Magnetic Structures and Excitations in the Superconductor HoNi$_{11}$B$_2$C studied by Neutron Scattering

ABHANDLUNG
zur Erlangung des Titels
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Abstract

The family of superconducting compounds of layered transition metal borocarbides RNi$_2$B$_2$C have been the subject of considerable investigation since their discovery in 1994. Here $R$ stands either for nonmagnetic Y, Lu and Sc or for lanthanide elements in a $R^{3+}$ state. Of particular interest are those members of the family that contain magnetic rare-earth ions (such as Er, Ho, Dy) as they provide an opportunity to study the interplay between magnetism and superconductivity. Below the magnetic ordering temperature the magnetic moments of HoNi$_2$B$_2$C are essentially confined to the basal ($a,b$)-plane, as a consequence of the crystalline electric field (CEF) splitting of the ground-state multiplet of the Ho$^{3+}$ ion. Several magnetic structures consisting of ferromagnetic Ho$^{3+}$ planes and of different stacking along the $c$-direction are stabilized as a function of an external magnetic field.

The primary aim of this work was to investigate the effect of an external magnetic field $H$ on the magnetic excitations in ordered HoNi$_2$B$_2$C single crystals by inelastic neutron scattering (INS) and to determine the leading exchange interaction via the field dependence of the low-lying CEF excitation energy. Furthermore, we intended to investigate the line-width of the excitation, which probes the interaction between magnetism and superconductivity. The application of a mean-field model to the measured energy renormalization of the CEF excitation resulted in exchange parameters of the RKKY interaction inconsistent with results obtained when the magnetic field was applied along the hard in-plane direction leading us to restudy the magnetic phases in a comprehensive neutron diffraction investigation. In a first step we performed macroscopic measurements in order to characterize the single crystals and moreover, they provide by means of AC-susceptibility valuable information about the phase border of the respective metamagnetic arrangement.

Single crystal neutron diffraction revealed the richness of magnetic phases in HoNi$_2$B$_2$C and yielded the discovery of additional magnetic modulations. Moreover, neutron diffraction has been used to determine the ($H,T$) magnetic phase diagram of HoNi$_2$B$_2$C for the magnetically easy and hard in-plane field direction. The analysis of the diffraction data combined with the INS investigation and the macroscopic studies improved decidedly the previously existing metamagnetic phase diagram. For a magnetic field applied along the hard in-plane direction we observed two metamagnetic structures with a stacking in the $c$-direction different to that proposed structures by other authors. For both metamagnetic structures we observed a reappearance of incommensurate magnetic modulations close to the Fermi nesting vector. We ascribe this to a weakening of the magnetostriction due to the applied magnetic field along the hard in-plane direction. We propose for the field induced magnetic structure of the high field regime a superposition of ferromagnetic ordering with the incommensurate $a^*$-structure. By neutron polarimetry we could unambiguously determine an incommensurate magnetic phase of HoNi$_2$B$_2$C which is related to the Fermi surface nesting vector, the same wave vector that is common throughout the heavy $RNi_2B_2C$ family.

Furthermore, we observed by INS a weak dispersive excitation starting from the magnetic $\Gamma$-point which exhibits magnetic as well as phononic characteristics. We propose that this
excitation is caused by a magnetovibrational scattering mechanism. With this comprehensive study we could expand the knowledge about the complex magnetic structures of the borocarbide HoNi$_2$B$_2$C and their influence on the dynamics. Moreover, we could solve the above-mentioned contradiction concerning the INS investigation. All discontinuities and broadenings of the energy renormalization of the magnetic excitation could be assigned to the now well-defined underlying metamagnetic phases and transitions. No evidence for the influence of superconductivity on magnetic excitations was found.
Zusammenfassung

Seit ihrer Entdeckung im Jahre 1994 sind die supraleitenden Verbindungen der Substanzklasse der Seltenerd-Nickel-Borokarbide \( RNi_2B_2C \) Gegenstand intensiver Forschung. Das \( R \) in der Summenformel steht für \( R^{3+} \) Ionen der nicht-magnetischen Elemente Y, Lu und Sc oder der Lanthaniden. Von besonderem Interesse sind die Nickel-Borokarbide der magnetischen Seltenerd-Ionen (wie Er, Ho, Dy), bei welchen das Wechselspiel zwischen Magnetismus und Supraleitung in einem experimentell gut zugänglichen Temperaturbereich untersucht werden kann. Das Kristallfeld in HoNi\(_2\)B\(_2\)C hebt die Entartung des Grundzustands der Ho\(^{3+}\) Ionen auf und beschränkt dadurch unterhalb der magnetischen Ordnungstemperatur die Ausrichtung der magnetischen Momente auf die (\( a,b \))-Ebene. Die Ho\(^{3+}\)-Momente sind ferromagnetisch in den (\( a,b \))-Ebenen angeordnet und diese in \( c \)-Richtung antiferromagnetisch gestapelt. Ein angelegtes äußeres Magnetfeld vermag nun die Stapelfolge in \( c \)-Richtung zu modifizieren, dadurch werden zusätzliche sogenannte metamagnetische Phasen beobachtet.


Mit einer Neutronen-Polarimetrie Messung konnten wir die mit dem "Fermi-Flächen-
nesting” in Verbindung gebrachte inkommensurable magnetische Struktur unzweifelhaft bestimmen. Der Propagationsvektor dieser magnetischen Struktur ist allgegenwärtig in den $R\text{Ni}_2\text{B}_2\text{C}$ Verbindungen und ist Gegenstand kontroverser Diskussionen. Bei einer weiteren INS Untersuchung haben wir eine schwache dispersive Anregung gefunden, welche am magnetischen $\Gamma$-Punkt entspringt. Die Anregung zeigt sowohl phononischen als auch magnetischen Charakter. Wir vermuten, dass der beobachtete Streuvorgang durch Magnetovibration erzeugt wird.

Mit dieser umfassenden Arbeit konnten wir die Kenntnisse über das komplexe magnetische System von $\text{HoNi}_2\text{B}_2\text{C}$ entscheidend erweitern. Durch die neu gewonnenen Erkenntnisse über das Phasendiagramm können nun die bei der INS Studie beobachteten Energie sprunge und Linienverbreiterungen in der Energienormalisierung der magnetischen Anregungen mit einem Modell in Molekularfeldnäherung gut erklärt werden. Wir fanden jedoch bei den inelastischen Messungen keinen Hinweis, dass die Supraleitung die magnetischen Anregungen von $\text{HoNi}_2\text{B}_2\text{C}$ beeinflusst.
List of acronyms

AF antiferromagnetic
BZ Brillouin zone
CEF crystalline electric field
DOS density of states
e-p electron-phonon
FM ferromagnet
FS Fermi surface
HFE Helmholtz free-energy
GL Ginzburg-Landau
ICM incommensurate magnetic
INS inelastic neutron scattering
mf mean Field
RKKY Ruderman-Kittel-Kasuya-Yoshida
SC superconductivity
FWHM full width half maximum
SDW spin density wave
r.l.u. relative lattice units
a.u. arbitrary units
SF spin-flip
PPMS Physical Properties Measurement System

List of symbols

\( B, H, M \) magnetic induction, magnetic field and magnetization
\( H_{ex} \) applied external magnetic field
\( C(T) \) specific heat
\( \delta \) CEF splitting energy
\( E_F \) Fermi energy
\( T_C \) superconducting transition temperature
\( T_N \) Néel temperature
\( T_m \) magnetic transition temperature
\( T_{IC} \) transition temperature incommensurate magnetic structure
\( |\Gamma\rangle \) CEF state
\( H_{C2} \) upper critical field of the superconductor
\( J(q) \) effective interaction between local moments
\( g \) Landé factor
\( J \) total angular momentum of f-shell
\( \mu, \mu_B \) magnetic moment, Bohr magneton
\( 2\Theta \) scattering angle
\( k_i, k_f \) initial and final wavevectors of neutron
\( Q = k_f - k_i \) scattering vector
\( \Omega \) angle between \( k_i \) and \( Q \)
\( \lambda \) wavelength or penetration depth superconductivity
\( N(E) \) quasiparticle DOS
\( k_F \) Fermi wave number
\( \xi_0 \) coherence length superconductivity
\( \Delta_0 \) energy gap of superconductivity
\( k_B \) Boltzmann constant
\( \chi' \) real part of the AC susceptibility
\( \chi'' \) imaginary part of the AC susceptibility
\( E \) CEF transition energy
\( O_{mn}^\text{CEF} \) CEF Stevens operators
\( B_{mn}^\text{CEF} \) CEF parameter in Stevens notation
\( M_{i}^{\alpha} \) transition matrix element \((\alpha = x, y, z)\) of the CEF transition \( \Gamma_4 \rightarrow \Gamma_5(i) \)
\( M_{\perp} \) transverse transition matrix element
\( M_{\parallel} \) longitudinal transition matrix element
\( B_{mf,i} \) mean-field of the respective magnetic phase
\( D_{\parallel} \) in-plane demagnetization factor
Chapter 1

Experimental techniques

1.1 Physical properties measurement system (PPMS)

This system is designed to perform a variety of automated measurements of physical properties such as DC-magnetization ($M$), AC-susceptibility ($\chi$), heat capacity ($C$) and resistivity ($\rho$). Sample environment controls include magnetic fields up to 9T and a temperature range of 1.8 - 400K. We used the PPMS to characterize our HoNi$_2$B$_2$C samples. A detailed description of the macroscopic measurements will be given in chapter 3. For more information about the technical specification of the PPMS, see http://www.qdusa.com/products/ppms.html

1.2 Three-axis spectroscopy

Neutrons of a defined wavelength are selected from the "white" beam by means of a monochromator M (first axis). The wavelength or incident energy of neutrons depends on the monochromator material and the angle $2\Theta_M$. The sample S diffracts by an angle $2\Theta_S$ (second axis). The scattered neutrons are further analyzed with regard to their energy (third axis) by the analyzer via further diffraction process by an angle $2\Theta_A$ and finally counted by the detector D. The scattering vector $Q$ and the energy transfer $\hbar\omega$ are unequivocally determined by the angles $2\Theta_M$, $2\Theta_S$ and $2\Theta_A$. Thereby, the wave vectors $k_i$ and $k_f$ are connected with vector $Q$ and energy $\hbar\omega$ by $Q = k_i - k_f$ and $\Delta E = \hbar^2(k_i^2 - k_f^2)/2m$. The sense of the energy transfer determines whether the neutron has gained ($k_i < k_f$, $\Delta E < 0$) or lost energy ($k_i > k_f$, $\Delta E > 0$) during the scattering process. Triple axis spectrometers are very versatile neutron instruments because an almost arbitrary point in the $(Q,\omega)$-space can be probed and the resolution of both, momentum- and energy-transfer, can be adapted for a wide range of experiments. Therefore, they are mostly used for the determination of dispersion curves of phonons or spin waves in single crystals. In such measurements, only limited regions of $(Q,\omega)$-space are of interest. Inelastic neutron scattering (INS) is the process of scattering neutrons from a sample, accompanied by a change in energy of the neutron. INS experiments have been performed both at PSI (RITA-II), ILL (IN14) and at the LLB...
1.3 Cold neutron single crystal diffraction

The measurement principle of diffractometry is based on the Bragg-equation $2d \cdot \sin(\theta) = \lambda$. By irradiation of the crystal with a fixed wave length $\lambda$ with a given lattice plane $d$ the neutrons are diffracted in the direction of $2\theta$ relative to the incoming beam. This is the
1.4 Neutron scattering

principle of coherent elastic neutron scattering. The experiments presented in this work have been performed on the neutron diffractometers DMC, HRPT and TriCS at the Paul Scherrer Institute (PSI), Switzerland. The main part of the elastic investigations were performed on DMC. We used a 1.8 Tesla horizontal cryomagnet to measure the temperature and field dependence of HoNi$_2$B$_2$C. For a schematic layout of the diffractometer DMC see Fig.1.3. The DMC combines high neutron intensity provided by a vertically focusing monochromator with a position sensitive BF$_3$ "banana-type" multidedector (400 single detectors with an angular separation of 0.2°). An oscillating radial collimator suppress Bragg peaks originating from the sample environment. For our experiments we used an additional graphite filter in front of the sample to avoid higher harmonics. Diffractograms of the aligned single crystal were collected by a sample rotation around the vertical axis. These combined data provide a complete visualization of the scattering intensities in the corresponding 2D-plane of the reciprocal space. The single crystal was turned in steps of 1/8 degree in a range of 180 degrees for each setting of applied external magnetic field and temperature. The collected data were analyzed by the TVtueb software tool developed for the flat-cone diffractometer D2 at the HMI Berlin. This technique is especially useful for the measurement of complicated structures, e.g. the detection of satellites reflections at magnetic phase transitions and for the investigation of diffuse scattering of disordered crystals.

More information about neutron scattering can be found in the literature, see e.g. [1], and on the web:
http://sinq.web.psi.ch
http://www.ill.fr
http://www.neutron-eu.net
http://www.hmi.de/bensc/misc/flat-cone/tvtueb/index_en.html

1.4 Neutron scattering

1.4.1 Introduction

Neutron scattering is a very strong tool in solid state physics since the accessible energy- and momentum-transfer cover the range that is most relevant for the determination of the properties of most materials:

1. Cold neutrons with energies of about 0.1 to 10 meV and more energetic thermal neutrons with energies up to several 100 meV are commonly produced in neutron sources. Therefore, the basic excitations of crystal lattices and spin structures are accessible.

2. The energy spectra of cold and thermal neutrons happens to be in the right range for solid state physics. The wavelength $\lambda = \frac{2\pi}{k}$ of cold neutrons matches the typical dimensions of the studied structures. As a consequence the basic excitations can be probed throughout the Brillouin zone with neutrons, which is not possible by any other technique.

In the neutron scattering two interactions of neutrons with matter are important:
Experimental techniques

DMC

Cryomagnet MAO2

monochromator

Graphite (002), vertically focusing

wavelengths

2.3 Å ÷ 6.5 Å, standard: 2.56 Å, 3.82 Å, 4.21 Å

detector

"Banana" type multidetector, BF3, 400 detectors with 0.2° steps

collimations

oscillating collimator system between sample and detector: 73 cadmium coated steel plates
(angular distance 1.2°, thickness 0.02 cm)

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**Figure 1.3:** Schematic layout of the cold neutron diffractometer DMC at PSI. For our investigation we used an horizontal-field cryomagnet with a maximum field of 1.8T. An important advantage for this type of measurements was the small blind angle of the cryomagnet of a few degree only. Some technical specification of the instrument are given in the table.

1. Neutrons interact through the strong nuclear force with the atomic nuclei of the sample. Consequently they are a good probe for the chemical structure and the corresponding excitations of the sample under investigation.

2. As the neutron carries a magnetic moment $\mu_n = -1.913\mu_N$, where $\mu_N$ is the nuclear magneton, it also couples to the magnetic field that is due the magnetic moments in the sample. This interaction makes neutron scattering a unique tool for the determination of magnetic structures and excitations (and it is a major advantage compared to X-ray scattering).

Another major advantage is the electric neutrality of neutrons. They can easily penetrate the sample and are therefore ideal for study bulk properties.
1.4 Neutron scattering

1.4.2 Theory of inelastic neutron scattering

For the theoretical interpretation of neutron experiments one uses the concept of the scattering cross-section

\[
\left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{k\sigma\lambda \rightarrow k'\sigma'\lambda'} = \frac{1}{\Phi} \frac{1}{d\Omega} \sum_{k' \in d\Omega} W_{k\sigma\lambda \rightarrow k'\sigma'\lambda'}
\]

where \( k \) is the wave vector of the incoming (resp. \( k' \) for the outgoing) neutron, \( \sigma \) is the spin state of the incoming (resp. \( \sigma' \) for the outgoing) neutron, \( \Phi \) is the neutron flux, \( d\Omega \) is the solid angle element containing \( k' \), and \( W_{k\sigma\lambda \rightarrow k'\sigma'\lambda'} \) is the scattering rate.

Eq. (1.1) gives the rate with which neutrons are scattered from the initial state \( |k\sigma\lambda\rangle \) into the final state \( |k'\sigma'\lambda'\rangle \) while the sample changes its state from \( |\lambda\rangle \) to \( |\lambda'\rangle \) normalized with the incident flux \( \Phi \). If we normalize the state \( |k\sigma\lambda\rangle \) in such a way that \( \langle k'\sigma'\lambda'|k\sigma\lambda\rangle \) has the dimension of a volume, we obtain the following expression for the cross-section:

\[
\left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{k\sigma\lambda \rightarrow k'\sigma'\lambda'} = \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \frac{k'}{k} \langle k'\sigma'\lambda' | V | k\sigma\lambda \rangle|^2 \times \delta(E_{k'\sigma'\lambda'} - E_{k\sigma\lambda})
\]

where \( m \) is the neutron mass and \( V \) the scattering potential. Because the initial state \( |\lambda\rangle \) and the final state \( |\lambda'\rangle \) of the sample cannot be controlled in an arbitrary way, one has to sum over the final states \( |\lambda'\rangle \) and average over the initial states \( |\lambda\rangle \). If no polarization analysis is performed, the same procedure has to be applied to the initial and the final spin state \( |\sigma\rangle \) and \( |\sigma'\rangle \) of the neutron:

\[
\left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{k \rightarrow k'} = \frac{1}{2} \sum_{\lambda',\sigma,\sigma'} p_\lambda \left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{k\sigma\lambda \rightarrow k'\sigma'\lambda'}
\]

where \( p_\lambda \) is the probability that the sample is initially in the state \( |\lambda\rangle \). In the usual non-relativistic approximation the neutron interacts through the strong nuclear force with the nuclei and with its magnetic moment with the magnetic field in the sample.

1.4.3 Magnetic neutron scattering

As this interaction is electromagnetic, the first Born approximation (Fermi’s golden rule) is applicable. The magnetic interaction of the neutron that is most important for this work is the interaction with localized magnetic moments of rare earth ions. Using the projection identity for the vector operators, it can be shown that the magnetic interaction of the neutron with the spin of the individual unpaired electron of the \( 4f \)-shell can be expressed by using the total angular momentum operator \( J = L + S \) of the rare earth ion. Making use of this, the magnetic neutron scattering cross-section is given by:

\[
\left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{magn.} = \left( \frac{\gamma e^2}{m_e c^2} \right)^2 k' \sum_{\delta_{\alpha,\beta}} \left( \delta_{\alpha,\beta} - \frac{Q_a Q_\beta}{Q^2} \right) \sum_{j, d, j', d'} \frac{g_\alpha^2}{4} F_d^\star(Q) F_d(Q) \times e^{-2W} \sum_{\lambda, \lambda'} p_\lambda \langle \lambda | e^{-iQ R_{j, d'}} J_{j, d'}^\alpha | \lambda' \rangle \langle \lambda' | e^{-iQ R_{j, d'}} J_{j, d'}^\beta | \lambda \rangle \times \delta(E_\lambda - E_{\lambda'} + \hbar \omega)
\]
where \( F_d(Q) \) is the magnetic form factor of the ion of type \( d \), \( p_\lambda \) is the probability for finding the sample in the initial state \( |\lambda\rangle \), \( g \) is the Landé factor, which is only valid within the lowest \( J \)-multiplet, and \( J_{jd} \) is the angular momentum operator of the ion in the unit cell \( j \) at the position \( d \).

### 1.4.4 Single-ion crystal-field excitations

The basic principles of magnetic neutron scattering will be further developed to inelastic neutron scattering and applied to the study of dynamical magnetic properties of condensed matter. If the coupling between the magnetic ions is weak, we are left with a single-ion problem, thus the excitation energies will be independent of the scattering vector \( Q \). Typical examples are rare-earth compounds which exhibit very low magnetic ordering temperatures or do not order at all. In this case the dominant mechanism is the crystal-field interaction [2]. In evaluating the cross-section for the crystal electrical field (CEF) transition \( \Gamma_n \rightarrow \Gamma_m \) we start from Eq. (1.4). Since we are dealing with single-ion excitations, we have \( j = j' \) and \( d = d' \), and consequently the sum over \( j \) and \( d \) can be carried out. The cross-section for single-ion CEF spectroscopy becomes:

\[
\frac{d^2\sigma}{d\Omega dE'}_{CEF} = N \left( \frac{\gamma e^2}{m_e c^2} \right)^2 \frac{k'}{k} \sum_\alpha \left( 1 - \frac{Q^2}{Q^2_\alpha} \right) \frac{g^2}{4} |F(Q)|^2 \times e^{-2W} \sum_{i,i'} p_i |\langle \Gamma_i | J^a | \Gamma_{i'} \rangle|^2 \delta(E_i - E_{i'} + \hbar \omega)
\]  

(1.5)

where \( |\Gamma_i\rangle \) is the eigenstate \( i \) of the CEF Hamiltonian.

\[
p_i = \frac{e^{-\beta E_i}}{Z}
\]

(1.6)

is the probability for finding an ion in the initial state \( |\Gamma_i\rangle \). \( Z \) is the partition function. The effect of the crystal field on a rare-earth ion is a partial or total lifting of the \((2J+1)\)-fold degeneracy of the ground-state \( J \)-multiplet. The crystal-field levels are denoted by the irreducible representations \( \Gamma_n \), and the corresponding wave functions are

\[
|\Gamma_n\rangle = \sum_{M=-J}^{J} a_n(M) |M\rangle
\]

(1.7)

From the sequence of the energy levels, properly identified by their irreducible representations \( \Gamma_n \), the crystal-field potential can be determined unambiguously [2]. In an experiment with unpolarized neutrons it cannot be avoided to measure both the CEF and the contribution from incoherent phonon scattering at the same time, so the measured spectrum is always a mixture of the two. But there are mainly two ways to get around this problem:

1. The magnetic form factor \( F(Q) \) of an ion is proportional to the Fourier transform of its normalized spin density, which has for 4f electrons a certain spacial spread around the rare-earth ion. Therefore, the magnetic scattering decreases when \( Q \) is
1.4 Neutron scattering

increased, while the incoherent signal from the phonons is proportional to $Q^2$. These different $Q$-dependencies can be used to identify the origin of a scattering-signal if measurements at different $Q$-values are available.

