferromagnetic type-III structure. It shows heavy fermion behavior ($\gamma = 270$ mJ/molK$^2$) accompanied by short range magnetic correlations far above $T_N$ ([91] and references therein). The CEF splitting constitutes of a $\Gamma_6$ ground-state doublet with an excited $\Gamma_8$ quartet and $\Gamma_7$ doublet at 220 K and 430 K, respectively [92]. Measurements of the electrical resistivity $\rho$ under hydrostatic pressure revealed a clear bend around 10 K at 0.75 GPa, which in [91] has been attributed to an anomalous enhancement of $T_N$ with pressure.

A large pressure dependence of the ordering temperature would make this compound an ideal candidate for a magnetically driven BCE. The corresponding large Zeeman splitting of the ground-state doublet would result in a considerable extensive BCE $\Delta S_M$, while the very low ordering temperature at ambient pressure would not limit the intensive BCE $\Delta T_{ad}$ as is the case for CeSb and HoAs.

BCE measurements have been carried out on a single crystal of YbAs (2.86 · 2.88·3.01 mm$^3$) with the very same setup as for the measurements on HoAs (section 3.1.3). However measurements in the temperature region between 1.7 K and 20 K with uniaxial pressures of up to 0.75 GPa did not show any trace of a BCE. On the contrary, a small heating is observed with the release of pressure which gains in magnitude with decreasing temperature or increasing pressure. The temperature and the pressure behavior of this heating effect are characteristic of friction presumably originating from the interface between the sample and the socket and the sample and the piston, respectively. Assuming that pressure releases a friction heat $Q_f$ independent of temperature, the corresponding signature in the sample temperature is (2.6)

$$\Delta T_f = \frac{Q_f}{C} \quad (4.8)$$

where $C$ denotes the heat capacity of the sample. Note that $\Delta T_f$ is diverging as $T$ approaches zero ($C \to 0$). Figure 4.22 shows the heating originating from friction at 2 K in function of the applied pressure. At $T = 20$ K neither heating nor cooling is observed, indicating that elastic heating, if present, contributes to less than 0.05 K.\textsuperscript{18}

The lack of any effective cooling down to $T = 1.7$ K clearly demonstrates that the ordering temperature $T_N$ is not sufficiently shifted by pressure, i.e. $T_N < 1.7$ K for $p \leq 0.75$ GPa. However uniaxial pressure may well lead to different effects than hydrostatic pressure does. Also note that a structurally driven BCE originating from a pressure-induced tetragonal distortion is absent in YbAs as the doublet-ground state of the Kramers ion Yb$^{3+}$ cannot be split by means of a structural change and because the quartet is well separated.

Though not fulfilling the necessary properties for a BCE, YbAs has served well in estimating the contributions from friction and elastic heating for all the other BCE measurements under uniaxial pressure done throughout this work. Both contributions are found to be very small within the temperature range of 2 K < $T < 20$ K

\textsuperscript{18}the relative temperature accuracy for this measurement
Figure 4.22: Friction effect $\Delta T_f$ in YbAs at $T = 2$ K. Teflon disks of 0.1 mm thickness were placed in between the sample and the socket or piston, respectively (section 3.1.3).

for $p < 0.4$ GPa.\textsuperscript{19}

A later published report [93] about neutron scattering measurements on YbAs under hydrostatic pressure up to 0.75 GPa has indeed stated no indications for a long range magnetic order in YbAs above 1.4 K and hence leaves the explanation of the bend in the $\rho(T)$ curve of [91] unexplained.

\textsuperscript{19}typically for uniaxial setup: $|\Delta T_{ela}| \leq 0.05$ K at $T \leq 20$ K and $p \leq 0.7$ GPa; $\Delta T_f \leq 0.05$ K at $T \geq 5$ K and $p \leq 0.7$ GPa
4.5 Ce$_3$Pd$_{20}$Ge$_6$

The Kondo lattice compound Ce$_3$Pd$_{20}$Ge$_6$ represents the first heavy-fermion system with an observed BCE. After isothermal application of uniaxial pressure the compound shows cooling by as much as -0.75 K per 0.3 GPa pressure release at 4.4 K. Based on entropy considerations the observed cooling effect can be explained by an increase of the Kondo temperature and by a structurally induced splitting of the $\Gamma_8$ ground-state quartet upon uniaxial pressure. Part of what follows has been published in [94].

4.5.1 Introduction

The metallic Kondo compound Ce$_3$Pd$_{20}$Ge$_6$ with a Kondo temperature $T_K$ of several Kelvin crystallizes in the cubic space group $Fm\bar{3}m$, structure type $C_6C_{23}$, with the Ce ions occupying two different crystallographic sites (4a) and (8c) of cubic point-symmetry. The compound shows ferroquadrupolar ordering at $T_Q = 1.25$ K and antiferromagnetic dipolar ordering below $T_N = 0.75$ K. At low temperatures the specific heat divided by temperature $C/T$ is very much enhanced with values up to $8 \text{ J/(mol Ce K}^2)$ [95, 96]. For both crystallographic sites (4a) and (8c) the ground state $J$-multiplet of the Ce$^{3+}$ Kramers ion is split by the CEF into a quartet ground-state $\Gamma_8$ and a doublet state $\Gamma_7$ at $\Delta_{CEF} = 60 \text{ K}$ and $\Delta_{CEF} = 46 \text{ K}$, respectively [97]. The rare case of a quartet ground-state for the Ce$^{3+}$ ion with a correspondingly large magnetic entropy makes this compound a promising candidate for the BCE. However a deficiency in magnetic entropy characteristic of Kondo compounds is apparent in Ce$_3$Pd$_{20}$Ge$_6$ from specific heat measurements by Kitagawa et al. [95] (Fig. 4.23). The magnetic entropy $S_{\Gamma_8} = R \ln 4 = 11.53 \text{ J/(mol Ce K}^2)$ associated with the $\Gamma_8$

![Figure 4.23: Magnetic entropy of Ce$_3$Pd$_{20}$Ge$_6$ determined experimentally by integration of $C_M(T)/T$ (non-magnetic entropy subtracted by the measurement of La$_3$Pd$_{20}$Ge$_6$). Note that not until 11 K is the magnetic entropy associated with the quartet ground-state reached (data from Kitagawa et al. [95]).](image)
ground state is not reached until $T > 11$ K.

Uniaxial pressure on a single crystal of Ce$_3$Pd$_{20}$Ge$_6$ is expected to have two effects on the magnetic entropy:

1. uniaxial pressure along [111] will result in a trigonal distortion of the crystal and hence to the splitting of the $\Gamma_8$ ground state into two doublet states,$^{20}$

2. the pressure-induced reduction in cell volume is expected to increase the $4f$−$sd$ hybridization and hence to enlarge $T_K$ (section 2.4.3 and [23]).

4.5.2 Direct observation of the intensive BCE

A single crystal grown by the Czochralski pulling method and cut by spark erosion into a cylinder of 2.77 mm diameter and 2.46 mm height along [111] was prepared for the BCE measurements. The standard setup described in section 3.1.3 was used with the exception that instead of Teflon disks a thin foil of tin was placed between the sample and the socket and the sample and the piston, respectively. The temperature of the sample was measured by an Au/Fe-Chromel thermocouple at a rate of 20 meas/sec. The measured cooling effect is shown in Figure 4.24 at $T = 2.83$ K for a pressure release of $p = 0.30(2)$ GPa.

Note that the measured temperature does not drop down instantaneously with the release of the pressure (black arrow), but rather continuously decreases until a minimum in temperature (gray arrow) is reached. The relatively slow relaxation rates in this sample make it possible to correct the measured BCE for the dynamics of the thermometry by means of the 2$\tau$-model described in section 3.1.5. The solid

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$^{20}$A similar splitting of the CEF induced by a structural distortion is observed in HoAs (section 4.3).
Figure 4.25: Experimentally determined and calculated temperature dependence of the BCE for a pressure release of $p = 0.3$ GPa in function of initial temperature $T_0$ (values for calculation listed in Table 4.3).

line in Figure 4.24 shows that this model indeed well describes the evolution of the thermocouple temperature and yields the effective (though not directly measurable) cooling effect $\Delta T$ of the sample. Figure 4.25 shows the cooling effect $\Delta T$ corrected by (3.13) and (3.14) as a function of the initial temperature $T_0$ when pressure is released. Cooling up to about $T_0 = 12$ K with a maximum of -0.75 K at 4.4 K and 0.3 GPa pressure release could be observed. The relaxation rate $\tau_1$ is found to reflect the specific heat of the sample for $T > 4$ K in analogy to the $1\tau$-model and varies between $\approx 0.2$ s and $\approx 0.5$ s ($T = 4$ K and 14 K, respectively). The relaxation rate $\tau_2$ associated with the heat load of the temperature sensor decreases from $\approx 0.1$ s to $\approx 0.04$ s within $T = 4$ K and 14 K, respectively.

4.5.3 Discussion

The observed BCE may be modelled taking into account issues specific for the magnetic entropy in Kondo systems. The deficiency in magnetic entropy (Fig. 4.23), which is characteristic for all Kondo systems, can be accounted for by the resonance-level model introduced by Schotte and Schotte [98].

The resonance-level model for Kondo systems

Schotte and Schotte [98] have proposed a model which is able to describe the basic thermodynamic properties of a Kondo system like specific heat, magnetization and magnetic susceptibility. Their model considers an arbitrary impurity spin $S$ in a Kondo system like e.g. the AgFe dilute alloy. With respect to the impurity spin $S$ the model assumes the Kondo effect to result in a resonance of Lorentzian shape and width $\Delta_K$ at the Fermi energy, where $\Delta_K$ turns out to be of the same order as the Kondo energy $kT_K$. Vice versa the resonance at the Fermi energy results in an effective dynamical broadening of the energy levels of the spin $S$ system with an
associated free energy of

\[ F_{2S+1} = -kT \int_{-\infty}^{\infty} \frac{(\Delta K/\pi)de}{e^2 + \Delta K^2} \ln \left( \sum_{-S}^{S} \exp(eS/kT) \right). \]  

(4.9)

This expression is readily recognized as a generalization of the free energy of a system with \( 2S + 1 \) discrete energy levels (2.23). With the formulation of the free energy the thermodynamic properties of the system are defined and can be calculated with the appropriate thermodynamic relations. The associated magnetic entropy is hence given by

\[ S_{2S+1} = -\frac{\partial}{\partial T} F_{2S+1} \]  

(2.24).

The above model may now be adapted for the case of \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) including the CEF. In the non-distorted case (\( p = 0 \)) the \( \Gamma_8 \) ground state may be treated as an effective \( S = 3/2 \) system neglecting the higher \( \Gamma_7 \) doublet as it is almost unpopulated for \( T < 20 \) K (for either site of the \( \text{Ce}^{3+} \) ion). In the distorted case the effective \( S = 3/2 \) system (i.e. the quartet \( \Gamma_8 \)) is split into two doublets with \( S = \pm 1/2 \) and \( S = \pm 3/2 \) states separated by the energy \( \Delta_d \). Hence (4.9) may be generalized to

\[ F_{\text{CEF}} = -kT \int_{-\infty}^{\infty} \frac{(\Delta K/\pi)de}{e^2 + \Delta K^2} \ln \left( \sum_{i=1}^{6} \exp(-E_i/kT) \right). \]  

(4.10)

with

\[ E_{1,2} = -\frac{\Delta_d}{2} \pm \frac{1}{2} \epsilon, \]  

(4.11)

\[ E_{3,4} = +\frac{\Delta_d}{2} \pm \frac{3}{2} \epsilon, \]  

(4.12)

\[ E_{5,6} = \Delta_{\text{CEF}}. \]  

(4.13)

\( E_{5,6} \) have been included for the sake of completeness and in order to describe \( S_{\text{CEF}} = -\frac{\partial}{\partial T} F_{\text{CEF}} \) correctly for high temperatures. The influence of the Kondo effect on these two states may though be neglected as \( \Delta_{\text{CEF}} \gg \Delta_K \).

**The model for the BCE in \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \)**

The actual calculation of the total entropy \( S \) in \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) at ambient and elevated pressure is based on \( c_p \) measurements of \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) and \( \text{La}_3\text{Pd}_{20}\text{Ge}_6 \) at ambient pressure by Kitagawa et al. [95].

