Doctoral Thesis

A high pressure low temperature study on rare earth compounds semiconductor to metal transition

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A High Pressure Low Temperature Study on Rare Earth Compounds:
Semiconductor to Metal Transition

A dissertation
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ZÜRICH
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Doctor of Natural Sciences

presented by
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1988
to my Parents
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Abstract

Many rare earth monochalcogenides exhibit under pressure a semiconductor to metal transition (SMT) and concomitant a change in valence of their rare earth ions. In this work we present and discuss high pressure low temperature experiments on single crystalline semiconducting TmSe_{1-x}Te_x (x = 0.55, 0.68), Tm_{1-x}Eu_xSe (x = 0.5), and SmS_{1-x}Se_x (x = 0.11, 0.44) alloys. At room temperature all of them reveal a steady decrease of the electrical resistivity \( \rho \) with increasing pressure \( p \) indicating the closing of the energy gap. As the metallic state is achieved the resistivity becomes essentially pressure independent. In TmSe_{0.45}Te_{0.55} and TmSe_{0.32}Te_{0.68} at temperatures below ~ 250 K and most prominent at 5 K, however, we observe in the semiconducting regime an unusual peak structure in the resistivity-pressure relation. With neutron diffraction no crystallographic phase transition is discernible; and magnetic susceptibility and magnetoresistance data make it unlikely that the phenomenon is due to magnetic interactions. We propose the electron-hole interaction to play an important role in TmSe_{1-x}Te_x under pressure and speculate that the resistance anomaly is triggered by an excitonic instability. We can derive for these compounds a temperature-energy-gap phase diagram which is typical for an excitonic insulator. Optical reflectivity measurements on TmSe_{0.45}Te_{0.55} at ambient pressure give evidence that the necessary presupposition for the occurrence of an excitonic insulator—the presence of an excitonic level within the energy gap—is fulfilled. The significant temperature dependence of the \( \rho(p) \) peak height is successfully described with a simple model which is based on the admixture of \( f \) character into the \( d \) conduction band with a corresponding decrease of mobility of carriers. No similar effect in \( \rho(p) \) at low temperatures has been observed in Tm_{0.5}Eu_{0.5}Se or SmS_{0.85}Se_{0.11}. Nevertheless, we have reasons to expect Se rich SmS_{1-x}Se_x compounds to be good candidates to exhibit also this peak structure at low temperatures. The character of the pressure induced SMT in TmSe_{0.45}Te_{0.55} changes from continuous at room temperature to discontinuous at temperatures below ~ 200 K. In the same compound a pressure induced transition from weak antiferromagnetism (\( T_N < 0.4 \) K; semiconducting state) to ferromagnetism (maximum \( T_C \approx 6 \) K; metallic state) is observed.

Tm_{0.5}Eu_{0.5}Se is a ferromagnetic semiconductor (\( T_C = 16 \) K). The electrical resistivity in the range 100 – 300 K is predominantly of extrinsic character, but near the ordering point a pronounced peak in \( \rho(T) \) occurs, and in the ordered region the resistivity becomes significantly reduced. This behavior is thought to be due to the spin disorder scattering and the exchange induced splitting of the conduction band (magnetic red shift). For pressures up to 9 kbar magnetic susceptibility measure-
Abstract

ments indicate a considerable increase of the ordering temperature with a rate of nearly 1 K/kbar. The resistivity peak shifts under pressure with the same rate to higher temperatures, but its height becomes reduced, presumably due to the presence of more free electrons (liberated 4f electrons). The susceptibility measurements suggest a pressure induced ferromagnetism to antiferromagnetism (with $T_N \approx 10$ K) transition concomitant to the pressure induced SMT. The situation is considerably complicated by the magnetic red shift of the energy gap.

In Sm$_{0.56}$Se$_{0.44}$ we have measured the volume-pressure relation at room temperature. We find this material to become very soft before the first-order valence transition occurs (at 23.7 kbar). This is in contrast to SmS which remains stiff up to the valence transition. Hence Sm$_{0.56}$Se$_{0.44}$ is similar to the TmSe$_{1-x}$Te$_x$ compounds which, even if the transition is first-order ($x = 0.4$), exhibit a significant softening of the lattice. We are left with the speculation that in analogy to TmSe$_{0.32}$Te$_{0.68}$ also in Sm$_{0.56}$Se$_{0.44}$ Poisson’s ratio might become negative already in the semiconducting state.
Zusammenfassung

Viele Monochalkogenide der Seltenen Erden zeigen einen druckinduzierten Halbleiter-Metall Übergang, damit verbunden ist eine Änderung der Valenz der Ionen der Seltenen Erden. In dieser Arbeit präsentieren und diskutieren wir Hochdruck-Tieftemperatur Experimente an einkristallinen, halbleitenden TmSe$_{1-x}$Te$_x$ ($x = 0.55$, 0.68), Tm$_{1-x}$Eu$_x$Se ($x = 0.5$), und Sm$_{1-x}$Se$_x$ ($x = 0.11$, 0.44) Verbindungen. Bei Zimmertemperatur zeigen alle diese Proben eine monotone Abnahme des elektrischen Widerstandes $\rho$ mit zunehmendem Druck $p$, was auf das Schliessen der Energielücke zurückzuführen ist. Sobald der metallische Zustand erreicht ist, wird der Widerstand praktisch druckunabhängig. In TmSe$_{0.45}$Te$_{0.55}$ und TmSe$_{0.32}$Te$_{0.68}$ beobachten wir jedoch bei Temperaturen unterhalb $\sim 250$ K, und am ausgeprägtesten bei $5$ K, im halbleitenden Bereich ein höchst seltsames Maximum in den Widerstands-Druck Kurven. Neutronenstreuung zeigt keine kristallographische Phasenumwandlung an. Im weiteren schliessen wir aus Messungen der magnetischen Suszeptibilität und des Magnetowiderstandes, dass es unwahrscheinlich ist, dass das Phänomen auf magnetische Wechselwirkungen zurückzuführen ist. Wir sind der Ansicht, dass die Elektron-Loch Wechselwirkung in TmSe$_{1-x}$Te$_x$ unter Druck eine bedeutende Rolle spielt und spekulieren, dass die Anomalie im Widerstand durch eine exzitonische Instabilität ausgelöst wird. Wir erhalten für diese Verbindungen ein Temperatur-Energielücke Phasendiagramm, welches typisch ist für einen exzitonenischen Isolator. Optische Reflektivitätsmessungen an TmSe$_{0.45}$Te$_{0.55}$ bei Normaldruck geben Evidenz, dass die notwendige Voraussetzung für das Auftreten eines exzitonischen Isolators—die Existenz eines exzitonischen Niveaus innerhalb der Energielücke—erfüllt ist. Die bedeutende Temperaturabhängigkeit des Maximums von $\rho(p)$ kann erfolgreich mit einem einfachen Modell beschrieben werden. Dieses basiert auf der Beimischung von $f$-Charakter zum $d$-Leitungsband mit entsprechender Abnahme der Beweglichkeit der Ladungsträger. Kein vergleichbarer Effekt in $\rho(p)$ bei tiefen Temperaturen wurde in Tm$_{0.5}$Eu$_{0.5}$Se oder SmS$_{0.89}$Se$_{0.11}$ beobachtet. Allerdings gibt es Gründe anzunehmen, dass Se-reiche SmS$_{1-x}$Se$_x$ Verbindungen gute Kandidaten sind, um bei tiefen Temperaturen ein vergleichbares Maximum in den Widerstands-Druck Kurven zu zeigen. Der druckinduzierte Halbleiter-Metall Übergang in TmSe$_{0.45}$Te$_{0.55}$ vollzieht sich kontinuierlich bei Zimmertemperatur, unterhalb $\sim 200$ K ist der Übergang dann aber sprunghafter Natur. In derselben Verbindung beobachtet man einen druckinduzierten Übergang von einem schwachen Antiferromagneten ($T_N < 0.4$ K; halbleitender Zustand) zu einem Ferromagneten (maximales $T_C \approx 6$ K; metallischer Zustand). Tm$_{0.5}$Eu$_{0.5}$Se ist ein ferromagnetischer Halbleiter ($T_C = 16$ K). Der elektrische
Zusammenfassung

Widerstand ist im Bereich 100 – 300 K hauptsächlich extrinsischen Charakters, nahe des Ordnungspunktes tritt dann aber eine ausgeprägte Spitze in $\rho(T)$ auf, und im magnetisch geordneten Zustand ist der Widerstand markant reduziert. Dieses Verhalten wird auf Spin-Disorder-Streuung und austauschinduzierte Aufspaltung des Leitungsbandes (Rotverschiebung) zurückgeführt. Für Drücke bis gegen 9 kbar zeigen Messungen der magnetischen Suszeptibilität eine bedeutende Zunahme der Ordnungstemperatur mit nahezu 1 K/kbar. Die Widerstandsspitze verschiebt sich dabei mit derselben Rate zu höheren Temperaturen, wobei ihre Höhe allerdings reduziert wird, was wahrscheinlich auf das Vorhandensein von zusätzlichen freien Elektronen (delokalisierte 4f Elektronen) zurückzuführen ist. Die Suszeptibilitätsmessungen deuten zudem daraufhin, dass der druckinduzierte Halbleiter-Metall Übergang begleitet wird von einem Ferromagnetismus-Antiferromagnetismus (mit $T_N \approx 10$ K) Übergang. Die Situation ist erheblich kompliziert durch die magnetische Rotverschiebung der Energielücke.

An SmS$_{0.56}$Se$_{0.44}$ haben wir bei Zimmertemperatur die Volumen-Druck-Kurve gemessen. Wir finden, dass dieses Material vor dem Valenzübergang 1. Ordnung (bei 23.7 kbar) sehr weich wird. Dieser Befund steht im Gegensatz zu SmS, welches bis hin zum Valenzübergang steif bleibt. SmS$_{0.56}$Se$_{0.44}$ ist somit den TmSe$_{1-x}$Te$_x$ Verbindungen ähnlich, die sogar im Falle eines sprunghaften Übergangs ($x = 0.4$) eine ausserordentliche Abnahme des Kompressionsmoduls aufweisen. Wir spekulieren, dass, in Analogie zu TmSe$_{0.32}$Te$_{0.68}$ auch in SmS$_{0.56}$Se$_{0.44}$ die Poissonzahl bereits im halbleitenden Zustand negativ werden könnte.
1. Introduction

The physical properties of rare earth compounds are essentially influenced by the rare earth’s \(4f\) electrons. The neutral, free rare earth atoms have the electronic configuration: \((\text{Xe})4f^n5d^06s^2\). In a crystal the rare earths are ions, and the \(4f\) shell is deeply buried in the xenon core. The latter has the consequence that in most solids the \(4f\) wave functions of neighbouring rare earth ions do not overlap, giving rise to energetically sharp \(4f\) levels. Since the \(4f\) electrons are so close to the nucleus they screen the nuclear charge very effectively. Hence the removal of a \(4f\) electron lets the ion shrink. That’s why the ionic radii of the rare earths vary noticeably with their valence: for example \([1]\) \(\text{Sm}^{2+}: 1.16\ \text{Ä}, \text{Sm}^{3+}: 0.98\ \text{Ä}, \text{and Tm}^{2+}: 1.04\ \text{Ä}, \text{Tm}^{3+}: 0.87\ \text{Ä}\). A striking effect of this is the variation of the lattice constant of the rare earth monochalcogenides as one goes through the rare earth series (Fig. 1.1). The divalent compounds (Sm, Eu, Tm, Yb), which are semiconductors, have a significantly larger lattice constant than the trivalent compounds, which are metals.

![Lattice constants of the rare earth monochalcogenides (From [2]).](image)

In a rare earth compound the system of the \(4f\) electrons may carry a magnetic moment. Such a material consists of an array of localized magnetic moments which,
1. Introduction

however, can interact with each other leading to long range magnetic order at low enough temperatures. Free carriers are able to mediate such a magnetic interaction according to the RKKY mechanism; a typical example is gadolinium metal [3]. But, exchange interactions can lead to magnetic order also in the absence of free carriers. The famous Eu monochalcogenides were the first rare earth compounds to become recognized as magnetically ordering semiconductors [4].

Among the rare earth compounds there is a fascinating class of solids called intermediate (or homogeneously mixed) valence compounds. The characteristic common feature of these materials is believed to be that their rare earth constituents are not in a stable state of well defined valence. Instead, one has a quantum mechanical mixture of the \(4f^n5d^0\) and \(4f^{n-1}5d^1\) configurations on each rare earth ion (also at \(T = 0\)). This situation is to be discriminated from inhomogeneously mixed valency where one encounters di- and trivalent ions on equivalent lattice sites (e.g. Eu\(_2\)S\(_4\), Sm\(_2\)S\(_4\) [5]). Experimental evidence for the coexistence of two different \(4f\) configurations in intermediate valence compounds is given by intermediate lattice constants compared to the ones corresponding to integral valence, by magnetic susceptibility at higher temperatures which detects the state of the \(4f\) shell, by a soft lattice and a negative Poisson's ratio, and by Mössbauer-, L-edge- and X-ray photoelectron spectroscopy. This coexistence leads to a hybridization of localized \(4f\) and extended \(5d\) states near the Fermi level \(E_F\) [6]. Over a narrow energy range (of order 10 meV) a large density of states (DOS) occurs. If there is a single peak at \(E_F\) the material is metallic (examples: CePd\(_3\), YbCu\(_2\)Si\(_2\) [7]). But, in other cases, there is a double-peak structure in the DOS with a tiny (of order meV) forbidden gap containing \(E_F\), making the material an insulator for \(T \rightarrow 0\) (example: SmB\(_6\) [8,9]). A pseudo gap (DOS is small but non-zero) may occur as in “gold” SmS [10]. A coexistence of intermediate valency and magnetic order has been found only in Tm based compounds; this is thought to be related to the fact that the (free) Tm ion has a magnetic ground state in both valencies (Tm\(^{2+}\): \(^2\)F\(_{7/2}\) and Tm\(^{3+}\): \(^3\)H\(_6\)), whereas intermediate valence compounds based on Ce, Sm, Eu and Yb happen to mix a magnetic and a non-magnetic (free ion) state.