2. Another difference between the scattering of neutrons from CEF transitions and phonons which can be used to distinguish the two is their temperature dependence. The occupation of a CEF state $|\Gamma_i\rangle$ is given by Boltzmann statistics while the population of a phonon-mode of branch $s$ with wave-vector $\mathbf{q}$ is determined by Bose-Einstein statistics: $\langle n_s(\mathbf{q}) \rangle = \frac{1}{e^{\beta \omega_s(\mathbf{q})} - 1}$. Therefore, the occupation of all phonon states increases (more phonons) with temperature while the CEF levels are getting more equally populated (constant number of states). Obviously, it is of advantage to go to low temperatures when looking for CEF transitions. Nevertheless, CEF measurements at higher temperatures may help to clarify the CEF level-scheme if the low-temperature data are not conclusive.
Chapter 2

Physical properties of HoNi$_2$B$_2$C

2.1 Crystal structure of HoNi$_2$B$_2$C

The rare earth nickel borocarbides, with the chemical stoichiometry $R$Ni$_2$B$_2$C, belong to the quaternary intermetallic superconductors. Here $R$ stands either for nonmagnetic Y, Lu and Sc or for lanthanide elements in a magnetic $R^{3+}$ state. Several excellent reviews are available already (Lynn et al. [3], Hilscher and Michor [4], Müller and Narozhnyi [5]), mostly focusing on the material physics and chemistry of these compounds. The crystal structure of HoNi$_2$B$_2$C, which is shown in Fig.2.1, is body centered tetragonal (symmetry group I4/mmm). The magnetism in these materials arises from ordering of the magnetic moment on the rare earth ion. The structure consist of R-C planes separated by Ni$_2$B$_2$ layers stacked along the c axis. Four B atoms are placed on the corners of a slightly distorted tetrahedron centered on Ni site. The bonds network include also B-C connections and, in spite of the apparent layered structure, the overall metallic behavior of the system is three dimensional [6]. The Ho$^{3+}$ ions are placed in the center of wide cavities and have a weak bonding with the rest of the structure, this makes the doping on this site particularly easy. The lattice parameters $a$ and $c$ have been determined [7] and are approximately $a = 3.51\text{Å}$ and $c = 10.51\text{Å}$. 
2.2 Types of magnetic order in HoNi$_2$B$_2$C

It has been shown by neutron diffraction that in the narrow temperature-range of 4.5K to 5.5K and at zero magnetic field three different types of magnetic structures occur in HoNi$_2$B$_2$C \cite{5}: a commensurate (CM) antiferromagnetic (AF) structure with a propagation vector of $\mathbf{\tau}_1 = (0 0 1)$, and two incommensurate (ICM) ones: with $\mathbf{\tau}_2 = (0 0 0.915)$ (c*-structure) and $\mathbf{\tau}_3 = (0.585 0 0)$ (a*-structure), see Fig.2.2. In the antiferromagnetic state the magnetic moments are aligned along magnetically easy directions $[\pm 1 \pm 1 0]$. This $\mathbf{\tau}_1$ magnetic structure consists of ferromagnetic planes of the Ho$^{3+}$ ions stacked antiferromagnetically along the c-direction. At temperatures below 4.5K only the CM $\mathbf{\tau}_1$ structure persists. Utilizing high-resolution x-ray scattering Hill et al. \cite{8} showed that this c-axis spiral is characterized by two wave vectors $\mathbf{q}_1 = (0 0 0.906)$ and $\mathbf{q}_2 = (0 0 0.919)$ r.l.u. The ICM $\mathbf{\tau}_2$ structure has been successfully analyzed in a quasi-linear meanfield model assuming a c-axis helix, taking into account CEF and the RKKY interaction, and supposing the presence of ferromagnetic sheets in the (a,b)-plane \cite{9}. Furthermore, in a small temperature range around $T_N \approx 5.2K$ an a*-incommensurate magnetization structure occurs with a modulation vector $\mathbf{\tau}_3 \approx (0.58 0 0)$ r.l.u. which is close to the nesting vector known from other borocarbide superconductors. The exact form of this a*-structure was still unknown \cite{5}. From results of neutron diffraction experiments on powder samples Loewenhaupt et al. \cite{11} concluded that the a*-structure has an oscillating
2.2 Types of magnetic order in HoNi$_2$B$_2$C

The net distribution of Ho moments then can have four possible configurations which are shown schematically in Fig. 6. For $\tau_1 \sim \hat{a}$, $\tau_2 \sim \hat{b}$, $\tau_3 \sim \hat{c}$, and $\tau_3 \sim \hat{b}$. These data originate from our neutron diffraction study described in detail in chapter [4].

Figure 2.2: Temperature dependence of three magnetic wave vectors of HoNi$_2$B$_2$C corresponding to: $\tau_1 = (1\ 0\ 0)$ r.l.u., ICM c*-modulation $\tau_2$, and ICM a*-modulation $\tau_3$. These data originate from our neutron diffraction study described in detail in chapter [4].

Figure 2.3: The phase-diagram at $T = 2K$ with the net distribution of magnetic moments shows four different regions. Note that moments are solely along one of the magnetically easy directions $\{\pm 1\ 1\ 0\}$ axes. $\Theta$ is the angle between the [1 1 0] direction and the applied magnetic field $H_{ax}$ in the basal plane (Canfield et al. [10]).

component of magnetic moments along the c-axis. In contrast, Hill et al. [8] suggested that the ICM $\tau_3$-structure has only magnetic moments perpendicular to the c-axis. Alternatively, the structure could be a transverse amplitude modulated wave with propagation vector along $\hat{a}$* (or $\hat{b}$*) [12]. U. Gasser has shown that the magnetic phases in a Co-doped sample like HoNi$_{1.8}$Co$_{0.2}$B$_2$C are very similar to the ones in HoNi$_2$B$_2$C. Essentially the same temperature dependencies of the commensurate $\tau_1$ and the ICM c*-structure are observed, whereas the ICM a*-structure has not been found in the doped sample. The magnetic c*-structures of HoNi$_2$B$_2$C have therefore turned out to be robust with respect to a reduction of the Fermi level $E_F$ and consequently to a variation of the Fermi-surface [13]. The modulation vector $\tau_3$ is ubiquitous in the quaternary borocarbides:

1. The borocarbide superconductors show Fermi-surface nesting characterized by nesting vector $\sim \tau_3$.

2. In some of the RNi$_2$B$_2$C compounds, in particular for $R = Y$, Lu, and Ho, phonon softening is observed for a modulation vector $\sim \tau_3$.

3. Zero-field incommensurate magnetization structures with a modulation vector $\sim \tau_3$.
occur in \( R\text{Ni}_2\text{B}_2\text{C} \) for \( R = \text{Gd, Tb, Ho and Er} \).

4. A metamagnetic phase with a modulation vector close to \( \tau_3 \) has been reported also for \( \text{TmNi}_2\text{B}_2\text{C} \).

Since the discovery of the two incommensurate magnetic modulations in the mid nineties a lively debate is going on concerning these structures and their influence on a near-reenterant behavior of superconductivity, as discussed in section 2.3.1.

**Figure 2.4:** The different magnetic structures of \( \text{HoNi}_2\text{B}_2\text{C} \) as determined by neutron scattering. (left) commensurate antiferromagnetic \( \tau_1 \), (middle) incommensurate \( \text{c}^*\)-structure (spiral) with the modulation vector \( \tau_2 = (0 \ 0 \ 0.916) \) and (right) incommensurate \( \text{a}^*\)-structure with a modulation vector of \( \tau_3 = (0.58 \ 0 \ 0) \) r.l.u. [5].

**Figure 2.5:** The incommensurate \( \text{a}^*\)-structure \( \tau_3 = (0.58 \ 0 \ 0) \) r.l.u. is a transverse amplitude modulated wave with the magnetic moments along the \( \text{b}^*\)-direction as we determined by neutron polarimetry, see chapter [4] It is conceivable that \( \tau_3 \) exists in superposition with \( \tau_1 \).

### 2.2.1 Metamagnetic transitions

For magnetic fields \( H_{ex} \) applied perpendicular to the tetragonal \( \text{c} \)-axis of \( \text{HoNi}_2\text{B}_2\text{C} \) single crystals, it was concluded that besides the paramagnetic phase at elevated temperatures and the simple antiferromagnetic phase(\( \uparrow \downarrow \)) at low temperatures and low field, three
2.2 Types of magnetic order in HoNi$_2$B$_2$C

Figure 2.6: Longitudinal x-ray scans in the vicinity of the (0 0 3) antiferromagnetic reciprocal-lattice point. Top: $T = 4.3$K. Only the commensurate peak is present. Inset: Schematic of reciprocal space. Closed (open) circles represent nuclear (antiferromagnetic) Bragg peaks. The crosses correspond to the incommensurate satellites present for temperatures above $T = 5.2$K. The ICM peak consists of two satellites at $(0 0 2 + q_1)$ and $(0 0 2 + q_2)$. The (0 0 3) commensurate peak is still present but significantly reduced and broadened. Bottom: Data taken at $T = 5.39$K, in the incommensurate phase. Inset: High-resolution neutron-scattering data taken at an equivalent temperature confirming that the splitting of the ICM satellite is a bulk effect. (Hill et al. [8])

Figure 2.7: Temperature dependence of the (0 0 3) commensurate antiferromagnetic Bragg peak. (a) The peak intensity. (b) The width, $\kappa$ of a Lorentzian fit to the data. At low temperatures the intensity is approximately constant, suggestive of a saturated order parameter. At $T = 5.2$K, the intensity abruptly falls. This coincides with the appearance of ICM satellite peaks, and marks the first-order CM-ICM transition. The (0 0 3) intensity decays more slowly as the temperature is increased further. Below the transition it is almost resolution limited. Above $T = 5.2$K the peak broadens. The solid line is a guide to the eye. (Hill et al. [8])

metamagnetic phases occur [10] (see Fig.2.3). Two basic assumptions were established by Canfield to describe the metamagnetic phase diagram:

1. The magnetic moment directions at $T = 2$K are extremely anisotropic and locked in one of the four in-plane easy direction $[\pm 1 \pm 1 0]$.

2. All metamagnetic states are built from ferromagnetic basal planes.
In other words, in all of the magnetically ordered phases the local magnetic moments are either near-parallel(↑), near-antiparallel(↓) or near-perpendicular (→, ←) to the [1 1 0]-direction. As an important result Detlefs et al. [14] found by neutron diffraction at $T = 2\text{K}$ that the second metamagnetic phase (↑↑→) has a modulation vector $\tau_3 \approx (4/7 \ 0 \ 0)$ r.l.u. In theirs study the magnetic field was oriented in the basal plane 15degree off the [1 1 0]-direction. A similar result has been reported by Campbell et al. [15] who measured for $H_{\text{ex}}$ parallel to [1 0 0], and observed in the second metamagnetic phase an incommensurate wave vector of about (0.61 0 0) r.l.u. Amici and Thalmeier [9] used a quasi-one-dimensional model in which the presence of ferromagnetically ordered Ho layers with their magnetic moments oriented perpendicular to the tetragonal c-axis is proposed from the very beginning and the competition of RKKY interaction along the c axis with the CEF is analyzed. The so-called clock model of Kalatsky and Pokrovsky [16] is also a semiclassical approximation which starts with the assumption that the strong single-ion anisotropy confines the Ho magnetic moments to the four directions [±1±1 0]. However, neither model can explain the origin of the $a^*$-modulation observed at zero field or at finite field as reported by Detlefs et al. [14]. But Rhee et al. explain this $a^*$-modulation in terms of electronic susceptibility [17]. Possibly these problems can only be solved by a more detailed description of the RKKY interaction, taking into account the Fermi-surface nesting features [5].

The metamagnetism of HoNi$_2$B$_2$C is caused by two antagonistic interactions, namely tetragonal CEF potential and the RKKY-interaction. Whereas the first tries to align the moments along the easy axis as determined by the CEF potential the second one prefers a helical modulation of moments with a wave vector that minimizes the exchange energy. The favored structure results from a compromise and may change with temperature and external field [18]. Property of the CEF potential is obtained from inelastic neutron
scattering experiments (Gasser et al. [19]) by fitting the observed energies and intensities of CEF transitions which determines the parameters of the model Hamiltonian \( H_{CEF} \). The start parameters for the fit were obtained by an extended point charge model. Then the CEF energies and wave functions are obtained explicitly. For \( \text{Ho}^{3+} \) (\( J=8 \)) the 17 CEF states split into two groups. A group of 13 states with energies > 10meV which is irrelevant in the interesting temperature range and four low lying CEF states consisting of a ground state singlet \( \Gamma_4 \) (0meV) and excited doublet \( \Gamma_5^* \) (0.15meV) and another singlet \( \Gamma_1 \) (0.32meV).

### 2.2.2 Magnetostriiction

A magnetoelastic effects in \( \text{HoNi}_2\text{B}_2\text{C} \) observed by diffraction experiments was reported by Kreyssig et al. [20]. At low temperatures the tetragonal lattice is distorted along the [1 1 0]-direction, in which the long-range ordered Ho moments are aligned. The length of the unit cell in [1 1 0]-direction is shortened by about 0.19% compared to its length in [1 1 0]-direction. This lattice distortion is considered to be related to the existence of the commensurate c-axis modulated antiferromagnetic structure. The magnetoelastic effect in \( \text{HoNi}_2\text{B}_2\text{C} \) might be a key issue for the understanding of the ICM \( a^*\)-structure. Detlefs et al. [14] concluded that for an external magnetic field \( H_{ex} \) one will have a reduction in the magnetostriction along [1 1 0] for those metamagnetic states, where the net magnetization points away from the [1 1 0]-direction. In other words, in the metamagnetic states with a non-collinear magnetic structure. The reduction of the magnetostriction and the resulting disturbance of the Fermi surface nesting along [1 0 0] could be the basic cause of the magnetic ordering vector \( 0.58a^* \), the same propagation vector which is common through out the heavy \( R\text{Ni}_2\text{B}_2\text{C} \) [14]. We will come back to this issue in section 4.4.
2.3 Superconductivity in HoNi$_2$B$_2$C

Superconductivity in a number of borocarbides was first reported in 1994 by Nagarajan et al. [21] and Cava et al. [22]. An excellent review on unconventional superconductivity and magnetism in lanthanide and actinide intermetallic compounds is available from Thalmeier and Zwicknagl [18]. There is evidence that the superconducting mechanism is primarily of the electron-phonon (e-p) type although this cannot explain the large anisotropy of the SC gap [18].

The superconducting condensate and magnetic moments are carried by different types of electrons, namely itinerant 3d-electrons for the Ni$_2$B$_2$ layers and localized Ho$^{3+}$ 4f-electrons for the R-C layers respectively. The coherence length $\xi_0$ at zero temperature is calculated in the BCS approximation, and the temperature dependence may be obtained using Ginzburg-Landau theory. The coherence length $\xi$ is important in the relation to ordered magnetic structures since the magnetic field emerging from an antiferromagnetic structure will not affect the order parameter of superconductivity, if the modulation of magnetic moments is zero in average on the length scale of the coherence length. This is the case in RNi$_2$B$_2$C where $\xi$ is of the order 100 Å [5]. The RNi$_2$B$_2$C compounds are type two superconductors with a Ginzburg-Landau parameter $\kappa = \frac{\lambda}{\xi}$ in the range of 5 - 10. The penetration depth $\lambda$ is defined as the length scale of the penetration of the magnetic field into the superconducting type II material: $B_i(x) = B_{\text{applied}} e^{-x/\lambda}$. The simple picture of a magnetic superconductor is that there are flux lines (flux quantum) penetrating regions with zero field superconductivity. In the RNi$_2$B$_2$C compounds the penetration depth is of the order 500 Å to 1000 Å thus for a moderate magnetic field the distance between the flux lines becomes smaller than the penetration depth. Therefore the picture to have in mind is an almost constant field throughout the superconducting phase, penetrated by regions of zero superconductivity. Superconductivity is suppressed in a type II superconductor at a field $H_{C2}$ when the density of flux lines becomes so high that the normal cores with a size comparable to the coherence length, are overlapping. Borocarbides which posses $R^{3+}$ ions with an open 4f shell, i.e., with Pr, Nd, Gd, Tb, Dy, Ho, Er and Tm, show strong magnetic properties and order magnetically in the same temperatures range in which several of them undergo the superconducting transition (Fig.2.11). The magnetic transition temperatures $T_m$, which is either equal to $T_{ICM}$ or to $T_N$ depending on the borocarbide, scale linearly with the de Gennes factor:

$$dG = (g - 1)^2 J(J + 1)$$

(2.1)

where $g$ is the Landé factor and $J$ is the total angular momentum of the $R^{3+}$ ions. This is consistent with the coupling between the conduction electrons and the local magnetic moments giving rise to the long range magnetic order via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

2.3.1 Reentrant behavior

Resistivity and upper critical field measurements by Eisaki et al. [24], performed on powder samples, demonstrated that this compound exhibits reentrant behavior of superconductivity even in zero field in a small temperature range around 5K. Their susceptibility
Figure 2.11: Some examples of the transition temperatures to superconducting and magnetically ordered states among the series of the borocarbides (Amici et al. [23]).
cause for the anomaly of the upper critical field in HoNi$_2$B$_2$C. As a general empirical rule for HoNi$_2$B$_2$C samples, the appearance of reentrant behavior caused by stoichiometric effects or pressure or magnetic field is always connected with a reduced value of $T_C$ [5].

2.3.2 Interplay of superconductivity and magnetism

The antiferromagnetic molecular field establishes a periodic perturbation characterized by a length scale of the order of the Fermi wavelength $k_F^{-1} \ll \xi_0$. This implies that the spatial extent of the Cooper pairs extends over many periods of the alternating molecular field. The latter is therefore effectively averaged to zero and does not suppress superconductivity via an orbital effect [18]. The magnetic order does not lead to depairing (Fulde and Keller [29]). The coupling between magnetic and superconducting order parameters is weak enough to be treated as a perturbation but still strong enough to lead to pronounced effects on the SC properties. In the RKKY mechanism IC modulation vectors should result from the maxima of the static electronic susceptibility $\chi(q)$ which has been approximately calculated by Rhee et al. [17]. It exhibits a pronounced peak at the nesting vector of the Fermi surface which is indeed quite close to observed a-axis magnetic modulation vectors $q \approx (0.55 \ 0 \ 0)$ of the Gd, Tb, Ho and Er borocarbide compounds. On the other hand in HoNi$_2$B$_2$C only a flat maximum of $\chi(q)$ is observed for the modulation vector $\tau_2 = (0 \ 0 \ 0.915)$ close to the AF vector $\tau_1 = (0 \ 0 \ 1)$ so that the observed helically modulated structures along the c-direction should not be associated with any FS nesting feature. These compounds should more appropriately be called superconducting magnets because the magnetic and superconducting energy scales given by $E_m = k_BT_m$ and $E_{SC} = k_B^2 T_C^2 / E_F$ differ strongly. If $T_m \approx T_C$ as in the present case then $E_{SC}/E_m = k_B T_C / E_F \approx 10^{-2}$ [18]. This is due to the fact that only a fraction $k_B T_C / E_F$ of the conduction electrons participates in the pair formation whereas the exchange energy
of all localized spins is involved in the magnetic ordering. Thus local moment magnetic order energetically completely dominates superconductivity whose influence on the former will therefore be negligible (Amici and Thalmeier [30]). This is assumed by neglecting the effect of superconductivity on the RKKY interaction via the conduction electron susceptibility. This is justified because the superconductivity would only be affected for $|q| \leq \xi_0^{-1}$, and we discuss the competition with AF order or ICM phases with modulation vectors close to $\tau_1$. Amici et al. mentioned that there is no big difference in the effect of helical order (below $T_C$) and commensurate AF order (below $T_N$), the overall depression is simply controlled by the increase of ordered magnetic moments $\mu(T)$ when $T$ decreases. The observed $[1 1 0], [0 0 1]$ anisotropy of $H_{C2}$ is due to the different magnetization response. Amici and Thalmeier interpreted the main anomaly of the upper critical field in HoNi$_2$B$_2$C via the reduction of the interaction between phonons and electrons in the Bloch states of the magnetic structure. In this respect, the effect of a helical magnetic background on superconductivity is identical to the effect of antiferromagnetism [31]. They have found that helical magnetic structures appear to affect superconductivity in essentially the same way an antiferromagnet does, hence allowing coexistence. In this case indeed the main effect on the superconducting properties is a slight weakening of the effective attractive interaction among conduction electrons in the magnetic Bloch-states. Cooper pairs formed by electrons in the Bloch states associated with any kind of magnetic ordered states do not decay, exactly as non-magnetic BCS pairs do not. Therefore, the detrimental effect on superconductivity is not produced by ”pair-breaking” and the effect on superconductivity of a magnetically ordered structure is completely different from the one of an isolated magnetic impurity [23]. Doh et al. [32] demonstrated with a phenomenological model that the magnetic fluctuations and order in HoNi$_2$B$_2$C lead to anomalous behavior of the upper critical field. Their model includes two magnetic and two superconducting order parameters which account for the multiband structure of in this system. Furthermore, they explain with this model the doping dependence of $T_C$ in Ho$_{1-x}$Dy$_x$Ni$_2$B$_2$C. I will not go through an evaluation of the basic properties of superconductivity, simply because this thesis focusses mainly on the magnetic properties of HoNi$_2$B$_2$C.
Physical properties of HoNi$_2$B$_2$C
Chapter 3

Macroscopic measurements

The aim of the macroscopic investigation was to characterize the HoNi$_2$B$_2$C single crystals and to determine the upper critical field $H_{C2}$ of superconductivity. We performed electro-transport measurements to extract $H_{C2}$ as function of temperature for an applied field along $H_{ex} \parallel [1\ 1\ 0]$, $H_{ex} \parallel [1\ 0\ 0]$ and $H_{ex} \parallel [0\ 0\ 1]$. We relate this findings to results for the imaginary part of the AC susceptibility $\chi''$. Furthermore, the AC susceptibility investigation reveals interesting locations of the respective ($H,T$)-phase diagram, where $\chi''$ shows a local maximum. The DC-magnetization measurements determine the field induced magnetic phase transitions and establish valuable information about the arrangement of the magnetic moments in the respective metamagnetic state.