In the first step the non-magnetic contributions were determined by fitting \( c_p(\text{La}) = \gamma(\text{La})T + \beta(\text{La})T^3 \) on the \( c_p \) data of \( \text{La}_3\text{Pd}_{20}\text{Ge}_6 \). In the second step the experimentally determined magnetic entropy of \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) obtained by integration of \( (c_p(\text{Ce}) - c_p(\text{La}))/T \) (Fig. 4.23) was fitted with \( S_M = \delta \gamma \cdot T + S_{\text{CEF}} \) yielding \( \Delta_K \) and \( \delta \gamma \equiv \gamma(\text{Ce}) - \gamma(\text{La}). \)\(^2\) The non-magnetic and the magnetic entropy add up to the total entropy of \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) for \( p = 0 \) shown in Figure 4.26 and compared with experimental values.

Finally the total entropy at \( p > 0 \) has been modelled to account for the observed BCE using the adiabatic equation (2.5). The only free parameters at this stage are \( \Delta_K \) and \( \Delta_d \). \( \gamma \) and \( \beta \) are assumed to be independent of pressure, the latter

\(^2\)Note that in this context the excess contribution in the electronic term of the entropy \( \delta \gamma \cdot T \) (compared to non-magnetic \( \text{La}_3\text{Pd}_{20}\text{Ge}_6 \)) is also associated with the magnetic entropy \( S_M \).
implies that elastic cooling/heating is neglected (section 2.4.2 and 4.4). The best fit is shown in Figure 4.25 with the total entropy at $p > 0$ shown in Figure 4.26, the corresponding parameters are listed in Table 4.3.

The model overestimates the BCE for $T \leq 3$ K as it does not take into account any short range order effects of the quadrupolar and dipolar moment. Note that with $\Delta_d < 0$ the trigonal distortion realizes a $S = \pm 3/2$ ground-state doublet for $p > 0$. The increase of the Kondo temperature by about 20 % is a direct consequence of the strengthened 4f conduction-band hybridization with decreasing cell volume how it is generally observed in Kondo lattice compounds (section 2.4.3 and e.g. [23, 99]).

In conclusion the pressure-induced reduction of the magnetic entropy in Ce$_3$Pd$_{20}$Ge$_6$ leading to a BCE is found to be caused by two factors, namely by a strengthening of the Kondo effect and by the splitting of the ground-state quartet due to a pressure-induced structural distortion. The two ordering temperatures $T_N$ and $T_Q$ do not shift to above $T = 1.5$ K for uniaxial pressure $p \leq 0.3$ GPa.

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Note that uniaxial pressure generally leads to a reduction of total volume as can be seen from (4.5).
4.6 EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$

Valence transitions represent another type of phase transition well-known to exhibit a strong pressure dependence due to the different radii of the ion in the respective valence states. Eu compounds are especially well suited for a valence driven BCE as the change from divalent magnetic Eu$^{2+}$ to trivalent non-magnetic Eu$^{3+}$ implies drastic changes in the magnetic entropy. The Eu compound EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ allows pressure-induced valence transitions at comparatively low pressures and temperatures. It constitutes the first system where a valence driven BCE could be observed. Unfortunately, up to now no single crystal samples were available for uniaxial BCE studies and the measurements under hydrostatic conditions have shown a severe lack in the adiabaticity of the setup. Therefore the directly observed BCE is reduced by more than an order of magnitude compared to what is expected from calculations.

4.6.1 Introduction

Among the Eu compounds with an intermediate valence regime and a strongly temperature dependent valence, EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ shows a very sharp and almost complete valence transition [100]. In the ternary compounds ErNi$_2$Ge$_2$ and ErNi$_2$Si$_2$, the Eu ion is found in the magnetic divalent ($4f^7 8S_7/2$) and non-magnetic trivalent ($4f^6 7F_0$) state, respectively. Both compounds realize the tetragonal ThCr$_2$Si$_2$ structure type (space group $I4/mmm$). The pseudo-ternary compounds EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$, exhibit Eu$^{2+}$ ions with antiferromagnetic ordering for $T < 40$ K at Si concentration $x < x_c$ ($x_c \approx 0.15$), while for $x \geq x_c$ an intermediate valence regime with strongly temperature dependent valence is observed.

It was first demonstrated by Abd-Elmeguid et al. [101] on Eu(Pd$_{1-x}$Au$_x$)$_2$ that pressure may lead to a collapse of magnetic order as it destabilizes the Eu$^{2+}$ state and shifts the valence towards 3. In EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ the pressure dependence of the valence transition was first studied by Wada et al. [102] for $0.10 \leq x \leq 0.15$ by means of electrical resistivity measurements. Hydrostatic pressure $p$ was found to have the same effect as Si doping $x$, i.e. chemical pressure.$^{23}$ Hence a generalized $(x, p)$-$T$ phase diagram can be drawn for EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ as shown in Figure 4.27. The temperature-induced transition was found to be of first order for $p$ close to the critical pressure and continuous for larger $p$. The pressure dependence of the valence transition temperature $T_v$ is linear with $dT_v/dp = 105$ K/GPa. In the intermediate valence regime the occupation probabilities for the Eu$^{2+}$ and Eu$^{3+}$ may be described by the interconfigurational fluctuation model [103]. Experimentally, XAS measurements on EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ estimate the mean valence of Eu to change from $\approx 2.2$ to $\approx 2.85$, for $x \approx 0.2$ [104]. Aside temperature and pressure, high magnetic fields have also been shown to be effective in inducing an opposite valence transition Eu$^{3+}$ $\rightarrow$ Eu$^{2+}$ for $0.18 \leq x \leq 0.25$ ($H_v \geq 36$ T) [104].

4.6.2 Preparation and characterization of the sample

In order to measure the BCE at the lowest possible temperature a sample with $x$ close to $x_c$ has been chosen. In the series prepared for this work $x_c$ was found to be

$^{23}$Note that Si doping leads to smaller cell volume of the compound as its atomic radius is smaller than for Ge.
somewhat smaller [105] than reported earlier [102]. Note that sample preparation was already mentioned earlier as a crucial point determining the specific properties of EuNi₂(SiₓGe₁₋ₓ)₂ [104, 100]. The sample used for the present measurements was prepared by arc melting and characterized by X-ray diffraction and measurements of the heat capacity, magnetic susceptibility and resistivity at the Max Planck Institute in Dresden [105]. The sample has shown no magnetic order and has exhibited a sharp valence transition with a large thermal hysteresis, i.e., \( T_v^- = 38 \) K for cooling and \( T_v^+ = 48 \) K for warming (Fig. 4.28).
4.6.3 Estimation of the BCE in EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$

The magnetic entropy difference between the Eu$^{2+}$ and Eu$^{3+}$ state is amongst one of the largest to be realized. In the Eu$^{3+}$ state the total angular momentum $J$ vanishes ($L = 3$, $S = 3$) and hence the ground-state $J$-multiplet is non-degenerate by definition yielding $S_M = 0$, $\forall T$. On the other hand the Eu$^{2+}$ state constitutes a half-filled 4$f$-shell ($L = 0$, $S = 7/2$) and thus in the paramagnetic state the $2J + 1$-fold degeneracy of the ground-state $J$-multiplet cannot be lifted by the CEF resulting in $S_M = R \ln 8$, $\forall T$. Note the temperature independence of $S_M$ in either state which is a specific feature for Eu. The magnetic entropy change associated with a pressure-induced valence transition Eu$^{2+}$→Eu$^{3+}$ is hence expected $\Delta S_M = R \ln 8 = 17.3$ J/Kmol.

Indeed based on the Clausius-Clapeyron relation (2.59) Wada et al. [102] estimate an entropy change $\Delta S \approx 18$ J/Kmol from the observed $dT_v/dp$ value and the giant volume shrinkage of $\Delta V/V = -3.5$ % below $T = T_v$. Hossain [105] estimates a lower value $\Delta S \approx 14.5$ J/Kmol from integration of the magnetic heat capacity in EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ with the non-magnetic contribution subtracted by comparison with EuNi$_2$(Si$_{0.125}$Ge$_{0.875}$)$_2$. $\Delta S \approx 14.5$ J/Kmol may serve as a lower limit as (i) integration of $\int C/TdT$ generally underestimates $S$ for first order transitions and (ii) the value of $R \ln 8$ must be considered an overestimation as the mean valence values are found $> 2$ and $< 3$, respectively. In what follows $\Delta S = 14.5$ J/Kmol is used.

The BCE may be estimated in a similar way as done for all other compounds. The non-magnetic entropy $S_N$ may be estimated for $T < T_v$ from direct integration of $c_p/T$ data taken at ambient pressure on EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$. Note that for $T < T_v$ the Eu$^{3+}$ is non-magnetic. These data may be conveniently fit by a Debye ansatz for the lattice entropy (2.28) and a linear term for the electronic entropy (2.36), yielding $\Theta_D = 265(5)$ K and $\gamma = 0.092(2)$ mJ/Kmol (Fig. 4.29).$^{24}$ In principle,

$^{24}$This Debye temperature is close to values found by Mössbauer spectroscopy: $\Theta_D$(EuNi$_2$Ge$_2$) =
Figure 4.30: Estimation for the expected, true intensive BCE with corresponding entropy curves in EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ for different pressures assuming an entropy change $\Delta S = 14.5$ J/Kmol associated to the valence transition.

subtracting $S_N$ from $\int C/TdT$ of EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ gives the magnetic entropy. Note however, that due to the first order nature of the phase transition the entropy becomes discontinuous at $T_v$ while $C$ essentially becomes infinite, so that in practice the difference $S_D = \int C/TdT - S_N$ reflects only a fraction of the true magnetic entropy. Nevertheless $S_D$ may serve as an estimate for the shape of $S_M$. It turns out that $S_D$ may be conveniently described by a sigmoid function$^{25}$ (Fig. 4.29, inset). The magnetic entropy $S_M$ may now also be parametrized by a sigmoid function of the same width but with an amplitude scaled in account for the true entropy change $\Delta S$.

The entropy curves for $p > 0$ may be obtained by simply shifting the sigmoid function for $S_M$ with $dT_v/dp = 105$ K/GPa. Neglecting elastic heating for the moment, the non-magnetic entropy may be assumed to be independent of $p$. Finally the expected true intensive BCE $\Delta T$ may be obtained by solving the adiabatic equation (2.5). Figure 4.30 shows the resulting intensive BCE together with the corresponding entropy curves for different pressures. Cooling of up to -14 K is expected over a temperature range considerably larger than what is found for any other studied BCE system.$^{26}$ The corresponding extensive BCE is shown in Figure 4.31. The maximum attainable extensive BCE is constant over a broad temperature range.

4.6.4 Direct observation of the BCE in EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$

The BCE measurements on EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ were carried out in the hydrostatic setup described in section 3.1.4. The sample was cut into a cylindrical shape ($h = 4.28$ mm, $m = 350.3$ mg). Figure 4.32 shows the effective cooling observed in function of temperature. A representative time-evolution of the measured temperature is

\begin{align*}
300 \text{ K and } \Theta_D(\text{EuNi}_2\text{Si}_2) &= 210 \text{ K }[100].
\end{align*}

$^{25}y = \frac{1}{1+e^{-x/w}}$

$^{26}$Assuming $\Delta S = 17.3$ J/Kmol results in a maximal cooling of -16 K.
Figure 4.31: Estimation for the expected true, extensive BCE (corresponding to Fig. 4.30).

Figure 4.32: Directly observed BCE in EuNi$_2$(Si$_{0.15}$Ge$_{0.85})_2$ (inset: representative time-evolution of temperature). Arrows denote the direction of measurement. The observed cooling of the sample is clearly caused by the valence transition, as $\Delta T$ vanishes at about $T_v^+$ and decreases above about $T = 80$ K. The cooling above 120 K is mostly caused by elastic heating from the pressure-transmitting medium$^{27}$ and the sample itself and to a lesser extent also from the BCE of the sample originating from pressures at the very edge of the pressure distribution (see below). The observed hysteresis may be explained by the 1st order nature of the valence transition. However the directly observed BCE is

$^{27}$NaCl
found more than one order of magnitude smaller than expected from the estimation made above. The following reasons may be responsible for the drastic reduction of the effect observed in the experiment:

1. non-adiabaticity of the hydrostatic setup (see section 3.1.6),
2. considerably broad pressure distribution (as to be expected when using a solid pressure medium),
3. heat load of the temperature sensor (see section 3.1.5).