We shall concentrate now on the rare earth monochalcogenides. These compounds crystallize in the NaCl structure (fcc lattice). In the semiconducting compounds the rare earth ion is divalent. A rough sketch of their energy level scheme is given in Fig. 1.2. The localized \(4f^n\) level is situated within the energy gap between a filled anion \(p\) band and an empty cation \(5d6s\) conduction band. The \(5d\) band is crystal field split into the upper \(5de_g\) and the lower \(5dt_{2g}\) branch; the bottom of the latter lies below the bottom of the \(6s\) band [4,11]. The relevant energy gap \(E_g\) for \(4f^n5d^0 \rightarrow 4f^{n-1}5d^1\) excitations is given by the separation of the \(4f^n\) level from the
1. Introduction

Fig. 1.2. Schematic energy level scheme of semiconducting rare earth monochalcogenides. $D(E)$ denotes the density of states at the energy $E$.

bottom of the $5d_{2g}$ band. To get some impression of the magnitudes, two examples shall be given: in SmSe $E_g = 0.46$ eV [12], the $4p - 5d$ separation is 2.7 eV [11] and the crystal field splitting of the $5d$ band amounts to 1.87 eV [11]; in EuSe the corresponding values are 1.80, 2.1 and 1.7 eV, respectively [13]. The application of high pressure brings the ions closer to each other which increases the strength of the crystalline field. It has been established [14] that the $5d_{eg}$ branch shifts towards higher and the $5d_{2g}$ towards lower energies with respect to the localized $4f$ level. Consequently the gap $E_g$ is narrowed (of order 10 meV/kbar) until eventu-
1. Introduction

ally a pressure induced semiconductor to metal transition (SMT) occurs. Such an electronic transition involves a change in the valence state of the rare earth ions leading to a considerable volume collapse of the crystal; the rare earth ions are no longer divalent but intermediate valent between \( 2+ \) and \( 3+ \). The crystal structure remains NaCl-type through these anomalies [15]. The Sm monochalcogenides were the first materials where this fascinating transition was found: in 1970 Jayaraman et al [12,16] established the pressure induced SMT and volume collapse in these compounds. Another pressure induced volume collapse occurs in some compounds (e.g. SmTe, EuTe [17]) which is due to a NaCl to CsCl structural change; the ions remain integer valent.

In this study we will investigate semiconducting rare earth monochalcogenide alloy systems. It's not only pressure which influences the electronic energy spectrum of a compound, the exchange of cations or anions has similar effects. For example the energy gap \( E_g \) and hence the pressure where the metallic state is achieved depends on stoichiometry, and a compositionally induced SMT may occur (e.g. in TmSe_{1-x}Te_x alloys [18]).

We have selected three essentially different alloy systems: TmSe_{1-x}Te_x (Sect. 3), Tm_{1-x}Eu_xSe (Sect. 4) and SmS_{1-x}Se_x (Sect. 5). Whereas in the first and third example the anions are exchanged, in the second example the cations are exchanged against each other. In all three systems a pressure induced SMT involving a valence change occurs. Magnetic order is found in TmSe_{1-x}Te_x and Tm_{1-x}Eu_xSe, but is absent in SmS_{1-x}Se_x. Despite the extensive high pressure studies performed on these materials, only few high pressure low temperature experiments have been done up to now. It's the main purpose of this work to extend the high pressure investigation of these materials to low temperatures \( T_{min} = 1.5 \) K.
2. Experimental Details

2.1. Pressure Equipment

2.1.1. Pressure Generation

To perform high pressure experiments at \textit{room temperature} two different steel piston cylinder devices were available. The smaller one was double walled with an inner bore of about 10 mm. Pressures up to 18 kbar could be realized. Petrol-ether served as pressure transmitting medium. The larger high pressure device had been designed for pressures up to 50 kbar. The cylinder consisted of three layers with a central bore of half an inch, into which a teflon cell containing the sample, manganin gauge and liquid (mixture of n-pentane and isoamylalcohol) was introduced [19]. These devices could be used to measure \textit{electrical resistivity} and \textit{volume} continuously in function of pressure.

For \textit{low temperature} measurements we have used a CuBe clamp cell combined with the teflon cell technique. The pressure medium was 1:1 n-pentane-isoamylalcohol. Pressures up to 18 kbar were generated and locked in at ambient temperature. The small size of the device (outer diameter: 1 inch, inner bore 6 mm) allowed it to be introduced into a cryostat. During the cooling process the pressure medium freezes, but the pressure is thought to remain quasihydrostatic [20]. There occurs a loss of pressure which, however, we were able to measure accurately (Sect. 2.1.2.). We used the CuBe cell to perform high pressure low temperature investigation of \textit{electrical resistivity}, \textit{magnetic susceptibility} and \textit{neutron diffraction}.

2.1.2. Pressure Measurement

The pressure $p$ has been determined in situ by measuring the resistance $R_{\text{mang}}$ of a manganin gauge. $R_{\text{mang}}$ increases linearly with pressure

$$R_{\text{mang}}(p) = R_{\text{mang}}(p = 0) (1 + cp).$$

We used silk insulated manganin wire (diameter 0.05 mm, resistivity 220 $\Omega/m$) which we had several times temperature and pressure cycled ($T : 300-77$ K, $p : 0-10$ kbar) to minimize thermal and pressure hysteresis. The pressure coefficient $c$ in Eq.(2.1) has been determined from a careful resistivity-pressure experiment on bismuth. This material undergoes at 25.5 kbar [21] a first-order phase transition (I-II) which served us as the calibration point. We have found

$$c = 2.49 \times 10^{-3} \text{kbar}^{-1}.$$
2. Experimental Details

For measurements at room temperature a two probe determination of $R_{\text{mang}}$ was sufficient. For low temperature measurements, however, $R_{\text{mang}}$ had to be determined with four probes since the resistance of the copper lead wires depended significantly on temperature.

At low temperatures we measured the pressure with the manganin gauge, using the method described by Thompson [20]. It is assumed that the pressure coefficient $c$ of the manganin gauge is independent of temperature over the entire range $0 < T < 300$ K and the pressure $p$ is calculated similar to Eq. (2.1) through the relation

$$ p(T) = \frac{1}{c} \frac{R_{\text{mang}}(p, T) - R_{\text{mang}}(0, T)}{R_{\text{mang}}(0, T)} . $$

$R_{\text{mang}}(p, T)$ is the resistance of the manganin gauge within the CuBe cell (Sect. 2.1.2.) at temperature $T$ when at room temperature some pressure was locked in. $R_{\text{mang}}(0, T)$ is the corresponding resistance at ambient pressure ($p = 0$). We find for our pressure cell a similar temperature dependence of the pressure (Fig. 2.1) as Thompson has found [20]. In the transformation of the measured $\rho(T)$ curves (for various pressures) into $\rho(p)$ curves (for fixed temperatures) we have always taken into account the temperature dependence of pressure (e.g. Figs. 3.1 and 3.3).

2.2. Low Temperature Cryostat

2.2.1. Glass Cryostat

Low temperatures have been realized with a glass-dewar cryostat. Liquid nitrogen and liquid helium served as cooling agents. By lowering the pressure above the helium bath it was possible to attain temperatures as low as 1.5 K. A heater allowed the continuous increase of temperature up to room temperature. The warming rate was kept low to minimize thermal gradients. The temperature was changed typically by $0.5 - 1$ K/min, but near interesting transitions much lower values were realized.

2.2.2. Temperature Measurement

We used two temperature sensors. A calibrated Au-0.07%Fe/chromel thermocouple combined with an electronic device to compensate changes of room temperature could be used for the whole temperature range. For 1.5 - 20 K we used also an Allen-Bradley carbon resistance, $R_{\text{AB}}$, which obeys the relation [22]

$$ \frac{(\log R_{\text{AB}} - b)^2}{\log R_{\text{AB}}} = \frac{a}{T} . $$

(2.4)
2. Experimental Details

Fig. 2.1. Temperature dependence of pressure inside the CuBe clamp cell.

The λ point (2.17 K) and the boiling temperature at ambient pressure (4.21 K) of liquid helium served as calibration points to derive the coefficients $a$ and $b$.

For 4.2 – 20 K possible temperature gradients were studied [23] with Allen-Bradley resistances. The temperatures within the CuBe cell and outside were found to agree within 0.05 K. The gradient outside, over the whole (vertical) cell was at maximum 0.2 K.

2.3. Samples

All our measurements have been performed on single crystalline samples. The relevant data are provided in Table 2.1. $a_0$ denotes the lattice constant at ambient conditions, $#$ is the number of the sample, and $q/l$ denotes the geometrical factor used in the resistivity measurement (Eq.(2.5)). The table also includes information about which measurement was performed on what sample.
2. Experimental Details

Table 2.1 Single crystalline samples used in our experiments.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Batch</th>
<th>$a_0$ [Å]</th>
<th>#</th>
<th>Volume [mm$^3$]</th>
<th>$q/I$ [cm]</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>TmSe$<em>{0.45}$Te$</em>{0.55}$</td>
<td>2142</td>
<td>6.137</td>
<td>4</td>
<td>$2.8 \times 1.3 \times 0.6$</td>
<td>0.101</td>
<td>$\rho(p, T, H), \chi(p, T)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>$2.2 \times 2.2 \times 1.9$</td>
<td></td>
<td>neutrons, optics</td>
</tr>
<tr>
<td>TmSe$<em>{0.32}$Te$</em>{0.68}$</td>
<td>1799</td>
<td>6.21$^a$</td>
<td>5</td>
<td>$2.2 \times 1.0 \times 0.5$</td>
<td>0.110</td>
<td>$\rho(p, T)$</td>
</tr>
<tr>
<td>Tm$<em>{0.3}$Eu$</em>{0.5}$Se</td>
<td>1615</td>
<td>6.06$^b$</td>
<td>1</td>
<td>$2.6 \times 1.5 \times 0.8$</td>
<td>0.141</td>
<td>$\rho(p, T), \chi(p, T)$</td>
</tr>
<tr>
<td>SmS$<em>{0.8}$Se$</em>{0.11}$</td>
<td>2174</td>
<td>6.003</td>
<td>1</td>
<td>$2.7 \times 1.5 \times 0.8$</td>
<td>0.128</td>
<td>$\rho(p, T)$</td>
</tr>
<tr>
<td>SmS$<em>{0.56}$Se$</em>{0.44}$</td>
<td>2117</td>
<td>6.084</td>
<td>2</td>
<td></td>
<td>0.250</td>
<td>$\rho(p)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>$V/V_0(p)$</td>
</tr>
</tbody>
</table>

$^a$Ref. [24], $^b$Ref. [25]

2.4. Electrical Resistivity

2.4.1. Measurement

The electrical resistivity has been measured with a four probe technique. The sample was contacted with electrochemically etched phosphorous bronze tips that were pressed in a linear equidistant arrangement onto the sample. We made the observation that the contacts were best when the surface of the single crystal was slightly polished. The specific electrical resistivity $\rho$ of the sample was determined according to

$$\rho = (U/I)(q/I),$$

where $U$ is the voltage measured across the inner two contacts, $I$ is the current introduced via the outer two contacts, $q$ is the cross section of the sample, and finally $I$ denotes the separation of the inner two contacts. Boppart has shown [2] that four-probe-resistivities with contacts either in a linear arrangement or in the van der Pauw geometry agree within about 20%, the ratio being pressure independent. We have used a lock-in technique with an alternating current of constant amplitude (0.01 – 10 mA; 8 – 860 Hz, usually ~ 86 Hz were used). We verified the absence of current or frequency dependence of the resistivity in the used current and frequency range.

Magnetoresistance could be measured in the temperature range 1.5 – 4.2 K. The magnetic field, generated with a superconducting coil, could be varied continuously in the range 0 – 43 kOe.

2.4.2. Energy Gap Determination

In semiconducting rare earth compounds the cations 4$f$ electrons are situated in a localized level between the lower lying $p$ bands and the higher lying $5d$ bands.
2. Experimental Details

This situation is similar to an n-doped insulator with the 4f electrons being the donor electrons. The number of donors corresponds, however, to the atomic density of about $10^{22}$ cm$^{-3}$. In spite of this high density of “donors” they do not overlap to form an “impurity band”. This is due to the concentration of the 4f charge distribution around the ion core and shielding of the 4f levels by the filled electron shells of the xenon configuration [13]. In pure compounds the number $n$ of thermally excited electrons over the $4f^{n}5d^{0} - 4f^{n-1}5d^{1}$ energy gap $E_g$ is in the Boltzmann approximation given by

$$n \propto e^{-E_g/2k_BT},$$  \hspace{1cm} (2.6)

where $k_B$ is the Boltzmann constant. In real materials, however, vacancy concentrations in both the anion and the cation sublattice in the order of percents are present [26] This can result in a pinning of the Fermi energy (or the chemical potential at $T > 0$) to the 4f level [13] with the consequence that the factor 1/2 in the exponent in Eq.(2.6) goes away and

$$n \propto e^{-E_g/k_BT}. \hspace{1cm} (2.7)$$

Conductivity measurements on EuO single crystals [27] revealed thermal activation energies between 1.1 and 0.55 eV, depending on the purity of the sample (the optical gap is about 1.1 eV [13]). This demonstrates the severe influence of impurities on the very position of the chemical potential.

In several Sm and Eu compounds it has been found that energy gaps (and energy gap closing rates under pressure) which are determined with optical methods agree with the resistivity measurements evaluated with Eq.(2.7) (see e.g. Ref. [15]). Although one should look at each case separately\(^1\) we will follow this experience

\(^1\) Boppart [2] has measured the number of conduction electrons in TmSe$_{0.32}$Te$_{0.68}$ under pressure at room temperature via Hall coefficient. Assuming a linear pressure-energy gap relation he could determine the pressure dependence of the chemical potential $\zeta$ relative to the bottom of the d conduction band. He treated the 4f level as a donor and found it to lie close to $\zeta$ with the energy separation $\zeta - E_{4f}$ being essentially pressure independent, indicating the pinning of the chemical potential to the 4f level. A recalculation with the same data and model, however, reveals that $\zeta$ lies about in the middle of the energy gap $E_g$ for all investigated pressures. Thus within the framework of this model in TmSe$_{0.32}$Te$_{0.68}$ $\zeta$ would not be pinned to the 4f level. It is doubtful, however, whether this model can give the exact position of $\zeta$ relative to the 4f level since it does not incorporate for example acceptors which can have severe influence on the position of the chemical potential [13].