3.1 DC-magnetization

The temperature and magnetic field ($H_{ex}$) dependencies of the static magnetization were measured using the magnetometer option of a Quantum Design PPMS 6000 based on a extraction magnetometry technique. Moving a magnetized sample through the detection coil induces a voltage in the detection coil set. The amplitude of the signal is proportional to the magnetic moment and speed of the sample during extraction. The magnetization data for an applied magnetic field along the easy and hard in-plane direction and for $H_{ex} \parallel [0\ 0\ 1]$ are shown in Fig. 3.1(left). At $T = 2K$ the $M_{DC}(H)$ data, taken with increasing and decreasing field, exhibit hysteretic metamagnetic transitions to a first metamagnetic phase ($\uparrow\uparrow\downarrow$) with increasing field near 0.4T and 0.5T for $H_{ex} \parallel [1\ 1\ 0]$ and $H_{ex} \parallel [1\ 0\ 0]$, respectively. A second transition takes place at 1.0T for $H_{ex} \parallel [1\ 1\ 0]$ to a near saturated magnetization and at 0.8T for $H_{ex} \parallel [1\ 0\ 0]$ to a phase of about $\sqrt{2}/2$ of the saturated magnetization. No correction of the field values for the demagnetization factor of the samples is included. We determined the saturated magnetic moment per Ho$^{3+}$ ion to be $\mu_S \approx 8.5 \mu_B$ for an applied magnetic field of 2.5T in $[1\ 1\ 0]$-direction and fixed $T = 2K$. However, our value for the saturated magnetic moments is $\approx 13\%$ smaller as the value reported by Canfield et al. [10]. The magnetization data received for $H_{ex} \parallel [1\ 0\ 0]$ and $H_{ex} \parallel [1\ 1\ 0]$ were measured on a single-crystal sample of 42mg. The measurements for $H_{ex} \parallel [0\ 0\ 1]$ have been carried out with a sample of 132mg. We like to emphasize that with the magnetometer one measures the projection of the net magnetic moment along the field-axis, e.g. we can not distinguish between $\langle \downarrow\uparrow\downarrow\rangle$ with an net moment along the
Figure 3.1: DC-Magnetization at $T = 2K$ for an applied magnetic field $H_{ex} || [1 1 0]$ and $H_{ex} || [1 0 0]$, respectively. Left: The obtained PPMS data without any correction factor. Right: The data for $H_{ex} || [1 0 0]$ are multiplied by $\sqrt{2}$.

Field direction and a ($\uparrow \uparrow \downarrow \downarrow$) arrangement of the moments. Both structures would result in a magnetization of $\sqrt{2}/2\mu_S$. If we assume the same first metamagnetic phase ($\uparrow \uparrow \downarrow$) for an applied field along $[1 0 0]$ as along $[1 1 0]$ we have to multiply the measured DC-magnetization by a factor $\sqrt{2}$, see Fig.3.1(right). The resulting curve lies $\approx 15\%$ higher at the plateau of the first metamagnetic state than the curve for the $H_{ex} || [1 1 0]$ data. This discrepancy is either due to a misalignment of the crystal in respect to the applied field or an indication that the so far proposed arrangement ($\uparrow \uparrow \downarrow$) [33] is not valid for an applied field in the hard in-plane direction. We will come back to this issue in section 4.4. Additional temperature-sweep measurements at constant magnetic field values and field-scans at fixed temperature for $H_{ex} || [0 0 1]$ are presented in Fig.3.2.

### 3.2 AC-susceptibility

To perform an AC susceptibility measurement on the PPMS, a signal with a frequency of 10Hz to 10kHz and an amplitude of 2mOe to 15Oe is applied to the drive coil and the sample is centered in one of the two detection coils. The system then records the voltage across the detection coils for a predetermined amount of time. On of the most notable feature of the AC magnetometry system is its ability to separate real and imaginary components of the AC response. The real part $\chi'$ represents the component of the susceptibility that is in phase with the applied AC field, while complex part $\chi''$ represents the component that is out of phase. $\chi''$ is related to the energy losses, or in other words, the energy absorbed by the sample from the AC field. We performed our experiments with an AC amplitude of 100e and a frequency of 1000HZ. Based on a preliminary work by Canfield et al. [33] in which $H_{C2}$ was estimated by magnetic susceptibility measurements.
3.2 AC-susceptibility

Figure 3.2: DC-Magnetization for an applied magnetic field $H_{ex} || [1 1 0]$. Left: At constant temperature $T = 3K$, 4.6K and 5.3K. Right: Temperature-scans at 0.4T, 0.55T, 0.7T, 1.05T and 1.6T.

we performed a comparable study on our HoNi$_2$B$_2$C single-crystals. But our attempts demonstrated the difficulties in extracting this quantity. The measurements access the superconducting phase on top of a strong and anisotropic magnetic answer. We measured the AC susceptibility as a function of the temperature for a fixed magnetic field. Every field value was achieved by setting the field at $T = 20K$ and cooling down to 2K afterwards. We combined the single temperature scans to a surface plot consisting of 30 to 40 data sets. Interestingly, in the surface plots of the imaginary part $\chi''$ of the AC susceptibility (Fig.3.3, Fig.3.5 and Fig.3.6) a similar characteristic of the contour lines was observed as in the corresponding resistivity measurements, see Fig.3.10, Fig.3.11 and Fig.3.12. The contrast of the respective surface plots was tuned to reproduce the $H_{C2}$ characteristics obtained by the resistivity measurements. A interesting feature of the surface plot for an applied field along $[1 1 0]$ is presented in Fig.3.4. At 3.5K and 0.4T we observed a local maximum of $\chi''$ akin to a triple point of phase boundaries. At this point the system seems to be in an indifferent state. Different magnetic arrangements possess the same energy and may coexist. But it was not possible to determine $H_{C2}$ directly out of the AC susceptibility data. Therefore a comparative resistivity investigation was performed, to be discussed below.

The physical properties, especially superconductivity of the rare-earth borocarbides, have a strong dependence on small variations in the crystal stoichiometry [34, 35, 36]. But we do not agree with the statement that AC susceptibility measurements are more sensitive to the re-entrant or near re-entrant behavior, than electrical resistance measurements at low temperatures as reported by Ref. [34, 35]. We observed in the resistivity measurements a relatively sharp transition of $\Delta T_C \approx 0.4K$ at $T_C \approx 8.5K$ without any re-entrant behavior below $T_C$ for zero magnetic field (see Fig.3.9 right)) whereas from the AC-Susceptibility measurement of the same crystal we would estimate a broad transition $\Delta T_C \approx 1K$ at
Macroscopic measurements

Figure 3.3: Imaginary part $\chi''$ of the AC-Susceptibility for an applied magnetic field along [1 1 0].

Figure 3.4: Triple point of magnetic phase boundaries in HoNi$_2$B$_2$C as measured by the imaginary part $\chi''$ of the AC-Susceptibility.

Figure 3.5: Imaginary part $\chi''$ of the AC-Susceptibility for an applied magnetic field along [1 0 0].

Figure 3.6: Imaginary part $\chi''$ of the AC-Susceptibility for an applied magnetic field along [0 0 1].

$T_C \approx 7$K and from the pronounced peak of the real part $\chi'$ at $\approx 5$K we would conclude a re-entrant behavior, see Fig.3.3. Due to the fact that the change in magnetic ordering dominates the AC-Susceptibility measurements and the before mentioned discrepancy we determined the superconducting properties, e.g. $H_{C2}$ of HoNi$_2$B$_2$C by conventional resistivity measurements. By definition, the most direct way to investigate the superconducting properties is by electro-transport measurements.
3.3 Resistance and determination of $H_{C2}$

The resistivity measurements were performed on small platelet-shaped single crystals (5x5x1mm$^2$). A Quantum Design four-probe AC resistance bridge was used in conjunction with the $T$ and $H_{ex}$ environment control of the PPMS to measure the in-plane four-probe resistance as a function of temperature, applied magnetic field, and crystal orientation relative to the field. Gold wires 0.06mm in diameter were attached to the surface of the crystal with a silver ink (Electrodag$^\text{TM}$ 1415). The contact resistance was less than 1Ω. The resistance data presented in this work were measured with a sampling current of 5mA at 100Hz. For the resistance measurements the magnetic field was set to the chosen constant value after zero field cooling down to 2K. The measurements directly provide the temperature dependence of $H_{C2}$ as a function of different applied field directions. The determined residual resistivity ratio (RRR) results in $\approx 11.5$. This ratio is an indicator for the quality of the HoNi$_2$B$_2$C single crystal. The RRR is defined as the ratio between the resistance of the crystal at 293K and the resistance just above $T_C$, see Fig 3.9. We measured the resistance as a function of the temperature (increasing) for a fixed magnetic field. Every field value was achieved by setting the field at $T = 20K$ and cooling down to 2K afterwards. We combined the single temperature scans to a surface plot consisting of 20 to 25 data sets. The $H_{C2}(T)$ curves for HoNi$_2$B$_2$C determined by resistivity measurements for the applied magnetic field along the [1 1 0]-axis, [1 0 0]-axis and [0 0 1]-axis are shown in Fig 3.10, Fig 3.11 and Fig 3.12, respectively. To compare our data to the preliminary work of Krug et al. [37] the criterion to determine $H_{C2}$ was set to the midpoint of the superconducting phase transition.

Qualitatively, the $H_{C2}(T)$ curves show the same features known from other groups’ investigations [37, 33, 38]. There is a local maximum at 6K and a deep minimum at $T_N \approx 5K$. 

\[\text{Figure 3.7:} \] Local maximum of $\chi''$ for an applied magnetic field along [1 1 0]. The maximum is located at the lower boarder of the second metamagnetic phase transition.

\[\text{Figure 3.8:} \] Real part $\chi'$ and imaginary part $\chi''$ of the AC-Susceptibility at zero static field. $f = 100Hz$, $H_0 = 10Oe$
Figure 3.9: PPMS resistance measurements as function of the temperature with a sampling current of 5mA along [1 1 0]. Left: The residual resistivity ratio (RRR) of the investigated HoNi$_2$B$_2$C single crystal is $\approx 11.5$. Right: The transition temperature to the superconduction state is $T_C \approx 8.5$K. whereas the temperature range amounts $\Delta T_C \approx 0.4$K.

Figure 3.10: Normalized resistivity and the determined $H_{C2}$ for an applied magnetic field $H_{ex} \parallel [1 1 0]$. The measurements were carried out at a sampling current of 5mA along [1 -1 0].

Figure 3.11: Normalized resistivity and the determined $H_{C2}$ for an applied magnetic field $H_{ex} \parallel [1 0 0]$. The measurements were carried out at a sampling current of 5mA along [0 1 0].

Quantitatively, our values for $H_{C2}$ are generally lower than the values presented by Krug. Comparing their data with ours, one finds agreement in the $H_{ex} \perp [0 0 1]$ curves, which are at lower values than the $H_{ex} \parallel [0 0 1]$ curve in the whole temperature range under investigation. For $H_{ex} \parallel [0 0 1]$, our value of the local maximum above $T_N$ is about 35% lower. Like reported in the investigation of Rathnayaka et al. we can confirm a char-
characteristic sampling current dependence of the measured resistance. One observes a shift of the $H_{C2}$-curve towards smaller field values for an increase of the sampling current (0.5 to 5mA). The effect clearly depends on the direction of the applied field. The sampling current dependence is more pronounced for an applied field along $H_{ex} || [0 0 1]$ than for a field in the (a,b)-plane.

### 3.4 Heat capacity

The specific-heat of a HoNi$_2$B$_2$C crystal of mass $\approx 9$mg was measured from 2 to 10K. On the PPMS a thermal relaxation technique was used with the sample attached to a micro-calorimeter platform by a small amount of a thermal coupling agent (Apiezon grease). The specific-heat data were corrected for an additive therm due to the addenda, the contribution of which was determined by a separate measurement. Following the notation of Park et al. [39] we identified by this investigation three magnetic transitions ($T_N$, $T^*$, $T_M$), see Fig.3.13. Where $T_N \approx 5.2$K is associated with the Néel temperature, $T^* \approx 5.5$K with the onset of the incommensurate $c^*$-structure and $T_M \approx 6.0$K with the onset of the incommensurate $a^*$-structure (compare to Fig.4.3 of the diffraction study). The expected indication for $T_C \approx 8.5$K could not be observed by the specific heat measurement, see Fig.3.13(inset). Park et al. [39] reported of a specific heat discontinuity at $T_C$ of $\approx 100$mJ/(mol·K) which should in principle be measurable with the accuracy of our investigation. However we didn’t observe any trace of this transition which might be buried in the huge magnetic background.
Figure 3.13: Zero-field heat capacity of HoNi$_2$B$_2$C measured on PPMS. The single crystal mass was 9.2(3)mg. Three magnetic transitions were identified at $T_N \approx 5.2$K, $T* \approx 5.5$K and $T_M \approx 6.0$K. Inset: We haven’t observed any indication for $T_C$ in the specific heat measurement.
Chapter 4

Structural investigation

In this chapter we present a comprehensive single crystal neutron-diffraction study of HoNi$_2$B$_2$C in the presence of a magnetic field applied along [1 1 0], [1 0 0], and [0 0 1]. This investigation stresses the richness of the system under investigation and reveals that the magnetic phase diagram of HoNi$_2$B$_2$C is more complicated as proposed so far. In zero field, spherical neutron polarimetry allow the determination of the incommensurate $a^*$-structure of HoNi$_2$B$_2$C. Combined diffraction data provide a complete visualization of the scattering intensities in the corresponding 2D-plane of the reciprocal space. Furthermore, the phase diagram for different magnetic modulations was determined for a magnetic field applied along the easy and the hard in-plane direction $H_{ex} || [1 1 0]$ and $H_{ex} || [0 1 0]$, respectively. The motivation to perform the structural investigation on HoNi$_2$B$_2$C was the inconsistency of the inelastic data with the proposed metamagnetic (↑↑→) phase.

4.1 Zero magnetic field

To perform the temperature and field dependent measurements we used a 1.8 Tesla horizontal cryomagnet. Since the discovery of the two incommensurate magnetic modulations in the mid-nineties a lively debate is going on concerning these structures and their influence on the near-reenterant behavior of superconductivity. Based on a high-resolution x-ray and neutron scattering study Hill et al. suggested for the $\tau_2$ structure a c-axis spiral modulation associated with two close wave vectors $q_1=0.906 \ c^*$ and $q_2=0.919 \ c^*$[8]. Furthermore, it has been proposed that the modulation is not perfectly sinusoidal: Since the first and third harmonic reflections are present, which points towards a ‘squaring’ of the spiral [12]. Also, the exact type of the $a^*$-structure still remained unclear [3]. From neutron diffraction results on powder samples Loewenhaupt et al. [11] concluded that the ICM $\tau_3$ has an oscillating component of magnetic moments parallel to c-axis. In contrast, Hill et al. [8] suggested that the ICM $\tau_3$ has only magnetic moments perpendicular to the c-axis. Alternatively, the structure could be a transverse amplitude modulated wave with propagation vector along $a^*$ (or $b^*$) [12]. Moreover, it has not been settled yet whether all these wave vectors may coexist in the same volume fraction or if they compete and are locally separated. A magnetoelastic effect in HoNi$_2$B$_2$C was reported by Kreyssig et al. [20]: At low temperatures $T<T_N$ the tetragonal lattice is slightly distorted along the [1 1 0]-axis, in which the long-range ordered Ho
moments are aligned. HoNi$_2$B$_2$C is a good example of a local moment system that manifests extreme basal plane single ion anisotropy at low temperature due to crystal electric field (CEF) interaction. Whether the magnetic long-range order is commensurate or incommensurate is the result of a competition between the CEF \[19\] and the Rudermann-Kittel-Kasuya-Yoshida (RKKY) interaction. Since this indirect exchange interaction is mediated by the conduction electrons, the incommensurate magnetic structure depends on details of the electronic structure. This is the reason why the nesting vector $q \approx (0.6 0 0)$ manifests itself as the modulation wave vector of different incommensurate structures found in various RNi$_2$B$_2$C compounds \[5\]. For HoNi$_2$B$_2$C a strong correlation between the near-reentrant behavior of superconductivity and the $a^*$-modulated structure was emphasized by Müller et al. \[40\] and other authors \[11, 14\]. On the other hand, a mean-field calculation of A. Amici \[23\] provides a completely different interpretation. According to him, the dip in the upper-critical-field curve of HoNi$_2$B$_2$C results from a small but rapid decrease of the effective electron-phonon interaction parameter due to the onset and fast increase of the magnetic order parameter. In this picture, the $a^*$-structure plays only a marginal role for the depression of superconductivity. Nevertheless, a direct manifestation of the electron-phonon coupling was observed in the softening of the phonon spectrum in HoNi$_2$B$_2$C at the nesting wave vector along the $a^*$-axis \[12\]. Altogether, there is evidence that the ICM $\tau_3$-structure is most probably connected to the Fermi surface nesting and therefore the relation of this structure to superconductivity still needs to be resolved.

4.1.1 Neutron polarimetry

We performed a spherical neutron polarimetry experiment on the D3 diffractometer with the CRYOPAD II at ILL in Grenoble, France. The study is based on high quality single crystals of $^{11}$B substituted HoNi$_2$B$_2$C. They were prepared by a high temperature flux-growth technique described in Ref. \[43\]. The crystal (5x5x1 mm$^3$) was mounted inside an ILL orange-type cryostat with the $b^*$-direction perpendicular to the scattering plane. The measurements were performed with a neutron wavelength of 0.843 Å (Cu$_2$MnAl monochromator) at temperatures 2K-5.3K. The polarization of the scattered beam was measured by a $^3$He neutron spin filter. Since the filter polarization decays with time, this decay was monitored by measuring the polarization of the (0 0 4) structural reflection and the appropriate polarization correction was applied. The scattered polarization was measured for three directions of the incident polarization: parallel to the vertical $z$-direction, along the scattering vector $Q \parallel x$ and in the $y$-direction that completes the right-handed Cartesian set. In this coordinate system the magnetic interaction vector $M_\perp$, being the projection of the Fourier transform of the magnetization $\mathbf{M}(r)$ onto the plane perpendicular to $Q$, lies in the $yz$-plane.

4.1.2 Data analysis

For a pure magnetic reflection, the cross section for Bragg scattering of a beam of neutrons with polarization $P_\parallel$ is \[44, 45\]

$$\frac{\partial \sigma}{\partial \Omega} = M_\perp \cdot M_\parallel + P_\parallel \cdot \Im (M_\perp \times M_\parallel)$$

(4.1)
4.1 Zero magnetic field

and the scattered polarization $P_s$ is

$$P_s \frac{\partial \sigma}{\partial \Omega} = -P_i (M_{\perp} \cdot M_{\perp}^*) + 2 \Re (M_{\perp} (P_i \cdot M_{\perp}^*)) - 2 \Im (M_{\perp} \times M_{\perp}^*)$$

(4.2)

$M_{\perp}^*$ denotes the complex conjugate of the magnetic interaction vector $M_{\perp}$, $\Re$ the real part and $\Im$ the imaginary part of a complex number. For an amplitude modulated wave in its simplest case the magnetic moment on the $j$th atom of the $l$th unit cell may be written as

$$S_{jl} = A_j \cos(\tau \cdot r_l + \phi_j)$$

(4.3)

and for a helix or cycloidal magnetic structure

$$S_{jl} = A_j \cos(\tau \cdot r_l + \phi_j) + B_j \sin(\tau \cdot r_l + \phi_j)$$

(4.4)

where $A_j$ and $B_j$ are perpendicular vectors. They correspond to the magnitude and direction of the major and minor axis of the elliptical envelope of the spin modulation on the $j$th atom. $r_l$ is the vector defining the origin of the $l$th unit cell and $\tau$ the propagation vector of the modulation. The phases of the modulation are given by $\phi_j$. By measuring the change in polarization state of neutrons scattered by the magnetic reflections one can undoubtedly distinguish whether a modulation of the amplitude or a modulation of the direction of the moments constitutes the magnetic structure.

For neutrons scattered by a pure magnetic reflection of collinear structures ($M_{\perp} \parallel M_{\perp}^*$) the polarization $P_s$ is related to the incident polarization $P_i$, by a precession of $180^\circ$ about $M_{\perp}$. In helical structures, where $M_{\perp}$ and $M_{\perp}^*$ are not parallel, the situation is different. In this case, if the incident polarization $P_i$ is perpendicular to the scattering vector $Q$, the polarization is flipped around the magnetic interaction vector $M_{\perp}$ and rotated towards $Q$.

In a multidomain sample, both the cross section and the scattered polarization have to be calculated for each magnetic domain separately and summed up with weights proportional to the domain fraction. The two most common types of domains are configuration ($K$-) and orientation ($S$-) domains. $K$-domains exist whenever the propagation vector $k$ describing the magnetic structure is not transformed either into itself, or itself plus a reciprocal vector, by all the symmetry operators of the paramagnetic group. When this is the case the operation of the paramagnetic symmetry on $k$ generates a set of inequivalent vectors which form the star of $k$. Each vector in the star generates a different configuration ($K$-) domain. The $S$-domains arise when the symmetry of a magnetic structure is lower than the configurational symmetry.

Each magnetic reflection arises from a single $K$-domain, but may have contribution from more than one $S$-domain. The presence of $S$-domains leads to depolarization of the scattered beam. For a detailed description of spherical neutron polarimetry we refer to Ref.[16].
4.1.3 ICM $a^*$-structure

Firstly, we examined the magnetic reflections corresponding to the $a^*$-structure $\tau_3 = (0.585 0 0)$. The results are presented in table 4.1. The scattered polarization of the $(h\pm\tau_3 0 0)$ reflections is not rotated when the initial polarization is parallel to $z$ (the $b^*$-direction), but is reversed when $P_i$ is parallel to $x$ ($a^*$) or $y$ ($c^*$). Besides, there is no significant depolarization of the beam in any of the three cases indicating the presence of only one $S$-domain for the studied $K$-domain. This behavior is unique to the situation where the magnetic interaction vector $M_\perp$ is along $b^*$, any component of the magnetic moment along the $c$-direction could, therefore, be excluded. The Ho moments must lie in the $(a,b)$ basal plane and its major component must point in $b^*$-direction. The existence of an $a$-component can be probed on the $(h\pm\tau_3 0 l)$ reflections ($l \neq 0$). The presence of an $a$-component should lead to the non-zero off-diagonal components $-P_{fy}$ for an incident $z$- and $P_{fz}$ for an incident $y$-polarizations, respectively. Under a captious view the entries in table 4.1 (for example (-0.415 0 1)) could be interpreted as a confirmation of a small $a$-component. However, since a single observation can be biased by experimental artifacts (errors in sample alignment, polarization correction, instrument adjustment), we performed a least-squares refinement based on a number of different $(h\pm\tau_3 0 l)$ reflections. This refinement confirms that the deviation of the magnetic moments from the $[0 1 0]$-direction does not exceed 4.0(4)$^\circ$. These results unequivocally show that the $a^*$-structure is the transverse amplitude-modulation of the magnetic moment along $b$ (see Fig.4.1). This corroborates one of the ICM-structures suggested by A.I. Goldman et al. [12].