The severe lack in adiabaticity of the hydrostatic setup is likely to be responsible for most of the reduction. Comparing the BCE in CeSb measured under uniaxial and hydrostatic pressure, the non-adiabaticity of the hydrostatic pressure cell is expected to reduce the effect by a factor 14 \ldots 21 at 20 K (see section 4.1.5). Hence an observed cooling of $\sim -0.5$ K only, must not be considered as contradicting the estimations made in the previous section. The non-adiabaticity of the setup may be accounted for by the stationary picture introduced in section 3.1.6. The intensive BCE is then calculated with (3.16) instead of the adiabatic equation (2.5). While the non-adiabaticity is found to reduce $\Delta T(T)$ almost uniformly, it cannot explain the shape of the observed BCE. Figure 4.32 clearly shows an effective cooling up to $T > 80$ K for the $p = 0.34, 0.48$ GPa data sets, in agreement with $dT_v/dp$. Thus one may feel confident in the value of mean pressure acting on the sample. However, for pressures $p > 0.2$ GPa broad plateaus of constant $\Delta T$ are expected (e.g. the rectangular shape of $\Delta T(T)$ for $p = 0.5$ GPa in Fig. 4.30). Within these plateaus the intensive BCE $\Delta T$ is essentially only limited by the extensive BCE $\Delta S$ and the slope of $S(T)$ (2.11), while outside of these plateaus $\Delta T$ is restricted by non-complete phase transitions. Therefore the widths of the plateaus and the shape of the flanks left and right are essentially determined by the width of the valence transitions at $p = 0$ and $p > 0$.

Using a solid pressure-transmitting medium for the experiment one must expect an inhomogeneous pressure distribution around the sample, resulting in locally different $T_v(p > 0)$ thanks to the large value of $dT_v/dp$. It has already been reported earlier that thermal processing and chemical inhomogeneities may affect the width of the valence transition considerably due to internal stress and strain in the sample [102, 104]. The present sample used for the experiment is characterized by an extraordinarily sharp valence transition. The value for the width of the transition used in the above estimations may even be reconsidered for $p = 0$, as the solid matrix of the pressure medium may leave the sample under stress on the surface after pressure release, but it will certainly not reflect the situation for $p > 0$.

In account for the many unknowns with respect to the non-adiabaticity and the pressure distribution, no attempt was made to correct the measured data for the heat load of the sensor. The above mentioned two factors responsible for the reduction of $\Delta T$ indeed have proved sufficient to account qualitatively for the observed value and shape of $\Delta T(T)$ as shown representatively for the $p = 0.34$ data set (warming) in Figure 4.33. The degree of non-adiabaticity $\eta = \Delta S/(\Delta S + \Delta T)$ was estimated to be about $\eta \approx 0.95$, while the transition width for $p > 0$ was found to be broadened by about a factor of 8 (it was assumed to be not broadened for $p = 0$, i.e. at the value determined in the previous section). Both values are given
for the sake of completeness and in support of the above made estimation of the BCE in EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ (section 4.6.3). They do not reflect the real temperature and pressure dependence of the non-adiabaticity of the setup nor the true pressure distribution in the pressure cell.

### 4.6.5 Conclusions

The principle of cooling by a pressure-induced valence transition could be demonstrated for EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$. The expected intensive BCE of -14 K for $p > 0.2$ GPa and the broad working range of a few 10 K for $p \approx 0.5$ GPa make this compound a very potent magnetic refrigerating material. The extensive BCE of 14.5 J/Kmol (theoretical value: 17.3 J/Kmol) is in fact competitive with the best, known MCE materials (Gd: $\sim 2$ J/Kmol, Gd$_5$(Si$_2$Ge$_2$): $\sim 18$ J/Kmol, ErAl$_2$ $\sim 8$ J/Kmol for $\Delta H = 5$ T) [1]. The exact working range of this compound may further be tuned seamlessly between 40 K and above room temperature via the Si doping.

Nevertheless, the direct measurement of the intensive BCE under hydrostatic pressure revealed cooling rates more than one order of magnitude below the calculated values. This discrepancy could be explained in terms of non-adiabatic conditions of the experimental setup, so that the experimentally observed values are not found to be necessarily in contradiction to the calculations. Hence EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ and other Eu compounds likely represent the best-suited BCE systems studied throughout this work, despite the small, directly observed effects.

The modest cooling effect observed in EuNi$_2$(Si$_x$Ge$_{1-x}$)$_2$ must be considered to be caused primarily by the deficiency of the experimental measurement technique, which may be considerably relaxed by (i) a hydrostatic pressure cell allowing for better thermal isolation of the sample or (ii) the measurement of the effect under...
uniaxial pressure on a single crystal sample.\textsuperscript{28}

These conclusions may raise further questions about the general applicability of the BCE for technical use, which are addressed in the concluding chapter of this work.

\textsuperscript{28}To the knowledge of the author it is not known whether the valence transition can be driven by uniaxial pressure at all.
Chapter 5

Neutron Scattering Studies under Pressure

This chapter summarizes some studies on compounds not used for the barocaloric cooling. The compounds presented here have either not been characterized under pressure before and hence were studied in view of being possible BCE candidates (like RAl$_x$Ga$_{1-x}$), or they served as suitably simple model compounds to test the pressure cell for inelastic neutron scattering developed throughout this work and to test the approximation schemes for the estimation of the CEF under pressure as were applied in the previous chapter.

It is shown that inelastic neutron scattering studies under pressure serve as an important tool to study the relation between structural, electronic and magnetic properties of a solid.
5.1 Phase diagram of the pseudo-ternary rare-earth compounds RAl\textsubscript{x}Ga\textsubscript{2−x}

Depending on the Al content \(x\) the pseudo-ternary compounds RAl\textsubscript{x}Ga\textsubscript{2−x} show different chemical structures in a sequence generic for all rare-earth ions R. The magnetic properties of the respective phases are found to differ considerably. In the paramagnetic state these are governed by the CEF and hence are linked to the respective chemical structure. As an example the chemical phase diagram of NdAl\textsubscript{x}Ga\textsubscript{2−x} [106] is shown in Figure 5.1 together with corresponding CEF splitting schemes obtained from INS measurements [107]. The CEF in the intermediate-\(c/a\) phase is drastically reduced compared to the case in the low-\(c/a\) phase. Therefore the magnetic entropy (2.42) of the two phases is expected to differ considerably. Assuming now that pressure may lead to a structural phase transition for compounds close to the border of these two phases, the NdAl\textsubscript{x}Ga\textsubscript{2−x} system would represent an interesting candidate for a structurally driven BCE (Fig. 5.2).

The aim of this project was to clarify whether pressure-induced structural phase transitions in RAl\textsubscript{x}Ga\textsubscript{2−x} exist, how the magnetic and structural properties are linked to each other and what mechanisms may determine the nature of the chemical phase diagram. Therefore high-pressure ND experiments were carried out on

![Chemical phase diagram](image)

Figure 5.1: Top: Chemical phase diagram of NdAl\textsubscript{x}Ga\textsubscript{2−x} with corresponding lattice parameters [106]. Bottom: CEF splitting schemes for different Al concentrations \(x\) (D: doublet, Q: quartet) [107].
Figure 5.2: Estimated BCE in NdAlGa for the pressure-induced phase transition intermediate—low-c/a. $S(T)$ denotes total entropies ($\Theta_D \approx 250$ K, $\gamma \approx 20$ mJ/K$^2$mol, CEF from [107]).

Figure 5.3: $AlB_2$ structure type. The family of RAl$_x$Ga$_{2-x}$ compounds realizes two phases of $AlB_2$ type with distinct lattice ratios c/a.

NdAl$_x$Ga$_{2-x}$ ($x = 1.00, 1.08$ and $1.46$) and the previously not determined CEF of ErAl$_x$Ga$_{2-x}$ ($x = 0.5, 1.0, 1.75$) was established and compared to other compounds of the RAl$_x$Ga$_{2-x}$ family.

The ND measurements revealed critical pressures too high to make these compounds suitable for barocaloric cooling, nevertheless the study of these systems has yielded some interesting new aspects which are summarized here. The results presented in this section have been published in [108, 33]

5.1.1 Introduction

The intermetallic compounds RAl$_x$Ga$_{2-x}$ show a wide variety of chemical and magnetic structures. The binary compounds RAl$_2$ (R=Ce, Pr, Nd, Sm, Tb, Gd, Dy, Ho, Er, Tm, Yb), i.e. $x=2$, all crystallize in the cubic MgCu$_2$ Laves phase (space group $Fd\bar{3}m$) and exhibit ferromagnetic order (except for R=Ce) with Curie temperatures between $T_C = 5.4$ K (TmAl$_2$) and $T_C = 120$ K (SmAl$_2$) [36]. Upon
partial substitution of the Al ions by Ga most of these pseudo-ternary compounds (e.g. R = Ce, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb) realize a hexagonal AlB$_2$ phase (space group $P6/mmm$). In this structure the B atoms form a graphite-like net with the A atoms located at $(0,0,c/2)$ above the centers of the hexagonal network (Fig. 5.3). This structure is found to occur in two modifications with distinct lattice ratios $c/a$ [109], namely the low-$c/a$ and the intermediate-$c/a$ phase with $c/a \approx 0.85$ and $c/a \approx 1.0$, respectively. Eventually some of the RAl$_x$Ga$_{2-x}$ systems realize the CeCu$_2$ structure for very high Ga-content [110, 106, 111, 112, 113]. This structure is closely related to the AlB$_2$ structure. All RAl$_x$Ga$_{2-x}$ systems feature chemical phase diagrams with broad regions of phase coexistence. The widths of the different phases are found to depend on the diameter of the specific rare-earth ion [114]. The observed chemical phase diagrams of these compounds are surprising as Al and Ga belong to the same chemical group (IIIB) with almost equal metallic atomic radii.

The magnetic structures of a few of the pseudo-ternary RAl$_x$Ga$_{2-x}$ systems have been studied in detail, e.g. for R=Nd, Er [115] and Ho [111, 116]. Both systems show a large variety of frustrated magnetic arrangements in a most simple hexagonal structure.

The CEF interactions of the binary, cubic compounds RAl$_2$ have been studied by various authors ([36], [117, 58] and references therein). Whereas to the knowledge of the author NdAl$_x$Ga$_{2-x}$ [107] and HoAlGa [116] represent the only systems in the hexagonal AlB$_2$ structure for which attempts in determining the CEF have been made so far. In the latter case, the CEF parameters, the magnetic exchange parameters and the magnetic periodicity at $T_N$ lead to a quantitative understanding of the complex magnetic phase diagram of HoAlGa [116].

5.1.2 Sample Preparation

The samples were synthesized by arc-melting under argon atmosphere starting from the elemental metals. They were remelted several times. Under He atmosphere the resulting ingots were then grained to powder and filled into standard Al (V) cans suited for the INS (ND) measurements under ambient pressure or filled into the pressure cells at ambient atmosphere. None of the samples showed a reaction when exposed to air.

5.1.3 Pressure-induced structural phase transition in NdAl$_x$Ga$_{2-x}$

Neutron diffraction (ND) measurements under hydrostatic pressure at room temperature have been carried out in order to clarify the question of whether pressure-induced transitions between the intermediate-$c/a$ and the low-$c/a$ AlB$_2$ phase and between the low-$c/a$ AlB$_2$ and the cubic MgCu$_2$ phase occur. The measurements on the isostructural phase transition intermediate $\rightarrow$ low-$c/a$ have first been tackled. In a series of samples with different Al content $1.0 \leq x \leq 1.18$ the border between the pure intermediate-$c/a$ phase and the mixed low/intermediate-$c/a$ phase has been found at $x_c = 1.12$ by means of X-ray diffraction at room temperature. The low-$c/a$ phase realizes a smaller volume compared to the intermediate-$c/a$ phase. Therefore the hypothetical pressure-induced transition was assumed to take place from the intermediate-$c/a$ to the low-$c/a$ phase.
Preliminary measurements up to 1.63 GPa, $x \approx 1.0$

In the first step ND experiments on NdAlGa ($x = 1.0$) have been carried out on the DMC diffractometer (SINQ) in a zero-matrix clamp cell at pressures up to $p = 1.5$ GPa. At the highest applied pressure small shoulders at the (101) and (110) Bragg reflection of the intermediate-$c/a$ phase could be observed. However the limited $Q$-range and the data quality did not allow for a non-ambiguous assignment of these shoulders to the low-$c/a$ phase. A repetition of the experiment on the powder diffractometer D2B (ILL, France) using a McWhan type pressure cell and pressures of up to 1.63 GPa supported the assumption that the high-pressure phase of NdAlGa is indeed represented by the low-$c/a$ AlB$_2$ phase which starts to establish for $p \gtrsim 1.5$ GPa in the presence of the low-pressure (intermediate-$c/a$) phase. Many large peaks originating from the pressure cell however resulted in some ambiguities and did not allow the refinement of the high-pressure phase in terms of a Rietveld analysis.