\(^2\) The optical gap of TmTe was found to be about 0.35 eV [28], this agrees with a comparison of resistivity values of TmTe and metallic TmSe$_{1-x}$Te$_{x}$ compounds at ambient conditions (with Eq.(2.7)) which yields 0.32 eV [18]. From the pressure dependence of the resistivity at room temperature assuming Eq.(2.7) only 0.20 eV result for the gap [16,29]. Thus it would be tempting to apply Eq.(2.6). However, the resistivity of the samples used in [29,30] was only 0.8 $\Omega$cm which is much below the resistivity of pure TmTe (18 $\Omega$cm [31], ~50 $\Omega$cm [18]). This lower resistivity
2. Experimental Details

and assume for our investigated compounds that the chemical potential is pinned to the 4f level.

Assuming simple carrier statistics and a pinning of the chemical potential to the 4f level the resistivity becomes

\[ \rho = \rho_0 e^{E_g/k_BT}. \]  

(2.8)

Many semiconducting rare earth compounds show an exponential decrease of resistivity under pressure (at ambient temperature) up to the SMT where the resistivity becomes more or less pressure independent [15]. This implies through Eq.(2.8) a linear closing of the energy gap \( E_g(p) \) under pressure \( p \)

\[ E_g(p) = E_g(p = 0) + p \frac{dE_g}{dp}. \]  

(2.9)

\( \rho_0 \) is taken to be pressure independent. \( E_g(p = 0) \) and \( dE_g/dp \) can be estimated from the resistivity pressure curve. On the other hand, the energy gap can also be evaluated from a measurement of the temperature dependence of the resistivity. The slope of \( \rho(T) \) in Eq.(2.8) in an Arrhenius plot (log\( \rho \) vs. 1/T) is determined by \( E_g \).

2.5. Magnetic Susceptibility

2.5.1. Definition

The magnetization \( M \) of a material depends on the internal magnetic field \( H_i \). The initial magnetic susceptibility \( \chi_{in} \) is defined as the slope of the \( M(H_i) \) curve at zero internal field:

\[ \chi_{in} \equiv \frac{dM}{dH_i} \bigg|_{H_i=0}. \]  

(2.10)

This definition is clear for para-, dia- and antiferromagnets since in these cases \( M(H_i) \) is a unique function. For ferromagnets the situation is more complicated (Fig. 2.2). Starting from a sample with no net magnetization, \( M(H_i) \) will follow the virgin curve (Fig. 2.2 curve a). If \( H_i \) has exceeded \( H_c \) considerably a cycling of the magnetic field will result in the saturation \( M(H_i) \) hysteresis (Fig. 2.2 curve b). The positive magnetic field \( H_c \) at the zero crossing of \( M(H_i) \) is called coercive force. Cycling of the magnetic field with smaller amplitude \( H_{max} \) leads to inner hysteretic curves (Fig. 2.2 curve c). For \( H_{max} \ll H_c \) the hysteresis degenerates to a straight line whose slope we shall define as the initial susceptibility \( \chi_{in} \) for a ferromagnet.

is probably due to defects and has the consequence that the energy gap derived from the pressure dependence of the resistivity will be too small. These data convince us to take here the chemical potential also to coincide with the 4f level.
2. Experimental Details

Fig. 2.2. The macroscopic magnetization \( M \) of a ferromagnet depends in a complicated manner on the inner magnetic field \( H_i \). (After [32])

2.5.2. Temperature Dependence

In an ideal paramagnet \( \chi_{in} \) diverges at zero temperature as \( \chi_{in} \propto \frac{1}{T} \). A ferromagnet reveals on the other hand a divergence of the susceptibility at a finite temperature which is called Curie temperature \( T_C \). The detailed temperature dependence of \( \chi_{in} \) below \( T_C \) is complex, and like the shape of the hysteresis it is very sensitive to the foregoing mechanical and heat treatment of the sample [32]. There is a very close correlation between the coercive force \( H_c \) and the initial susceptibility \( \chi_{in} \) [33] due to the fact that both quantities depend on the mobility of the Bloch-walls. One finds approximately [32]:

\[
H_c = \frac{\text{const}}{\chi_{in}}.
\]  

The coercive force increases with decreasing temperature, hence \( \chi_{in} \) decreases. The decrease of the initial susceptibility below \( T_C \) is larger in a hard ferromagnet (large \( H_c \)) than in a soft or nearly isotropic ferromagnet (small \( H_c \)).

In an antiferromagnet above the ordering point \( T_N \) (N\'eel temperature), the susceptibility again increases with decreasing temperature, however, it remains finite. Close to \( T_N \) there is a maximum, below which \( \chi_{in}(T) \) depends on the relative orientation of the applied field with respect to the sublattice magnetization. According to Fischer [34] \( T_N \) lies slightly below the maximum of \( \chi_{in}(T) \) and coincides with the temperature where \( \chi_{in}(T) \) has maximum slope.
2. Experimental Details

2.5.3. Measurement

As discussed in the previous section (Sect. 2.5.2.), the initial susceptibility has a marked structure at the magnetic ordering temperature. If we want to determine this temperature (in function of pressure), rather than the detailed $\chi_{in}(T)$-structure, we can use a transformerlike arrangement containing the sample [35] (Fig. 2.3) introduced into the CuBe pressure cell. A primary coil generates via induction an ac-voltage in a secondary coil which contains the sample. Since the induced voltage depends on the sample’s susceptibility, its measurement gives information about the magnetic behavior. It has been shown by Schwob [35] that the applied magnetic induction (of the order of $10^{-3}$ T) in the method to be described in detail below, is small enough not to disturb the ordering process.

![Schematic drawing of the coils used for the study of the magnetic susceptibility. The various quantities are explained in the text.](image)

The relation between the measured signal (induced voltage $V_{ind}$) and the initial susceptibility $\chi_{in}$ shall be elaborated in the next part of this section. Imagine an alternating current $I(t) = I_0 \sin(\omega t)$ passing through the primary coil $P$ ($N_P$ windings, length $a_P$) generating the magnetic field $H_{ext}(t)$ (index $ext$ stands for external

\[3\] The calculation will be made in the SI system
2. Experimental Details

with respect to the sample) in the secondary coil. We assume the coils to be long and slim. In this approximation

\[ H_{\text{ext}}(t) = \frac{N_p I_0}{a_p} \sin(\omega t). \]  

(2.12)

The associated inductance becomes

\[ B_{\text{ext}}(t) = \mu_0 H_{\text{ext}}(t) \]  

(2.13)

when the (very small) permeability of the coil body and the pressure liquid is neglected. \( \mu_0 \) is the permeability of the vacuum. The secondary coil consists of two oppositely wound subcoils \( S_1 \) and \( S_2 \) of equal length \( a_S \) and numbers \( N_S \) of windings but with slightly different average cross sections \( A_1 \) and \( A_2 \) (with this we take into account the inability to create two exactly identical subcoils). The induced voltage \( V_{\text{ind}} \) in the whole secondary coil is the sum of the voltages \( V_1 \) and \( V_2 \) induced into the connected subcoils \( S_1 \) and \( S_2 \):

\[ V_{\text{ind}}(t) = V_1(t) + V_2(t) \]  

(2.14)

\[ V_1(t) = N_S A_1 \left( \frac{a_{\text{sample}}}{a_S} \frac{dB_1(t)}{dt} + (1 - \frac{a_{\text{sample}}}{a_S}) \frac{dB_{\text{ext}}(t)}{dt} \right) \]  

(2.15)

\[ V_2(t) = -N_S A_2 \frac{dB_{\text{ext}}(t)}{dt}. \]  

(2.16)

The negative sign in Eq.(2.16) is due to the opposite winding orientations of \( S_1 \) and \( S_2 \). \( B_i \) (index \( i \) for internal) is the inductance within the sample (length \( a_{\text{sample}} \), cross section \( A_1 \)) which is situated within the subcoil \( S_1 \). We make use of the general relations

\[ B_i = \mu_0 (H_i + M) \]  

(2.17)

\[ H_i = H_{\text{ext}} - N M, \]

where \( N \) denotes the demagnetization factor, \( M \) the magnetization and \( H_i \) the magnetic field inside the sample. With \( M = \chi_{\text{in}} H_i \) we can get \( B_i \) as a function of the external field \( H_{\text{ext}} \):

\[ B_i = \mu_0 H_{\text{ext}} \frac{1 + \chi_{\text{in}}}{1 + N \chi_{\text{in}}}. \]  

(2.18)

From Eqs.(2.12)-(2.18) and with \( A_1 a_{\text{sample}} = W_{\text{sample}} \) being the volume of the sample we get for the induced voltage

\[ V_{\text{ind}}(t) = V_{\text{ind}}^0 \cos(\omega t) \]  

\[ V_{\text{ind}}^0 = \mu_0 N_S \frac{N_P}{a_P} I_0 \omega \left( \frac{W_{\text{sample}}}{a_S} \frac{1 - N}{1/\chi_{\text{in}} + N} + (A_1 - A_2) \right). \]  

(2.19)
2. Experimental Details

Since in a usual experiment not amplitudes but effective values of current and voltage are measured we introduce

\[ i = \frac{I_0}{\sqrt{2}} \quad \text{and} \quad \hat{V}_{\text{ind}} = \frac{V_{\text{ind}}}{\sqrt{2}} \]  

(2.20)

and find the final formula for the effective induced voltage:

\[
\hat{V}_{\text{ind}} = \mu_0 N_S \frac{N_P}{a_P} \hat{I} \omega \left( \frac{W_{\text{sample}}}{a_S} \frac{1 - N}{1/N + N} + (A_1 - A_2) \right). 
\]

(2.21)

This equation gives now the quantitative relation between the measured signal \( \hat{V}_{\text{ind}} \) and the initial susceptibility \( \chi_{\text{in}} \). In this work the susceptibility measurements are always presented in the form:

Induced Voltage (\( \hat{V}_{\text{ind}} \)) versus Temperature (T).

Let us discuss Eq.(2.21) in certain limits.

a) \( \chi_{\text{in}} = 0 \):

\[
\hat{V}_{\text{ind}}(\chi_{\text{in}} = 0) = \mu_0 N_S \frac{N_P}{a_P} \hat{I} \omega (A_1 - A_2). 
\]

(2.22)

Due to the lack of identical subcoils an induced voltage is measured even if the secondary coil is empty.

b) \( \chi_{\text{in}} \ll 1/N \):

\[
\hat{V}_{\text{ind}}(\chi_{\text{in}}) - \hat{V}_{\text{ind}}(\chi_{\text{in}} = 0) = \mu_0 N_S \frac{N_P}{a_P} \hat{I} \omega \frac{W_{\text{sample}}}{a_S} (1 - N) \chi_{\text{in}}. 
\]

(2.23)

If the susceptibility is low enough we find it to be proportional to the voltage (difference).

c) \( \chi_{\text{in}} \to \infty \):

\[
\hat{V}_{\text{ind}}(\chi_{\text{in}} \to \infty) = \mu_0 N_S \frac{N_P}{a_P} \hat{I} \omega \left( \frac{W_{\text{sample}}}{a_S} \frac{1 - N}{N} + (A_1 - A_2) \right). 
\]

(2.24)

A nonvanishing demagnetization factor \( N \) (1/3 for a sphere) has the consequence that the induced voltage remains finite even if the susceptibility diverges.

In a typical experiment the various quantities had the following values

\[
N_P = 386 \quad A_1 \approx A_2 = 5.52 \text{ mm}^2
\]

\[
N_S = 193 \quad W_{\text{sample}} = 3.22 \text{ mm}^3
\]

\[
a_P = 5.0 \text{ mm} \quad \hat{I} = 10 \text{ mA}
\]

\[
a_S = 2.5 \text{ mm} \quad \frac{\omega}{2\pi} = 88.6 \text{ Hz}.
\]
2. Experimental Details

Thus the primary coil generated an external effective magnetic induction of about $9.7 \times 10^{-4}$ T. In this experiment we measured $V_{\text{ind}}(\chi_{\text{in}} \to \infty) - V_{\text{ind}}(\chi_{\text{in}} = 0) \approx 280 \mu V$, from which the demagnetization factor $N = 0.32$ can be estimated. The induced voltage of the empty coil ($\chi_{\text{in}} = 0$) is quite small and depends on the quality of the windings. For a frequency of 88.6 Hz various coils revealed $V_{\text{ind}}(\chi_{\text{in}} = 0)$ to be in the range of $1 - 30 \mu V$ which is according to Eq.(2.22) equivalent to $(A_1 - A_2)/A_1 = 0.2\% - 5\%$.

2.5.4. Examples

In this section we shall give examples of the temperature dependence of the induced voltage measured with the technique described above. $V_{\text{ind}}(T)$ is briefly described for soft and hard ferromagnets, for antiferromagnets, and for paramagnets.

EuO and EuS are typical soft (or isotropic) ferromagnets with Curie temperatures of 69.3 K and 16.6 K respectively [4]. Their $V_{\text{ind}}(T)$ (also in function of pressure) has been measured by Schwob [35]. Below $T_C$ $V_{\text{ind}}$ is constant, and above $T_C$ $V_{\text{ind}}$ monotonically decreases with increasing temperature. At the ordering point itself a distinct kink is present. The data can well be interpreted with $\chi_{\text{in}}$ diverging at $T_C$ (as discussed in Sect. 2.5.3. $V_{\text{ind}}(\chi_{\text{in}} \to \infty)$ stays finite) and remaining very large below $T_C$. The latter is via Eq.(2.11) equivalent to a very small coercive force. Pronounced kinks at their respective Curie temperatures are also present in magnetization measurements in low external fields of e.g. Co [36], Fe [37], Ni [38] and CdCr$_2$Se$_4$ [39].