4.1.4 ICM $c^*$-structure

Secondly, we examined the magnetic reflections corresponding to the $c^*$-structure $\tau_2 = (0 \ 0 \ 0.915)$. These reflections appear very close in the reciprocal space to the magnetic reflections $(h \ 0 \ l)$ $(h+l ~\text{odd})$ of the commensurate $\tau_1 = (0 \ 0 \ 1)$ structure. As the spacial resolution was rather poor, the $\tau_2$ and $\tau_1$ peaks could not be separated. Therefore, we analyzed the polarization in the center of the $(0 \ 0 \ 3)$ peak and at the right and left wings at $T = 5.34$K (see Fig.4.4). The scattered polarization is rotated, when the initial polarization is parallel to the scattering vector $Q$ (table 4.2) at these three positions, therefore, the scattering is purely magnetic. However, the scattered beam is completely depolarized for the $P_{iy}$, $P_{iz}$ incident polarizations. Due to this depolarization it is not possible to unambiguously deduce a model of the magnetic structure but two classes of models could be proposed:

1. long-range $\tau_2$ incommensurate magnetic structure with equally populated orientation ($S^-$) domains or chiral domains.

2. $\tau_1$ commensurate magnetic structure disturbed by discontinuities appearing regularly at $c/(1-|\tau_2|)$.

Fig.4.2 offers a simplified overview of possible spin arrangements. From the first class of models the transverse amplitude wave and circular helix magnetic structure are the simplest cases. The helical $ab$-plane spin modulation in Fig.4.2c1 is the most probable
model, since the mean-field theory calculations of Amici et al. based on this assumption correctly predict the commensurate-to-incommensurate transition in the expected temperature range \[9\]. Since single-ion CEF anisotropy is significant the structure becomes more complicated. The anisotropy might not be uniform within the basal plane, being larger for specific directions. This could lead to a bunched helix structure or modulated helix illustrated schematically in Fig. 4.2(a, b). Also a cycloidal modulation can not be excluded.

For the second class of models the presence of disturbances in the long-range collinear \(\tau_1=(0 \ 0 \ 1)\) magnetic structure could lead to appearance of the incommensurate peaks. These disturbances appearing at \(c/(1-|\tau_2|)\approx 11c\) could be stacking faults, domain walls, defects, spin-slips (see Fig. 4.2(c_2)). From the available data we cannot specify more exactly the origin of such disturbances. But in such a case reflections should be broaden as disturbances appear not absolutely regular. This is, however, not in agreement with observations of Hill et al. \[8\], who reports that the \(q_1\) reflections remain resolution limited indicative of an extremely well-ordered structure, whereas the \(q_2\) modulation has a correlation length \(\xi\) similar to the CM \(\tau_1\)-structure near the transition temperature (\(\xi\approx 600\,\text{Å}\) at \(T=5.44\,\text{K}\)). Therefore, we tend to give preference to a long-range helical structure as the origin of the \(\tau_2\) reflections.
Figure 4.3: Temperature dependence of three magnetic wave vectors of HoNi$_2$B$_2$C corresponding to: $\mathbf{q} = (1\ 0\ 0)$ r.l.u., ICM $c^*$-modulation $\tau_2$ and ICM $a^*$-modulation $\tau_3$. The onset of the CM $\tau_1$-structure e.g. (1 0 0) is correlated with an pronounced intensity increase of the pure nuclear reflections e.g. (2 0 0). We ascribe this to a strong extinction effect caused by a pronounced change of the domain structure.

Figure 4.4: $\omega$-scan through the (0 0 3) reflection at several temperatures. Arrows point to the $\omega$-values where the polarization analysis has been performed. We attribute the doublepeak structure to two slightly twisted crystallites. The solid lines are guides to the eye.

Table 4.1: Selected polarimetric data for the wave vector $\tau_3=(0.58\ 0\ 0)$ for HoNi$_2$B$_2$C.

<table>
<thead>
<tr>
<th>(H K L)</th>
<th>$T$(K)</th>
<th>$P_i$</th>
<th>$P_{xf}$</th>
<th>$P_{yf}$</th>
<th>$P_{zf}$</th>
</tr>
</thead>
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<tr>
<td>(-0.585 0 0)</td>
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<td>1016(20)</td>
<td>0.012(15)</td>
<td>0.076(20)</td>
<td></td>
</tr>
<tr>
<td>5.34K</td>
<td>010</td>
<td>-0.002(16)</td>
<td>-1.042(20)</td>
<td>-0.029(21)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>001</td>
<td>0.117(22)</td>
<td>-0.055(25)</td>
<td>1.019(21)</td>
<td></td>
</tr>
<tr>
<td>(-0.415 0 1)</td>
<td>100</td>
<td>-1.025(28)</td>
<td>0.014(22)</td>
<td>0.047(25)</td>
<td></td>
</tr>
<tr>
<td>5.34K</td>
<td>010</td>
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<td>-1.024(28)</td>
<td>-0.120(22)</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>-0.102(21)</td>
<td>1.023(27)</td>
<td></td>
</tr>
<tr>
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<td>-0.053(22)</td>
<td>-0.026(28)</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>001</td>
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<td>0.082(21)</td>
<td>1.032(29)</td>
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4.1 Zero magnetic field

HoNi$_2$B$_2$C, $T = 5.3$K

Figure 4.5: Single crystal diffraction measured in HoNi$_2$B$_2$C at $T=5.3$K and zero field. Left: ICM $a^*$-structure; Right: ICM $c^*$-structure. A high-resolution investigation of Hill et al. [8] reveals that the ICM $c$-axis satellite $\tau_2$ consists of two peaks. We observe this occurrence in our investigation by the splitting of the $3^{rd}$ order reflection $3\tau_2$ at the positions $(0\ 0\ 1\pm \delta_1, 2)$ with $\delta_1 \approx 0.24$ and $\delta_2 \approx 0.28$.

Table 4.2: Polarimetric data for $\tau_2 = (0\ 0\ 0.915)$ and $\tau_1 = (0\ 0\ 1)$ reflections for HoNi$_2$B$_2$C. $P_i$ and $P_f$ are the polarization matrices of the incident and diffracted beams.

<table>
<thead>
<tr>
<th>$(H\ K\ L)$</th>
<th>$T$ (K)</th>
<th>$P_i$</th>
<th>$P_{xf}$</th>
<th>$P_{yf}$</th>
<th>$P_{zf}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-1.027(30)</td>
<td>-0.007(20)</td>
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<td>$(0\ 0\ -3.0)$</td>
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<td>-1.011(25)</td>
<td>-0.002(20)</td>
<td>-0.012(22)</td>
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<tr>
<td>$(0\ 0\ -3.085)$</td>
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<td>-1.026(30)</td>
<td>0.008(21)</td>
<td>-0.016(25)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$P_{xf}$</th>
<th>$P_{yf}$</th>
<th>$P_{zf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.020(25)</td>
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<td>0.015(26)</td>
<td>-0.070(28)</td>
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<td>0.008(22)</td>
<td>-0.070(28)</td>
</tr>
<tr>
<td>-0.005(22)</td>
<td>-0.070(28)</td>
<td>-0.005(22)</td>
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Figure 4.6: Neutron powder diffraction pattern of HoNi$_2$B$_2$C at $T=5.25$K. The 1$^{st}$ row of the vertical markers denotes the chemical structure, the 2$^{nd}$ row the CM $\tau_1$, the 3$^{rd}$ row the ICM $\tau_2$, the 4$^{th}$ the ICM $\tau_3$, and the 5$^{th}$ row denotes the 3$^{rd}$ harmonic of the ICM $\tau_2$-structure. The regions from 66.5$^\circ$ to 68.5$^\circ$ and from 77.5$^\circ$ to 81.5$^\circ$ with Bragg peaks from the aluminium sample container were excluded from the refinement.

4.2 Magnetic field along [1 1 0]

Single-crystal diffraction investigation in HoNi$_2$B$_2$C has been performed to study the complicated magnetic structure as a function of applied external magnetic field and temperature. Diffractograms of the aligned single crystal (see Fig.4.8) were collected by a sample rotation around the vertical axis by 180 degrees. These combined data provide a complete visualization of the scattering intensities in the corresponding 2D-plane of the reciprocal space. To perform the temperature and field dependence measurements we used a 1.8 Tesla horizontal cryomagnet with only a small blind angle of $\approx 2^\circ$. This technique is especially useful for the measurement of complicated structures, e.g. the detection of satellites reflections at magnetic phase transitions. We performed these experiments on the diffractometer DMC at PSI. The collected data were analyzed by the TVtueb software tool developed for the flat-cone diffractometer D2 at the HMI Berlin. This is schematically shown in Fig.4.7. The crystallographic axes of the crystal were oriented in respect of the horizontal magnetic field in the cryomagnet. The sample table was turned in steps of 1/8 degree over a range of 180 degree in $\Omega$. A diffractogram was taken for every $\Omega$-position an combined to a ($\Omega$,2$\Theta$)-plot and finally transformed into a
4.2 Magnetic field along [1 1 0]

Figure 4.7: The sample table was turned in steps of 1/8 degree in a range of 180 degrees. For every Ω-position a diffractogram was taken and combined to a (Ω,2Θ)-plot. With the TVtueb software we transformed the data into a Q-plot (a disk in reciprocal space).

Q-plane in reciprocal space. A representative illustration of such a Q-plane is shown by Fig.4.10 for T = 5.3K and zero magnetic field. In order to complete the phase diagrams of the different magnetic modulations in HoNi₂B₂C we made some additional measurements on the single crystal diffractometer TriCS at SINQ, PSI. The integrated intensities of the different Bragg reflections are obtained by fitting one Gaussian function to the respective profile of an Ω-scan.

4.2.1 a*-modulations

A detailed analysis of the magnetic reflections was performed as function of the temperatures and a magnetic field applied along [1 1 0]. At T = 2K we observed the ICM τ₃-structure at the second metamagnetic phase transition at Hₑₓ ≈ 1T up to 1.7T. The region of existence of the ICM τ₃-structure is shown in Fig.4.11, whereas the interpolated data presented in Fig.4.13 give a picture of the intensity distribution. The maximal intensity at T = 2K was observed for Hₑₓ ≈ 1.3T. The maximal integrated intensity of the ICM τ₃-modulation in the investigated (T,H)-phase diagram is located at (T ≈ 4.9K, H ≈ 0.9T).
Figure 4.8: For the purpose of the single crystal neutron diffraction investigation a plaquette-like single crystal was mounted on an aluminium holder. The [0 0 1]-direction of the crystal is oriented parallel to the long axis of the aluminum cylinder. The mass of this HoNi$_2$B$_2$C sample amounts to $\approx 125$mg.

It extends curve-shaped form ($T \approx 4.2$K, $H \approx 1.1$T) to ($T \approx 5.1$K, $H \approx 0.5$T). As can be seen in Fig.4.12 higher harmonics associated with $\tau_3$ appear, a second harmonic $\tau_4 \approx (0.86 0 0)$ and a third harmonic $\tau_5 \approx (0.29 0 0)$. Fig.4.11 shows the phase diagram for the respective modulation. The intensities of this higher harmonics ($\tau_4$ and $\tau_5$) are correlated to the intensity of $\tau_3$, see Fig.4.14. At $T=2$K the value of the ICM $\tau_3$ propagation vector changes slightly from 0.569 at $H_{ex} = 1.1$T to 0.560 for 1.5T. The temperature dependence of the propagation vector at zero field and as function of an applied magnetic field at fixed $T = 5.3$K is presented in Fig.4.9. Various field- and temperature-scans of the phase diagram for the ICM a*-structures are presented in appendix A.

Figure 4.9: Dependence of the ICM $\tau_3$ propagation vector. Left: As function of the Temperature at zero field. Right: As function of an applied magnetic field at $T = 5.3$K.
4.2 Magnetic field along [1 1 0]

4.2.2 c*-modulations

As the applied magnetic field at \( T = 2 \text{K} \) is increased the first metamagnetic state \((\uparrow \uparrow \downarrow)\) is stabilized above the first metamagnetic phase transition \( H_{ex} \approx 0.4 \text{T} \). \( \mathbf{q} = 1.0 \mathbf{c}^* (\tau_1) \) disappears and a new wave vector \( \mathbf{q} = 2/3 \mathbf{c}^* \) can be observed, see Fig. 4.18 (left). This is the wave vector which was predicted by theory and is consistent with the net distribution of moments deduced from the magnetization measurements. The phase diagram of the \( 2/3 \mathbf{c}^* \)-structure is presented in Fig. 4.15. There is a plateau-like maximum in the region of the first metamagnetic state \((\uparrow \uparrow \downarrow)\), whereas for the field-scan at \( T = 5.3 \text{K} \) the \( 2/3 \mathbf{c}^* \)-structure appears only weakly, see Fig. 4.18 (right). Furthermore, we examined the phase diagram of the ICM \( \mathbf{c}^* \)-structure \( \tau_2 = (0 \ 0 \ 0.915) \), as shown in Fig. 4.16. Interestingly, there is a small region around \( H_{ex} = 0.4 \text{T} \) where we observed the \( \tau_2 \)-structure only if we cooled in an applied magnetic field, whereas in the field-scans at \( T = 2 \text{K} \) and \( T = 3 \text{K} \) the \( \tau_2 \)-structure was absent. Fig. 4.17 (left) shows a comparison between a diffractogram measured during a field scan and a diffractogram obtained after field cooling (FC). The satellites of the \( \tau_2 \)-structure are only present in the (FC) diffractogram. The criterium to compared the \( H_{ex} = 0.4 \text{T} \) FC data with the field scan at \( H_{ex} = 0.42 \text{T} \) was the almost equal intensity of the \( 2/3 \mathbf{c}^* \)-satellites. Fig. 4.17 (right) shows the field dependence of the different \( \mathbf{c}^* \)-structures at \( T = 2 \text{K} \) between 0.35T and 0.52T (field-cooled for every value). The lowest temperature at which the \( \tau_2 \)-structure can be observed by a field-scan, is between 4.6K and 3K, see Fig. 4.16. Various field- and temperature-scans of the phase diagrams for the \( \mathbf{c}^* \)-structures are presented in appendix A.
Figure 4.10: Single-crystal diffraction study on DMC ($\lambda = 2.57\text{Å}$) at zero field and fixed $T = 5.3\text{K}$. The values of the Q-plane ($h$ and $l$) are given in relative lattice units. The two weak circles belong to the aluminum of the sample holder. At this temperature the ICM $a^\times$-structure coexists with the ICM $c^\times$-structure. For a better overview and based on the symmetry of the investigated system we mirrored the transformed sector of the $Q$-plane and obtained a entire disk in reciprocal space.
4.2 Magnetic field along $[1 \ 1 \ 0]$

**Figure 4.11:** Phase diagram of the ICM $a^e$-structures for an applied magnetic field $H_{ex} \parallel [1 \ 1 \ 0]$. The squares indicate an experimentally determined point $(H,T)$ at the border of the respective phase. Various intersections of this phase diagram are presented in appendix A.

**Figure 4.12:** Section of the $Q$-plane at $H_{ex} = 1.1\,\text{T}$ and $T = 2.0\,\text{K}$. Higher harmonics of the ICM $\tau_3$-structure appear for a sufficiently high magnetic field.

**Figure 4.13:** $H_{ex}-T$ phase diagram of the ICM $\tau_3$-structure for an applied magnetic field $H_{ex} \parallel [1 \ 1 \ 0]$. The contour lines are interpolated from various temperature- and field-scans and give a picture of the intensity distribution of the observed phase.
Figure 4.14: Field-scans at $T=2\text{K}$ and $T=5.3\text{K}$. $a^*\text{-modulations}$ observed for an applied magnetic field in easy-direction. Whereas $(1\ 0\ 0)m$ and $(1\ 1\ 0)n$ denote the magnetic and the nuclear Bragg peak, respectively.

Figure 4.15: $H_{\text{ex}}-T$ phase diagram of the $2/3c^*\text{-structure}$ for an applied magnetic field $H_{\text{ex}} \parallel [1 \ 1 \ 0]$. The squares indicate an experimentally determined point $(H,T)$ at the border of the phase. The level curves are interpolated from the data and give a picture of the intensity distribution of the observed phase.

Figure 4.16: $H_{\text{ex}}-T$ phase diagram of the ICM $\tau_2\text{-structure}$ for an applied magnetic field in [1 1 0]-direction. At $T=2\text{K}$ and $T=3\text{K}$ we observed the $\tau_2\text{-structure}$ only if we cooled in an applied magnetic field $H_{\text{ex}} \approx 0.4T$, whereas for field-scans at the mentioned temperatures the $\tau_2\text{-structure}$ was absent.
4.2 Magnetic field along [1 1 0]  

Figure 4.17: Left: Comparison between the diffractogram measured during the field-scan at $H_{ex} = 0.42T$ (increasing field, ZFC) and the diffractogram obtained for FC at $H_{ex} = 0.4T$. We chose the 0.42T field-scan data for this comparison because the intensity of the $2/3c^*$-structure is as high as that of the field-cooled measurement at 0.4T. The $\tau_2$-structure appears field-cold only. Right: The integrated intensity of $\tau_2$ reaches its maximum at $\approx 0.39T$. The lines are guides to the eyes.

Figure 4.18: Field-scans at $T = 2K$ and $T = 5.3K$. $c^*$-modulations observed for an applied magnetic field in easy-direction.
4.3 Magnetic field along [0 1 0]

In this section, the magnetic structure of HoNi$_2$B$_2$C is examined when applying the external magnetic field along [0 1 0], which is one of the hard in-plane axis of magnetization. In this case, one has to distinguish between $a^*$-modulations (or propagation vectors perpendicular to the applied field) and $b^*$-modulations whose propagation vectors are parallel with respect to the field direction. Fig. 4.25 shows a $(k,l)$-plane at $H_{ex} = 1.1$T and $T = 2.0$K and stresses the richness of the system under investigation and reveals that the magnetic phase diagram of HoNi$_2$B$_2$C is more complicated than proposed so far. Our intention was to identify the fundamental magnetic structures and to determine their $H_{ex}$-$T$ phase diagram. Because we don’t have as much data as for the easy field direction it is not possible to create reasonable interpolations for contour plots. Nevertheless, the development of the different propagation vectors may be estimated from the individual field- and temperature-scans. Beside this chapter, various field- and temperature-scans of the phase diagrams for the $a^*$-, $b^*$-, and $c^*$-structures are presented in appendix B. In addition, higher harmonics of the fundamental magnetic structures are present and complicated a detailed analysis.

4.3.1 $a^*$ & $b^*$-modulations

Three different varieties of the ICM $\tau_3$-structure have been observed for an external field along [0 1 0]. We define the structure which is perpendicular to the field direction and arises from the phase at zero field as $\tau_3$. The second structure arising from the phase at zero field, which is oriented parallel in respect to the applied field we define as $\tau_3'$, see Fig. 4.19. The third structure $\tau_3''$ is also parallel to the field but present only above 0.8T. Increasing the applied magnetic field $H_{ex} || [0 1 0]$ at $T = 2$K a first metamagnetic phase transition takes place at $\approx 0.5$T and according to the phase diagram of Canfield et al. [10] the metamagnetic state ($\uparrow \uparrow \downarrow$) is stabilized. Interestingly, at this metamagnetic state the ICM $a^*$-modulation $\tau_3''$ can be observed, see Fig. 4.20(right). The field dependence of the propagation vectors $\tau_3''$ and $\tau_3'$ at $T = 2$K is presented in Fig. 4.21(left). Note, the intensity ratio $I(\tau_3'')/I(\tau_3')$ changes if we starting the scan from $H_{ex} = 1.75$T field-cooled, as can be seen in Fig. 4.21(right). At 2K the dominant magnetic structure above 0.8T is the ICM $\tau_3''$-modulation. Unfortunately, the accessible field values are limited by the cryomagnet to 1.75T. The field dependence of the ICM $a^*$-modulations at fixed $T = 5.3$K is presented in Fig. 4.22. At 2K the positions of $\tau_3'$, $\tau_3''$ and $\tau_3'$ remain constant as a function of the applied field, see Fig. 4.23. In contrast to this, at $T = 5.3$K the position is more sensitive, as shown in Fig. 4.24. The position ($h$-value) of the magnetic propagation vector $\tau_3$ which is perpendicular to the applied field varies between 0.573 and 0.588. For $\tau_3'$ the position ($k$-value) is slightly larger and varies between 0.582 and 0.597. Whereas, the $k$-values of $\tau_3''$ are decidedly larger and lie between 0.610 and 0.620. As shown in Fig. 4.26 various higher harmonics of the fundamental magnetic structures are present. Due to the limited instrumental resolution we were not able to identify all of the magnetic reflections yet.
4.3 Magnetic field along [0 1 0]

Figure 4.19: \( \tau_3 \)-phase diagrams for an applied magnetic field \( H_{ex} || [0 1 0] \). Left: ICM \( \tau_3 \)-structure, perpendicular to the applied field. Right: ICM \( \tau_3' \)-structure, parallel to the field direction. The squares indicate an experimentally determined point \((H,T)\) at the border of the phase.

Figure 4.20: Left: \( H_{ex}-T \) phase diagrams of the ICM \( \tau_{3p} \)-structure for an applied magnetic field \( H_{ex} || [0 1 0] \). Right: Field-scan at \( T = 2K \), dependence of the ICM \( \tau_3 \) propagation vector.
Figure 4.21: Field-scans at $T = 2K$. $\mathbf{a}^*$-modulations observed for an applied magnetic field in easy-direction. *Left*: Zero field-cooled (ZFC) *Right*: Field-scan at $T = 2K$, starting from $H_{ex} = 1.75T$ field-cooled.