Measurements up to 5.2 GPa, $x \approx 1.0$

In order to proof the above stated thesis and to find out more about the phase fractions of the two phases, high-pressure ND measurements using sapphire-anvil pressure cells have been carried out on the powder diffractometer DN12 (Dubna, Russia) for the two Al concentrations $x = 1.00$ and $x = 1.08$. The measurements were carried out without the use of an additional pressure transmitting medium. All diffraction data were taken at a constant scattering angle of 90°. The data of the 16 detectors were normalized and summed, except for detectors contaminated with Bragg peaks from the sapphire anvils. The data were refined for lattice parameters $a$, $c$ and volume phase fractions $r_{\text{int}}, r_{\text{low}}$ using the program MRIA [118]. Figure 5.4 shows refined diffraction patterns of NdAl$_{1.08}$Ga$_{0.92}$ at different pressures (similar results were obtained for the NdAlGa sample). Note that for $p = 0$ the sample was wrapped in aluminium foil and measured without the pressure cell, hence additional Bragg peaks from Al appear in Figure 5.4. The measurement at $p = 1.9$ GPa already shows the occurrence of the high-pressure phase (indicated by arrows). The Bragg peaks of the high-pressure phase become gradually more pronounced as pressure increases. For $p \geq 3.8$ GPa additional Bragg peaks from sapphire become visible at $d = 1.01, 1.61, 1.65$ Å. These peaks are present in all detectors and hence result from small cracks in the anvils. Table 5.1 lists the refined parameters for both samples.

### Table 5.1: Refined room-temperature parameters of the NdAl$_x$Ga$_{2-x}$ system at ambient and elevated pressures. (data for $x = 1.13$, $p = 0$ from Martin [119], X-ray).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$p$ [GPa]</th>
<th>$a_{\text{int}}$ [Å]</th>
<th>$c_{\text{int}}$ [Å]</th>
<th>$(c/a)_{\text{int}}$</th>
<th>$r_{\text{int}}$ [%]</th>
<th>$a_{\text{low}}$ [Å]</th>
<th>$c_{\text{low}}$ [Å]</th>
<th>$(c/a)_{\text{low}}$</th>
<th>$r_{\text{low}}$ [%]</th>
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<td>4.209(1)</td>
<td>0.97</td>
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<td>35(3)</td>
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<td>4.132(4)</td>
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<td>56(2)</td>
<td>4.418(3)</td>
<td>3.723(4)</td>
<td>0.84</td>
<td>44(2)</td>
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<td>4.195(1)</td>
<td>0.97</td>
<td>100</td>
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<td>3.754(4)</td>
<td>0.85</td>
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<td>0.84</td>
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<td>3.699(2)</td>
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91
Figure 5.4: Refined diffraction patterns of NdAl$_{1.08}$Ga$_{0.92}$ at different pressures. Residua are given in units of standard deviation. Solid and dashed lines indicate the low- and high-pressure phase, respectively. Thick arrows indicate Bragg peaks occurring from the high-pressure phase. At high pressures contamination with sapphire peaks could not be avoided.
Figure 5.5 shows the lattice parameters and volume fractions in NdAl$_{1.08}$Ga$_{0.92}$. In both samples the high-pressure phase could be indexed by the low-c/a AlB$_2$ phase with lattice parameters close to the values found for NdAl$_x$Ga$_{2-x}$ ($x > 1.12$) at ambient pressure (for comparison the values for $x = 1.13$ are also given in Table 5.1). In the presented refinement of the data no corrections due to preferred orientation are taken into account even though preferred orientation must be expected at these pressures. In particular, Bragg peaks above $d = 2$ Å are most affected by preferred orientation, which may explain the difficulties in fitting their relative intensities for $p > 3.8$ GPa. Note, however that (i) the preferred orientation does not influence the total integrated intensities and thus has little influence on the refined volume fraction values and (ii) the implementation of a preferred orientation model based on this limited number of observed Bragg peaks must be considered with caution.

Even at the highest applied pressure of 5.2 GPa both samples still show more than 50% of their volume in the low-pressure phase. This is in accordance with the chemical phase diagram where the pure intermediate-c/a phase is followed by a region of phase coexistence with the low-c/a phase upon reduction of the Ga-content. In conclusion, together with the results from the earlier measurements at lower pressures, both samples ($x = 1.00, 1.08$) can be assigned a critical pressure of $p_c \approx 1.5$ GPa for the isostructural transition from the intermediate-c/a to the low-c/a phase.
In search for the hexagonal-cubic phase transition

Measurements on NdAl$_{1.46}$Ga$_{0.54}$ close to the border between the low-c/a AlB$_2$ and MgCu$_2$ phase have been carried out up to $p = 4.5$ GPa in search for a hypothetical pressure-induced transition into the cubic phase. However up to the highest applied pressure no precursor for the high-pressure phase was found, like e.g. an anomalous softening of the lattice parameters, broadening of Bragg peaks etc. At $p = 4.5$ GPa the cell volume of the sample amounted to about the cell volume of the MgCu$_2$ phase. It must hence be concluded that the hexagonal-cubic transition cannot be induced by pressure of up to 4.5 GPa.

In the context of using NdAl$_x$Ga$_{2-x}$ as a possible BCE candidate, it remains to state that the nature of the crystal field in the two isostructural AlB$_2$ phases comply very well with the requirements for a large entropy change and hence a large BCE (Fig. 5.2). However the critical pressure needed for the phase transition is too high for a practical use of NdAl$_x$Ga$_{2-x}$ as a BCE refrigerating material.

5.1.4 CEF in ErAl$_x$Ga$_{2-x}$ and implications on the chemical phase diagram of the RAl$_x$Ga$_{2-x}$ family

The ErAl$_x$Ga$_{2-x}$ system constitutes another possible candidate for a structurally driven BCE. ErAl$_x$Ga$_{2-x}$ has a similar chemical phase diagram (Fig. 5.6) as NdAl$_x$Ga$_{2-x}$. The CEF of ErAl$_x$Ga$_{2-x}$ has not yet been determined and hence INS measurements for $x = 0.5$ (MgCu$_2$) and $x=1.0$, 1.5 (low-c/a AlB$_2$) have been carried out.$^2$ The ground-state $J$ multiplet of Er$^{3+}$ ($J = 15/2$) is expected to be

---

$^1_{x_c = 1.50(2)}$

$^2$The INS measurements on ErAl$_x$Ga$_{2-x}$ have been carried out before the high-pressure ND measurements on NdAl$_x$Ga$_{2-x}$, hence at that time the large critical pressures needed for the transitions...
Figure 5.7: CEF level scheme of $\text{ErAl}_x\text{Ga}_{2-x}$ resulting from parameters final listed in Table 5.3. Arrows denote observed energy transitions, dashed arrows indicate observed but unresolved transitions. Numbers on arrows give the relative strength of the corresponding transition-matrix elements. (*$\text{ErAl}_2$ after [117].

split into 3 quartet states and 2 doublet states for the cubic case ($x = 0.5$) and into 8 Kramers doublet states for the hexagonal cases ($x = 1.0$ and $x = 1.5$) (Fig. 5.7). The structural and magnetic properties of $\text{ErAl}_x\text{Ga}_{2-x}$ for $x = 2$, 1.75, 1.0 and 1.5 are listed in Table 5.2

The measurements were carried out on DrüchaL (SINQ) with a fixed analyzer energy of $E_f = 4.9$ meV and constant scattering vectors $Q = 1.0, 1.2, 1.6$ and 2.1 Å$^{-1}$. Higher-order contamination was suppressed by use of a cooled Be-filter after the sample. For cooling of the sample a closed-cycle He-refrigerator was used except for $\text{ErAl}_{1.75}\text{Ga}_{0.25}$ which was measured in a standard ILL cryostat. The ND measurements on $\text{ErAl}_{1.75}\text{Ga}_{0.25}$ were performed on DMC (SINQ) with a neutron wavelength of $\lambda = 2.56$ Å.

**CEF in $\text{ErAl}_{1.75}\text{Ga}_{0.25}$ (cubic $\text{MgCu}_2$)**

The measured INS spectra of $\text{ErAl}_{1.75}\text{Ga}_{0.25}$ for temperatures above and below the magnetic ordering temperature $T_C = 10.5$ K are shown in Figure 5.8. In the paramagnetic state the spectrum shows some unresolved inelastic intensity near the elastic line and a broad bump at around 6 meV. Based on this experimental data no unambiguous set of CEF parameters can be found. Hence additional measurements in the ordered state were carried out, where the Zeeman splitting of the CEF levels into separate singlet states serves as a crucial check for the corresponding eigenfunctions.

were unknown.
Table 5.2: Structural and magnetic properties of the ErAl\(_x\)Ga\(_{2-x}\) system (\(M_0\): saturated magnetic moment, \(\vec{k}\): magnetic propagation vector, *: values calculated from parameters indicated in last column, †: present work, lattice constants at room temperature).

<table>
<thead>
<tr>
<th>(x)</th>
<th>struct. (M)</th>
<th>(a) [(\text{Å})]</th>
<th>(c) [(\text{Å})]</th>
<th>(T_C) [K]</th>
<th>(T_N) [K]</th>
<th>(M_0) [(\mu_B)]</th>
<th>(\vec{k}) [r.l.u]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>MgCu (_2)</td>
<td>7.794</td>
<td></td>
<td>14(1)</td>
<td>4.83</td>
<td>7.9(1) (</td>
<td></td>
<td>\ 11\ 1)</td>
</tr>
<tr>
<td>1.75</td>
<td>MgCu (_2)</td>
<td>7.778</td>
<td></td>
<td>14(1)</td>
<td>4.81</td>
<td>7.9(1) (</td>
<td></td>
<td>\ 11\ 1)</td>
</tr>
<tr>
<td>1.0</td>
<td>(\text{Al}_2)</td>
<td>4.425</td>
<td>3.515</td>
<td>2.8(3)</td>
<td>4.9(1)</td>
<td>4.9(1) (\perp\ 001)</td>
<td>((\frac{1}{2},\frac{1}{2},0))</td>
<td>0.472</td>
</tr>
<tr>
<td>0.5</td>
<td>(\text{Al}_2)</td>
<td>4.371</td>
<td>3.581</td>
<td>2.5(3)</td>
<td>3.8(1)</td>
<td>3.8(1) (\perp\ 001)</td>
<td>((\frac{1}{2},\frac{1}{2},0))</td>
<td>0.461</td>
</tr>
</tbody>
</table>

According to earlier work [36, 117, 119] the direction of the magnetic moments is along \(\langle\ 11\ 1\rangle\). Based on the Hamiltonians (2.40) and (2.50) a self-consistent least-squares procedure yielded the CEF parameters \(B_4\) and \(B_6\) and the molecular field \(\vec{H}_{mf} = \lambda g\mu_B \langle \vec{J} \rangle\). The resulting parameters are listed in Table 5.3. The molecular field \(\vec{H}_{mf}\) accounts for \(T_C \approx 17.7\text{ K}\) - higher than actually observed and to a saturated moment of \(M_0 = M(T \to 0) = 8.45\ \mu_B\).