USe is an example for a hard ferromagnet. Magnetization measurements [40,41] have shown the coercive force to vary strongly with temperature, at 4.2 K in the <111> direction it is as large as $\sim 10$ kOe. This implies (Eq.(2.11)) the initial susceptibility to become very small below $T_C$. Indeed we have found for USe a pronounced peak structure (Fig. 2.4) in $V_{\text{ind}}(T)$ demonstrating the striking difference between a soft and a hard ferromagnet. The fact that the maximum induced voltage, indicating $T_C$, occurs at 174 K rather than at 160 K [40] is probably the result of a sample dependence of the Curie temperature [42].

In antiferromagnets the susceptibility is always finite. As discussed in Sect. 2.5.2. the susceptibility has a maximum close to the ordering point, and at $T_N$ itself $\chi_{\text{in}}(T)$ has maximal slope. This behavior is clearly seen in the antiferromagnet EuTe [35]. It shall be mentioned that due to Eq.(2.21) the maximal slope of $V_{\text{ind}}(T)$ occurs at a temperature which is slightly below $T_N$. An estimation for $\text{TM}_{0.5}\text{Eu}_{0.5}\text{Se}$ under high pressure, however, reveals this difference to be quite small ($< 0.1$ K at an ordering temperature of about 10 K).

The temperature dependence of the induced voltage above the ordering point
2. Experimental Details

Fig. 2.4. Induced voltage $V_{\text{ind}}$ (magnetic susceptibility) as a function of temperature of the hard ferromagnet USe at ambient pressure: $p = 0$ kbar.

is given quite well by Eq.(2.21). As an example we will look at Tm$_{0.5}$Eu$_{0.5}$Se at ambient pressure. According to Batlogg [18] this material reveals in the range of 50 - 300 K a Curie-Weiss behavior $\chi_{\text{in}} = C/(T - \theta)$. We introduce this temperature
2. Experimental Details

dependence of $\chi_{in}$ into Eq.(2.21) and derive

$$\dot{V}_{ind} = \frac{f_1}{T + f_2} + f_3,$$

where

$$f_1 \equiv \mu_0 N_S \frac{N_P}{a_P} I_\omega W_{sample} C(1 - N)$$

$$f_2 \equiv NC - \theta$$

$$f_3 \equiv \mu_0 N_S \frac{N_P}{a_P} I_\omega (A_1 - A_2).$$

We have treated $f_1$, $f_2$, and $f_3$ as free parameters such as to give the best fit to the experimental $\dot{V}_{ind}(T)$ data (Fig. 2.5, dots). The solid line in Fig. 2.5 represents the fit with $f_1 = 1.57 \times 10^{-4}$ VK, $f_2 = -3.6$ K, and $f_3 = -8.5 \times 10^{-6}$ V. The agreement is astonishingly well if one is aware of the idealizations that led to Eq.(2.21). In principle it would be possible to determine the effective moment of the magnetic ions. Indeed we get the correct order of magnitude; however, the scattering of the data is too large to see for example a pressure dependence. This is not amazing since in the very temperature range, under the given experimental conditions, the induced voltage changes only a few $\mu$V so that the thermal expansion of the pressure medium and the coil itself disturbs a perfect measurement.

2.6. Elastic Neutron Scattering

These experiments have been performed at the Saphir reactor in Würenlingen, in cooperation with the Laboratorium für Neutronenstreuung, ETH Zürich.

2.6.1. Double Axis Spectrometer

This set-up allows the investigation of the elastic neutron diffraction pattern of single crystals. For our measurements a fixed neutron wavelength of $\lambda = 2.35$ Å was used. The sample (angle $\omega$), sitting in the neutron beam, and the detector (angle $2\theta$) could be rotated independently about a common vertical axis. After the crystal had been orientationally adjusted, a certain portion of reciprocal space could be investigated. Various computer controlled scans were possible, e.g. (see Fig. 2.6)

- $\omega$ or rocking scan: only the crystal ($\omega$) is rotated, the detector is kept in a fixed position. In k-space this results in a circle around the origin.

- 2:1 scan: both angles are changed simultaneously. $2\theta$ is incremented twice as much as $\omega$, leading in k-space to a straight line pointing towards the origin.

- constant k increment scan: the angles are changed such as to give in k-space an arbitrary straight line. The 2:1 scan is a special case of this more general type of

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2. Experimental Details

- Figure 2.5. Induced voltage $V_{ind}$ (magnetic susceptibility) versus temperature of Tm$_{0.5}$Eu$_{0.5}$Se at ambient pressure. The dots indicate the measured data (for clarity only few data points are shown) and the solid line represents a fit with Eq.(2.21) and a Curie-Weiss law for $\chi(T)$ (see text).

scan. Moreover, in the region where such a straight line is the tangent of a rocking scan both type of scans are nearly identical.

2.6.2. Low Temperature Equipment

From room temperature down to 10 K a closed-He-cycle-refrigerator was available. For temperatures down to 1.5 K (but also up to 300 K) a cryostat with liquid nitrogen and liquid helium combined with a vacuum pump was used. The temperature was monitored with a Au-Fe/Chromel thermocouple and a carbon resistor. The low temperature device was mounted onto a goniometer which was attached on the rotation table (angle $\omega$).

2.6.3. High Pressure Equipment

We have used the CuBe pressure cell described in Sect. 2.1.1. Due to attenuation, only about 7% of the incident neutrons passed the pressure cell. Fig. 2.7 shows
2. Experimental Details

![Diagram of reciprocal space with labels: constant k-increment scan, 2:1 scan, rocking scan, [011], [100], 000, 100, 200, 300, 400, 033, 133, 233, 333, 433, 022, 122, 222, 322, 422, 011, 111, 211, 311, 411.]

Fig. 2.6. The plane in reciprocal space defined by the directions [100] and [011] for a cubic lattice. Various possible scans of Bragg reflections are indicated: rocking scan, 2:1 scan, and constant k increment scan.

the Debye-Scherrer pattern of the pressure cell containing the teflon cell filled with the liquid but without any sample \((p = 0)\). The two peaks can be identified as the 111 and the 200 reflection of copper which is the most abundant element present in the bulk of the pressure cell.

2.6.4. Sample

Neutron scattering has been performed on single crystalline TmSe_{0.45}Te_{0.55} sample #5 (Sect. 2.3.), which had a volume of \(\sim 9 \text{ mm}^3\). The sample was bounded by equivalent \{100\} planes. We put the crystal inside the pressure cell such that the (011) plane coincided with the scattering plane. This made it possible that all points (being close enough to the origin) in reciprocal space lying in the plane defined by [100] and [011] were accessible (Fig. 2.6).

2.6.5. Bragg Reflections

Our diffraction experiments have been performed with unpolarized neutrons, thus the total intensity \(I_{tot}\) of a Bragg reflection \(hkl\) can be expressed as

\[
I_{tot}(hkl) = I_N(hkl) + I_M(hkl). \tag{2.25}
\]
2. Experimental Details

Fig. 2.7. Debye-Scherrer pattern of the CuBe pressure cell containing the teflon cell filled with the liquid, but without any sample (p = 0). The two peaks can be identified as the 111 and the 200 reflection of copper which is the most abundant element present in the wall of the pressure cell. The measurement was made without collimation of the neutron beam.

$I_N$ and $I_M$ are the intensities due to nuclear and magnetic scattering, respectively. For the nuclear scattering

$$I_N(hkl) = C|F_N(hkl)|^2,$$  

(2.26)

where $F_N$ stands for the nuclear structure factor and $C$ denotes a constant. The TmSe$_{1-x}$Te$_x$ compounds crystallize in the NaCl structure, for which holds

$$F_N = 0 \quad \text{if } hkl \text{ are even and odd}$$

$$F_N = 4 \left( b_{Tm} + (-1)^{(h+k+l)} b_{Se,Te} \right) \quad \text{if all } hkl \text{ are even or all are odd.}$$

(2.27)

$b_{Tm}$ and $b_{Se,Te}$ are the scattering lengths of the cations and anions. We assume

$$b_{Se,Te} = (1-x)b_{Se} + xb_{Te}.$$  

(2.28)
2. Experimental Details

If numerical data for TmSe₀.₄₅Te₀.₅₅ [43] are introduced into Eqs.(2.27) and (2.28) one finds that the intensity $I_N$ of nuclear reflections with odd $hkl$ (e.g. 111, 311) is three orders of magnitude smaller than the intensity of those with even $hkl$ (e.g. 200, 400, 220, 222). This has the consequence that in the absence of magnetic scattering only the latter reflections are measurable. If, however, there is an onset of magnetic order, the diffraction pattern changes. Ferromagnetism results in an additional intensity $I_M$ to all allowed nuclear reflections. In TmSe₀.₄₅Te₀.₅₅ e.g. the 111 reflection should become observable with the intensity [44]

$$I_M = C \frac{2 f^2 (\sin \theta/\lambda)}{3 \mu_{Tm}^2 (0.270 \times 10^{-12} \text{ cm})^2 4^2}, \quad (2.29)$$

where $C$ denotes the same constant as in Eq.(2.26), $f(\sin \theta/\lambda)$ is the magnetic form factor of the Tm ions and $\mu_{Tm}$ their ordered moment in units of $\mu_B$ (Bohr magneton). The factor $\frac{2}{3}$ stems from the assumption that the sample is divided up into domains whose directions of magnetization are oriented in a random manner [45]. $\frac{4}{4}$ is the number of lattice points in the unit cell. We take for the magnetic form factor the free ion value in the dipole approximation [46]

$$f(\sin \theta/\lambda) = \langle j_0 \rangle (\sin \theta/\lambda) + \langle j_2 \rangle (\sin \theta/\lambda) \frac{J(J + 1) + L(L + 1) - S(S + 1)}{3J(J + 1) - L(L + 1) + S(S + 1)}. \quad (2.30)$$

$\langle j_0 \rangle (\sin \theta/\lambda)$ and $\langle j_2 \rangle (\sin \theta/\lambda)$ are radial integrals containing the electronic density and spherical Bessel functions [47] and $J, L, S$ describe the Hund's rule ground state of Tm. The magnetic form factor $f(\sin \theta/\lambda)$ depends on the valence state of the ion; however, in the case of the 111 reflection Tm$^{2+}$ and Tm$^{3+}$ have within 1% the same $f(\sin \theta/\lambda)$.

In the presence of antiferromagnetism (AF) new reflections will occur. Different types of AF lead to different reflections. For a fcc lattice the following connection holds

$$\text{AF(I)} : 100, 011$$
$$\text{AF(II)} : \frac{111}{2} \frac{111}{2} \frac{111}{2}. \quad (2.31)$$

Taking the ratio $I_M/I_N$ (Eqs.(2.26) and (2.29)), the unknown constant $C$ drops out, and it is possible to derive the absolute value of the sublattice magnetization $\mu_{Tm}$. It has to be kept in mind that the observed intensities must be multiplied by the Lorentz factor $\sin(2\theta)$ [48]. The temperature dependence of the sublattice magnetization can also be investigated.
2. Experimental Details

2.7. Volume Measurement

The pressure dependence of the volume has been determined at room temperature with the strain gauge technique [49]. Strain sensitive resistance foils were glued onto two opposite sides of the crystal to be measured and a reference crystal with known compressibility (silicon). The four resistances have been connected to a full Wheatstone bridge supplied by a constant current source. The measured bridge voltage is directly proportional to the strain difference of the sample and the reference.

2.8. Optics

Optical reflectivity at near normal incidence has been measured at ambient pressure with two different apparatus covering the energy ranges 1 – 500 meV and 0.5 – 4.3 eV, respectively. The experiment has been performed at room temperature in the whole energy range, and at 6 K in the low energy range.

For the Raman scattering an argon ion laser was used. The incident wave length was 514 nm. The scattered light was analysed with the resolution of 1 meV. In the present study energy shifts from 0 – 185 meV were investigated.
3. TmSe–TmTe Alloys

3.1 Introduction

The TmSe–TmTe alloy system exhibits a compositionally induced semiconductor to metal transition (SMT). TmTe, on the one end of the system, is an ionic semiconductor with an energy gap $E_g$ of about 300 meV [24]. This gap is determined by the separation in energy between the Tm$^{2+}4f^{13}$ level and the bottom of the 5$d_{t^2_g}$ band. The exchange of (large) Te$^{2-}$ by more and more (small) Se$^{2-}$ leads to a reduction of the lattice constant. The consequence is an increase of the strength of the crystalline field which increases the separation of the 5$d_{t^2_g}$ and the 5$d_{e_g}$ sub-bands, leading to a decrease of the energy gap. In TmSe$_{0.60}$Te$_{0.40}$, $E_g$ is reduced to about 40 meV [24]. The Se rich TmSe$_{1-x}$Te$_x$ compounds ($x < 0.18$), on the other hand, are intermediate valent metals [18,24]. The variation of stoichiometry does not lead to a continuous SMT; in the range 0.18 < $x$ < 0.4 there is a miscibility gap [24,50].

The semiconducting compounds TmSe$_{1-x}$Te$_x$ (0.4 ≤ $x$ ≤ 1) can be transformed into a metallic state on the application of external pressure [15,24]. The SMT is continuous for 0.5 ≤ $x$ ≤ 1, but discontinuous for 0.4 ≤ $x$ < 0.5. Now it is the pressure which reduces the lattice constant and hence decreases, via crystalline field splitting of the 5$d$ band, the energy gap. Resistivity measurements at room temperature give clear evidence for the pressure induced SMT [24]. Hall effect data of TmSe$_{0.32}$Te$_{0.68}$ under pressure [24] indicate the conductivity to be mainly determined by the thermal excitation of localized 4$f^{13}$ electrons into 4$f^{12}5d^1$ bandlike states. Concomitant with the SMT, there occurs a valence transition of the Tm ions which gives rise to a softening of the lattice and a negative Poisson’s ratio [2,51]. Intermediate valency is indicated further by high pressure investigations of susceptibility [2,24] and L-edge absorption [52,53].