Figure 4.22: Field scans at $T = 5.3K$ for an applied magnetic field along [0 1 0]. *Left*: $\mathbf{a}^*$-modulations and the nuclear Bragg peak at $Q = (1 1 0)$ r.l.u. *Right*: $\mathbf{b}^*$-modulations.
Figure 4.23: Dependence of the ICM $\tau_3$ propagation vector as function of the applied magnetic field $H_{ex} \parallel [0 1 0]$ at $T = 2$K. Left: ICM $\tau_3'$, perpendicular to the applied field. Right: ICM $\tau_3'$ and ICM $\tau_3''$, in field direction.

Figure 4.24: Dependence of the ICM $\tau_3$ propagation vector as function of the applied magnetic field $H_{ex} \parallel [0 1 0]$ at $T = 5.3$K. ICM $\tau_3$ is oriented perpendicular to the applied field and the propagation vector ICM $\tau_3'$ is along the field direction.
Figure 4.25: $Q$-plane at $H_{ex} = 1.1T$ (FC) and $T = 2.0K$. We observe a complicated multi-$\tau$-structure along the field direction $H_{ex} \parallel [0 1 0]$. Furthermore, a weak $2/3c^*$-structure can be observed which disappears as the applied magnetic field at $T = 2K$ is increased.
4.3 Magnetic field along [0 1 0]

Figure 4.26: Intersection of the Q-plane at $T=2.0\text{K}$ along $(\xi 0 0)$ r.l.u. The black an the red solid line correspond to $H_{\text{ex}} = 1.1\text{T}(\text{FC})$ and at $H_{\text{ex}} = 1.75\text{T}(\text{FC})$, respectively. The magnetic Bragg peak $(0 1 0)$ is weakly visible at $1.1\text{T}$ and disappears for higher fields. The two peak profile of ICM $\tau_3'$ and $\tau_3''$ is located at $\approx 26^\circ$ and the corresponding satellites at $\approx 61^\circ$. Additionally, various satellites of higher harmonics are observed.

4.3.2 $c^*$-modulations

The qualitative behavior of the $c^*$-modulations is similar to the situation for an applied field in easy direction. In the first metamagnetic state ($\uparrow\uparrow\downarrow$) at $T=2\text{K}$ the propagation vector $\mathbf{q} = 2/3c^*$ may be observed, as shown in Fig.4.28(left). The phase diagram of the $2/3c^*$-structure is presented in Fig.4.27(left). Remarkably, the maximal integrated intensity of this modulation is distinct smaller compared to the one of the the $2/3c^*$-structure for an applied field in easy direction (with respect to $\tau_1$). Similar, to the investigation for the easy field direction we do not observe the $\tau_3$ structure in the field-scan at fixed $T=2\text{K}$, but if we cooled in an applied magnetic field of $\approx 0.7\text{T}$, see Fig.4.27(right). Consistent with the findings of Detlefs et al. [14] we haven’t observed any $c^*$-modulation above $1.2\text{T}$, e.g. no $2/3c^*$-structure in the proposed second metamagnetic phase ($\uparrow\uparrow\rightarrow$).
Figure 4.27: $H_{ex}$-$T$ phase diagrams of the $2/3c^*$-structure and the ICM $\tau_2$-modulation for an applied magnetic field $H_{ex} \parallel [0 1 0]$. The squares indicate an experimentally determined point $(H,T)$ at the border of the phase. At $T = 2K$ we observed the $\tau_2$-structure only if we cooled in an applied magnetic field $H_{ex} \approx 0.5T$, whereas for field-scans at the mentioned temperatures the $\tau_2$-structure was absent.

Figure 4.28: Field-scans at $T = 2K$ and $T = 5.3K$. $c^*$-modulations observed for an applied magnetic field in hard-direction.
Figure 4.29: Q-planes for an applied magnetic field along [0 1 0] at 0.5T, 1.0T and 1.75T ($T = 2.0K$). We observed in the low field state at 0.5T $a^*$-modulations perpendicular to the applied field direction, whereas for the higher field state at 1.0T and 1.75T the propagation vectors turn by 90° and point towards the field direction.
4.4 Discussion

4.4.1 ICM modulations at zero field

Within the statistical accuracy of our experiment, the zero field ICM \( a^* \)-structure of HoNi\(_2\)B\(_2\)C is a *transverse amplitude modulated wave with the magnetic moments along the \( b^* \)-direction*. We cannot, however, unambiguously determine the \( c^* \)-structure from polarimetric data. We give preference to a model of a helimagnetic arrangement for the \( c^* \)-structure based on the fact that the RKKY exchange, favoring incommensurate helical (or cycloidal) ordering, competes with the single-ion CEF anisotropy, which allows only a limited number of magnetically easy directions. The 3\(^{rd} \) harmonics which we observed in a neutron diffraction experiment for both ICM \( c^* \)-modulations (see Fig.4.5, right) might arise from a bunching of the moment directions due to the competition of the RKKY exchange and the CEF anisotropy. Though the presence of regular discontinuities seems to us a less probable reason of the \( \tau_2 \) reflections, it is worth noting that the microstructure plays an important role in HoNi\(_2\)B\(_2\)C. Below the antiferromagnetic transition crystallo-graphic domains form due to magneto-elastic coupling in order to minimize the energy. Recently Vinnikov et al. [48] reported on magnetic flux-line structures (vortices) in the superconducting phase of HoNi\(_2\)B\(_2\)C caused by pinning at magnetic domain boundaries. The vortex structure of the basal plane consists of stripes along [1 0 0] (respectively [0 1 0]) with a typical spacing of 1\( \mu \)m. From the observed line-width broadening of x-ray diffraction peaks Hill et al. [8] concluded that in the 5.2K-5.44 K regime magnetic domains of the CM \( \tau_1 \)-structure remain, but the coherence length in \( c \)-direction is distinctly reduced. Comparing the coherence length obtained by Hill of the short-range ICM \( c^* \)-modulations (\( q_2 \)) with the one they observed for the CM \( \tau_1 \)-structure we tentatively conclude that these two structures coexist in the same domain but that the long-range ICM \( c^* \)-modulation (\( q_1 \)) exists in separate domains. Whether the long-range \( a^* \)-modulation exists in distinct domains occupying only part of the crystal or whether this structure is present, superposed on the other modulations throughout the whole volume remains an open question.

The apparent coexistence of the \( a \)- and \( c \)-axis modulations in the \((T,H)\)-phase diagram implies that the two structures have similar free energies and regions of each structure may be stabilized by, e.g., strain, lattice defects or impurities. In fact, it is also conceivable that the magnetoelastic energy could determine whether the \( c^* \)-structure is helical or a spin density wave, thus stabilizing one of the two states depending on the total energy balance [23].

The absolute value of the Ho moment cannot be determined reliably from the polarimetric data, therefore we deduced these values based on neutron powder diffraction data. Due to the very similar temperature dependence of the ICM-structures in both powder and single crystal samples we believe that such an approach is appropriate. For the ICM \( c^* \)-modulation we imposed a helix spin structure with moments restricted to the basal plane. We performed a Fullprof refinement (see Fig.4.6) assuming the presence of three independent magnetic structures. At \( T=5.3K \) the refined value for the ordered moment of the CM \( \tau_1 \)-structure was 4.34(3)\( \mu_B/\text{Ho} \), for the ICM \( c^* \)-structure 4.09(4)\( \mu_B/\text{Ho} \) and for the ICM \( a^* \)-structure 3.95(7)\( \mu_B/\text{Ho} \). Note, for the refinement we assumed that the different magnetic phases are present in the entire crystal. A constrain to a fraction of the crystal would result in a higher magnetic moment for the respective phase. Further-
more, we refined the magnetic moment from powder diffraction data measured for the antiferromagnetic phase at \( T = 2K \). The 2K ordered moment value is 9.06(8) \( \mu_B/\text{Ho} \) for the \( \tau_1 \)-structure. Based on this, the moments calculated for the \( \tau_1, \tau_2 \) and \( \tau_3 \) structures at \( T = 5.3K \) could not belong to the same Ho-ion, since the total ordered moment would reach as much as 11.5 \( \mu_B/\text{Ho} \) for certain Ho sites. Even when the 3\(^{rd}\) harmonic of the ICM c*-modulation is included in the calculation (its upper estimate is \(< 1.0 \mu_B\)), the total moment would be 10.5 \( \mu_B/\text{Ho} \). This estimation provides strong evidence that the magnetic intensity cannot arise from a single magnetic phase with the total moment attributed to one Ho atom, but the moment should be distributed in 2 or 3 different types of domains. This is in agreement with the conclusion of Hill et al. \[8\] that the ICM a*-structure and the ICM c*-structure do not exist in the same volume of the crystal. Furthermore, the superconductivity of these different domains might be unequal. It is possible, that just in one sort of these domains the superconductivity is weakened or even suppressed by the respective magnetic arrangement. We like to underline that the domain formation due to the magnetic order may considerably affect the transport properties (e.g. pinning at the domain walls).

It is worth noting that the onset of the \( \tau_1 \)-structure is correlated with an pronounced intensity increase of the pure nuclear reflections e.g. (2 0 0) (see Fig.4.3).

The intensity variation of nuclear reflections is most probably caused by a change of extinction due to the magnetoelastic effect. By reason of multiple scattering, the strong extinction causes weakening of the diffracted intensity in perfect crystals of HoNi\(_2\)B\(_2\)C. The formation of the commensurate magnetic structure leads to reduction of nuclear domain size resulting in less multiple scattering and increase in intensity of the nuclear reflections. To exclude that the additional intensity originate from a ferromagnetic contribution we performed polarized measurements at the nuclear Bragg peak \( Q = (1 1 0) \) r.l.u. in the paramagnetic and in the antiferromagnetically ordered phase at \( T = 10K \) and \( T = 2K \), respectively (see Fig.4.30). Magnetic scattering would cause additional intensity in the spin flip (SF) channel. Within statistics, there is no magnetic contribution on the nuclear Bragg peak \( Q = (1 1 0) \). Therefore, we ascribe this intensity increase of the nuclear Bragg peaks in the magnetically ordered phase to a lifting of the strong extinction. Interestingly, the intensity of the nuclear reflections seems not to be affected by the onset of the ICM a*-modulation. These observations imply that the onset of the \( k_1 \)- and \( k_2 \)-structure is associated with a breakdown in crystal perfection, whereas the onset of \( k_3 \) is not.

### 4.4.2 0.58a* for \( H_{ex} \parallel [1 1 0] \)

To our knowledge, these experimental results prove for the first time the presence of the 0.58a*-modulation stabilized for an applied magnetic field in easy direction at \( T = 2K \). The second and third harmonic of the 0.58a*-modulation are observable for a sufficiently high magnetic field. Additional information lies in the higher harmonics of a magnetic propagation vector. In the picture of a sinusoidal amplitude modulated wave, the intensity of the odd order reflections reveals the squaring up of the structure and the intensity of the even order reflections reveals the net ferromagnetic moment of the structure. Regarding the simple magnetic structure at zero field and \( T = 2K \) the temptation for an one-dimensional model is obvious from a theoretical point of view. Two basic assumption
Figure 4.30: Polarized measurements at the nuclear Bragg peak \( \mathbf{Q} = (1 1 0) \) r.l.u. in the paramagnetic and in the antiferromagnetically ordered phase at \( T = 10K \) and \( T = 2K \), respectively. Left: Due to the strong extinction effect we observed an intensity increase for the non spin flip channel (NSF) in the ordered phase. Right: Within statistics there is no difference in intensity for the spin flip channel (SF). The continuous lines are fits to a Gaussian profile for the respective data.

are established in existing theories [9, 16], but these theories are not able, by construction, to explain the existence of an \( \mathbf{a}^* \)-modulation. The first assumption is, that the moments at \( T = 2K \) are extremely anisotropic and locked in one of the four in-plane easy directions \([±1 ±1 0]\) and the second, that all metamagnetic states are built from ferromagnetic basal planes. Even for a applied field along \([1 1 0]\) one has to question the correctness of the two assumptions. As the applied magnetic field at \( T = 2K \) is increased the 0.58\( \mathbf{a}^* \)-modulation appears at the transition (\( H_{ex} \approx 1.0T \)) from the first metamagnetic state (\( ↑↑↓ \)) to the paramagnetic state (\( ↑ \)) and reaches its maximum at \( ≈ 1.3T \). The integrated intensity of this field induced modulation is of similar size as the respective modulation at zero field. The appearance of the 0.58\( \mathbf{a}^* \) modulation suggests a momentary non-collinear structure which will be discussed in detail in the next paragraph.

4.4.3 ICM modulation for \( H_{ex} \parallel [0 1 0] \)

The most striking result of the diffraction experiment is for an applied field in \( \mathbf{b}^* \)-direction at \( T = 2K \) the presence of the 0.58\( \mathbf{a}^* \) propagation vector in the first metamagnetic phase and the switch-over to the 0.62\( \mathbf{b}^* \) propagation vector in the second metamagnetic phase (\( H_{ex} > 0.8T \)), in coexistence with a weaker 0.60\( \mathbf{b}^* \)-modulation. In almost the whole region of existence higher harmonics of the respective fundamental magnetic structures are present. Keeping in mind the basic assumptions of the existing theories mentioned in the previous paragraph one has to come across the question, which of these two assumptions become void for an applied magnetic field along the hard in-plane direction, in order to explain the appearance of the \( \mathbf{a}^* \)- and \( \mathbf{b}^* \)-modulations. Acting on a hypothesis of Detlefs et al. [14] that the \( \mathbf{a}^* \)-modulation only manifests itself in non-collinear structures. They argue that in ErNi\(_2\)B\(_2\)C and TbNi\(_2\)B\(_2\)C [49] the single ion anisotropy due to the CEF
forces the magnetic moments along \([1 0 0]\) and the low temperature magnetic ordering wave vector is close to \(0.58a^*\), whereas in HoNi\(_2\)B\(_2\)C and DyNi\(_2\)B\(_2\)C [10] the magnetic moments are along \([1 1 0]\) and the low temperature ordering wave vector is \(1.0c^*\). As cooling down through the Néel temperatures, there are clear magnetostricions observed in members of the \(R\)Ni\(_2\)B\(_2\)C family [50, 51, 20]. By symmetry arguments, a distortion along \([1 1 0]\) is far more likely to disturb a Fermi surface nesting along \([1 0 0]\) than a distortion along \([1 0 0]\) [17]. For HoNi\(_2\)B\(_2\)C Detlefs et al. conclude that for an external magnetic field \(H_{ex}\) one will have a reduction in the magnetostriction along \([1 1 0]\) for those metamagnetic states, where the net magnetization points away from the \([1 1 0]\)-direction. In other words, in the metamagnetic states with a non-collinear magnetic structure. The reduction of the magnetostriction and the resulting disturbance of the Fermi surface nesting along \([1 0 0]\) will lead to a magnetic ordering vector \(0.58a^*\), the same propagation vector which is common throughout the heavy \(R\)Ni\(_2\)B\(_2\) [14]. Different non-collinear metamagnetic states are imaginable.

If we retain the two basic assumptions we have to consider the C6 phase (\(\uparrow\downarrow\uparrow\rightarrow\leftarrow\rightarrow\)) and the F2 phase (\(\uparrow\rightarrow\)) suggested by Amici et al. [9] based on a model calculation. A compilation of the suggested phases is given in table 4.3. As the applied magnetic field \(H_{ex} \parallel [0 1 0]\) at \(T = 2K\) is increased C6 and F2 would be stabilized above the first and second metamagnetic phase transition, respectively. There are several arguments that the C6 phase is the arrangement of the first metamagnetic state instead of A3 (see table 4.3), based on the fact that:

1. We observe by neutron scattering a \(2/3c^*\)-modulation in this phase, but clearly weaker than for \(H_{ex} \parallel [1 1 0]\) in the first metamagnetic phase.

2. In contrast to the Bragg reflection \((0 1 0)\) we observe intensity on \((1 0 0)\).

3. \(\tau_1\) is still observable with approximately \(1/2\) of the intensity measured for the AF2 state.

The C6 phase is a non-collinear magnetic structure which could lead to a magnetic ordering vector \(0.58a^*\) due to a reduction of the magnetostriction and the resulting disturbance of the Fermi surface nesting. For the second metamagnetic phase we initially considered the possibility, that the basal plane arrangement of magnetic moments is a fishbone-pattern (see Fig. 4.31), whereas the net magnetization points towards the applied field direction.

1. There is no \(2/3c^*\)-modulation observed in this phase.

2. Beside the lack of the reflection \((0 1 0)\) we neither observed \((1 0 0)\).

3. \(\tau_1\) is not observable in this phase as well.

4. There are no \(1/2a^*\) (\(1/2b^*\) respectively) modulations observed.

The last point exclude a a fishbone-pattern for the second metamagnetic phase. Based on our neutron diffraction study we propose for this metamagnetic phase a superposition of ferromagnetic ordering (in-plane and along \(c\)-direction) with the above mentioned ICM \(b^*\)-modulations. In ErNi\(_2\)B\(_2\)C the zero field ordering wave vector is found to be along the
Figure 4.31: Fishbone-pattern of the magnetic moments in the (a, b)-plane like we initially suggested for the second metamagnetic phase \( H_{ex} \parallel [0 1 0] \) would lead to \( 1/2a^* \)-Bragg reflections in a neutron diffraction experiment. But we did not observe such Bragg reflections in our neutron diffraction investigation.

(a) (b)-axis and the ordered moments are along the b (a)-axis perpendicular to the ordering wave vector, with \( q = 0.55 \). In HoNi\(_2\)B\(_2\)C at \( T = 2\)K we observed in the low field state at \( \approx 0.5\)T a modulation perpendicular to the applied field direction. Interestingly, for the higher field state at \( \approx 1.0\)T the propagation vector turns by 90° and points towards the field direction, see Fig. 4.29. Assuming an transverse amplitude modulated wave with the magnetic moments perpendicular to the propagation one would expect rather an opposite behavior. For the second metamagnetic phase our elastic investigations confirm the previous findings reported by Detlefs et al. They observed for the second metamagnetic state an magnetic propagation vector \( q = 0.58a^* \) and no magnetic ordering vector along the c*-axis. In theirs study the magnetic field was oriented in the basal plane 15degree off the [1 1 0]-direction. Furthermore, they observed no ordering with a modulation in b*-direction. A similar result has been reported by Campbell et al. They observed for \( H_{ex} \) parallel to [0 1 0] in the second metamagnetic phase a modulation along the b*-direction with a wave vector (0 0.61 0). He already mentioned the possibility of an alternating fishbone pattern. In contrast to our investigation they observed a pronounced hysteresis for the second metamagnetic transition (also for \( H_{ex} \parallel [1 1 0] \)).

In our investigation we found for an applied field in [0 1 0]-direction two magnetic propagation vectors for the second metamagnetic state. Both propagation vectors are parallel to the applied field direction [0 1 0]. At \( T = 2\)K the dominant magnetic propagation vector in the second metamagnetic phase is \( \tau_{3r} \approx (0 0.62 0) \), whereas above \( T = 3.5\)K the propagation vector \( \tau_{3r} \approx (0 0.59 0) \) becomes more pronounced, see Fig. C.4. In addition, we observed a magnetic propagation vector \( \tau_3 \approx (0.57 0 0) \) in the first metamagnetic state perpendicular to the applied field direction.

For an applied magnetic field perpendicular to the c-direction the a*-modulation is even more pronounced in several regions of the \( H_{ex}-T \) phase diagram compared to zero field. Therefore we like to underline the requirement for any further theoretical attempts to account for the metamagnetic transitions in HoNi\(_2\)B\(_2\)C to incorporate the ICM a*-structure. Possibly a more extended description of the RKKY interaction, taking into account the Fermi surface nesting features is required to improve the theoretical analysis and to explain the magnetism in HoNi\(_2\)B\(_2\)C. The magnetic properties of HoNi\(_2\)B\(_2\)C, shape up a challenging problem by themselves, even before considering their interplay with superconductivity.
4.4 Discussion

Table 4.3: Stacking sequence of ferromagnetically ordered (a,b)-planes along the [0 0 1]-direction for the magnetic phases in HoNi$_2$B$_2$C at $T = 2$K, proposed by Amici et al.\cite{Amici}. The arrows illustrate the direction of the Ho moments within the (a,b)-planes. The nomenclature of the phases is according to\cite{Amici}. For selected reflections we calculated the neutron diffraction intensities for the respective magnetic arrangement. The reflection intensities are normalized to $I_{(001)}$(AF2) = 100% (powder sample). ↑(→) signifies the [1 1 0](1 -1 0)-direction. In the last two columns the value (in $\mu_B$/Ho) and the direction of the net magnetization are given for the corresponding phase. The saturated magnetic moment determined by our DC-magnetization measurements amounts $\mu_S \approx 8.5\mu_B$/Ho.

<table>
<thead>
<tr>
<th>magnetic Phase</th>
<th>Structure</th>
<th>reflection intensities (magnetic contribution)</th>
<th>net magnetization $\mu_B$/Ho</th>
<th>direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF2</td>
<td>↑↑↑↑↑↓</td>
<td>(0 0 1) 100 0 0 60 60</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>AF2'</td>
<td>←−←−←−←−</td>
<td>(0 0 $2/3$) 0 0 60 60</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>AF3</td>
<td>↑↑↑↑↑↓</td>
<td>0 100 2.7 0 0</td>
<td>$\frac{1}{3}\mu_S$ [1 1 0]</td>
<td></td>
</tr>
<tr>
<td>AF3'</td>
<td>↑→←↑→←←</td>
<td>0 100 2.7 0 0</td>
<td>$\frac{1}{3}\mu_S$ [1 1 0]</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>↑↑↑←←→</td>
<td>51 51 1.4 60 0</td>
<td>$\sqrt{2}\mu_S$ [1 0 0]</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>↑↑→↑→→</td>
<td>0 51 14 0 0</td>
<td>$\frac{\sqrt{3}}{3}\mu_S$ [3 1 0]</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>↑→↑↑→</td>
<td>51 0 12 60 0</td>
<td>$\sqrt{2}\mu_S$ [1 0 0]</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>↑↑↑↑↑↑↑↑↑↑</td>
<td>0 0 24 0 0</td>
<td>$\mu_S$ [1 1 0]</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Summary of the main propagation vectors observed in HoNi$_2$B$_2$C for an applied magnetic field $H_{ex} \parallel [1 1 0]$ and $H_{ex} \parallel [0 1 0]$.