In order to check the CEF parameters, specific heat and ND measurements were carried out. Both resulted in \(T_C = 10.5(1)\text{ K}\) in contrast to \(T_C = 14\text{ K}\) published.
in earlier works [115, 119]. The Rietveld refinement of the diffraction data yielded a magnetic moment of $M = 7.9(1) \mu_B$ at $T = 1.5$ K. However regarding the mean-field approach as being the simplest way to incorporate magnetic order, one may well accept $T_C$ and $M_0$ reconstructed from the CEF. Figure 5.9 shows the dependence of the reduced magnetic moment versus reduced temperature obtained from the ND measurement in comparison with the CEF calculation. The agreement is satisfactory. The obtained CEF parameters also account well for the [111] axis being the easy magnetic axis up to room temperature. The values found for ErAl$_{1.75}$Ga$_{0.25}$ are close to the ones of ErAl$_2$ [36, 117], they match within 7 % for $B_4$ and 20 % for $B_6$. Note that they follow a trend to smaller values as the lattice constant $a$ is reduced.

**CEF in ErAlGa (hexagonal low-c/a AlB$_2$)**

The neutron spectra for ErAlGa are shown in Figure 5.10. At $T = 15$ K two broad peaks can be observed. At higher temperature $T = 50$ K the peak around 6 meV develops a shoulder at the right side and a new weak peak around 9 meV appears. The magnetic origin of the peaks is established by noting that the dependence of their intensity with momentum transfer $Q$ follows the form factor $F(Q)$ in (3.17). Obviously the two additional features at $T = 50$ K result from CEF transitions from excited states that are not sufficiently populated at $T = 15$ K. All peaks are distinctly broader than the instrumental resolution ($\Gamma_{\text{inst}}(\Delta E = 0$ meV) $\approx 0.22$ meV, $\Gamma_{\text{inst}}(\Delta E = 6$ meV) $\approx 0.42$ meV), which is likely caused by inhomogeneities in the Al-Ga content of the samples [33]. A least-squares fit on (2.41) resulted in two CEF sets both describing the observed neutron spectra equally well (Table 5.3), i.e. resulting in the same energy splitting and transition-matrix elements except for one of the eight Kramers doublets namely $\Gamma_9^{(2)}$. However no strong INS transition from or
Figure 5.10: INS spectra for ErAlGa with $E_f = 4.9$ meV, $Q = 1.2$ and 1.6 Å$^{-1}$ (corrected for magnetic form factor, background subtracted, height of elastic line is around 24 counts). The curve denotes the least-squares fit by CEF parameters final given in Table 5.3.

to the $\Gamma_9^{(2)}$ state can be observed in either set. In Figure 5.10 the solid line indicates the fit by the first set of parameters given in Table 5.3 to which also the energy-level scheme of Figure 5.7 and labelling in Figure 5.10 refer. On the basis of other experimental methods presented below, it will be shown that in analogy to ErAl$_{0.5}$Ga$_{1.5}$ this CEF set is the favored one.

**CEF in ErAl$_{0.5}$Ga$_{1.5}$ (hexagonal low-c/a AlB$_2$)**

The neutron spectra of ErAl$_{0.5}$Ga$_{1.5}$ show the same characteristics as for ErAlGa with a smaller overall splitting (Fig. 5.11). The data were fitted using the same procedure as for the ErAlGa sample and similarly resulted in two possible CEF sets as listed in Table 5.3. For both samples the two sets differ by the sign of the second-order CEF parameter $B_2^0$. It has been shown in [120] that the second-order term of the $1/T$ expansion of the magnetic susceptibility (or the constant term in the inverse susceptibility) depends only on the second-order CEF and on the bilinear exchange and thus entirely governs the magnetic anisotropy in the high-temperature limit. Indeed a mean-field calculation of the magnetic susceptibility shows that for the ErAl$_{0.5}$Ga$_{1.5}$ sample the two CEF sets yield different easy axes at temperatures $T > 20$ K (Fig. 5.12), whereas for the ErAlGa sample the easy axis is oriented along [001] for both CEF sets. Hence the determination of the easy axis of ErAl$_{0.5}$Ga$_{1.5}$ at elevated temperatures serves as a crucial check for the CEF parameters.

In order to check the single-ion anisotropy, grain-aligned samples of ErAl$_{0.5}$Ga$_{1.5}$
Figure 5.11: INS spectra for ErAl$_{0.5}$Ga$_{1.5}$ with $E_f = 4.9$ meV, $Q$=1.3, 1.6 and 2.1 Å$^{-1}$ (corrected for magnetic form factor, background subtracted, height of elastic line is around 27 and 50 counts, respectively). The curve denotes the least-squares fit by CEF parameters final given in Table 5.3.

and ErAlGa were prepared by mixing well-grained powder with epoxy resin. The resin was filled in Torlon cylinders of 6 mm diameter and was hardened at room temperature in a magnetic field of 9 T perpendicular to the cylinder axis. Slices of the cylinders were then analyzed on the single-crystal neutron diffractometer TriCS (SINQ) and on a magnetometer. The chosen geometry allowed to measure the susceptibility without correcting for shape anisotropy. Both samples exhibited pronounced preferred orientation along the c-axis coinciding with the direction of the magnetic field used for the alignment. This allowed to conclude that in ErAl$_{0.5}$Ga$_{1.5}$ the first CEF set with the c-axis being the easy axis at room temperature must be preferred ($B_0^2 < 0$).

Finally the close analogy in the geometry and in the sequence of energy levels between ErAlGa and ErAl$_{0.5}$Ga$_{1.5}$ suggests, that the first CEF set with $B_0^2 < 0$ is favored in ErAlGa too.

**Comparison of the CEF within the RAl$_x$Ga$_{2-x}$ family**

The obtained CEF parameters of ErAl$_x$Ga$_{2-x}$ at different Al content $x$ may now be compared to each another as well as to the two other RAl$_x$Ga$_{2-x}$ compounds for which the CEF has been determined, namely NdAl$_x$Ga$_{2-x}$ and HoAl$_x$Ga$_{2-x}$. Already a first view at the CEF parameters of the two cubic ErAl$_x$Ga$_{2-x}$ samples with $x$ = 2 and $x$ = 1.75 reveals that the differences cannot be ascribed to geometric

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3Single crystal samples of ErAl$_x$Ga$_{2-x}$ were not available.
Figure 5.12: Calculated inverse magnetic susceptibility $1/\chi$ for the two CEF sets of ErAl$_{0.5}$Ga$_{1.5}$. Only the final set leads to the c-axis being the easy direction of magnetization for $T > 20$ K in accordance with the results obtained for the grain-aligned sample. The inset compares the measurements on powder with the powder-averaged calculation.

Table 5.3: Crystal-field parameters (Stevens) obtained by least-squares fits to the observed INS spectra (ErAl$_2$ after [36], all values in meV). For ErAlGa and ErAl$_{0.5}$Ga$_{1.5}$ two CEF sets are given. The easy axis of magnetization at room temperature favors the first set labelled final. Note that the sign of $B_6^0$ remains undetermined in $6/mmm$ point-symmetry [27].

<table>
<thead>
<tr>
<th>Set</th>
<th>$B_4 \times 10^3$</th>
<th>$B_6 \times 10^5$</th>
<th>$H_{mf}$ [kOe]</th>
<th>$\lambda_{mf} \times 10^2$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl$_2$</td>
<td>0.110</td>
<td>-0.134</td>
<td>75(7)</td>
<td>7.9(7)</td>
</tr>
<tr>
<td>ErAl$<em>{1.75}$Ga$</em>{0.25}$</td>
<td>0.102(20)</td>
<td>-0.111(6)</td>
<td>75(7)</td>
<td>7.9(7)</td>
</tr>
<tr>
<td>AlB$_2$-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ErAlGa</td>
<td>final</td>
<td>-0.38(16)</td>
<td>0.36(12)</td>
<td>-0.698(13)</td>
</tr>
<tr>
<td>alternative</td>
<td>0.05</td>
<td>0.50</td>
<td>-0.689</td>
<td>0.161</td>
</tr>
<tr>
<td>ErAl$<em>{0.5}$Ga$</em>{1.5}$</td>
<td>final</td>
<td>-0.51(27)</td>
<td>0.66(17)</td>
<td>-0.588(26)</td>
</tr>
<tr>
<td>alternative</td>
<td>0.49</td>
<td>0.97</td>
<td>-0.566</td>
<td>0.128</td>
</tr>
</tbody>
</table>

factors solely. ErAl$_{1.75}$Ga$_{0.25}$ has a slightly smaller lattice constant $a$ than ErAl$_2$, nevertheless it shows a smaller overall CEF splitting of only about 8.5 meV compared to about 10.5 meV in ErAl$_2$ (Fig. 5.7) despite $B_n^m \propto a^{-(n+1)}$ (2.49). In order to compare the CEF parameters along different chemical structures ($MgCu$_2$ \leftrightarrow$ low-$c/a$ AlB$_2$ \leftrightarrow$ intermediate-$c/a$ AlB$_2$) and along different rare earth ions (R=Er ,Nd, Ho), the CEF parameters must be reduced by means of the extended point-charge model described in section 2.4.4. Assuming strong screening due to the conduction electrons, only the closest shell of neighboring ions around the rare-earth ion may be considered in order to calculate the coordination factors $\gamma_n^m$ in (2.46). Specifically for
the cubic case only the 4 closest rare-earth neighbors are considered\(^4\), while for the hexagonal case the 12 nearest Al/Ga ions plus the two close apex rare-earth ions are considered. In the reduction of the CEF parameters the corrections by Morrison are also taken into account according (2.47). The values of the radial moments are taken from [26]. Table 5.4 lists the resulting reduced CEF parameters \(a^m_n\) of ErAl\(_x\)Ga\(_{2-x}\) together with CEF parameters for R=Nd and Ho taken from [107, 116] and reduced by the same procedure. Except for \(a^0_2\) for which the approximation of considering only nearest neighbor ions proves to be too poor (compare section 2.4.4), the values of all reduced CEF parameters are very close to each another and show the same tendency to lower absolute values upon an increase of the Ga concentration within the whole family of RAl\(_x\)Ga\(_{2-x}\) compounds. As pure geometric effects are cancelled out by the reduction of the CEF parameters, the large decline of the CEF potential upon Ga increase directly reflects the change in the electronic properties of these systems. According to (2.48) the model may ascribe this effect by a reduction of the effective charge of the ligands (\(\propto a^m_n\)) or equally by an increase of the screening (\(k_{0}^2\)).

Assuming a linear relationship between the free-electron concentration \(n\) and Ga-content \(y \equiv 1 - x\) one expects for the functional dependence of \(a^m_n\) on \(y\) in the free-electron approximation (Eq. (2.48) with \(k_{0}^2 \propto D(E_F) \propto n^{1/3} \propto (y + y_0)^{1/3}\))

\[
a_n(k_0) = a_n(0)(1 - \alpha_n(y + y_0)^{1/3})
\]  \(5.1\)

with proportionality factor \(\alpha\) and offset constant \(y_0\). A fit of the most dominant and experimentally best determined parameter \(a^0_6\) on (5.1) is shown in Figure 5.13 for ErAl\(_x\)Ga\(_{2-x}\) and supports this simple model qualitatively.

\(^4\)The similarly distanced, spherically arranged 12 surrounding Al/Ga ions lead to small contributions in \(\gamma^m_n\) only.
Table 5.4: Reduced CEF parameters $a''_n$ found in the RAl$_x$Ga$_{2-x}$ family with Morrison’s corrections applied (all values in units of $[10^4\text{meV} \cdot \AA]$, M=Al/Ga, (*) these compounds crystallize in the $AlB_2$ structure with intermediate c/a-ratio where the two rare-earth apex ions have not been considered for coordination).