The magnetic properties of TmSe$_{1-x}$Te$_x$ are of special interest since in this system a coexistence of intermediate valence and magnetic order occurs. Stoichiometric TmSe exhibits antiferromagnetism (type I) below $T_N \approx 3$ K [54]. But the type of order can easily be changed to ferromagnetism either through the application of a moderate magnetic field (3 – 4 kOe) [54] or through the exchange of some Se by Te. Metallic TmSe$_{1-x}$Te$_x$ in the range 0.1 ≤ $x$ ≤ 0.18 is ferromagnetic [2,18,55,56] with $T_C = 1.8 – 3.7$ K. The semiconducting TmSe$_{1-x}$Te$_x$ compounds have a completely different magnetic behavior. They are antiferromagnets with very low ordering points: 0.4 ≤ $x$ ≤ 1: $T_N = 0.2 – 0.3$ K [24] and $x = 0$ (TmTe): $T_N = 0.2 – 0.4$ K (AF II) [57,58]. Under pressure, however, they reveal a SMT which has significant
3. 

\begin{align*}
3. \text{ TmSe-TmTe Alloys} \\
\text{implications on magnetic order. Wohlleben et al} \ [59] \text{ have found that at } 30-50 \text{ kbar TmTe (metallic at these pressures) has an ordering point lying above liquid helium temperature. And Batlogg et al} \ [60] \text{ showed that metallic pressed TmSe}_{0.60}\text{Te}_{0.40} \text{ can have the magnetic ordering point as high as 5.6 K.}
\end{align*}

With our low temperature high pressure study of semiconducting TmSe_{1-x}\text{Te}_x compounds we want to investigate the SMT at low temperatures. Theoretical considerations predict the continuous SMT (at 300 K) to be first-order at low temperatures \[61]\). Also the pressure-volume phase diagram of TmSe_{1-x}\text{Te}_x \[24\], which is reminiscent of the van der Waals gas, suggests a discontinuous behavior at low temperatures. We will show that this indeed is the case for TmSe_{0.45}\text{Te}_{0.55}. Furthermore, we have discovered a novel feature in the pressure dependence of the resistivity at low temperatures. A fascinating interpretation could be the transition to an excitonic insulator state. Finally, the evolution of magnetic order has been studied under pressure.

3.2. Experimental Results

3.2.1. Electrical Resistivity

We have measured at \textit{room temperature} the resistivities of TmSe_{0.45}\text{Te}_{0.55} \text{ and TmSe}_{0.32}\text{Te}_{0.68} \text{ as a continuous function of pressure (Figs. 3.3 and 3.4). We observe an exponential decrease of resistivity which indicates according to Eq.(2.8) a linear closing of the energy gap under pressure (Eq.(2.9)). As the resistivity becomes pressure independent, the gap is closed, and a \textit{continuous SMT has taken place. From our data we can estimate } dE_g / dp = -11.8 \text{ and } -13.0 \text{ meV/kbar, } E_g(p = 0) = 135 \text{ and 185 meV, and the SMT taking place at 11.4 and 14.2 kbar for TmSe}_{0.45}\text{Te}_{0.55} \text{ and TmSe}_{0.32}\text{Te}_{0.68}, \text{ respectively. These values compare well with measurements by Boppart [2,24].}

We then have investigated the temperature dependence of resistivity of the same samples, being subjected to various pressures (Figs. 3.1 and 3.2). The \textit{ambient pressure} curve of both (semiconducting) compounds reveal a resistivity increase from room temperature down to the lowest temperature (1.5 K) of about three orders of magnitude. The slope of the curve in the Arrhenius plot gradually decreases with decreasing temperature, which is probably due to extrinsic carriers. At room temperature the slope corresponds to (Eq.(2.8)) \textit{E_g} = 108 \text{ meV and 156 meV for TmSe}_{0.45}\text{Te}_{0.55} \text{ and TmSe}_{0.32}\text{Te}_{0.68}, \text{ respectively, being in reasonable agreement with the gap estimated from high pressure data.}

In order to study the influence of pressure, we have transformed all measured curves into a log ρ(p)-plot, the temperature being a parameter (Figs. 3.3 and 3.4). It
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Fig. 3.1. Temperature dependence of the electrical resistivity of TmSe$_{0.45}$Te$_{0.55}$. The pressures at room temperature are $a = 0$, $b = 9.7$, $c = 11.0$, $d = 12.9$, $e = 15.0$, and $f = 17.0$ kbar, respectively. Note the linear scale for the resistivity in the insert. For clarity not all measured curves are shown.

came to a surprise that for temperatures below about 250 K and most prominent at the lowest temperature (5 K in Figs. 3.3 and 3.4) the resistivity-pressure relations of TmSe$_{0.32}$Te$_{0.68}$ and TmSe$_{0.45}$Te$_{0.55}$ show a novel feature. After the initial decrease of resistivity, we observe, above a temperature and composition dependent critical pressure, an increase of resistivity with increasing pressure, followed again by a decrease and a SMT. The lower the temperature the larger is the increase of the resistivity. At 5 K the resistivity goes up by a factor of 370 for TmSe$_{0.45}$Te$_{0.55}$. In this pressure region the slope of the log $\rho(p)$-curves is considerably increased on cooling, at 5 K we find $d\log \rho/dp \geq 2.5$ kbar$^{-1}$ and even a first-order transition cannot be ruled out. For comparison, the rate of the resistivity decrease under pressure at room temperature $d\log \rho/dp \approx -0.2$ kbar$^{-1}$ for the same sample.

The pressure induced SMT cannot be studied directly at low temperatures with our CuBe clamp cell, since we cannot change the pressure at a fixed low temperature. Nevertheless, an indirect study is possible. In our experiments, the pressure cell is loaded at room temperature. On cooling, a certain amount of the pressure is
lost which, however, we can measure accurately (see Sect. 2.1.2.). Now, when we have driven the sample at room temperature slightly into the metallic state, the SMT can be reversed when the temperature is decreased. Depending on the initial
Fig. 3.3. Pressure dependence of the electrical resistivity of TmSe$_{0.45}$Te$_{0.55}$ for various temperatures. The thin solid lines are guides to the eye. For temperatures below 200 K a first-order SMT is suggested.

Pressure at room temperature, the SMT can be studied at various temperatures. This behavior is depicted in Fig. 3.5 for three different pressures for TmSe$_{0.45}$Te$_{0.55}$. While curve 1 shows a continuous transition, curve 2 exhibits a jump at 192 K and 11.0 kbar: the resistivity changes almost by a factor of 4 within less than 0.5 K (which causes a pressure change of less than 0.02 kbar; Sect. 2.1.1. and Fig. 2.1). This clearly indicates a first-order SMT. For lower temperatures (curve 3) the transition is still quite sharp—it takes place over about 0.14 kbar—and we think that the discontinuous behavior is masked only by some nonhydrostatic behavior of the frozen pressure transmitting medium. We observe only a very small hysteresis $\Delta p \leq 0.04$ kbar which, however, is just about the experimental error. We would
like to remark here that the hysteresis $\Delta p$ of the pressure driven first-order SMT in TmSe$_{1-x}$Te$_x$ compounds is considerably smaller (TmSe$_{0.60}$Te$_{0.40}$: $\Delta p \approx 0.3$ kbar [2,24]) than for example in SmS$_{1-x}$Se$_x$ compounds (e.g. SmS: $\Delta p \approx 5.7$ kbar [12]). The first-order SMT of TmSe$_{0.45}$Te$_{0.55}$ below ~ 200 K has been introduced into Fig. 3.3. The SMT in TmSe$_{0.32}$Te$_{0.68}$ seems to be continuous also at low temperatures.

At the highest pressures (Fig. 3.1, curve f: $p(5\text{ K}) = 14$ kbar), the compound TmSe$_{0.45}$Te$_{0.55}$ could be studied in the metallic state over the whole temperature range (Fig. 3.1). The variation of resistivity with temperature is considerably smaller compared with the semiconducting state. We observe an increase of resistivity with
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![Graph showing the temperature dependence of the electrical resistivity of TmSe₀.₄₅Te₀.₅₅ for three different pressure runs. At room temperature the pressure is 12.0, 12.9, and 13.9 kbar and at the transition it is reduced to 10.7, 11.0, and 11.0 kbar for the curves 1, 2, and 3, respectively.]

**Fig. 3.5.** Temperature dependence of the electrical resistivity of TmSe₀.₄₅Te₀.₅₅ for three different pressure runs. At room temperature the pressure is 12.0, 12.9, and 13.9 kbar and at the transition it is reduced to 10.7, 11.0, and 11.0 kbar for the curves 1, 2, and 3, respectively.

Decreasing temperature down to about 6 K, followed by a resistivity decrease.

*Magnetoresistance* has been studied on TmSe₀.₄₅Te₀.₅₅ under three different pressures (Fig. 3.6). In our experiments, both the current and the external magnetic field were parallel to the [100] direction. In Table 3.1 some values are compiled. The indicated pressures are the values at 4.2 K. ρ₀ denotes the resistance at H = 0; H_max is the applied magnetic field, where Δρ(H)/ρ₀ has a maximum.

At 7.5 and 12.8 kbar the sample is in the semiconducting state, whereas at 15.2 kbar it is metallic. We observe in the metallic state a more pronounced magnetoresistance; and at low fields there is a distinct maximum. The field dependence of ρ is found to be the same for increasing and decreasing fields.
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Table 3.1 Magnetoresistance of TmSe$_{0.45}$Te$_{0.55}$ under pressure.

<table>
<thead>
<tr>
<th>$p$ [kbar]</th>
<th>$T$ [K]</th>
<th>$\rho_0$ [$\Omega$cm]</th>
<th>$H_{\text{max}}$ [kOe]</th>
<th>$\Delta \rho/\rho_0(H_{\text{max}})$</th>
<th>$\Delta \rho/\rho_0(43$ kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>4.2</td>
<td>8.81</td>
<td>3.5</td>
<td>+0.1%</td>
<td>−6.3%</td>
</tr>
<tr>
<td>12.8</td>
<td>4.2</td>
<td>1.64 x $10^{-3}$</td>
<td>−</td>
<td>−</td>
<td>−4.9%</td>
</tr>
<tr>
<td>15.2</td>
<td>4.2</td>
<td>1.45 x $10^{-4}$</td>
<td>1.4</td>
<td>+1.3%</td>
<td>−20.9%</td>
</tr>
<tr>
<td>15.2</td>
<td>2.0</td>
<td>4.01 x $10^{-4}$</td>
<td>2.6</td>
<td>+4.9%</td>
<td>−17.1%</td>
</tr>
</tbody>
</table>

3.2.2. Magnetic Susceptibility

The initial susceptibility $\chi_{in}$ of TmSe$_{0.45}$Te$_{0.55}$ has been measured via induced voltage (Eq.(2.21)) at four different pressures (Fig. 3.7). In the semiconducting state ($p(5$ K$) = 8.5$ and $13.6$ kbar) there is only a slight increase of the susceptibility upon cooling. This is characteristic for paramagnetism. The magnetic ordering point lies well below 1.5 K. In the metallic state, on the other hand, there is a pronounced peak structure at $T_{\text{max}}$ indicating the onset of magnetic order; $T_{\text{max}} = 5.8$ and $5.1$ K for $p(5$ K$) = 14.3$ and $16.4$ kbar, respectively.

3.2.3 Neutron Scattering

Neutron scattering has been performed on TmSe$_{0.45}$Te$_{0.55}$. Although faced with the problem of a small transparency of the CuBe pressure cell, we were lucky to find clear cut Bragg reflections (Fig. 3.9). It took somewhat more than an hour to perform one scan over a position in reciprocal space. A scan along a certain direction (e.g. from the origin to 022) took 6 to 13 hours.

The observeability of reflections has been discussed in Sect. 2.6.5. Three different pressure runs were realized:

a) $p(300$ K$) = 11.9$ kbar: At 10 K the pressure is reduced to 8.5 kbar. At this pressure the sample is in the state with the anomalously enhanced resistivity. We made this experiment in order to look for a possible crystallographic phase transition which could be the cause for the resistance anomaly. We performed $\omega$- and $2\omega$-scans at positions 200, 400, 220, 222, 111, 100, 011 and 211 in reciprocal space at temperatures 300 K and 10 K. The reflections 200 and 400 have been measured in the whole temperature range 10 – 300 K. The fcc allowed nuclear Bragg reflections 200, 400, 220 and 222 could be observed very well. No other reflections were present and there was also no broadening of the nuclear Bragg reflections at 10 K with respect to 300 K (for 200 and 400 see Fig. 3.8). These findings indicate the absence of a structural phase transition. At room temperature the sample was in the metallic state with Tm being intermediate valent. Upon cooling, the SMT is reversed and
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Fig. 3.6. Relative change of the electrical resistivity $\Delta \rho / \rho^0$ of TmSe$_{0.45}$Te$_{0.55}$ in function of a magnetic field at various pressures and temperatures.
Fig. 3.7. Induced voltage $V_{\text{ind}}$ (magnetic susceptibility) as a function of temperature of TmSe$_{0.45}$Te$_{0.55}$ for various pressures, whose magnitudes are indicated for $T = 5$ K. In the metallic state ($p = 14.3$ and 16.4 kbar) a pronounced peak structure can be observed, whereas in the semiconducting state ($p = 8.5$ and 13.6 kbar) the susceptibility remains very small.
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Tm becomes more divalent, which increases the lattice constant \(a_0\) considerably. From the neutron data it is possible to calculate \(a_0\) via

\[
a_0 = \frac{4\pi}{Q_{400} - Q_{200}}. \tag{3.1}
\]

\(Q_{400}\), \(Q_{200}\) are the lengths of the scattering vectors of the 400 and 200 Bragg reflection, respectively. Between 255 – 210 K the lattice constant increases by remarkably 1.6\%\(^4\) (Fig. 3.8). Over this temperature range the pressure is reduced by about 0.8 kbar. To get the same change of the lattice constant at room temperature the pressure has to be changed by about 3 kbar [2]. This is further evidence that the valence transition goes towards first-order at low temperatures. In this experiment a closed-He-cycle-refrigerator was used (see Sect. 2.6.2.) where the temperature could be kept constant only within a few K. Due to the considerable temperature dependence of the lattice constant at the valence transition this lead to the slight increase of the width of the reflections in this temperature range (Fig. 3.8).

\[\text{b) } p(300K) = 17.7 \text{ kbar:} \]