<table>
<thead>
<tr>
<th>propagation vector</th>
<th>reflection r.l.u.</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>(0 0 1)</td>
<td></td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>(0 0 0.91)</td>
<td>consists of $q_1$ and $q_2$</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>(0.585 0 0)</td>
<td></td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>(0.84 0 0)</td>
<td>$2^{nd}$ harmonic of $\tau_3$</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>(0.26 0 0)</td>
<td>$3^{rd}$ harmonic of $\tau_3$</td>
</tr>
<tr>
<td>2/3$c^*$</td>
<td>(0 0 0.67)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>propagation vector</th>
<th>reflection r.l.u.</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>(0 0 1)</td>
<td></td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>(0 0 0.91)</td>
<td>consists of $q_1$ and $q_2$</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>(0.585 0 0)</td>
<td>perpendicular to the field direction</td>
</tr>
<tr>
<td>$\tau_3'$</td>
<td>(0.60 0 0)</td>
<td>in field direction</td>
</tr>
<tr>
<td>$\tau_3''$</td>
<td>(0.62 0 0)</td>
<td>in field direction</td>
</tr>
<tr>
<td>2/3$c^*$</td>
<td>(0 0 0.67)</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5

Inelastic neutron scattering (INS)

In this chapter the effect of an external magnetic field \( H \) on magnetic excitations in ordered \( \text{HoNi}_2\text{B}_2\text{C} \) is investigated by inelastic neutron scattering. A Zeeman-like renormalization of the low-lying transition \( \Gamma_4 \rightarrow \Gamma_5(1,2) \) is observed as function of an external magnetic field \( H \perp [0 \ 0 \ 1] \) and at fixed \( T = 2 \text{K} \). The direct study of the singlet-doublet \( \Gamma_4 \rightarrow \Gamma_5(1,2) \) CEF transition reveals the intrinsic mean-field CEF nature of the experimental observation. The field dependence of the excitation energy is successfully related by first principles to the leading exchange interactions between the rare-earth ions, allowing their direct determination both in the basal planes and between the planes. In addition, a dispersive excitation was observed arising from the magnetic \( \Gamma \)-point at \( Q = (0 \ 0 \ 3) \).

5.1 The crystal electric field (CEF)

Rare earth ions in compounds are very often found to be in the trivalent state \( \text{R}^{3+} \) with the electronic configuration \([\text{Xe}]4f^N\). The magnetic properties are due to the \( f \)-electrons, because only the \( f \)-shell is incomplete. Inside a material the states of the \( f \)-shell differ from the ones of the free \( \text{R}^{3+} \)-ion, because they are influenced by conduction electrons and the surrounding atoms in the crystal lattice, which reduce for instance the rotational symmetry at the position of the rare earth from the group of all to the rotations contained in the point group of the rare earth site. This effect of the charge contribution of the surroundings can be decisive for the magnetic properties of the \( \text{R}^{3+} \)-ion and, therefore deserves special attention.

If a \( \text{R}^{3+} \)-ion is placed inside a material its interaction with the surrounding has to be taken into account for a determination of its eigenstates. in the case of the \( 4f \)-shell the CEF is the dominant interaction with the surrounding. The CEF is due to the electrostatic potential

\[
V_{\text{CEF}}(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{5.1}
\]

that is generated by all electric charges in the environment of the rare earth ion. The \( J \)-multiplets of a free rare earth have full rotational symmetry. Because the CEF reduces the symmetry the degeneracy of the ground-state \( J \)-multiplet is at least partially removed. This effect can be described by group theory. If the CEF is taken into account,
the eigenstates are labeled by the irreducible representations of the point group of the rare earth site. Each irreducible representation corresponds to a certain behavior with respect to the symmetry operations of the point group. Table 5.1 shows how the degeneracy of the ground state $J$-multiplet of Ho$^{3+}$ is lifted in a tetragonal surrounding (point symmetry $D_{4h}[\frac{4}{m}mm]$).

<table>
<thead>
<tr>
<th>$J$</th>
<th>8</th>
</tr>
</thead>
</table>
| singlets| +2$\Gamma_2^+$
|         | +2$\Gamma_3^+$
|         | +2$\Gamma_4^+$
| doublets| +4$\Gamma_5^+$

Table 5.1: irreducible representations $\Gamma_n$ of Ho$^{3+}$ formed in an environment with $D_{4h}$ symmetry.

The CEF Hamiltonian $H_{CEF}$ can be expressed in a general way in terms of spherical tensor operators $C^m_n$ that are defined in, e.g. [53].

$$H_{CEF} = \sum_{n,m} A^m_n C^m_n$$  \hspace{1cm} (5.2)

The $A^m_n$ are the CEF parameters, which are treated as adjustable parameters in most cases. The CEF parameters have the form

$$A^m_n = \gamma^m_n \langle r^n \rangle,$$  \hspace{1cm} (5.3)

where $\langle r^n \rangle$ is the $n$'th moment of the radial 4$f$-wave function and the factor $\gamma^m_n$ contains the geometrical information of the spatial distribution of the charges. For the point group $D_{4h}$ the number of CEF parameters is reduced to 5 ($A^0_2, A^0_4, A^4_4, A^6_0, A^6_6$) if the conventional axes of the unit cell are chosen.

In insulating materials the CEF splitting is of the order of 100meV. As there are no conduction electrons, only the charges of the ions contribute to the potential Eq.(5.1). In this case the energy splitting caused by $H_{CEF}$ is of the same order of magnitude as the splitting between $J$–multiplets due to spin-orbit coupling ($H_{ls}$). Therefore, $H_{CEF}$ and $H_{ls}$ have to be diagonalized at the same time. In this case, the notation of Eq.(5.2) with tensor operators has to be used.

On the other hand, in most metals the CEF splitting is smaller than 10meV. This is because $V_{CEF}$ is screened by the conduction electrons and its effect on the 4$f$-shell is therefore reduced. Then, it can be sufficient to consider only the subspace of the lowest $J$-multiplet and treat the CEF as a small perturbation. As long as only the lowest $J$-multiplet is considered, the Wigner Eckart theorem can be used to rewrite $H_{CEF}$ in terms of the angular momentum operators $J_x, J_y$ and $J_z$. In this way one arrives at:

$$H_{CEF} = \sum_{n,m} B^m_n O^m_n,$$  \hspace{1cm} (5.4)
where the $O_m^n$ are the Stevens operators constructed from the angular momentum operators $J_i$ \((i = x, y, z)\) and the $B_m^n$ are the CEF parameters in the Stevens notation. The CEF parameters $A_m^n$ are related to the $B_m^n$ by $B_m^n = \chi_n^R A_m^n$. The $\chi_n^R$ are reduced matrix elements dependent on the rare earth $R$ ion \([53]\). The determination of the crystal-field splitting of a rare-earth ion inside a crystal matrix is a difficult task. The usual first step in such procedure is to derive a reasonable set of crystal-field parameters by means of the extended point-charge model. The starting set of crystal-field parameters can then be independently adjusted, by means of a least-squares fitting procedure, until they provide a good agreement between the measured and calculated energy spectra. It is also important to check the reliability of the received crystal-field parameters by calculating various thermodynamic properties of the respective material and to compare the theoretical values with experimental data. These are, for example, the magnetization:

$$M_\alpha = \frac{1}{k_BT} \frac{\partial \ln Z}{\partial H_\alpha} = g\mu_B \sum_i p_i |\langle \Gamma_i | J_\alpha | \Gamma_i \rangle|$$ \hspace{1cm} (5.5)

the single-ion susceptibility:

$$\chi_{\alpha\alpha} = \frac{\partial M_\alpha}{\partial H_\alpha} = g^2 \mu_B^2 \left[ \sum_i \frac{|\langle \Gamma_i | J_\alpha | \Gamma_i \rangle|^2}{k_BT} p_i + \sum_{i \neq j} \frac{|\langle \Gamma_j | J_\alpha | \Gamma_j \rangle|^2}{E_i - E_j} (p_i - p_j) \right]$$ \hspace{1cm} (5.6)

and the heat capacity:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = k_B \left[ \sum_i \left( \frac{E_i}{k_BT} \right)^2 p_i - \sum_i \left( \frac{E_i}{k_BT} p_i \right)^2 \right]$$ \hspace{1cm} (5.7)

where $p_i$ is the Boltzmann population factor for the $i^{th}$ crystal-field level and $Z$ the partition function, given by:

$$p_i = \frac{1}{Z} e^{-\frac{E_i}{k_BT}} \quad \text{and} \quad Z = \sum_i e^{-\frac{E_i}{k_BT}}$$ \hspace{1cm} (5.8)

### 5.2 Exchange interaction RKKY

A magnetic interaction which is important for the borocarbides is the RKKY interaction (after Ruderman, Kittel, Kasuya and Yosida). This interaction originates from the polarization of conduction electrons due to the rare earth magnetic moments. Direct exchange coupling between the magnetic ion and the conduction electrons at the Fermi surface results in spin polarization of the conduction electron sea around the ion. This polarization is far reaching and a periodic function of distance from the magnetizing ion. The magnetic ion at a certain site is therefore influenced by conduction electrons that have been polarized by magnetic ions at other lattice sites. This interaction is long range and its
Inelastic neutron scattering (INS) sign depends on the distance between the magnetic ions. When the conduction electrons are approximated by a gas of free electrons, the RKKY interaction can be written in its simplest form [53]:

\[ H_{RKKY} = -\sum_{i,j} J(r_i - r_j)J_i \cdot J_j, \]  

(5.9)

with

\[ J(r_i - r_j) = -\frac{9\pi N^2}{2E_F}\Gamma^2(g_J - 1)^2 F(2k_F|r_i - r_j|), \]  

(5.10)

and

\[ F(x) = \frac{x \cos x - \sin x}{x^4}, \]  

(5.11)

where \( N = N_- - N_+ \) is the difference of the number of up and down spin conduction electrons, \( E_F \) is the energy at the Fermi level, \( k_F \) is the wave-vector at the Fermi level, \( \Gamma \) is the effective exchange integral of the \( s-f \) interaction, \( g_J \) is the Land \( g \)-factor, and \( J_i \) is the total angular momentum of the \( i \)'th magnetic ion. Eq.(5.9) shows that the strength of the RKKY exchange is expected to be proportional to the de Gennes factor \( (g_J - 1)^2J(J + 1) \). This proportionality is also expected for the Curie temperature calculated in a mean-field approach [54]. The scaling of the transition temperature \( T_m \) with the de Gennes factor and the observation of incommensurate spin structures is an indication for the importance of the RKKY interaction.

The exchange integral \( J(r_i - r_j) \) between the ions at \( r_i \) and \( r_j \) (see, Eq.(5.10)) depends on the detailed band structure and the Fermi-surface. The magnetic structure that is realized below \( T_m \) is then expected to be described by the wave-vector \( k \) at which the Fourier transformed exchange integral

\[ J(q) = \sum_r J(r)e^{-iq\cdot r}, \]  

(5.12)

reaches its absolute maximum (minimum of energy). This maximum can occur anywhere in the Brillouin zone. As a consequence, the chemical lattice has no direct influence on the magnetic order that is favored by the RKKY exchange and incommensurate spin structures are commonly observed in materials with dominant RKKY interaction.

The influence of the Fermi-surface becomes especially clear for \( R = \) Gd, Tb, Ho, and Er in the borocarbides. In all four compounds an incommensurate magnetic structure with the wave-vector \( k \approx (0.55, 0, 0) \) r.l.u. is observed [13]. This structure is favored by a maximum in the susceptibility of the conduction electrons, which is due to Fermi surface nesting.

### 5.3 Experimental setup and samples

For the present investigation single crystals of isotopically substituted HoNi\textsuperscript{11}B\textsubscript{2}C and of sufficient size were prepared (by P.C. Canfield) by a high temperature flux-growth technique described in reference [43]. The crystal shape was plaquette-like, with the plaquette
face perpendicular to the [0 0 1]-direction. The typical size of such crystals is about 5x5x1mm$^3$ ($m \approx 190$mg). The quality of the samples was tested by bulk magnetization and resistivity as function of temperature and external field (see Chapter 3). For the purpose of the INS investigations, several crystals were mounted on a common aluminum plate to obtain a total sample mass of the order of 3g. The alignment of the single crystals in the [1 1 0],[0 0 1] scattering plane was performed piecewise by the conventional two-axis mode (see Fig.5.1). The geometry of the sample holder allows to turn the combined sample around the crystallographic c-axis to adjust the [1 0 0],[0 0 1] scattering plane likewise. The mosaicity of the total sample was smaller than 2.5 deg as obtained by the measured FWHM of the rocking scans at the Bragg reflections. The INS measurements were performed on the RITA-II triple-axis spectrometer installed at the Swiss Spallation Neutron Source SINQ, Villigen PSI, on the 4F2 spectrometer at the Laboratoire Leon Brillouin (LLB), CEA/Saclay, France, and on the IN14 spectrometer at the Institut Laue-Langevin (ILL), Grenoble, France. Instruments were operated at fixed final energies $E_f = 5.0$meV and $E_f = 3.5$meV, respectively, in their standard focusing conditions with open geometry after the sample. Horizontal incoming beam collimation was 60' and 80', respectively. A cold beryllium filter in front of the analyzer was used in all measurements with a fixed final energy $E_f = 5.0$meV to suppress higher order contaminations. For the investigation at a fixed analyzer energy of $E_f = 3.5$meV a cold beryllium oxid filter was used instead. The measurements were performed at fixed temperatures in the range of $T = 2K$ to $T = 10K$. The measurements devoted to the investigation of the CEF magnetic excitons in the AF phase of HoNi$_2$B$_2$C at $T = 2K$ were organized according to the preceding INS investigation of N. Cavadini et al. [55]. We chose the energy range, where the peak of the low-lying $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition has been identified. The spectrometer RITA-II at SINQ has a 30x50cm$^2$ position-sensitive detector (PSD) with a resolution of 128x128 pixels. For our investigation we defined different windows of the detector matrix all centered at the nominal PSD middle in order to optimize the peak-to-background ratio. A cryomagnet was used to apply a vertical magnetic field up to 5T. Every magnetic field setting was achieved by warming up the sample above $T \approx 20K$ applying the appropriated external magnetic field and re-cooling down to the temperature were we performed the measurements (field cooling).
5.4 The $\Gamma_4 \rightarrow \Gamma_5(1,2)$ transition at zero field

The lowest CEF transition is of singlet-doublet nature, which, at $T = 2K$ and zero applied magnetic field, is centered at the energy $E \approx 1.7\text{meV}$. Interestingly, former powder INS investigations reported the broad nature of the low-lying transition, see references [19, 56]. Cavadini et al. [55] ascribed this broadening of the $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition to an overall doublet splitting of about $0.18\text{meV}$, which is decidedly larger than the theoretical prediction, see Table 5.4. In our investigation, even in the high resolution mode at $E_f = 3.5\text{meV}$ with an energy resolution of about $0.09\text{meV}$, we were not able to see the doublet splitting of the CEF transition. The tetragonal (I4/mmm) to orthorhombic (Fmmm) distortion along [1 1 0]-direction is quantified as $0.19\%$ in reference [57]. Estimates from a point charge model show that the minor symmetry lowering does not perceptibly affect the tetragonal CEF scheme of Ho$^{3+}$. Especially the doublet splitting of the low-lying $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition remains the same. If we assume a doublet splitting of $\delta \approx 0.017\text{meV}$ calculated within a mean-field CEF model approach and apply the spectral weight (Table 5.4) of the distinct CEF transitions $\Gamma_4 \rightarrow \Gamma_5(1,2)$ to a least square fitting procedure we obtain a FWHM of $0.35(2)\text{meV}$, see Fig.5.6. From the novel single crystal INS investigations performed on different samples the broad nature of $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition is unambiguously ascribed to an intrinsic feature present at each wave vector and not to a doublet splitting effect. Within experimental accuracy, the absence of resolvable energy dispersion of the low-lying singlet-doublet transition is in agreement with the same model approach explaining the higher singlet-singlet transitions [55]. According to the theoretical considerations of N. Cavadini et al. [55], almost vanishing dispersive behavior is expected for the $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition. Due to the absence of a resolvable energy dispersion (see Fig.5.3 and 5.4) we concentrated our INS investigation mainly on $Q = (0 \ 0 \ 3)\ \text{r.l.u.}$ and $Q = (0.6 \ 0 \ 0)$. $Q = (0 \ 0 \ 3)$ is at the magnetic
zone center whereas $\mathbf{Q}=(0.6\ 0\ 0)$ reflects the Fermi-surface nesting vector as mentioned in the introduction.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\tilde{E}$ (meV)</th>
<th>$M^\perp$</th>
<th>$M^\parallel$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_4 \rightarrow \Gamma_5(1)$</td>
<td>1.719</td>
<td>0.23</td>
<td>0.03</td>
</tr>
<tr>
<td>$\Gamma_4 \rightarrow \Gamma_5(2)$</td>
<td>1.736</td>
<td>0.14</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Table 5.2:** Renormalized low-lying CEF transitions calculated for the $J = 8$ ground state multiplet of Ho$^{3+}$ with $B_{mf} = 3.0T$. The list is restricted to the energy range of interest, here $\tilde{E}$, $M^\perp$ and $M^\parallel$ denote the transition energy (meV), the transverse and the longitudinal transition matrix elements, respectively [55].
Inelastic neutron scattering (INS) permits a direct study of the field-dependence of the low-lying CEF transition (E ≈ 1.7meV).

Figure 5.2: CEF-level scheme of HoNi$_2$B$_2$C. The energy of the degenerated free-ion ground state splits into CEF energy levels. A numerical diagonalization in the 2J+1 spin space of the ground state multiplet yields an exchange mean-field $B_{mf}$ of 3T. For Ho$^{3+}$ (J=8) the 17 CEF states split into two groups. A group of 13 states with energies > 10meV which is irrelevant in the interesting temperature range and four low lying CEF states consisting of a ground state singlet $\Gamma_4$, a doublet $\Gamma_5(1,2)$ and another singlet $\Gamma_1$. Note, the transition matrix elements for $\Gamma_4 \rightarrow \Gamma_1$ are close to zero. The calculated doublet splitting for $\Gamma_5(1,2)$ results in $\delta \approx 0.017$meV.
5.4 The $\Gamma_4 \rightarrow \Gamma_5(1,2)$ transition at zero field

Figure 5.3: $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition energy measured for several wave vectors along the $a^*$-direction $Q = (\xi \ 0 \ 2)$ r.l.u., at zero external magnetic field and $T = 2K$. The plotted values show the mean energy position of the respective excitation extracted from the gaussian fit. The dashed line indicates the averaged transition energy.

Figure 5.4: $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition energy measured for $Q = (0 \ 0 \ 2)$, $Q = (0 \ 0 \ 2.5)$ and $Q = (0 \ 0 \ 3)$ r.l.u., at zero field and at selective values of the external magnetic field at $T = 2K$. The lines are guides to the eyes.
Inelastic neutron scattering (INS)

Figure 5.5: Magnetic field renormalization of the low-lying $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition measured for $Q = (0 \ 0 \ 3)$ r.l.u. and $T = 2K$. The external magnetic field was applied in [1 1 0]-direction and $T = 2K$. The continuous line is a fit function according to Cavadini et al. [58], the dashed line is the Zeeman-like renormalization calculated from the non-interacting Ho$^{3+}$ ion. Discontinues of the energy renormalization were observed at the metamagnetic phase transitions $H_{ex} \approx 0.4T$ and $H_{ex} \approx 1.0T$.

Figure 5.6: Representative neutron profile of the CEF transition energy measured in HoNi$_2$B$_2$C for $Q = (0 \ 0 \ 3)$, at zero field and $T=2K$. The solid line correspond to a Gaussian fit function with a mean excitation energy of $E=1.72(1)\text{meV}$ and a FWHM of $0.35(2)\text{meV}$, based on the CEF mean-field calculation with a doublet splitting of $0.017\text{meV}$. The spectral weight of the respective CEF transition is denoted by the dashed Gaussian peaks. The horizontal bar illustrates the calculated energy resolution(FWHM).
5.5 Data analysis for the external field along [1 1 0]

As far as magnetic properties are concerned, we will neglect the degree of freedom of the conduction electrons (superconductivity), assuming that the only way they enter the magnetic properties is via an effective temperature- and field-independent RKKY-exchange interaction among the stable Ho 4f moments. The appropriate Hamiltonian is then given by [9].

\[
\mathcal{H} = \sum_i [\mathcal{H}_{CEF}(J_i) - \mu_i \cdot B] - \frac{1}{2} \sum_{i,j} \mathcal{J}(i,j)J_i \cdot J_j, \tag{5.13}
\]

This Hamiltonian includes the crystalline electric field single-ion part \(\mathcal{H}_{CEF}(J_i)\) expressed in terms of the total angular momentum \(J_i\), the Zeeman interaction between the local magnetic induction \(B\) and the magnetic moment \(\mu_i = \mu_B g J_i\), and the effective RKKY
Inelastic neutron scattering (INS)

**Figure 5.8:** Transition matrix elements from a mean-field calculation with $B_{mf} \parallel [1 1 0] = 3.0T$ and $H_{ex} \parallel [1 1 0]$ out of ground state $\Gamma_4$. $M^\uparrow_{\Gamma_5(2)}$ and $M^\downarrow_{\Gamma_5(1)}$ denote the planar and the longitudinal transition matrix elements, respectively. $M^\perp_i = M^x_i = M^y_i$, $M^\parallel_i = M^z_i$.

**Figure 5.9:** Transition matrix elements from a mean-field calculation with $B_{mf} \parallel [-1 -1 0] = 3.0T$ and $H_{ex} \parallel [1 1 0]$ out of ground state $\Gamma_4$.

**Figure 5.10:** Expected intensity developing for the doublet branches shown in Fig. 5.7 for a scattering vector $Q=(H 0 0)$. The two doublet intensities of each branch are added together.