<table>
<thead>
<tr>
<th>Compound</th>
<th>coord.</th>
<th>$a'_2$</th>
<th>$a'_4$</th>
<th>$a'_6$</th>
<th>$\pm a'_6$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl$_2$</td>
<td>4R</td>
<td>-1.20</td>
<td>-5.34</td>
<td></td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>ErAl$<em>{1.75}$Ga$</em>{0.25}$</td>
<td>4R</td>
<td>-1.10</td>
<td>-4.34</td>
<td></td>
<td></td>
<td>present work</td>
</tr>
<tr>
<td>ErAlGa</td>
<td>12M+2R</td>
<td>-0.043</td>
<td>-0.113</td>
<td>-3.63</td>
<td>1.15</td>
<td>present work</td>
</tr>
<tr>
<td>ErAl$<em>{0.5}$Ga$</em>{1.5}$</td>
<td>12M+2R</td>
<td>-0.051</td>
<td>-0.195</td>
<td>-3.37</td>
<td>0.918</td>
<td>present work</td>
</tr>
<tr>
<td>HoAl$_2$</td>
<td>4R</td>
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<td></td>
<td></td>
<td>[36]</td>
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<tr>
<td>HoAlGa</td>
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<td>0.030</td>
<td>-0.249</td>
<td>-3.00</td>
<td>1.40</td>
<td>[116]</td>
</tr>
<tr>
<td>NdAl$_2$</td>
<td>4R</td>
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<td>-5.90</td>
<td></td>
<td></td>
<td>[36, 107]</td>
</tr>
<tr>
<td>NdAl$<em>{1.25}$Ga$</em>{0.75}$</td>
<td>12M+2R</td>
<td>0.025</td>
<td>-0.261</td>
<td>-4.45</td>
<td>1.58</td>
<td>[107]</td>
</tr>
<tr>
<td>NdAlGa$^*$</td>
<td>12M</td>
<td>-0.052</td>
<td>-0.103</td>
<td>-2.12</td>
<td>2.02</td>
<td>[107]</td>
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<tr>
<td>NdAl$<em>{0.5}$Ga$</em>{1.5}$ $^*$</td>
<td>12M</td>
<td>-0.043</td>
<td>-0.099</td>
<td>-1.29</td>
<td>1.45</td>
<td>[107]</td>
</tr>
<tr>
<td>NdGa$_2^*$</td>
<td>12M</td>
<td>-0.025</td>
<td>-0.056</td>
<td>-0.356</td>
<td>0.628</td>
<td>[107]</td>
</tr>
</tbody>
</table>

5.1.5 Conclusions

Within the same chemical structure the observed change in the CEF upon the increase of the Ga-content cannot be solely attributed to the change in lattice dimensions. Point-charge model calculations suppose a modification in the electronic properties of the solid upon the addition of Ga-ions resulting in an increase of the electron concentration. This finding is in accord with the observed structural phase transitions common to most members of the RAl$_x$Ga$_{2-x}$ family. The change from the cubic $MgCu_2$ Laves phase to the hexagonal $AlB_2$ follows the general sequence $MgCu_2$-$MgZn_2$-$ThSi_2$ found for many of the MN$_2$ phases upon the increase of the electron concentration [121]. However in the rare-earth compounds (M=R) only the $MgCu_2$ and the $AlB_2$ structure are realized, the latter being in close relation to the $MgZn_2$ structure. The isostructural phase transition within the $AlB_2$ phase upon further increase of the Ga concentration can also not be explained on geometric arguments only. On basis of well-established near-neighbor diagrams of the $AlB_2$ structure [122], the difference in atomic radii of Al and Ga [123], though in sign correct, proves to be too small in order to cause the change in c/a (i.e. the transition).\textsuperscript{5} However for intermetallic MN$_2$ phases with the $AlB_2$ structure, Pearson [109] has shown that depending on the valence of the M atom the reduced strain parameter is shifted resulting in two distinct families of MN$_2$ phases with different c/a-ratios. Although Al and Ga correspond to the same group in the periodic system the increase of Ga concentration obviously influences the electronic properties of the solid. Further experimental evidence for an increase of the electron concentration is found from the following arguments: (i) the lattice constant $a$ decreases with Ga, in agreement with Pauling’s empirical equation (e.g. in [122]) applied on the bond lengths of the B atoms ($B-B = \sqrt{3}a$ in $AlB_2$), which implies an increased valence electron concentration (VEC) for the Ga-rich compounds. (ii) ErGa$_2$ shows a larger electric conductivity than ErAl$_2$ [124, 125]. Hence it can be concluded that the observed structural phase transitions are rather electronically driven by a Hume-Rothery like

\textsuperscript{5}metallic atomic radii: $r(Al^{3+}) = 1.432$ au; $r(Ga^{3+}) = 1.411$ au [123]
mechanism\textsuperscript{6} than by mere geometric factors.

In addition it is noteworthy to mention that the observed pressure-induced isostructural phase transition in NdAl\textsubscript{x}Ga\textsubscript{1−x} is in accordance with these findings. Pressure is generally found to decrease the density of states at the Fermi level (section 2.4.3) and hence is expected to have a similar effect on the electronic properties like the decrease of the Ga-content. Therefore the observed pressure-induced transition may well be electronically driven too.

The main conclusion drawn from this work on the RAl\textsubscript{x}Ga\textsubscript{2−x} family of compounds, namely, that the different structures of these compounds are driven by a Hume-Rothery like mechanism in the case of chemical substitution Al→Ga or in the case of pressure-induced transitions, is subject to further confirmation by theoretical calculations.

\textsuperscript{6}The Hume-Rothery rules state that contacts of the Fermi sphere with the Brioullin zone boundary are often observed to be avoided by a change of chemical structure of the respective system. E.g. in the Cu-Zn alloy system the structure sequence α(fcc) → β(bcc) → γ(complex) → ε(hcp) → γ(hcp) found for increasing Zn content is explained by the different number of valence electrons of Cu (\(n = 1\)) and Zn (\(n = 2\)) [22].
5.2 Pressure dependence of the CEF in NdAl$_3$ and CEF of PrAl$_3$

This section illustrates the use of the pressure cell developed for the TOF spectrometer FOCUS at SINQ (section 3.2.2). The CEF of the binary rare-earth compounds PrAl$_3$ and NdAl$_3$ have been examined at ambient pressure by means of INS. The CEF of the latter compound has also been measured under hydrostatic pressure ($p = 0.84$ GPa). Substantial changes of the CEF under pressure have been observed. They are briefly discussed within the simple point-charge model.

5.2.1 Introduction

The relation between local structure and microscopic properties of a physical system has often proved to play a key role in the understanding of striking macroscopic phenomena. In many cases chemical substitution fails to address the primary question about local effects on altered atomic distances in a compound, as the substituting ion brings in its intrinsic electronic properties and is implanted discretely into the host lattice. INS under pressure addresses directly the question about the relation between structure and microscopic properties by primarily only changing interatomic distances, which though may have secondary effects on the electronic properties too.

PrAl$_3$ and NdAl$_3$ crystallize in the hexagonal structure type $\text{Ni}_3\text{Sn}$ (space group $P6_3/mmc$). The CEF splitting of PrAl$_3$ and NdAl$_3$ have been determined earlier in [126, 127, 128, 129] and [130], respectively. The particular sequence of CEF transitions in PrAl$_3$ made the interpretation of earlier INS results somewhat awkward, hence different possible sets of CEF parameters have been proposed in literature. The hexagonal structure of these simple binary compounds allows a change of the lattice ratio $c/a$ under hydrostatic pressure. Together with the low magnetic ordering temperature of NdAl$_3$ $T_N = 4.1(2)$ K (PrAl$_3$ shows no ordering at all) they make ideal candidates for the study of pressure effects on the CEF in metallic rare-earth compounds as broadening of the CEF transitions due to magnetic dispersion effects is expected to be small.

5.2.2 Experimental

Both samples have been characterized by X-ray diffraction. The PrAl$_3$ sample has shown no impurity phase, whereas for the NdAl$_3$ sample tiny amounts of NdAl$_2$ and Nd$_3$Al$_{11}$ have been found. The lattice constants at room temperature correspond to published values [131]. The only free atomic position parameter of Al is found $x_{\text{Al}} = 0.858(1)$ for both compounds. The INS experiments have been carried out on the TOF spectrometer FOCUS. The incoming neutron wavelength was chosen 2.9 Å with time-focusing at 10 meV. All measurements were carried out in neutron energy loss configuration. For the measurements at ambient pressure the polycrystalline powder samples were placed in standard vanadium containers of 10 mm diameter and were cooled in a standard ILL cryostat. The measurements of NdAl$_3$ under pressure were carried out in the pressure cell described in section 3.2.2. The lattice constants of the sample and of the pressure calibrant were determined on the powder diffractometer HRPT at 10 K in the very same sample environment prior to the INS measurements. For the measurements of the magnetic susceptibility under pressure,
Figure 5.14: Observed inelastic neutron spectra for PrAl\textsubscript{3} at ambient pressure together with calculated spectra using the best-fit parameters listed in Table 5.5 (note the different scaling).

the cell described in section 3.3.1 has been used. In order to avoid screening of the sample due to the Meissner effect, the sample was placed in an aluminum capsule with a lead cap ($T_N$(NdAl\textsubscript{3}) $< T_c$(Pb)).

5.2.3 Results

The inelastic neutron spectra of PrAl\textsubscript{3} are shown in Figure 5.14 for ambient pressure. The strong transition at 4.5 meV can readily be ascribed to a transition from the ground state. Note that this transition dominates over the incoherent elastic scattering. All additional intensity in the $T = 65$ K spectrum are attributed to transitions from excited CEF levels. For the hexagonal point-group D\textsubscript{3h} of the rare-earth site the CEF can be described by the Hamiltonian (2.41). The best-fit parameters found by the profile matching procedure described in section 3.2.2 are listed in Table 5.5. The resulting CEF level scheme is shown in Figure 5.18. The CEF parameters determined in this work are in accordance with values published earlier by Alekseev [127] on the basis of less resolved thermal TOF INS spectra.

The spectrum at 10 K found for NdAl\textsubscript{3} is characterized by three large CEF transitions (Fig. 5.15). The least-squares fitting of the spectrum resulted in the parameters listed in Table 5.5. The values found are close to the ones published by Alekseev et al. [130], which to the knowledge of the author constitute the only CEF set based on INS measurements. The corresponding level scheme is depicted in Figure 5.18. As opposed to the CEF by Alekseev the ground-state is not found to be a $\Gamma_8$ but a $\Gamma_9$ doublet state. Hence this set results in a somewhat larger saturated
Figure 5.15: Observed inelastic neutron spectrum for NdAl$_3$ at ambient pressure ($T = 10$ K) together with calculated spectra using the best-fit parameters listed in Table 5.5.

Figure 5.16: INS spectra for NdAl$_3$ at ambient pressure (in the pressure cell) and at $p = 0.84(5)$ GPa ($T = 10$ K). The solid lines denote calculations based on best-fit parameters listed in Table 5.5.

The spectra of NdAl$_3$ in the pressure cell at ambient pressure and at $p = 0.84(5)$ GPa are presented in Figure 5.16. The measurement at ambient pressure corresponds well to the measurement done in the vanadium container aside an effective loss in intensity by a factor of six due to absorption by the cell (for about the same sample volume). Pressure leads to an overall shift of the spectrum to higher energies without any principally new features. The peaks for $p > 0$ are found to be broader than for $p = 0$ as a consequence of pressure distribution. Starting from
Table 5.5: Lattice parameters and best-fit parameters for the CEF in PrAl$_3$ and NdAl$_3$ (Stevens notation, all parameters in [meV]; lattice constants of PrAl$_3$ from X-ray diffraction at room temperature, NdAl$_3$ from ND at 10 K). Note that the sign of $B^6_6$ remains undetermined in $D_{3h}$ point-symmetry [27].