At this pressure the sample was in the metallic state down to the lowest temperature \((p(1.5K) = 15.0 \text{ kbar})\). The purpose was now the study of magnetic order. We performed \(\omega\)- and 2:1-scans at 10 and 1.5 K at positions 200, 400, 022 (nuclear), 111 (F), 100 (AF I) and \(\frac{11h}{2}, \frac{3h}{2}, \frac{3h}{2}\) (AF II). Furthermore we made at 1.5 K 2:1-scans in three directions in reciprocal space (in steps of 0.2° in \(2\theta\)): from the origin out to 200, 022 (including the AF(I) reflection 011) and 111. At 10 K only nuclear Bragg reflections were present in the diffraction pattern. At 1.5 K, however, in addition to these we observed also the 111 reflection (Fig. 3.9) but no antiferromagnetic (AF) peaks. We conclude that the sample is ferromagnetic at low temperatures in zero external field. A comparison of the integrated neutron intensity \(I_M\) (Eq.(2.29)) of the 111 with \(I_N\) (Eq.(2.26)) of the 200 peak yields an ordered moment of the Tm ions of \(1.8 \pm 0.4 \mu_B\). We have also measured the temperature dependence of the maximum intensity of the 111 peak (Fig. 3.10). This yields the sublattice magnetization \(M\) (Fig. 3.11). The data can be fitted astonishingly well with the power law

\[
M \propto e^{\beta} \text{ where } \epsilon = \frac{T_0 - T}{T_C}. \tag{3.2}
\]

From this evaluation we derive the Curie temperature \(T_C = 5.07 \pm 0.1 \text{ K}\) and the critical exponent \(\beta = 0.32 \pm 0.03 (\epsilon = 0.002 - 0.3)\). A last important result of the neutron scattering at this pressure is that the lattice constant \(a_0 = 5.90 \pm 0.05\AA\) at 2 K is significantly smaller than at \(p = 0\) (6.137\AA) indicating that the sample is indeed in the collapsed intermediate valence phase. The variation of the temperature

\[^4\text{This is of the same order as the pressure induced first-order change in lattice constant of TmSe}_{0.60}\text{Te}_{0.40} \text{ at room temperature [2,24]}

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Fig. 3.8. Neutron scattering on TmSe_{0.45}Te_{0.55} at p(300 K) = 11.9 kbar.

a) Temperature dependence of the peak width of the nuclear Bragg reflections 200 and 400 in a 2:1 scan. FWHM = full width at half maximum. The horizontal straight lines are guides to the eye.

b) Temperature dependence of the lattice constant a₀. Below 255 K a₀ increases by 1.6% indicating the valence transition.
3. TmSe-TmTe Alloys

\[ \text{TmSe}_{0.45}\text{Te}_{0.55} \]

Fig. 3.9. Rocking scans of 200 and 111 Bragg reflections of TmSe_{0.45}Te_{0.55} under pressure (15 kbar: metallic; 5.8 kbar: semiconducting).
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Fig. 3.10. Temperature dependence of the maximum intensity of the 111 reflection of TmSe$_{0.45}$Te$_{0.55}$ at $p(1.5\,\text{K}) = 15\,\text{kbar}$. The horizontal solid line represents the background. The intensity above the background is due to magnetic scattering, and is according to Eq. (2.29) proportional to $M^2$.

through $T_C$ has no effect on the position of the nuclear Bragg reflections which proves that intermediate valency and magnetic order can coexist in this compound.

c) $p(300\,\text{K})=9.8\,\text{kbar}$: This measurement was made to check the absence of magnetic peaks at 1.5 K ($p = 5.8$ kbar) in the semiconducting state. At this temperature we performed $\omega$- and 2:1-scans at positions 200, 400, 022 (nuclear), 111 (F), 100, 011 (AF I) and $\frac{1}{2}1\frac{1}{2}$, $\frac{3}{2}1\frac{1}{2}$ (AF II). Again 2:1-scans from the origin to the 200, 111, 022 Bragg reflections were made. Beside the nuclear reflections no other peaks
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Fig. 3.11. Temperature dependence of the sublattice magnetization of the Tm ions of pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ at 15 kbar. The dashed curve is a power law fit as described in the text.

were present proving the absence of magnetic order (Fig. 3.9).

3.2.4. Optics

We have performed at ambient pressure near normal incidence optical reflectivity measurements on TmSe$_{0.45}$Te$_{0.55}$ at 6 and 300 K in the energy range 1 meV – 4.3 eV (Fig. 3.12). With the Kramers-Kronig analysis all optical constants could be derived.

The most obvious feature is a phonon structure around 16 meV. The increase of
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Fig. 3.12. Near normal incidence reflectivity of TmSe\(_{0.45}\)Te\(_{0.55}\) at \(p = 0\) kbar as a function of the photon energy. Solid line: \(T = 6\) K; dashed line: \(T = 300\) K.

The reflectivity towards 1 meV at room temperature is due to the presence of thermally activated carriers. At 6 K they are frozen out and hence the reflectivity levels off at the lowest energies and also the phonon structure becomes more pronounced with the maximum followed by a minimum. The energy gap is estimated from high pressure resistivity data to be about 135 meV (Sect. 3.2.1.). The imaginary part of the dielectric function \((\varepsilon_2)\) (Fig. 3.13) reveals indeed the beginning of a structure around this energy. At about 60 meV, however, there is an additional structure. An analysis with Lorentz oscillators reveals it to lie at \(\sim 63\) meV at 6 K and at \(\sim 57\) meV at room temperature. We suggest this structure to be due to excitations of 4\(f\) electrons to an excitonic level lying below the 5\(d\) conduction band.

A Raman scattering experiment has been performed on the same sample at \(p = 0\) in order to look for a structure near 60 meV (484 cm\(^{-1}\)). The spectrum has
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Fig. 3.13. Imaginary part ($\varepsilon_2$) of the dielectric function of TmSe$_{0.45}$Te$_{0.55}$ at $p = 0$ kbar as a function of the photon energy ($\hbar\omega$). Solid line: $T = 6$ K; dashed line: $T = 300$ K. In the insert $\varepsilon_2(\hbar\omega)$ is magnified in the energy range $10^{-2}$ – $10^{0}$ eV; the structure at 60 meV (arrow) is suggested to be due to an exciton.

been investigated with energy shifts 0 – 125 meV (300 K) and 0 – 185 meV (50 K) (Fig. 3.14). Both spectra reveal at about 20 meV a peak which has been found in all semiconducting TmSe$_{1-x}$Te$_x$ compounds [62] and represents a weighted phonon density of states. Beside this structure we find no other peaks in TmSe$_{0.45}$Te$_{0.55}$. An explanation could be that the 60 meV phenomenon is infrared-active but not Raman-active. It would be informative to perform resonant Raman scattering where the incident laser beam energy is close to the gap energy (135 meV).

The absorption constant $K$ can be deduced from the Kramers-Kronig analysis of the reflectivity spectrum. For TmSe$_{0.45}$Te$_{0.55}$ at 6 K we derive $K \approx 6000$ cm$^{-1}$ at 60 meV. To get a transmission of a few tenth of a % the crystal should be as
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Fig. 3.14. Raman scattering of TmSe_{0.45}Te_{0.55} at p = 0 kbar and T = 50 K. a. u. = arbitrary units; 1 eV ≈ 8066 cm⁻¹.

thin as 10 μm which is not feasible with cleaving. Thinning by mechanical polishing, on the other hand, has to be avoided since it induces the valence transition on the surface. We think that the 60 meV phenomenon in TmSe_{0.45}Te_{0.55} can be studied in transmission only on thin films of this material.

3.3. Discussion

3.3.1. Novel Pressure Induced Semiconductor to Metal Transition

The most fascinating feature of our high pressure investigation of TmSe_{1−x}Te_{x} compounds is without any doubt the unusual pressure dependence of resistivity at low temperatures (Figs. 3.3 and 3.4).
In a theoretical paper [61] a certain similarity of semiconducting Tm\textsubscript{Se\textsubscript{1-x}Te\textsubscript{x}} with expanded ScN has been suggested. Real ScN is a semimetal. Local density approximation, however, predict it to be a narrow (indirect) gap material [61]. Monnier et al [63] have demonstrated that the electron-hole correlation effects play an important role in ScN. Taking into account these effects they could show that the electron-hole liquid (EHL) is the true ground state. Expanded ScN, on the other hand, is a semiconductor, which is expected to undergo a first-order transition to the EHL state as the lattice parameter is reduced. The transition of semiconducting expanded ScN to an excitonic insulator is ruled out [63] with the observation that for such indirect gap materials the binding energy per pair of the EHL is always larger than the binding energy of the free exciton. The argument is essentially based on the existence of three equivalent minima of the conduction band at the X point which reduces the kinetic energy of the EHL. Jansen et al [64] have calculated the band structure of TmSe over a wide range of volumes and find that through the interaction with the ligand p orbitals, the 4f bands acquire a finite curvature. The position of the 4f $\Gamma_{15}$ level is much higher than one would extrapolate from the flat f bands in other parts of the Brillouin zone. Furthermore at the X point three degenerate minima of the conduction band occur. Jansen et al [61] have noticed that the band structure of semiconducting Tm\textsubscript{Se\textsubscript{1-x}Te\textsubscript{x}} in the neighborhood of the Fermi energy is close to that of expanded ScN. On the basis of this comparison they predict that the pressure induced SMT of Tm\textsubscript{Se\textsubscript{1-x}Te\textsubscript{x}} which is continuous for 0.5 \leq x \leq 1 should be discontinuous at low enough temperatures.

Our resistivity measurements on Tm\textsubscript{Se\textsubscript{0.45}Te\textsubscript{0.55}} definitely show that the very transition from the semiconducting to the metallic state is discontinuous at low temperatures whereas at room temperature it is continuous (Figs. 3.3 and 3.5). The neutron scattering data reveal the valence transition to take place over a considerably smaller pressure range at low temperature (Fig. 3.8) than at 300 K. And finally an abrupt SMT at about liquid helium temperature is also indicated by the immediate onset of magnetic order as determined from susceptibility measurements (Fig. 3.7). These findings taken alone would support the above presented theoretical considerations. But if we look at the whole picture (Figs. 3.3 and 3.4) we perceive immediately that with increasing pressure there is not a simple transition from the normal semiconducting state to the metallic state but there is first a transition to a new, more insulating state. To our knowledge no other rare earth compound has been found yet to show a similar effect.

One could imagine that the resistivity peak (Figs. 3.3 and 3.4) is due to magnetism. Our experiments on Tm\textsubscript{Se\textsubscript{0.45}Te\textsubscript{0.55}} under pressure tell us, however, that a magnetic field has only little influence on the resistivity peak height (Sect. 3.2.1.). It
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shall be mentioned in this context that SmS [65] and TmSe [66,67] show a considerable magnetoresistance. Furthermore we find the magnetic ordering temperature of TmSe$_{0.45}$Te$_{0.55}$ to be well below 1.5 K at the resistance peak. Since the peak structure of $\rho(p)$ can be seen already at temperatures as high as 250 K these experimental results make it unlikely that this phenomenon is due to magnetic interactions.

The neutron diffraction data point to the absence of a structural phase transition which could have been another explanation of the resistance peak.

A fascinating interpretation [68] of the resistivity anomaly could be the onset of an excitonic instability. This idea shall be discussed in detail in the following section. In another section we shall present a simple model which describes, however, the temperature dependence of the resistivity peak heights astonishingly well. The root idea here is a reduced mobility of carriers in the lower bound of the conduction band.

3.3.1.1. Excitonic Insulator

Imagine a semiconductor at $T = 0$ having an indirect energy gap $G$. The minimum of the empty conduction band and the maximum of the filled valence band in reciprocal space shall be separated by $w$. The promotion of a valence band electron to the conduction band leaves a positive hole in the valence band. Via screened Coulomb interaction electron and hole can be bound (binding energy $E_B$) and hence form an exciton. The exciton is a sharp excited state of the system. It is situated within the energy gap, $E_B$ below the conduction band. In the Mott-Wannier limit the electron-hole pair is loosely bound (radius $r_{E_x}$) and it extends over many unit cells in real space. In this case holds [69]

$$E_B = \frac{\mu}{m_0} \times 13.6 \text{ eV}$$

$$r_{E_x} = \frac{\epsilon}{\mu/m_0} \times 0.53 \text{ Å}.$$  (3.4)

$\epsilon$ denotes an appropriate dielectric constant, $\mu = (1/m_e + 1/m_h)^{-1}$ is the reduced mass of electron mass $m_e$ and hole mass $m_h$, and $m_0$ is the mass of the free electron. Examples are Si and Ge with $E_B \approx 13$, $\approx 3$ meV, and $r_{E_x} \approx 50$, $\approx 180$ Å, respectively [70]. The Frenkel exciton, on the other hand, is fairly localized in real space and has a large binding energy. It represents essentially an excited state of a single atom. Solid krypton and KCl with $E_B \approx 1.5$ and $\approx 0.4$ eV [71], respectively, are examples of this type of excitons.