**Figure 5.11:** Expected intensity developing for the doublet branches $\Gamma_5(1,2)$ and $\Gamma'_5(1,2)$ shown in Fig. 5.7 for a scattering vector $Q=(0 0 L)$. 
5.5 Data analysis for the external field along [1 1 0]

exchange interaction (with \( \mu_B \) the Bohr magneton and \( g = \frac{5}{4} \) the gyromagnetic ratio for Ho\(^{3+} \)). This expression explains the magnetic ground state and the metamagnetic phase transitions observed as a function of the applied external magnetic field \( [9] \). For the CEF single ion Hamiltonian we use the parameters (see Table 5.3) extracted from neutron spectroscopy and diffraction data \([19]\).

Table 5.3: The crystal-field parameters (meV) of HoNi\(_2\)B\(_2\)C (Gasser et al. \([19]\)).

<table>
<thead>
<tr>
<th>( B_2^0 )</th>
<th>( B_4^0 )</th>
<th>( B_4^1 )</th>
<th>( B_6^0 )</th>
<th>( B_6^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.22 (-10^{-2} )</td>
<td>-7.66 (-10^{-5} )</td>
<td>2.40 (-10^{-3} )</td>
<td>5.43 (-10^{-7} )</td>
<td>-1.51 (-10^{-5} )</td>
</tr>
</tbody>
</table>

A three-dimensional system of large angular momenta (\( J_{Ho} = 8 \)) justifies to treat the Hamiltonian of Eq.5.13 at a mean-field level \([9]\). It is possible to decouple the dynamics of different Ho sites by introducing the mean thermal average \(< J_i >\) and neglecting the two sites fluctuations. The single-ion mean-field Hamiltonian for the \( i \)th ion results in \([9, 59]\):

\[
H_{mf}(i) = H_{CEF}(J_i) - J_i(\mu_B g B + \sum_j J(i, j) \langle J_j \rangle) + \frac{1}{2} \langle J_i \rangle \sum_j J(i, j) \langle J_j \rangle \tag{5.14}
\]

with \( B = H + 4\pi DM \). \( H \) is the applied magnetic field and the value of the demagnetization factor \( D \) is between 0 and 1. The last term in Eq.5.14 just adds a constant contribution to the free energy, without affecting \(< J_i >\). To estimate the demagnetization factor \( D \) of our plaquette-shaped crystals we used the following approximation of an oblate spheroid with the magnetization \( M \) parallel to the circular plane \([60]\):

\[
D_{||} = \frac{1}{2} \left( \frac{q^2}{(q^2 - 1)^{3/2}} \sin^{-1} \sqrt{\frac{q^2 - 1}{q}} - \frac{1}{q^2 - 1} \right) \quad \tag{5.15}
\]

where \( q = \text{diameter/thickness} \) of the oblate spheroid. For the HoNi\(_2\)B\(_2\)C single crystals we estimated an average value of \( q \approx 7 \) which leads to an in-plane demagnetization factor of \( D_{||} \approx 0.09 \). The only dipole term which is included in a explicit way is the demagnetization field. Hence, this allows us to use a magnetic induction \( B \) independent of the position. A homogeneous magnetization of the crystal is calculated as

\[
M = g \mu_B \frac{1}{V_c} \sum_i \langle J_i \rangle \tag{5.16}
\]

where \( V_c \approx 65 \text{Å}^{-3} \) is the unit-cell volume and the bar on the momentum signifies the average on all ions. The contribution of the magnetization to the Helmholtz free-energy (HFE) is \( E_M^{\text{HFE}} = 2\pi DM^2 = D \cdot 8.1 \cdot 10^{-3} \text{meV} \).

We assume ferromagnetic alignment in the basal plane and we argue based on the magnetization data (see chapter 3), that at \( T = 2 \text{K} \) the magnetic moments of the Ho\(^{3+} \) ions are almost at the saturation value \( \langle J_i \rangle \approx J_{Ho} = 8 \) and are locked in one of the in-plane
Inelastic neutron scattering (INS)

Figure 5.12: The effective descriptions of the exchange interactions are within the planes \((J \perp c^*)\) and between the planes \((J \parallel c^*)\), the latter running between the nearest, second nearest and third nearest neighboring planes, respectively.

easy directions. This reduces the RKKY interaction to c-dependence only. Taking the magnetic moment in the site 0 as reference the RKKY interaction may be parameterized as \[ J_i = \sum_{j_i} J(0, j_i) \] (5.17) whereas \(j_i\) is running over all sites of the \(i^{\text{th}}\) plane. The effective description of the exchange interaction results in \(J \perp c^* = J_0\) and \(J \parallel c^* = J_1, J_2, J_3\). The interactions are within the planes \((J \perp c^*)\) and between the planes \((J \parallel c^*)\), the latter running between the nearest, second nearest and third nearest neighboring planes, respectively. Furthermore, we assume that the moments lie in the basal plane for the whole temperature range where we performed our measurements and therefore, neglecting any out-of-plane component.

Bases on Eq. 5.14 and the mentioned assumptions we define the mean-field Hamiltonian for the \(i^{\text{th}}\) ion as

\[
\mathcal{H}_{mf}(i) = \mathcal{H}_{cef} - g\mu_B J_i (B_{mf} + B_{ex}).
\] (5.18)

The first term in Eq 5.18 denotes the CEF energy splitting of the single ion. To describe the magnetic excitations at finite fields we assume an effective field consisting of the exchange mean-field \(B_{mf} \parallel [1 1 0]\) and the applied external magnetic field \(B_{ex} = H_{ex} - 4\pi D M\). A numerical diagonalization in the 2\(J+1\) spin space of the \(J=8\) ground state multiplet of the Ho\(^{3+}\) ion yields an exchange mean-field of \(B_{mf} \approx 3.0T \parallel [1 1 0]\).

Characteristic metamagnetic phases are stabilized as a function of the external magnetic field \(H_{ex} \parallel [1 1 0]\). The comparison of the spectra obtained for the antiferromagnetic and the metamagnetic phases, respectively allows the determination of the exchange interaction between the rare-earth ions. The metamagnetic phases are described by the propagation wave vectors \(q = c^*\) (antiferromagnetic), \(q = 2/3c^*\) (helicoidal) and \(q = 0c^*\) (ferromagnetic), see [10].
5.5 Data analysis for the external field along [1 1 0]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>$H_{\text{ex}} \parallel [1 1 0]$ (T)</th>
<th>$B_{m,f}$ in units of $\langle \frac{\delta J}{g\mu_B} \rangle$</th>
<th>$E_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF2</td>
<td>↑↓</td>
<td>$0 \leq H_{\text{ex}} \leq 0.4$</td>
<td>$B_{m,f,1}=4J_0 - 2J_1 + 2J_2 - 2J_3$</td>
<td>0</td>
</tr>
<tr>
<td>AF3</td>
<td>↑↑↓</td>
<td>$0.4 &lt; H_{\text{ex}} \leq 1.0$</td>
<td>$B_{m,f,2}=4J_0 + 2J_3$</td>
<td>$^{1/3}D_\parallel \cdot E_M^0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B_{m,f,3}=4J_0 - 2J_1 - 2J_2 + 2J_3$</td>
<td>$^{1/3}D_\parallel \cdot E_M^0$</td>
</tr>
<tr>
<td>P</td>
<td>↑↑</td>
<td>$1.0 &lt; H_{\text{ex}}$</td>
<td>$B_{m,f,4}=4J_0 + 2J_1 + 2J_2 + 2J_3$</td>
<td>$D_\parallel \cdot E_M^0$</td>
</tr>
</tbody>
</table>

Table 5.4: Stacking sequence of ferromagnetically ordered planes along the [0 0 1]-direction for the magnetic phases observed for an applied external magnetic field $H_{\text{ex}} \parallel [1 1 0]$ at $T=2$K. The nomenclature of the phases is according to Amici et al.\[9\]. In the third column the expansions for the respective mean-fields are given. $E_M^0$ denotes the maximal contribution of the magnetization to the HFE per unit cell and $D_\parallel$ is the in-plane demagnetization factor.

A comparison of the $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition energy between the antiferromagnetic ground-state ($\uparrow\downarrow$), the first metamagnetic state ($\uparrow\uparrow\downarrow$) and the ferromagnetic ground-state ($\uparrow\uparrow\uparrow$) enables to determine the exchange interaction, as reflected by the change in $B_{m,f}$, see Table 5.4. Within the model, a positive (negative) sign denotes a ferromagnetic (antiferromagnetic) exchange interaction. Our model approach envisages for the first metamagnetic phase two different mean-fields, $B_{m,f,2}$ for the Ho$^{3+}$ ions of planes with ferromagnetically stacked first neighbor planes and $B_{m,f,3}$ for planes with antiferromagnetic first neighbors in $c$-direction. The magnetization $B_M = \frac{1}{2} \mu_0(g\mu_B\langle J \rangle)/V_c = 0.9$T, is included in the model as introduced before and multiplied by the in-plane demagnetization factor $D_\parallel \approx 0.09$. From the least square fit of the INS data at $Q=(0 \ 0 \ 3)$ and $T=2$K we extracted for the antiferromagnetic ground-state $B_{m,f,1}=2.99(3)$T, $B_{m,f,2}=2.29(3)$T resp. $B_{m,f,3}=3.34(3)$T for the first metamagnetic phase and $B_{m,f,4}=1.27(3)$T for the forced ferromagnetic phase. In the global fit procedure we adopted for the analysis of the INS profiles four Gaussian peaks on top of a common background for each external magnetic field value. The FWHM of the peaks is overall fixed at 0.35meV obtained from a fit of the zero-field profile, see Fig 5.3. The relative intensities of the four Gaussian peaks as function of the external magnetic field is given by the spectral weight of the respective CEF transition calculated from the model approach. The relative energy positions of each Gaussian peak as function of the field are also determined by the model. The only free parameters are the four mean-fields $B_{m,f,i}$ for the respective magnetic phase, a scaling factor for the CEF profile at zero-field and a common linear background. Denoting with $\tilde{E} = E_i - E_4$ the corresponding energy expectation of the $\Gamma_4 \rightarrow \Gamma_i$ CEF transition, the resulting inelastic neutron cross section is

$$I_i(Q, \omega) \sim |f(Q)|^2 \left(1 - \frac{Q^\alpha Q^\alpha}{Q^2} \right) M_i^{\alpha\alpha} \delta \left(\hbar\omega - \tilde{E}_i \right)$$

(5.19)

where $f(Q)$ is the form factor of the Ho$^{3+}$ ion, the polarization factor $(1 - Q^\alpha Q^\alpha/Q^2)$ permits discrimination between transverse $\alpha=x,y$ and longitudinal $\alpha=z$ crystal field transition by measuring at different scattering vectors $Q$. For $Q \parallel c$ only transverse transition may observed, whereas for $Q \perp c$ both transverse and longitudinal transitions are
Determined values for the different mean-fields $B_{mf,i}$. 

Discontinues of the energy renormalization at the metamagnetic phase boundaries were set according to the macroscopic data, $H_{ex} \approx 0.4T$ resp. $H_{ex} \approx 1.0T$. The gray stripes accompanying the respective CEF doublet indicate the fixed global FWHM of 0.35 meV used in the model approach. The solid and the dashed lines belong to the collinear and anti-collinear aligned moments, respectively. The arrows indicate the different magnetic phases.

Accessible. $M_{i}^{\alpha\alpha} = |\langle \Gamma_{i} | J^{\alpha} | \Gamma_{4} \rangle |^{2}$ are the transition matrix elements whereas the index $i$ distinguishes the CEF transition ($i = 5(1)$ or $5(2)$, $\alpha = x,y,z$) denotes the spin coordinate and $J^{\alpha}$ the irreducible spin operator within the Ho$^{3+}$ ground state multiplet. $\Gamma_{i}$ and $\Gamma_{4}$ stays for the excited CFE state and ground state, respectively. $\tilde{E} = E_{i} - E_{4}$ is the according transition energy. $M_{i}^{\alpha\alpha}$ explicitly depend on the strength of the internal mean-field $B_{mf}$. The dominant tetragonal site symmetry justifies a further simplification of the transition matrix elements in planar and axial terms with respect to the [0 0 1]-direction, see Fig.5.8 and 5.9. $M_{i}^{\perp} = M_{i}^{xx} = M_{i}^{yy}$ and $M_{i}^{\parallel} = M_{i}^{zz}$ denotes the planar and the longitudinal transition matrix elements, respectively.

Because the linear combinations of the exchange parameters $\mathcal{J}_{i}$ for the different magnetic phases are not linearly independent (see Table 5.4) we need a additional criteria. Then the RKKY-interaction function along the c-axis is given by \textbf{23}.
5.5 Data analysis for the external field along [1 1 0]

Figure 5.14: INS profiles of the $\Gamma_4 \rightarrow \Gamma_5$ (1,2) CEF transition measured for $Q = (0 0 3)$ r.l.u. and the extracted mean-field $B_{mf,1}$ for the antiferromagnetic ground-state ($0T \leq H_{ex} || [1 1 0] \leq 0.4T$). The profile for $H_{ex} || [1 1 0] = 0.4T$ is at the metamagnetic phase transition and contains therefore a slight fraction of the first metamagnetic state. The continuous line corresponds to the global fit procedure addressed in the text and the horizontal bar denotes the calculated energy resolution (FWHM). The time required for one scan at a fixed magnetic field was approximately 12h.

$$J(q_z) = J_0 + 2 \sum_{i=1}^{3} J_i \cos \left( i q_z \frac{2\pi}{c} \right).$$  \hspace{1cm} (5.20)

The effective exchange parameters $J_i$ ($i=0..3$) are considered to be empirical parameters and a necessary condition is that the 1D Fourier transform $\mathcal{J}(q_z)$ of $J_i$ has a maximum at the incommensurate modulation vector $q$. We obtain the additional criteria in our model by taking the experimental observed value of the incommensurate magnetic $c^*$-structure $q = 0.91c^*$ [8] and claim

$$\frac{\partial \mathcal{J}(q_z = 0.91c^*)}{\partial q_z} = 0.$$ \hspace{1cm} (5.21)

The temperature independence of the RKKY-interaction function justifies that Eq.5.21 is valid in the ordered phase at $T = 2K$ as well. The incommensurate magnetic $c^*$-structure

$$B_{mf,1} = 2.99(2)T$$
Inelastic neutron scattering (INS)

Figure 5.15: INS profiles for the first metamagnetic phase (0.4T < \( H_{\text{ex}} \parallel [1\ 1\ 0] \leq 1.0T \)) and the extracted mean-field \( B_{mf,2} \) resp. \( B_{mf,3} \). The profile for \( H_{\text{ex}} \parallel [1\ 1\ 0] = 1.0T \) is at the border of the second metamagnetic phase transition and contains a contribution of the ferromagnetic state, visible by the broadening of the peak at 1.3meV. The continuous line corresponds to the global fit procedure addressed in the text and the horizontal bar denotes the calculated energy resolution (FWHM).

can be the ground state of the system only as long as the average moment per ion is small enough, i.e. close to the transition temperature, \( T \approx 5.3K \). By decreasing the temperature the ordered state develops and the CEF part of the HFE force the structure to find a commensurate compromise and direct the magnetic moments to lie in one of the four easy directions \([\pm 1\ \pm 1\ 0]\). From Eq.5.21 and the mean-field expansion \( B_{mf,1} \), \( B_{mf,2} \) and \( B_{mf,3} \) we obtain the exchange parameters \( J_0, J_1, J_2 \) and \( J_3 \). A fist validity check of the obtained exchange parameters is the expansion for \( B_{mf,4} = 4J_0 + 2J_1 + 2J_2 + 2J_3 + D_||E_0 \) of the forced ferromagnetic phase \( H_{\text{ex}} \parallel [1\ 1\ 0] \leq 1.0T \). The outcome of this expansion is \( B_{mf,4} = 1.30T \) which is within the estimated error of the fitted value for this mean-field.

The determined exchange function \( J(q_z) \) is shown in Fig.5.17. Within the statistics, no distinction in the energy renormalization for \( H_{\text{ex}} \parallel [1\ 1\ 0] \) at different Q-points is observed.

\[
B_{mf,2} = 2.29(3)T
\]

\[
B_{mf,3} = 3.34(3)T
\]
5.5 Data analysis for the external field along [1 1 0]

Figure 5.16: INS profiles for the ferromagnetic phase (1.0T < $H_{ex} \parallel [1 1 0]$) and the extracted mean-field $B_{mf,4}$. The continuous line corresponds to the global fit procedure addressed in the text and the horizontal bar denotes the calculated energy resolution (FWHM).

<table>
<thead>
<tr>
<th>$\mathcal{J}$</th>
<th>$\langle T \rangle$</th>
<th>$\langle \mu eV \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{J}_{\perp c^*}$</td>
<td>0.55(3)</td>
<td>4.8(3)</td>
</tr>
<tr>
<td>$\mathcal{J}_{\parallel c^*}$</td>
<td>-0.49(3)</td>
<td>-4.3(3)</td>
</tr>
<tr>
<td>$\mathcal{J}_0$</td>
<td>-0.04(3)</td>
<td>-0.4(3)</td>
</tr>
<tr>
<td>$\mathcal{J}_2$</td>
<td>0.04(3)</td>
<td>0.4(3)</td>
</tr>
</tbody>
</table>

Table 5.5: Empirical coupling parameters obtained from the INS investigation in combination with the RKKY interaction function $\mathcal{J}(q_L)$. The values are given in units of $\langle J \rangle/g\mu_B$ and in $\mu eV$. Within the model, positive (negative) signs denote ferromagnetic (antiferromagnetic) exchange interaction.
Figure 5.17: The obtained RKKY interaction function $J(q_z)$ from our model approach. The criteria was to have a maximum at the incommensurate magnetic wave vector $q = 0.91e^*$ as shown in the inset.
In order to confirm the exchange parameters $J_i$ ($i=0..3$) of HoNi$_2$B$_2$C we applied the model to the data obtained from the INS experiment for an external magnetic field in $[0\ 1\ 0]$-direction. Furthermore, we performed INS measurement with a rod shaped single crystal (see Fig.5.1, right) to verify the neutron profiles of our compounded sample. There is no significant deviation in the energy profiles for the two samples. The observed data for the AF and the first metamagnetic phase are in good agreement with the model calculation, see Fig.5.19 and Fig.5.20. Therefore, the determined exchange parameters $J_i$ ($i=0..3$) are consistent with our experimental results for an applied magnetic field in hard direction. For $H_{ex} > 0.8$T the experimental observations disagree with the previously proposed metamagnetic phase ($\uparrow\uparrow\rightarrow$) [10]. The calculation for the ($\uparrow\uparrow\rightarrow$)-phase results in two mean-fields : $B_{mf} \approx 1.7$meV for the spins aligned in $[1\ 1\ 0]$-direction and $B_{mf} \approx 2.3$meV for an alignment in $[-1\ -1\ 0]$-direction. Due to the fact, that $2/3$ of the Ho spins would sense in this phase a mean-field of 1.7 meV and the corresponding transition matrix elements become larger for smaller mean-field values, only the model profile for this lower mean-field is plotted in Fig.5.19 and Fig.5.20. As shown in Fig.5.18, the transition energies of the singlet-doublet transition $\Gamma_4 \rightarrow \Gamma_5(1,2)$ splits up as function of the external field whereas the $\Gamma_5(1)$-branch stays at the same energy the $\Gamma_5(2)$-branch increases with a slope of $\approx 0.8$ meV/T. The main disagreement compared to the experimental data is in the second metamagnetic phase where the flat CEF branch should be observable for an investigation at $Q=(0\ 0\ L)$, see Fig.5.19 and Fig.5.25. For $Q=(0.6\ 0\ 0)$ the calculated rising CEF branch lays above the observed profile at $H_{ex}=1$T and $H_{ex}=2$T, see Fig.5.25. There is evidence that the effective mean-field of this second metamagnetic phase amounts to clearly less than expected. If we take the observed peak of the rising CEF branch at $\approx 2.2$meV for $Q=(0.6\ 0\ 0)$ at $H_{ex}=2$T as reference (see Fig.5.25) we obtain a mean field $B_{mf} \approx 1$T for this magnetic phase. This suggests, together with the knowledge about the lack of any propagation vector for magnetic ordering in c-direction (see chapter 4), that the moments are not any longer ferromagnetically aligned in the planes $\perp c$. As already mentioned in the discussion of the structural investigation, we assume, that the basal plane arrangement of magnetic moments is a fishbone-pattern (see Fig. 4.31), whereas the net magnetization points towards the applied field direction. For some measurements an additional peak at $\approx 1$meV was observed, i.e. for all the profiles shown in Fig.5.20 except the one at $H_{ex}=0.3$T. Due to the fact, that this peak remains at the same energy as function of the field (for the respective Q), disappears above 2.5K and shows a $Q$-dependence, we do not ascribe this peak to an intrinsic property of HoNi$_2$B$_2$C. It is probable that the origin of this peak is an excitation of Helium (roton).
Figure 5.18: Mean-field calculation for an applied magnetic field in [0 1 0]-direction in the ordered state of HoNi$_2$B$_2$C. Assuming a mean-field of $B_{mf} = 3.0\,\text{T}$ the transition energy of the doublet $\Gamma_5(1, 2)$ splits up as a function of the external field whereas $\Gamma_5(1)$ stays at the same energy $\Gamma_5(2)$ increases with a slope of $\approx 0.8\,\text{meV/T}$. In this case the Ho moments are aligned in [1 1 0]-direction (continuous lines). For the alignment in [-1 -1 0]-direction (dashed lines) the transition energy of $\Gamma_5'(1)$ decreases whereas the energy of $\Gamma_5'(2)$ remains constant.
5.6 Renormalization for a field along $[0 \ 1 \ 0]$  

Figure 5.19: INS profiles of the $\Gamma_4 \rightarrow \Gamma_5(1,2)$ CEF transition measured at $Q=(0 \ 0 \ 3)$ for $H_{ex} \parallel [0 \ 1 \ 0]$. The continuous line corresponds to the model calculation based on the extracted $B_{mf,i}$ mentioned in the previous section. The observed data for the antiferromagnetic ground-state($\uparrow \downarrow$) and the first metamagnetic phase ($\uparrow \uparrow \downarrow$) are in good agreement with the model calculation. Above 0.8T the proposed metamagnetic phase ($\uparrow \uparrow \rightarrow$) fails to describe the experimental data within the model.
Figure 5.20: INS profiles of the $\Gamma_4 \rightarrow \Gamma_5 (1,2)$ CEF transition measured at $Q=(0.6 \ 0 \ 0)$ for $H_{\text{ex}} \parallel [0 \ 1 \ 0]$. It is again above 0.8T where the model for the $(\uparrow\uparrow\rightarrow)$-phase fails to describe the experimental data. The additional peak at $\approx 1\text{meV}$ is most probably not a feature of HoNi$_2$B$_2$C as mentioned in the text.
Figure 5.21: Renormalization scheme for an applied magnetic field in \([0 1 0]\)-direction. The showed mean-fields values \(B_{mf,i}\) stem from the fit for the applied field in easy-direction. The metamagnetic phase boundaries were set according to the macroscopic data to \(H_{ex} \approx 0.5\) T resp. \(H_{ex} \approx 0.8\) T. The gray stripes accompanying the respective CEF transition energy indicate the fixed global FWHM. The arrows indicate the different magnetic phases. For \(H_{ex} > 0.8\) T the experimental observations disagree with the previously proposed metamagnetic phase \([10]\).
Figure 5.22: Transition matrix elements from a mean-field calculation with $B_{mf} \parallel [1 1 0] = 3.0T$ and $H_{ex} \parallel [0 1 0]$ out of ground state $\Gamma_4$.