<table>
<thead>
<tr>
<th></th>
<th>$p$ [GPa]</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
<th>$B^0_0$</th>
<th>$B^0_4 \cdot 10^2$</th>
<th>$B^0_6 \cdot 10^3$</th>
<th>$B^6_6 \cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrAl$_3$</td>
<td>0</td>
<td>6.5121(4)</td>
<td>4.6038(3)</td>
<td>0.203(9)</td>
<td>-0.166(10)</td>
<td>0.114(3)</td>
<td>± 0.151(6)</td>
</tr>
<tr>
<td>NdAl$_3$</td>
<td>0</td>
<td>6.455(1)</td>
<td>4.589(4)</td>
<td>0.095(2)</td>
<td>-0.061(5)</td>
<td>-0.071(1)</td>
<td>± 0.082(1)</td>
</tr>
<tr>
<td>NdAl$_3$</td>
<td>0.84(5)</td>
<td>6.432(4)</td>
<td>4.564(9)</td>
<td>0.105(8)</td>
<td>-0.056(11)</td>
<td>-0.078(2)</td>
<td>± 0.087(5)</td>
</tr>
</tbody>
</table>

the CEF parameters of NdAl$_3$ at $p = 0$ the corresponding parameters at $p > 0$ are readily fitted. Table 5.5 lists the best-fit parameters of the CEF together with the lattice constants at $p = 0$ and $p = 0.84$ GPa. With the exception of $B^0_4$ (which has the largest experimental uncertainty) all parameters increase in magnitude. $B^0_6$ dominates the splitting scheme and increases by as much as 10%. Note that the neutron diffraction data did not allow for a refinement of the atomic position $x_{Al}$ of the Al ion. The value for $p > 0$ however is in agreement with the value found for $p = 0$, hence it may be assumed to be independent of pressure. In order to rule out any anomalous pressure dependence of the ordering temperature $T_N$, additional DC magnetization measurements under pressure were carried out yielding a modest pressure dependence of $dT_N/dp = 0.51(6)$ K/GPa (Fig. 5.17). Hence the pressure-induced change in the CEF must be addressed due to changes in the structure and in the electronic properties of the system.
Figure 5.18: Energy level schemes for NdAl$_3$ and PrAl$_3$ (arrows denote observed transitions).

Table 5.6: Reduced CEF parameters of NdAl$_3$ and PrAl$_3$ (all values in [10$^4$meVÅ])

<table>
<thead>
<tr>
<th></th>
<th>$a^0_2$</th>
<th>$a^0_4$</th>
<th>$a^0_6$</th>
<th>$a^0_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdAl$_3$</td>
<td>0.998</td>
<td>-1.753</td>
<td>-1.892</td>
<td>2.278</td>
</tr>
<tr>
<td>PrAl$_3$</td>
<td>0.634</td>
<td>-1.578</td>
<td>-1.681</td>
<td>2.327</td>
</tr>
</tbody>
</table>

5.2.4 Discussion

The CEF of NdAl$_3$ and PrAl$_3$ may now be discussed in terms of the extended point-charge model (section 2.4.4). The same procedure as applied to the CEF of the RAl$_x$Ga$_{1-x}$ family in section 5.1 yields the reduced CEF parameters $a^m_n$ (2.47) from the experimentally determined $B^m_n$. The resulting values for NdAl$_3$ and PrAl$_3$ are listed in Table 5.6. The radial moments $\langle r_n \rangle$ are taken from [26]. The geometric coordination factors $\gamma^m_n$ are calculated from the two closest shells of Al neighbors (6 Al, $d \sim 3.142$ Å; 6 Al, $d \sim 3.240$ Å) and rare-earth neighbors (6 R, $d \sim 4.376$ Å; 2 R, $d \sim 4.589$ Å). X-ray determined lattice constants at room temperature were used. The reduced CEF parameters are found to be very close to each other with the exception of $a^0_2$ (see sections 5.1 and 2.4.4). They may even be put in relation to the parameters found for the RAl$_x$Ga$_{1-x}$ family of compounds.

The effect of pressure on the CEF of NdAl$_3$ is more difficult to tackle by the extended point-charge model and shall be discussed only briefly here. The procedure to estimate the CEF for $p > 0$ based on the data set at $p = 0$ is outlined in section 2.4.4 and performed analogously to section 4.3 for the tetragonal distortion in HoAs. In the first step the CEF parameters $B^m_n$ at ambient pressure are parametrized

---

$^7$NdAl$_3$: $a = 6.4710(1)$ Å, $c = 4.6005(4)$ Å
Table 5.7: Effect of pressure on the CEF parameters of NdAl$_3$ as expected from the extended point-charge model (xPCM) (all values in [meV], Stevens notation).

<table>
<thead>
<tr>
<th>$p$ [GPa]</th>
<th>$B_0^0$</th>
<th>$B_0^1 \cdot 10^2$</th>
<th>$B_0^3 \cdot 10^3$</th>
<th>$B_6^6 \cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>observed</td>
<td>0</td>
<td>0.095(2)</td>
<td>-0.061(5)</td>
<td>-0.071(1)</td>
</tr>
<tr>
<td>xPCM</td>
<td>0</td>
<td>(-0.055)</td>
<td>-0.095</td>
<td>-0.081</td>
</tr>
<tr>
<td>observed</td>
<td>0.84</td>
<td>+11%</td>
<td>-9%</td>
<td>+10%</td>
</tr>
<tr>
<td>xPCM</td>
<td>0.84</td>
<td>+2%</td>
<td>+4%</td>
<td>+2%</td>
</tr>
</tbody>
</table>

yielding for the effective charge of the Al ion $q_{Al} \approx +1.64$ e as the only fit parameter ($q_{Nd} \equiv +3$e, $\gamma_n^m$ from above, no effective screening$^8$; $B_2^0$ was not fitted). In the second step the CEF is recalculated for the lattice constants at $p > 0$. The resulting parameters are given in Table 5.7. The model underestimates the effect of pressure (with the exception of $B_2^0$, which however is least accurately determined by the experiment). Note that the model in this form only accounts for pure geometrical changes. In fact pressure is expected to decrease the density of states at the Fermi level resulting in less screening due to conduction electrons. Consequently, the CEF splitting tends to become larger for $p > 0$ on account of the changed electronic properties at $p > 0$. *Ab initio* DFT calculations on NdAl$_3$ [132] are in progress to reveal the effect of pressure in more detail and to provide a comparison with the experimental findings. The results extend the scope of the present work and will be communicated separately.

$^8$On account of the observed size of CEF splitting, the screening due to conduction electrons was found weak.
5.3 Dimer exchange-striction in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$

The interplay between magnetism, electronic properties and structure represents an important aspect of solid state physics. Many compounds do not only show a change in their magnetic or electronic properties induced by a change in their structure but the virtual opposite: a change of their structure is needed in order to optimize their magnetic or electronic features. The most prominent mechanisms include: Jahn-Teller distortions, Peierls distortions, Hume-Rothery phase transitions, valence transitions and magneto striction, i.e. exchange-striction.

In what follows the mechanism of exchange-striction between two isolated ions forming a dimer is discussed, and based on neutron spectroscopy, experimental evidence for dimer exchange-striction in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$ is presented.

5.3.1 Formalism of exchange-striction

A pair of two isolated ions is considered. In the case of a non-magnetic pair, the two ions shall have a relative distance $r_0$ in equilibrium. An increase or decrease of this distance $r \rightarrow r_0 + \Delta r$ causes the ions to pull back to equilibrium position with the force (Hook’s law)

$$F(r) = -f \cdot \Delta r = -f \cdot (r - r_0) \quad (5.2)$$

where $f > 0$ denotes an effective force constant between the two ions. Let us now assume the pair consists of magnetic ions with spins $\hat{S}_1$ and $\hat{S}_2$ coupled by isotropic, bilinear antiferromagnetic exchange $J < 0$. The corresponding energy is

$$W_{ex} = -2J \hat{S}_1 \hat{S}_2 \quad (5.3)$$

with $\hat{S}_1$ and $\hat{S}_2$ denoting spin operators.

Any distance dependence in $J$ will cause the spins to alter their distance $r$ in order to minimize $W_{ex}$ (Fig. 5.19). The corresponding gain in exchange energy (5.3) implies a cost in elastic energy $W_{el}$ according to (5.2)

$$W_{el} = \int_{r_0}^{r} F(r) dr = \frac{1}{2} f \cdot (r - r_0)^2. \quad (5.4)$$

Hence the equilibrium distance between the two ions is given by balancing $W_{ex}$ and $W_{el}$, i.e., by minimization of the total energy [133, 134]

$$W = W_{ex} + W_{el} = -2J(r) \hat{S}_1 \hat{S}_2 + \frac{1}{2} f \cdot (r - r_0)^2 \quad (5.5)$$

$$= -2[J(r_0) + (r - r_0)J'] \hat{S}_1 \hat{S}_2 + \frac{1}{2} f \cdot (r - r_0)^2 \quad (5.6)$$

where $J(r)$ is expanded up to first order and $J' = dJ/dr|_{r_0}$. Minimization with respect to $r$

$$\frac{dW}{dr} = -2J' \hat{S}_1 \hat{S}_2 + f \cdot (r - r_0) = 0 \quad (5.7)$$

yields

$$r_{str} = r_0 + \frac{2J'}{f} \hat{S}_1 \hat{S}_2. \quad (5.8)$$

\[9\] The term exchange-striction will be used here for local phenomena, whereas magnetostriction will refer to corresponding collective phenomena.
Figure 5.19: Exchange-striction in a magnetic dimer. Left: non-magnetic dimer at equilibrium position $r_0$. Right: magnetic dimer with adapted distance $r$ in order to increase bilinear exchange.

Substituting $r_{str}$ back into (5.6), the total energy can be written

$$W = -2J(r_0)\hat{S}_1\hat{S}_2 - \frac{2J'^2(r_0)}{f} (\hat{S}_1\hat{S}_2)^2. \quad (5.9)$$

Note that the elastic contribution in $W$ now depends on spins $S_1$ and $S_2$ via the distance dependence of $J$, hence the second term in (5.9) may be associated with the biquadratic term in the spin Hamiltonian

$$\mathcal{H} = -2J\hat{S}_1\hat{S}_2 - K(\hat{S}_1\hat{S}_2)^2. \quad (5.10)$$

The effective force constant $f$ may now be expressed by $J'$ and $K$

$$f = \frac{2J'^2}{K}. \quad (5.11)$$

### 5.3.2 Dimer excitations in CsMn$_x$Mg$_{1-x}$Br$_3$

The ternary compound CsMnBr$_3$ may be considered a good approximation for a 1-dimensional Heisenberg-antiferromagnet (see [135] and references therein). The hexagonal compound of $P6_3/mmc$ space group ($a = 7.61$ Å, $c = 6.50$ Å) forms chains of face-sharing MnBr$_6$ octahedra along the c-axis with intra- and interchain distances $3.26$ Å $= c/2$ and $7.91$ Å, respectively (Fig. 5.20). The Mn$^{2+}$ ions are found in $^6S$ state with spin $s = 5/2$. The magnetic exchange $J$ within the chain is found about three orders of magnitude larger than between the chains. Substitution of Mn$^{2+}$ ions by non-magnetic Mg$^{2+}$ ions results in magnetic clusters via fragmentation of the magnetic Mn$^{2+}$ chains, while leaving the chemical structure of the compound unchanged.\(^{10}\)

The size distribution of the clusters is given by the Mn$^{2+}$ concentration $x$. In what follows dimers of Mn$^{2+}$ are discussed, which are the most probable cluster type to occur for $x = 0.28$. Treating for the moment the exchange between the two Mn$^{2+}$ ions in terms of isotropic bilinear exchange only, the corresponding Hamiltonian reads

$$\hat{\mathcal{H}} = -2J\hat{S}_1\hat{S}_2 \quad (5.12)$$

with six $2S + 1$-fold degenerate eigenstates of energy

$$E(S) = -J \left( S(S + 1) - \frac{35}{2} \right), \quad S = 0, \ldots, 5 \quad (5.13)$$

where $S = S_1 + S_2$ denotes the total dimer spin ($S = 0, \ldots, 2s+1$). The energy levels of $\mathcal{H}$ fulfill the Landé interval rule $E(S) - E(S - 1) \propto S$. However, INS studies on the $^{10}$CsMnBr$_3$ and CsMgBr$_3$ are found to exhibit equal unit cells within the experimental accuracy.
dimer excitations $|S-1\rangle \rightarrow |S\rangle$ in CsMn$_x$Mg$_{1-x}$Br$_3$ up to $S=4$ revealed a violation of Landé’s rule. The observed energy levels could be far better described by the Hamiltonian (5.10) including a biquadratic term in the exchange. Experimentally, for $x=0.28$ the bilinear and biquadratic exchange were found [135]:

$$J = -838(5)\mu eV$$

$$K = +8.8(8)\mu eV$$

### 5.3.3 Evidence for exchange-striction in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$

With the observed biquadratic exchange constant $K$ at hand, one may now try to explain $K$ in terms of exchange-striction. Given that the distance dependence of the bilinear exchange parameter $J'$ was known, the effective force constant $f$ could be readily calculated via (5.11) and compared to elastic properties of CsMn$_{0.28}$Mg$_{0.72}$Br$_3$. Hence the singlet-triplet dimer excitation $|0\rangle \rightarrow |1\rangle$ of CsMn$_{0.28}$Mg$_{0.72}$Br$_3$ has been measured for dilated and reduced Mn-Mn distances by means of measurements at high temperature and high pressure, respectively. The experiments were carried out on FOCUS (SINQ) with an incoming neutron wavelength of $\lambda_i = 4.8$ Å. The sample was placed in a standard vanadium can for the measurements at ambient pressure and $T = 4.2, 15, 50, 100, 150, 200$ K. The measurements under hydrostatic pressure were carried out in the pressure cell described in section 3.2.2 up to $p = 0.73$ GPa at $T = 4.2$ K. The lattice parameters of the sample (and pressure calibrant) were measured on HRPT (SINQ) in the very same sample environments.