In the following discussion $G$ shall denote the energy gap of an indirect semiconductor in the absence of electron-hole interaction. Let us assume a process (e.g. pressure, alloying) which reduces the energy gap $G$ but retains the excitonic binding energy $E_B$. It has been suggested by Knox [72] in 1963 that as soon as $G < E_B$
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the conventional insulating ground state would be unstable against the formation of excitons, and a transition to a new phase, which is called excitonic insulator [73] would result. Only if the gap $G$ is reduced to a critical value $G_c$ (usually $G_c < 0$) the material becomes a metal. Subsequently the theory of the new phase in the Mott-Wannier exciton limit was developed (e.g. des Cloizeaux [74], Kozlov and Maksimov [75], Keldysh and Kopaev [76], Jérome et al [73], and Halperin and Rice [77]). For a discussion we follow [73]. We introduce creation and destruction operators: $a^*_k$, $a_k$ create and destroy electrons in the valence band with wave vector $k$; $b^*_k$, $b_k$ create and destroy electrons in the conduction band with wave vector $w + k$. Then the conventional, insulating ground state in the Hartree-Fock approximation is given by

$$\Phi = \prod_k a^*_k |\text{vac}\rangle,$$  \hspace{1cm} (3.5)

where $|\text{vac}\rangle$ is the state with no electrons, and $k$ runs over the Brillouin zone. The ground state of the excitonic insulator, however, is of the form

$$\Psi = \prod_k a^*_k |\text{vac}\rangle,$$  \hspace{1cm} (3.6)

where $a^*_k$ creates an electron in a linear combination of valence and conduction band states,

$$a_k = u_k a_k - v_k b_k,$$  \hspace{1cm} (3.7)

This represents a correlated mixing of valence and conduction band states. It has been found that in the excitonic insulator state the actual energy gap $E_g$ is larger than the gap $G$ (in absence of electron-hole interaction) according to

$$E_g = \sqrt{G^2 + \Delta^2}.$$  \hspace{1cm} (3.8)

$\Delta$ is the gap due to electron-hole correlation and has been calculated as a function of $G$ [75] (Fig. 3.15). The transition into the excitonic insulator state is predicted to be second order [73,75] or first-order [78,79]. Due to the coupling of valence and conduction band states, which are separated by $w$ in reciprocal space, a new periodicity $2\pi/|w|$ occurs in the crystal [77]. This can result either in a charge density wave (CDW) leading to a crystallographic distortion or in a spin density wave (SDW) giving rise to antiferromagnetism.

The excitonic insulator occurs (at $T = 0$) when $G = E_B$. For a loosely bound exciton $E_B \propto e^{-2}$ (Eq.(3.3)). Hence the excitonic insulator state can only exist if $e$ does not increase without any limit when the energy gap is reduced. $e$, however, is
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Fig. 3.15. The electron-hole correlation gap $\Delta$ as a function of $G$, which is the gap in absence of electron-hole interaction. (After [83])

expected to be roughly proportional to $E_d^{-2}$ [77], where $E_d$ is the direct energy gap. Since the direct gap is still large when the indirect gap $G$ is closed, the situation $G = E_B$ seems to be realizable. The occurrence of a Mott-Wannier excitonic insulator phase has been questioned by Kübler [80]. He studied the dielectric screening of the electron-hole interaction for a simple (direct gap\(^5\)) band structure and found that the case considered does not become unstable toward exciton formation. We are left with the speculation that for more localized (Frenkel) excitons the screening of the Coulomb interaction is less effective and hence the excitonic insulator phase nevertheless can exist. This is supported by the study on expanded fluid mercury [81], to be discussed below.

We would like to draw the attention now to the possible excitonic insulator behavior of TmSe\(_{1-x}\)Te\(_x\) under pressure. In Fig. 3.16 a schematic $E(k)$ dispersion of semiconducting TmSe\(_{1-x}\)Te\(_x\) at ambient pressure is drawn. The conduction band is the 5\(d\)-derived $\Delta_{2'}$ band having its minimum at the X point. The “valence band” is formed by the 4\(f\) states. $G$ is the energy gap in absence of electron-hole interaction. We assume below the conduction band the existence of an exciton with binding energy $E_B$ which shall be in first approximation independent of $G$. Let’s look at our log $\rho(p)$ curves for fixed temperature of TmSe\(_{0.45}\)Te\(_{0.55}\) and TmSe\(_{0.32}\)Te\(_{0.68}\) (Figs.

\(^5\) Kübler [80] expects no essential change for an indirect semiconductor
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The initial decrease of $\rho$ is due to the decrease of $G$. We speculate now that the point of the *increase of resistivity* with increasing pressure is the onset of an excitonic instability. The ground state is no longer a pure $4f^n$ state, but $5d$ conduction band states get mixed in according to Eqs. (3.6) and (3.7). In other words, in the excitonic insulator state the TmSe$_{1-x}$Te$_x$ acquire a certain amount of intermediate valency. Within the framework of the above mentioned theory the energy gap in the excitonic insulator is larger than in the absence of the electron-hole interaction (Eq.(3.8)). Furthermore, in the excitonic insulator state not only has the ground state conduction band states mixed in, but also the excited states acquire a certain amount of valence band character \[82\]. In our case this means that the carriers have a certain $4f$ character which reduces their mobility. Both effects tend to an increase of resistivity just as we observe in the experiment. Further increase of pressure reduces the gap again until finally a metallic state is realized in TmSe$_{1-x}$Te$_x$. These data can be interpreted as evidence for a *sequence of pressure induced transitions from normal semiconductor to excitonic insulator to normal semimetal*.

![Diagram](image)

**Fig. 3.16.** Schematic $E(k)$ dispersion of semiconducting TmSe$_{1-x}$Te$_x$. $G$ denotes the energy gap in absence of electron-hole interaction. Below the conduction band minimum at the $X$-point an excitonic level is assumed.

What about the above mentioned new periodicity $2\pi/|w|$ which should be present in the excitonic insulator state? We have investigated the neutron diffraction...
3. TmSe–TmTe Alloys

tion pattern of TmSe\textsubscript{0.45}Te\textsubscript{0.55} at a pressure where the resistivity was enhanced, but found neither any new reflections nor a broadening of the fcc Bragg reflections, so there is no hint of any CDW or SDW. Also there is no anomaly in the susceptibility (under pressure) down to 1.5 K which could be due to a SDW. A SDW state may be detectable by its effect on nuclear magnetic resonance [77]. Several reasons could account for the absence of a new periodicity in our experiments. It is remarked in [77] that it is hard to detect this distortion, and if the exciton radius is more than a few lattice constants the magnitude of the distortion will be too small to be detected by neutrons or x-rays. Another argument is based on the observation of Jansen et al [64] that in TmSe\textsubscript{1-x}Te\textsubscript{x} the 4fΓ\textsubscript{15} level is pushed up in energy by interaction with the lower lying p states. According to these considerations, TmSe\textsubscript{1-x}Te\textsubscript{x} could be termed indirect semiconductors with |w| = ΓX = 2π/a\textsubscript{0} (fcc lattice [71]). But this has the consequence that the new periodicity 2π/|w| will be equal to the old lattice constant a\textsubscript{0} and no distortion of the lattice will occur. If, on the other hand, the 4f states are considered as completely localized, it is not clear whether any new periodicity in the excitonic insulator state should occur at all, since no w can be defined.

| Table 3.2 Excitonic insulator behavior of TmSe\textsubscript{1-x}Te\textsubscript{x}. |
|---|---|---|---|
| TmSe\textsubscript{1-x}Te\textsubscript{x} | x | E\textsubscript{B} [meV] | γ |
| TmSe\textsubscript{0.45}Te\textsubscript{0.55} | 0.55 | 75 | 0.33 |
| TmSe\textsubscript{0.32}Te\textsubscript{0.68} | 0.68 | 65 | 0.38 |

In [83] we find a qualitative phase diagram of the excitonic insulator in the temperature-gap (T–G) plane (Fig. 3.17). An essential feature of it is that at T = 0 the excitonic instability occurs at G = E\textsubscript{B} but as the temperature is increased the instability occurs at G < E\textsubscript{B}. The maximum transition temperature T\textsubscript{c} is given by

\[ k_B T_c = \gamma E_B, \]  

(3.9)

where γ is of order unity. In order to compare our data with this phase diagram we make now the crude assumption that both dE\textsubscript{g}/dp and E\textsubscript{g}(p = 0) of our compounds are temperature independent. This enables us to estimate the value of the (critical) energy gap E\textsubscript{g}\textsuperscript{c} at the moment of the onset of the resistivity increase with increasing pressure (Figs. 3.3 and 3.4), in function of temperature (Fig. 3.18). Striking features of our data are first the near coincidence of the T(E\textsubscript{g}) relations of both TmSe\textsubscript{0.45}Te\textsubscript{0.55} and TmSe\textsubscript{0.32}Te\textsubscript{0.68}, and second the surprising good agreement with the phase diagram of the excitonic insulator (Fig. 3.17). For T → 0 we can deduce E\textsubscript{B}, and taking T\textsubscript{c} = 300 K also γ = k\textsubscript{B}T\textsubscript{c}/E\textsubscript{B} can be estimated (Table 3.2).
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We see that $\gamma$ is really of the order unity and it compares well to $\gamma \approx 0.45$ taken in a theoretical work [73]. The magnitude of the binding energy of the exciton suggests them to be rather localized.

![Fig. 3.17. Qualitative phase diagram of an excitonic insulator. $k_B T_c = \gamma E_B$, where $\gamma$ is of order unity. (After [83])](image)

We have looked for an exciton in TmSe$_{0.45}$Te$_{0.55}$ at ambient pressure with optical means. The transition from the 4f level to the exciton should occur at $E_{ex} = E_g - E_B = (135 - 75) \text{ meV} = 60 \text{ meV}$. This is just the energy where we really have observed in the Kramers-Kronig analysed reflectivity spectrum a peak (Sect. 3.2.4.). Thus the necessary presupposition for the occurrence of an excitonic insulator, the presence of an exciton in the normal semiconducting state, seems to be fulfilled.

To our knowledge no material has been found up to now which shows without any doubt the transition to the excitonic insulator state. A promising candidate, however, seems to be TiSe$_2$ [84,85]. This is a semimetal at ambient conditions with a very small negative gap ($-50 \text{ meV}$) but at 200 K it exhibits a structural instability where the lattice constants are doubled. In the new state an energy gap occurs which is proposed [84] to be due to the realization of the excitonic insulator.

So far we have compared our data with existing theory of the Mott-Wannier type excitonic insulator. If we evaluate the Mott-Wannier formula (Eq.(3.3)) for the excitonic binding energy with experimental data of TmSe$_{0.32}$Te$_{0.68}$ ($\mu \approx m_e \approx 9 m_0$ [2], $\epsilon_{stat} \approx 10$, $\epsilon_{opt} \approx 6.7$ [86]) we get unrealistic large values for $E_B$ (more than 1 eV $\gg E_g$). This indicates that the excitons in TmSe$_{1-x}$Te$_x$ are rather localized, in which case Eq.(3.3) is not valid any more. The theory of the Frenkel excitonic
insulator is not yet well developed. We would like to draw the attention now to two examples which are discussed in literature as excitonic insulators of the Frenkel type.

a) The first is expanded fluid mercury (Hg). Turkevich and Cohen [81] have calculated the energy spectrum of Hg in function of the density \( \rho_{Hg} \). At infinite dilution \( (\rho_{Hg} = 0) \) the ground state is \( 6^1S_0 \), 6.7 eV above which a Frenkel exciton with \( E_B = 4.3 \) eV exists. Increasing the density spreads the excitonic level into a band, the bottom of which comes down and finally at \( \rho_{Hg} \approx 3 \) g/cm\(^3\) has the same energy as the \( 6^1S_0 \) level. At this density the binding energy of the exciton is only reduced to 3.7 eV. The normal insulating ground state, derived from the \( 6s^2 \) atomic configurations, becomes unstable to condensation of Frenkel excitons. This point is experimentally identified with an anomaly in the dielectric constant. The new insulating ground state now possesses correlated \( 6s - 6p \)
mixing. Above a certain, higher density Hg then becomes a normal metallic liquid. The transition to the excitonic insulator state is expected to be first-order. A similar $\rho_{Hg} - T$ phase diagram is predicted as for the Mott-Wannier case [83].

b) Another Frenkel excitonic insulator has been proposed by Logan [82]: alkali doped rare gas solids (e.g. Na in Ar, Kr or Xe solids). At low impurity concentration there is no impurity-impurity interaction so that there are sharp alkali levels. The Hamiltonian takes the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int} + \mathcal{H}_{RG}. \quad (3.10)$$

Here $\mathcal{H}_0$ is the electronic Hamiltonian for the free alkali atom, $\mathcal{H}_{RG}$ is the Hamiltonian depending solely on the rare gas atoms' degrees of freedom and $\mathcal{H}_{int}$ describes the coupling of the degrees of freedom of the impurity atom to those of the rare gas atoms. The calculations of Logan suggest that there is a critical density $\rho_{RG}^c$ of the rare gas solid such that for $\rho_{RG} < \rho_{RG}^c$ the material is in the normal insulating domain in which the impurity electronic ground state is a spherically symmetric $s$ state. For $\rho_{RG} > \rho_{RG}^c$, however, there is an excitonic insulator phase in which the impurity atoms posses electric dipole moments due to a $sp$ hybridized ground state. In the excitonic insulator the energy difference between ground state and first excited state is increased with respect to the normal insulator.

Is it possible at all that in TmSe$_{1-x}$Te$_x$ there occurs a transition to the excitonic insulator? As mentioned at the beginning of Sect. 3.3.1., in expanded ScN this transition is ruled out [63] with the observation that three degenerate conduction band minima exist. Considering the similar band structure [61] the same argument would hold for TmSe$_{1-x}$Te$_x$. However, in the latter compounds each Tm ion has a statistically different anion surrounding. The resulting different ligand field splitting influences the bottom of the conduction band which appears somewhat warped. This mechanism has been proposed by Boppart [2] to explain a change in slope of his log $\rho(p)$ curves (at 300 K) of TmSe$_{1-x}$Te$_x$ at higher pressures. The warping of the conduction band could remove the degeneracy of the three conduction band minima at the X point and hence increase the kinetic energy of the EHL ground state. This favors the transition to the excitonic insulator.

---

6 Contrary to Hg the alkali atoms shall be dilute for all densities $\rho_{RG}$ of interest. The excitonic level remains sharp.
3.3.1.2. Change of Mobility

In this section we propose a simple model for the quantitative analysis of the temperature dependence of the peak heights of the measured resistivity-pressure curves of TmSeₐ0.₄₅Te₀.₅₅ and TmSe₀.₃₂Te₀.₆₈. The electrical transport shall be described in terms of an effective mass \( m^* \) (i.e. parabolic band) and a mobility \( \mu \) of the conduction band electrons. We start from the normal semiconducting state at \( p = 0 \) (Fig. 3.19). We assume the following scenario. At a fixed temperature \( T \), for \( p > 0 \) the conduction band moves downward in energy (relative to the 4\( f \) level) initially without any change of its shape (\( m^* \) remains constant). In this pressure regime we observe the usual decrease of resistivity with increasing pressure. For higher pressures, however, there is an increase of resistivity, which in the present model shall be ascribed to the onset of a distortion of the bottom of the conduction band. The energy gap shall not be influenced by this process. We suppose the excitonic instability to be the trigger of this rearrangement of the energy spectrum. We discuss the new state at the point of maximum resistivity.