Figure 5.23: Transition matrix elements from a mean-field calculation with $B_{mf} \parallel [-1 -1 0] = 3.0T$ and $H_{ex} \parallel [0 1 0]$ out of ground state $\Gamma_4$.

Figure 5.24: Expected intensity developing for the different CEF transitions shown in Fig. 5.21 for a scattering vector $Q=(H 0 0)$. The intensities of the branches $\Gamma_5(1)$ and $\Gamma_5(2)$ which remains constant in energy are added together.

Figure 5.25: Expected intensity developing for the different CEF transitions shown in Fig. 5.21 for a scattering vector $Q=(0 0 L)$. In contrast to $Q=(H 0 0)$ the flat CEF branches retain the intensity.
5.7 Field along [0 0 1]

Inelastic neutron scattering (INS) investigations of low-lying crystal electric field (CEF) transition have been performed in the magnetically ordered state at different \( \mathbf{Q} \)-points as a function of an applied external magnetic field in \( \mathbf{c} \)-direction. In order to gain more information about the interplay between superconductivity and magnetism, the renormalization of the magnetic excitation has been measured at fixed \( T=2\text{K} \) and finite magnetic field \( H_{ex} \parallel [0 0 1] \). This direction corresponds to a hard axis of the Ho\(^{3+} \) ions and lacks the metamagnetic transitions reported for an applied field perpendicular to the \( \mathbf{c} \)-direction. Neither a renormalization nor a significant broadening of the CEF-transitions for the selected \( \mathbf{Q} \)-points was observed.
Figure 5.26: Representative neutron profiles of the $\Gamma_4 \rightarrow \Gamma_5 \{1,2\}$ CEF transition measured for $\mathbf{Q}=(0.6 \ 0 \ 0)$ and $\mathbf{Q}=(0 \ 0 \ 3)$ r.l.u. at zero field, at $H_{ex} \parallel \{0 \ 0 \ 1\}=0.8T\approx H_{c2}$ and at $H_{ex} \parallel \{0 \ 0 \ 1\}=1.5T$ in the antiferromagnetically ordered phase of HoNi$_2$B$_2$C. For this field direction no renormalization of the CEF transition energy was observed. No line-width broadening of the CEF transition was measured at the upper critical field of superconductivity $H_{c2} \approx 0.8T$ (at $T=2K$). The continuous line is a single Gaussian peak fit and the horizontal bar denotes the calculated energy resolution (FWHM).
In the magnetically ordered state at $T = 2K$, we observed a dispersive excitation starting from the magnetic $\Gamma$-point at $Q = (0 \ 0 \ 3)$ r.l.u. (Fig. 5.27). A comparison with the almost identical slope of the low-energy phonon dispersion along $(\zeta \ 0 \ 0)$ r.l.u. [42] and the consultation of the work about multiple scattering by H. Rønnow et al. [61] led us to the suspicion of a multiple scattering phenomena (Fig. 5.28). A first scattering process in this case would be elastic scattering at the magnetic Bragg peak $Q = (0 \ 0 \ 3)$ r.l.u. followed by an inelastic scattering caused by the acoustic phonons or vice versa. If we vary the $k_i/k_f$ ratio for a constant energy transfer the intensity of the mentioned excitation will change continuously if a single scattering process causes the excitation, whereas for a multiple scattering process this intensity will oscillate as function of the $k_i/k_f$ ratio. Therefore we performed $k_i/k_f$ ratio scans at a fixed transition energy $E = 2.3$ meV and on the maximum of intensity of the mentioned excitation $Q = (-0.07 \ 0 \ 3)$ in the magnetically ordered phase at $T = 2.0K$ (Fig. 5.29). Due to the continuous intensity increase of the excitation as function of $k_f$ we abandoned the multiple scattering hypothesis. A linear extrapolation of the dispersive excitation towards $Q = (0 \ 0 \ 3)$ r.l.u. results a finite transition energy of approximately 0.6meV which is also in contradiction with the multiple scattering hypothesis. The $Q$-dependence of an excitation can be used to distinguish between magnetic and vibrational origin. The magnetic scattering is dominant at low $Q$-values, i.e., in HoNi$_2$B$_2$C the square of the magnetic form factor drops from $|f(Q)|^2 = 0.97$ at $Q = (0 \ 0 \ 1)$ r.l.u. to 0.64 for $Q = (0 \ 0 \ 5)$ r.l.u. The contribution from phonons is proportional to $Q^2$ and, therefore, shows an opposite behavior. The observed $Q$-dependence (Fig. 5.30) shows an intensity increase of the dispersive excitation for higher $Q$-values pointing towards a phononic origin. Nevertheless, a magnetic character must be assumed due to their occurrence in the magnetically ordered state and its absence above $T_N$. This leads us to the suggestion, that the cause of this excitation could be a magnetovibrational scattering mechanism. This is scattering which is inelastic in the phonon system but elastic in the spin system, i.e. the orientation of the electron spins remains unchanged, but the neutron excites or de-excites phonons in the crystal lattice via the magnetic interaction [1]. Furthermore, at the wave vector $Q = (0 \ 0 \ 3)$ r.l.u. and fixed $T = 2K (< T_N)$ an additional excitation was observed around 0.8meV (Fig. 5.31), which is located far below the first crystal-field transition at 1.7meV. We observed this additional 0.8 meV excitation on two different samples measured by different instruments. The appearance in the magnetically ordered state and its absence for $T = 9K (> T_N)$ suggested a magnetic character of this excitation. But what is the nature of this excitation and why does it appear at a magnetic $\Gamma$-point? Is it a magnetic gap or is this peak linked to the superconductivity? Because we probably observed the phonon in a magnetic or electronic channel, the understanding of the scattering mechanism is important to gain deeper insight to the electron-phonon coupling and the origin of a possible gap.
Figure 5.27: Dispersive excitation along $(\xi \ 0 \ 3)$ r.l.u. in HoNi$_2$B$_2$C at $T=2K$ and fixed $k_f=1.55\text{Å}^{-1}$. Different $Q$-scan were performed at transition energies between 0.7meV and 9.0meV to follow the dispersive excitation. The time required for one scan at a given transition energy was approximately 6h resp. 6min/point.

Figure 5.28: Comparison between the dispersive excitation along $(\xi \ 0 \ 3)$ r.l.u. in HoNi$_2$B$_2$C at $T=2K$ and the low-energy phonon mode along $(\xi \ 0 \ 0)$ r.l.u. The plotted values show the mean peak position of the respective excitations extracted from the fits. The lines are guides to the eyes. The inset shows a representative neutron profile of the excitation along $(\xi \ 0 \ 3)$ r.l.u. for a energy transfer of 2.3meV at $T=2K$ measured on IN14.
Figure 5.29: $k_f$-scan for constant energy transfer of 2.3 meV and at $T = 2K$. We measured at the intensity maximum of the dispersive excitation $Q = (-0.07 \ 0 \ 3)$ and in addition at $Q = (-0.1 \ 0 \ 3)$ for the background.

Figure 5.30: Comparison of the dispersive excitation along $(\xi \ 0 \ n)$ r.l.u. (n=1..5) in HoNi$_2$B$_2$C for a energy transfer of 4.2 meV at $T = 2K$ and fixed $k_f = 1.55 \text{Å}^{-1}$. The lines are guides to the eyes.
Figure 5.31: Neutron profiles measured in HoNi$_2$B$_2$C for $Q=(0\ 0\ 3)$ r.l.u. at $T=2K$ and fixed $k_f=1.15\,\AA^{-1}$, resp. $k_f=1.55\,\AA^{-1}$. On IN14 the time required for this profile was approx. 3.5 min/point, in total approx. 4 h/scan. On RITA-II we measured $\approx 12$ h/scan. As mentioned in the text we observed in the antiferromagnetic ground state an additional excitation next to 0.8 meV was observed. Up to the present the nature of this weak excitation remains vague.
Chapter 6

Summary and outlook

The quaternary borocarbides $R\text{Ni}_2\text{B}_2\text{C}$ are ideal systems to study an interesting variety of commensurate and incommensurate magnetic structures as well as the interplay of magnetism and superconductivity. The aim of this work was to study the effect of an external magnetic-field $H_{\text{ex}}$ on the low-energy magnetic excitations of $\text{HoNi}_2\text{B}_2\text{C}$ by inelastic neutron scattering. Furthermore, we performed a comprehensive neutron diffraction study in order to identify the basic physical ingredients involved in the extraordinary rich magnetic phases of $\text{HoNi}_2\text{B}_2\text{C}$. In addition, it proved to be very useful to combine the results of the inelastic neutron scattering investigation with the structural neutron experiments and the data obtained by macroscopic studies.

In a first stage the characterization of the $\text{HoNi}_2\text{B}_2\text{C}$ single crystals and the determination of $H_{\text{C}2}$ by electro-transport measurements as function of temperature and applied magnetic field are presented in chapter 3. We related these findings to results for the imaginary part of the AC susceptibility $\chi''$. Furthermore, the AC susceptibility investigation reveals interesting regions of the respective $(H,T)$-phase diagram, where $\chi''$ exhibits a local maximum. To our knowledge, the neutron diffraction investigation presented in chapter 4 is the most elaborate experimental effort specifically devoted to the structural magnetic properties of $\text{HoNi}_2\text{B}_2\text{C}$. By neutron polarimetry we unambiguously determined the zero field ICM $a^*$-structure ($\tau_3$) of $\text{HoNi}_2\text{B}_2\text{C}$ as a transversal amplitude modulated wave consisting of magnetic moments restricted to the basal plane and perpendicular to the propagation vector $0.585a^*$. We give preference to a model of helimagnetic arrangement for the ICM $c^*$-structure of $\text{HoNi}_2\text{B}_2\text{C}$ since the Ruderman-Kittel-Kasuya-Yosida interaction, favoring incommensurate helical ordering, competes with the strong single-ion crystal-electric-field anisotropy, which allows only a limited number of magnetic easy directions. A possible next step to further clarify the ICM $c^*$-structure ($\tau_2$) would be to apply uniaxial pressure to change the population of the domains in a neutron polarimetry experiment. We conclude from neutron powder diffraction data measured at $T = 5.3\text{K}$ that the amplitude of the refined magnetic moment of the ICM $a^*$-structure ($\tau_3$) is similar to the one of the ICM $c^*$-modulation ($\tau_2$). Moreover, there is evidence from the refinement that not all of the four coexisting magnetic phases at $T = 5.3\text{K}$ and zero field ($\tau_1$, $\tau_3$ and the two modulations of $\tau_2$) may be located in the same volume of the crystal. In other words, some of these magnetic phases have to exist in different domains.

We proved the presence of the $0.58a^*$-modulation ($\tau_3$) stabilized for an applied magnetic field in the easy direction at fixed $T = 2\text{K}$. This diffraction investigation reveals for the
Summary and outlook

first time the appearance of higher harmonics for the above mentioned structure. To our knowledge, we report for the first time the presence of a ICM a*-modulation (τ₃) in the first metamagnetic phase for an applied field along the b-direction. This structure is accompanied by higher harmonics as well. As the magnetic field (Hₑₓ || b) is increased and exceeds the second metamagnetic phase transition one observes a switch-over to a complicated multi τ-structure (ICM b*-modulations). This structure consists mainly of a 0.62b*-modulation (τ₃") in coexistence with a weaker 0.60b*-modulation (τ₃'). In almost the whole region of their existence higher harmonics of the fundamental magnetic structure are present. In contrast to the proposed phase diagram for the metamagnetic states in HoNi₂B₂C we report two different metamagnetic phases observed for an applied magnetic field along the hard in-plane direction. Both structures are non-collinear and support the hypothesis that the a*-modulation (τ₃) exists in those phases were the magnetostriction is abated. We conclude, that the metamagnetic state C6 (↑↓↑←→←↑) theoretically proposed by Amici et al. is stabilized after the first metamagnetic phase transition Hₑₓ ≈ 0.4T up to the second transition Hₑₓ ≈ 0.8T. Furthermore, for the second metamagnetic phase there are strong arguments that the magnetic moments are not any longer strictly ferromagnetically aligned in the basal plane. There is evidence, that the magnetic structure is a superposition of ferromagnetic ordering and the a*-modulation (τ₃). The arguments for the existence of these two metamagnetic phases stabilized for an applied field in the magnetically hard direction are mainly based on the neutron diffraction study but are in addition supported by the INS investigation and the macroscopic data.

In chapter 5 we report inelastic neutron scattering investigations. The measurements were performed for both Q || c* and Q ⊥ c*, including the nesting vector Q ≈ (0.6 0 0) r.l.u. Energy and spectral weight of the observed neutron profiles are compared to model predictions developed on the basis of the J = 8 ground state multiplet of Ho³⁺ in an effective mean-field. The applied theoretical model is in remarkable agreement with the observed neutron profiles as function of an applied magnetic field in easy direction. Comparing the neutron profiles at zero field with those for a applied magnetic field, one observes a distinct line-width broadening of the mentioned CEF transition. We are able to explain this broadening in terms of energy position dependence of the investigated singlet-doublet Γ₄ → Γ₅(1,2) CEF transition due to the Zeeman term of the appropriate Hamiltonian. Based on a fit to the zero field data adopting a doublet splitting δ ≈ 0.017meV obtained by the mean-field calculation we assumed for our model approach a field-independent and nondispersive intrinsic line-width of the investigated CEF transition (FWHM ≈ 0.35meV). The relative variation of the internal mean field by virtue of field-induced metamagnetic transitions is shown to unambiguously renormalize the Ho³⁺ crystal field level. The field dependence of the Γ₄ → Γ₅(1,2) CEF excitation energy is successfully related by first principles to the leading exchange interactions between the rare-earth ions. The comparison of the CEF excitation energy for the different magnetic states allows the determination of the exchange interactions of both: in the basal planes and between the planes. The inapplicability of the model for the high field regime (Hₑₓ || a(b)) provides strong evidence that the assumption of ferromagnetic alignment within the basal plane has to be rejected for this metamagnetic state. In our opinion however, the more remarkable outcome of chapter 5 that we could not identify an additional indication for the competition between
magnetism and superconductivity, rather the opposite: we have found no peculiarities
from the INS study of the \( \Gamma_4 \rightarrow \Gamma_5(1,2) \) CEF transition measured at \( T = 2K \) as function
of an applied magnetic field. We like to mention, however, that the energy of the low-
est CEF transition \( \Gamma_4 \rightarrow \Gamma_5(1,2) \) of HoNi\(_2\)B\(_2\)C is within the superconducting gap at zero
field, which is estimated from the BCS expression: \( 2\Delta_0 = 3.52k_BT_C \sim 2.58\text{meV} \) \( (T_C = 8.5K \)
assumed).

We demonstrated that for an applied external magnetic field in the basal plane the ICM
\( \mathbf{a}^* \)-modulation (\( \tau_3 \)) is even more pronounced in several regions of the \((T,H)\)-phase diagram
as for zero magnetic field. This underlines the requirement of a more sophisticated theory
to comprehend this magnetic structure, up to now no theoretical models can explain the
origin of the ICM \( \mathbf{a}^* \)-structure (\( \tau_3 \)). Possibly a more extended description of the RKKY
interaction, taking into account the Fermi surface nesting features is required to improve
the theoretical analysis and may help to clarify the role of the ICM \( \mathbf{a}^* \)-modulation (\( \tau_3 \))
in the interplay between superconductivity and magnetic order in HoNi\(_2\)B\(_2\)C.

The magnetism of HoNi\(_2\)B\(_2\)C appears as a challenging problem by itself, even before con-
sidering its interplay with superconductivity. Undoubtedly, the results presented in this
thesis, will be of importance for answering remaining questions concerning the borocar-
bide HoNi\(_2\)B\(_2\)C e.g. the interplay between magnetic order and superconductivity. We are
confident that our experimental work will be valuable in a further theoretical treatment
to reveal additional peculiarities in the superconducting behavior of HoNi\(_2\)B\(_2\)C. Just one
open interesting issue shall be mentioned here in order to conclude. The influence of the
different metamagnetic structures on the magnetostriction and the resulting disturbance
of the Fermi surface nesting.
Appendix A

Macroscopic measurements

A.1 Resistance

In this appendix we show selected resistance measurements as described in section 3.3. The data were measured as function of the applied magnetic field along the [1 1 0]-axis, [1 0 0]-axis and [0 0 1]-axis, respectively.

![Graphs showing resistance measurements](image-url)

**Figure A.1:** PPMS resistance measurements as function of an applied magnetic field in easy direction $H_{ex}||[1 1 0]$ at fixed $T = 2K$ and $T = 2K$ 5.3K, respectively. current of 5mA along [1 1 0].
Figure A.2: PPMS resistance measurements as function of an applied magnetic field in hard direction $H_{ez} || [1 0 0]$ at fixed $T = 2K$ and $T = 2K, 5.3K$, respectively. current of 5mA along $[0 1 0]$.

Figure A.3: Normalized Resistivity as function of an applied magnetic field in easy direction $H_{ez} || [1 1 0]$ and temperature. The sampling current of 5mA was applied along $[1 -1 0]$. 
Figure A.4: Normalized Resistivity as function of an applied magnetic field $H_{ex}||[0 0 1]$ and temperature. The sampling current of 5mA was applied along [1 0 0].
Appendix B

Elastic investigation, $H_{ex} \parallel [1\ 1\ 0]$

In this appendix we show different cuts of the in section 4.2 presented phase diagrams of HoNi$_2$B$_2$C for an applied magnetic in easy direction. Beside the principal ICM-structures higher harmonics and some comparisons to commensurate structures are shown.

B.1 $a^*$-modulations

![Graphs showing temperature scans for different magnetic fields along [1 1 0] (FC). Left: Temperature dependence of the ICM $\tau_3$-structure. Right: Temperature dependence of $\tau_4$ (2nd harmonic of $\tau_3$).]

Figure B.1: Temperature scans for different magnetic fields along [1 1 0] (FC). Left: Temperature dependence of the ICM $\tau_3$-structure. Right: Temperature dependence of $\tau_4$ (2nd harmonic of $\tau_3$).
Figure B.2: Field-scan of the $\mathbf{a}^*$-structures at fixed $T = 2\,\text{K}$ and $T = 3.5\,\text{K}$.

Figure B.3: Left: Temperature scan of the $\mathbf{a}^*$-structures at $H_{\text{ex}} = 1.7\,\text{T}$ (FC). Right: Temperature dependence of the ICM $\tau_5$-structure (3$^{rd}$ harmonic of $\tau_3$).
B.2 c*-modulations

Figure B.4: Field-scan of the c*-structures at fixed $T = 3$K and $T = 4.6$K.

Figure B.5: Temperature scan of the c*-structures at zero field and $H_{ex} = 0.3$T (FC).
Figure B.6: Temperature scan of the $c^*$-structures at $H_{ex} = 0.4T$ (FC) and $H_{ex} = 0.6T$ (FC).
Appendix C

Elastic investigation, $H_{ex} \parallel [0 1 0]$

In this appendix we show different cuts of the in section 4.3 presented phase diagrams of HoNi$_2$B$_2$C for an applied magnetic in the hard in-plane direction. Beside the principal ICM-structures higher harmonics and some comparisons to commensurate structures are shown.

C.1 $a^*$ & $b^*$-modulations

![Graphs of temperature scans for applied field $H_{ex} = 0.3T$ (FC) along [0 1 0]. Left: ICM $\tau_3$, perpendicular to the applied field. Right: ICM $\tau_3'$, in field direction.]

**Figure C.1:** Temperature scans for an applied field $H_{ex} = 0.3T$ (FC) along [0 1 0]. *Left:* ICM $\tau_3$, perpendicular to the applied field. *Right:* ICM $\tau_3'$, in field direction.
Figure C.2: Field-scans of $a^*$-modulations at fixed $T = 4$K.

Figure C.3: Field-scans of $b^*$-modulations at fixed $T = 4$K.
Figure C.4: Temperature-scans of $b^*$-modulations at $H_{ex} = 1.1T$ (FC) and $H_{ex} = 1.75T$ (FC) along [0 1 0].

Figure C.5: Field-scans at fixed $T = 2K$ and $T = 4.6K$. 
Elastic investigation, $H_{ex} \parallel [0 1 0]$

**Figure C.6:** Dependence of the ICM $\mathbf{\tau}_3$ propagation vector as function of the temperature at $H_{ex} = 1.1T$ (FC) and $H_{ex} = 1.75T$ (FC) along $[0 1 0]$.

**Figure C.7:** Dependence of the ICM $\mathbf{\tau}_3$ propagation vector as function of the applied magnetic field $H_{ex} \parallel [0 1 0]$ at $T = 4K$. 
Figure C.8: Dependence of the ICM $\mathbf{\tau}_4$ propagation vector as function of the temperature at $H_{ex} = 1.1\,\text{T}$ (FC) and $H_{ex} = 1.75\,\text{T}$ (FC) along [0 1 0].
C.2 $c^*$-modulations

Figure C.9: Temperature-scans of $c^*$-modulations at $H_{ex} = 0.3$T (FC) and $H_{ex} = 0.5$T (FC).

Figure C.10: Left: Temperature-scans of $c^*$-modulations at $H_{ex} = 0.65$T (FC). Right: Field-scans of $c^*$-modulations at fixed $T = 4$K.
Bibliography


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