Figure 5.21 shows representative spectra for dilated, nominal$^{11}$ and reduced Mn-Mn distance. The corresponding bilinear exchange parameter $J$ in function of Mn-Mn distance is shown in Figure 5.22 assuming $K$ is constant.$^{12}$ The dis-

---

$^{11}$In what follows nominal conditions refer to $T = 15$ K at ambient pressure.

$^{12}$One may argue that in [135] the observed violation of Landé’s rule is caused by thermal depen-
Figure 5.21: INS spectra of the singlet-triplet dimer excitation of CsMnBr$_3$ for dilated, nominal and reduced Mn-Mn distance.

Figure 5.22: Distance dependence of the bilinear exchange parameter $J$ (empty markers: $p \equiv 0$, $T = 15, 50, 100, 150, 200$ K, filled markers: $T \equiv 4.2$ K, $p = 0, 0.73(2)$ GPa; the solid line shows a fit to an empirical power law).

tance dependence can be fitted by an empirical power law [134] and yields a value $J' = dJ/dr = +4.35$ meV/Å at nominal conditions. Eventually, one obtains for the force constant using (5.11):

$$f \approx 4300 \text{ meV/Å}^2 = 70 \text{ N/m}. \quad (5.14)$$

dence in $J$ as the spectra were taken at different $T$ for different $S$. However a recalculation of the energy scheme taking into account $J(T)$ determined from this work yields a renormalization of $K$ by less than -10 % only.
This value is deduced solely from the magnetic properties of the compound. It must be put in relation to elastic properties to judge the validity of the above proposed mechanism of exchange-striction. The estimation of the force constant \( f \) from macroscopic properties of the system is though non-trivial as \( f \) describes a pure microscopic property. The altered distance, i.e. striction, between the two ions forming the dimer is local and does not result in an overall distortion of the crystal.\(^{13}\)

The effective force constant \( f \) may be derived from the atomic force constants given that they are known. The parametrization of the phonon dispersion spectrum by the Born-von Karman model in theory allows all atomic force constants to be determined. However no comprehensive study of the phonon spectrum of CsMn\(_{0.28}\)Mg\(_{0.72}\)Br\(_3\) is currently at hand. Nevertheless, phonon dispersion studies on isostructural CsNiF\(_3\) have revealed a pronounced anisotropy of the phonon spectrum [136]. The anisotropy is explained in terms of stiff rods formed by the NiF\(_6\) chains along the \( c \)-axis. The stiffness in the \( c \)-axis is also reflected in the present neutron diffraction measurements on CsMn\(_{0.28}\)Mg\(_{0.72}\)Br\(_3\) under hydrostatic pressure, where the \( a \)-axis is found to be softer than the \( c \)-axis (\( \Delta a = -1.2\% \) and \( \Delta c = -0.8\% \) for \( p = 0.73 \) GPa). Hence assuming that the rods are stiff with small elastic coupling between them and that the Cs atoms act as a soft sublattice, the force constant \( f \) is expected to be of the same order as the macroscopic elastic constant along the \( c \)-axis, i.e., \( c_{33} \). The two constants are linked to each other via the elastic energy density, which for hexagonal symmetry reads

\[
\begin{align*}
\varepsilon_{el} &= \frac{1}{2} c_{11} (\varepsilon_{xx}^2 + \varepsilon_{yy}^2) + \frac{1}{2} c_{33} \varepsilon_{zz}^2 + c_{13} (\varepsilon_{xx} \varepsilon_{zz} + \varepsilon_{yy} \varepsilon_{zz}) + c_{12} \varepsilon_{xx} \varepsilon_{yy}. \\
\end{align*}
\]

(5.15)

Assuming the rods to be responsible for the stiffness along \( c \), one may set \( \varepsilon_{xx} = \varepsilon_{yy} = 0 \), i.e. considering only a local, longitudinal distortion of the unit cell \( \varepsilon_{zz} \neq 0 \). The associated energy per dimer which occupies half of the unit cell (\( V_{uc} = \sqrt{3} a^2 c / 2 \), \( r_0 = c / 2 \)) is

\[
W_{el} = \frac{V}{2} \varepsilon_{el} = \frac{\sqrt{3}}{4} a^2 c_{33} \varepsilon_{zz}^2 = \frac{\sqrt{3}}{4} a^2 c_{33} \left( \frac{r - r_0}{r_0} \right)^2.
\]

(5.16)

This energy may now be compared with (5.4) yielding for the effective force constant

\[
f = \frac{\sqrt{3} c_{33}}{c} \frac{a^2}{c}.
\]

(5.17)

With \( a = 7.533 \) Å, \( c = 6.454 \) Å and \( c_{33} = 64 \) GPa, where the latter value is taken from CsNiF\(_3\) [136], one finds \( f \approx 100 \) N/m. Rescaling the elastic constants from CsNiF\(_3\) to CsMn\(_{0.28}\)Mg\(_{0.72}\)Br\(_3\) by the rough relation \( c_{ij} \approx 1/\sqrt{M} \) with \( M \) the respective molar mass, one finds for CsMn\(_{0.28}\)Mg\(_{0.72}\)Br\(_3\)

\[
f \approx 100/1.28 \approx 80 \text{ N/m}.
\]

(5.18)

A similar, less physically sound calculation assuming constant unit cell volume, i.e. \( \varepsilon_{xx}, \varepsilon_{yy} \neq 0 \) yields \( f \approx 120 \) N/m.

\(^{13}\) \( \neq \) macroscopic magnetostriction
5.3.4 Discussion

The value of $f$ derived from magnetic properties of $\text{CsMn}_{0.28}\text{Mg}_{0.72}\text{Br}_3$ via exchange-striction is in striking agreement with the value derived from elastic properties and supports the concept of exchange-striction. Nevertheless one should note the two following points:

1. The above made approximations to derive the microscopic force constant $f$ from macroscopic elastic constants of an isostructural compound is crude. The two values of $f$ may hence be compared qualitatively only: they likely match within one order of magnitude.

2. Anderson [137] has shown the existence of a higher order term $(S_1S_2)^2$ in a perturbational approach for the magnetic exchange in insulators. He has estimated the $(S_1S_2)^2$ term to be about 1 \% of the $S_1S_2$ term for most insulating antiferromagnets. In the case of $\text{CsMn}_{0.28}\text{Mg}_{0.72}\text{Br}_3$ with Hamiltonian (5.10) the biquadratic term constitutes only about 0.5 \% of the bilinear term ($2J = -1676 \text{ \mu eV}$, $K = 8.8 \text{ \mu eV}$). Hence without further direct experimental determination of the effective force constant $f$, the above proposed origin of the biquadratic exchange, namely exchange-striction, may be equally well be ascribed to intrinsic biquadratic exchange.

In conclusion, the mechanism of exchange-striction accounts for an effective force constant with correct order of magnitude. Furthermore with the experimentally confirmed large distance dependence of the bilinear exchange, there is little reason to assume that the mechanism of exchange-striction is absent in $\text{CsMn}_{0.28}\text{Mg}_{0.72}\text{Br}_3$. 

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Chapter 6

Concluding remarks (BCE)

The barocaloric effect (BCE) potentially extends the techniques commonly used for magnetic refrigeration, a research topic which has gained increasing interest in the last decade for its economical potential. In the BCE, as opposed to other techniques, the entropy of the refrigerating material is reduced by the application of pressure without the need of large magnetic fields.

The present work constitutes the first Ph.D. thesis devoted to this topic. The aim of the work was to verify experimentally the effect, to find various mechanisms for it to occur and to explain it theoretically. Throughout this work, aside from the original idea of using a pressure-induced structural phase transition ((Pr,La)NiO$_3$ [4] and RAl$_x$Ga$_{2-x}$, HoAs) other mechanisms were found leading to a BCE, namely by

- pressure-induced magnetic phase transitions (CeSb, HoAs)
- pressure effects on Kondo systems (Ce$_3$Pd$_{20}$Ge$_6$)
- pressure-induced valence transitions (EuNi$_2$(Si,Ge)$_2$)
- pressure-induced spin-fluctuations

and combinations of the above. With the exception of the last mechanism all the others could be verified experimentally and described theoretically.$^1$

The extensive caloric effect, i.e. the change in magnetic entropy $\Delta S$ upon the isothermal change of pressure, was found in the BCE to the degree where it is a viable alternative to the MCE. It is in this stage of adiabatic cooling, where heat is transferred from or to the refrigerating material. Hence the value of $\Delta S$ is of considerable importance for possible applications of these refrigerating materials. It is worth mentioning that $\Delta S$ cannot be measured directly neither in the BCE nor

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$^1$The use of pressure-induced spin-fluctuations was considered in the system YMn$_2$ which shows large magnetic frustration, but eventually orders antiferromagnetically. Hydrostatic pressure is found to suppress the magnetic order via a transition critical in $p$ leaving the system in a state with large spin-fluctuations and hence very much enhanced electronic entropy. The change in total entropy is expected to be large as determined on basis of $c_p$ measurements of the compound under pressure [138]. Nevertheless the BCE in YMn$_2$ could not be verified experimentally.
The intensive caloric effect, i.e. the change in temperature $\Delta T$, was found to be less in the experiment compared to the theoretically expected values. This reduction is mainly caused by the non-adiabaticity during the change of pressure. While this turned out to be not too much of a problem for uniaxial pressure, it is for hydrostatic pressure. Since the present experimental setups allow for many improvements concerning thermal isolation of the system under investigation, considerably larger $\Delta T$ might be attained. Nevertheless, changing pressure adiabatically will remain a lot more difficult to achieve than changing an external magnetic field adiabatically. The theoretically expected values $\Delta T$ under the assumption of fully adiabatic conditions though are very much comparable with what is expected from MCE compounds.

The variety of different mechanisms leading to a reduction of magnetic entropy may be considered a superior feature of the BCE extending the range of potential refrigerating materials over the MCE. It is important to keep in mind that the application of a few 0.1 GPa pressure or a few Tesla magnetic field must be considered a minor perturbation for the majority of solid state systems. It is only thanks to special circumstances in a few compounds that the MCE and BCE become large enough to be considered for technical application. It is in this context that pressure-induced valence transitions (especially in europium compounds) must be considered a very promising way to implement the BCE.

From this work it evolved that the BCE is best implemented using uniaxial pressure, where quasi-adiabatic conditions can be realized far better than for hydrostatic pressure.

Future development may include the technique of piezo actuators to bring up the needed uniaxial force. Dilations in solid state systems are relatively small and piezo actuators are well capable of achieving forces of a few ten tons (in situ at low temperatures). An experimental arrangement as shown in Figure 6.1 may show considerably better adiabaticity than presently realized. Several building blocks may be put in series to increase cooling power. Likewise they may be built in very small
dimensions and therefore be able to be used in a new range of applications.

Other ideas involve the direct use of piezo-electric compounds as the active BCE system. In these compounds an externally applied electric field may lead to a change in symmetry. Given that the system owns a suitable crystal field\(^2\) the change in \(S_M\) may be used for adiabatic cooling in the very same way as for the structurally driven BCE (Fig. 6.2). The *piezo-induced magnetic cooling* may be achieved under very well adiabatic conditions and hence promises to be fairly efficient.

It is hoped, that the present work has aroused interest in the reader for the topic of magnetic cooling in general and specifically for some alternative approaches of how magnetic cooling may be implemented.

\[^2\text{One may also consider to dope known piezo-electric compounds with rare-earth ions.}\]
Bibliography


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