![Fig. 3.19](image)

**Fig. 3.19.** Evolution of the energy levels of semiconducting TmSe\(_{1-x}\)Te\(_x\) under pressure within the framework of the model discussed in this section.

Electrons in the lower part of the conduction band (from the bottom of the band at \( E_c \) to \( E_c + \delta E \)), due to the admixture of \( f \) character, shall have a reduced
mobility \( \mu \) and an enhanced effective mass \( m^* \) (index \( l \) for lower) (Fig. 3.19). At higher energies (\( E > E_0 + \delta E \)) the corresponding values shall be \( \mu_u \) and \( m^*_u \) (index \( u \) for upper), which we take to be equal to the values at \( p = 0 \) (\( \mu \) and \( m^* \)). \( m^*_l \gg m^*_u \) leads to a peak structure in the density of states \( D(E) \) for \( E_c < E < E_c + \delta E \). We take \( \delta E \) to be temperature independent. The conductivity \( \sigma \) can be expressed as

\[
\sigma = n_l q_e \mu_l + n_u q_e \mu_u. \tag{3.11}
\]

\( q_e \) denotes the charge of the electron. \( n_l \) and \( n_u \) are the number of thermally activated electrons into the lower and upper part of the conduction band

\[
n_l = 2 \int_{E_c}^{E_c+\delta E} D_l(E)F(E)\,dE \tag{3.12}
\]

\[
n_u = 2 \int_{E_c+\delta E}^{\infty} D_u(E)F(E)\,dE, \tag{3.13}
\]

where \( D_l, u \) is the density of states and \( F(E) \) is the Fermi distribution [87]:

\[
D_{l, u} = \frac{V}{4\pi^2} \left( \frac{2m^*_{l, u}}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} \tag{3.14}
\]

\[
F(E) = \frac{1}{e^{(E-\zeta)/k_B T} + 1} \tag{3.15}
\]

with \( \zeta \) denoting the chemical potential and \( V \) the volume, respectively. We assume the chemical potential to lie in such a way in the energy gap as to allow the approximation of the Fermi function \( F(E) \) by the Boltzmann function \( B(E) \)

\[
B(E) = e^{-(E-\zeta)/k_B T}. \tag{3.16}
\]

If we introduce Eqs.(3.16) and (3.14) into Eqs.(3.12) and (3.13) we get for the number of electrons in the two different parts of the conduction band

\[
n_l = 2 \frac{V}{4\pi^2} \left( \frac{2m^*_l}{\hbar^2} \right)^{3/2} e^{-(E_c-\zeta)/k_B T(k_B T)^{3/2} \gamma(3/2, 3/2, \delta E/k_B T)} \tag{3.17}
\]

\[
n_u = 2 \frac{V}{4\pi^2} \left( \frac{2m^*_u}{\hbar^2} \right)^{3/2} e^{-(E_c-\zeta)/k_B T(k_B T)^{3/2} \Gamma(3/2, 3/2, \delta E/k_B T)}, \tag{3.18}
\]

where \( \gamma \) and \( \Gamma \) are the incomplete gamma functions [88] which are defined as

\[
\gamma(a, x) \equiv \int_0^x e^{-t^a} \,dt \tag{3.19}
\]

\[
\Gamma(a, x) \equiv \int_x^\infty e^{-t^a} \,dt. \tag{3.20}
\]
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The ordinary gamma function is defined as

\[ \Gamma(a) \equiv \int_0^\infty e^{-t} t^{a-1} dt \]  

(3.21)

and is related to the incomplete gamma functions via

\[ \Gamma(a) = \Gamma(a, x) + \gamma(a, x). \]  

(3.22)

To evaluate \( \Gamma(a, x) \) we have used the series representation

\[ \Gamma(a, x) = \sum_{n=0}^{\infty} \frac{(-1)^n x^{a+n}}{n! (a+n)}. \]  

(3.23)

We make now the definition

\[ \eta \equiv \frac{m^*_1}{m^*_u} \frac{\mu_1}{\mu_u}. \]  

(3.24)

\( \eta \) describes how different the lower and upper part of the conduction band are. \( \eta = 1 \) means that they are equal. We will see that it is useful to introduce a new function

\[ A(\delta E/k_BT, \eta) \equiv \eta + (1 - \eta) \frac{\Gamma(3/2, \delta E/k_BT)}{\sqrt{\pi}/2}. \]  

(3.25)

\( A \) is a monotonic function of the argument \( \delta E/k_BT \) and has the extrema \( A = 1 \) for \( \delta E/k_BT \to 0 \), and \( A = \eta \) for \( \delta E/k_BT \to \infty \), respectively. \( A \equiv 1 \) for \( \eta = 1 \). If we introduce Eqs.(3.17) and (3.18) into Eq.(3.11), apply Eqs.(3.22), (3.24) and (3.25) we derive for the conductivity

\[ \sigma = \frac{V}{4\pi^2} \left( \frac{2}{\hbar^2} k_BT m^*_u \right)^{3/2} q_e \sqrt{\pi} \mu_u e^{-(E_C-C)/k_BT} A(\delta E/k_BT, \eta). \]  

(3.26)

The absence of any distortion of the conduction band is equivalent to \( \delta E = 0 \) or \( \eta = 1 \). In both cases \( A = 1 \), hence we define the normal conductivity

\[ \sigma_{\text{norm}} = \frac{V}{4\pi^2} \left( \frac{2}{\hbar^2} k_BT m^*_u \right)^{3/2} q_e \sqrt{\pi} \mu_u e^{-(E_C-C)/k_BT}, \]  

(3.27)

and we can write for the conductivity

\[ \sigma = \sigma_{\text{norm}} A(\delta E/k_BT, \eta). \]  

(3.28)

The effect of the admixture of \( f \) character to the \( d \) band is represented entirely by the function \( A(\delta E/k_BT, \eta) \). To compare this result with the experiment we proceed as follows. We change to resistivities

\[ \rho = 1/\sigma \]

\[ \rho_{\text{norm}} = 1/\sigma_{\text{norm}} \]  

(3.29)
and take the logarithm
\[ \log \rho = \log \rho_{\text{norm}} - \log A(\delta E/kBT, \eta). \] (3.30)

Let's look now at the \( \log \rho(p) \) curves for fixed temperatures (Figs. 3.3 and 3.4). With our model we intend to describe the height \( \Delta \log \rho \) of the resistivity anomaly above extrapolated values from above and below the \( \log \rho(p) \) peak. \( \Delta \log \rho(T) \) is plotted in Fig. 3.20. We identify now
\[ \Delta \log \rho(T) := \log \rho - \log \rho_{\text{norm}} = -\log A(\delta E/kBT, \eta). \] (3.31)

In this analysis it is assumed that the chemical potential does not change when \( \eta \) becomes different from one. \( \delta E \) and \( \eta \) are assumed to be temperature independent and are treated as fit parameters such as to give the best representation of the experimental \( \Delta \log \rho(T) \) data. The model parameters are collected in Table 3.3.

<table>
<thead>
<tr>
<th>( \text{TmSe}_{1-x}\text{Te}_x )</th>
<th>( x )</th>
<th>( \delta E [\text{meV}] )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TmSe}<em>{0.45}\text{Te}</em>{0.55} )</td>
<td>0.55</td>
<td>26</td>
<td>( 1 \times 10^{-3} )</td>
</tr>
<tr>
<td>( \text{TmSe}<em>{0.32}\text{Te}</em>{0.68} )</td>
<td>0.68</td>
<td>17</td>
<td>( 13 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

The theoretical curve with these parameters follows the experimental data astonishingly well (Fig. 3.20). The values of \( \delta E \) are of a reasonable magnitude. For the interpretation of the \( \eta \) values it is instructive to look at the case where the mobility is dominated by the scattering of the carriers by thermal vibrations of the ions, then \( \mu \propto m^* \eta^{-5/2} \) [89]. Introducing this relation into Eq.(3.24) we get \( \eta = m^*_e/m^*_i \). Since we find \( \eta \ll 1 \) this would imply the effective mass to have high values in the lowest part or the conduction band, which means a considerable enhancement of the density of states.

This simple two-parameter model gives a reasonable well description of the peak heights of \( \log \rho(p) \) as a function of temperature. We have assumed in this model that in the normal semiconducting state at low pressures \( \delta E = 0 \), and that at the maximum of the resistivity \( \delta E \) has the above mentioned magnitude for the two \( \text{TmSe}_{1-x}\text{Te}_x \) compounds. The detailed structure of the \( \log \rho(p) \) curves is not explained and we think that the introduction of a pressure dependence of \( \delta E \) and \( \eta \) would not bring any further insight. A more realistic model should take into account also an increase of the energy gap, as it is predicted by the excitonic insulator model. If one wants to make the calculations with the Fermi function, the knowledge of the exact position of the chemical position is required.
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![Graph showing temperature dependence of resistivity peak heights](image)

**Fig. 3.20.** Temperature dependence of the resistivity peak heights (Figs. 3.3 and 3.4) above extrapolated values from above and below the peak. Open symbols are measured values for TmSe$_{0.45}$Te$_{0.55}$ and TmSe$_{0.32}$Te$_{0.68}$ and the solid lines represent the model calculations as described in the text.

### 3.3.2. Magnetism Under Pressure

Susceptibility and neutron scattering experiments on TmSe$_{0.45}$Te$_{0.55}$ indicate that the magnetic ordering point is well below 1.5 K when the sample is in the semiconducting state. In the pressure induced metallic state, however, the ordering point is significantly enhanced and reaches nearly 6 K. Similar results have been found for the SMT in TmTe [59] and TmSe$_{0.80}$Te$_{0.20}$ [60]. With neutron scattering experiments we could prove that in pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ magnetic
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It is an open question, why semiconducting TmSe$_{1-x}$Te$_x$ have such a low ordering temperature ($T_N < 0.4$ K). TmTe has an appreciable ordered moment (2.3 $\mu_B$ [58]) and on the basis of the exchange mechanism discussed for the Eu chalcogenides, one would expect [90] it to be a high Néel temperature antiferromagnet. Instead $T_N$ is below 0.4 K [57,58]. The considerable enhancement of the ordering temperature in the metallic state could be due to a qualitative change in the exchange mechanism. Whereas in the semiconducting state a virtual $f-d-f$ exchange is effective, in the metallic state a real exchange occurs. The presence of free carriers could give rise to RKKY interaction. On the other hand, in the metallic state the Tm ions are intermediate valent, and Varma [91] has proposed for this situation that the double exchange mechanism could play an important role.

In the vicinity of the Curie temperature, a ferromagnetic metal exhibits a decreasing resistivity with decreasing temperature [92]. If we compare resistivity (Fig. 3.1) and susceptibility (Fig. 3.7) data we find this characteristic of a ferromagnet to be present in metallic TmSe$_{0.45}$Te$_{0.55}$. Furthermore, there is a striking similarity of the temperature dependence of the resistivity of TmSe$_{0.45}$Te$_{0.55}$ in the metallic state (Fig. 3.1) with TmSe$_{0.83}$Te$_{0.17}$ [55] and TmSe in a magnetic field ($H = 10$ kOe) [67], which both exhibit ferromagnetic order. These findings suggest that ferromagnetism is also present in metallic TmSe$_{0.45}$Te$_{0.55}$. This supposition is finally proved by our neutron scattering data (see Sect. 3.2.3.). The ordered moment (at 1.5 K) of the Tm ions amounts to $\mu_{Tm} = 1.8 \mu_B$. This moment is far below the free ion values of 4 and 7 $\mu_B$ for Tm$^{2+}$ and Tm$^{3+}$ but is comparable to the corresponding values of TmSe (1.7 $\mu_B$ [54], 1.9 $\mu_B$ [93]) and TmTe (2.3 $\mu_B$ [58]). In the ferromagnetic metallic compounds TmSe$_{1-x}$Te$_x$ with $0.1 \leq x \leq 0.18$ the moment $\mu_{Tm} \leq 1.6 \mu_B$ [2,56]. The reduced moments are not yet understood. In the case of the metallic compounds one could imagine that the valence instability reduces the magnetic moment. In TmTe, however, Tm is strictly divalent, making this argument worthless. In TmTe, furthermore, the observed reduced moment can not be explained by crystal field splitting of the Tm $4f$ ground state [132].

The shape of the susceptibility curve of pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ (Fig. 3.7) is similar to those of TmSe$_{0.80}$Te$_{0.40}$ under pressure [60] and ferromagnetic TmSe$_{0.83}$Te$_{0.17}$ at $p = 0$ [2,56]. The peak structure could point to antiferromagnetic correlations. Although any long range order of this type is excluded by the neutron diffraction data. However, antiferromagnetic short range order is still possible. On the other hand, Tm has a non-vanishing orbital moment, which destroys isotropy leading to some coercive force $H_c$. As discussed in Sect. 2.5.2. the occurrence of $H_c \neq 0$ leads to a reduction of the susceptibility below $T_C$, giving rise to another
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The temperature dependence of the sublattice magnetization $M$ of ferromagnetic TmSe$_{0.45}$Te$_{0.55}$ obeys for $T < T_C$ a power law with the critical exponent $\beta = 0.32 \pm 0.03$ (Fig. 3.11). Many magnetic materials have a $\beta$ of such a magnitude ($0.33 - 0.37$ [94]), which is definitely different from the mean field value $\beta = 0.5$. Theory indicates $\beta = 0.325$ for 3d-Ising systems, $\beta = 0.345$ for the 3d-ZY model and $\beta = 0.365$ for the 3d-Heisenberg case [95]. Although the measured value of $\beta$ favours the 3d-Ising model, we think that a definite decision for a specific model cannot be made. The error-bar of $\beta$ represents just an estimate based on various fits.

Above $T_C$ a slight tail in the magnetization is indicated by our data. Although the magnitude is less than the error-bar, the fact that for four successive temperatures above $T_C$ the magnetization is non-vanishing, makes the phenomenon plausible. One explanation is the existence of spin fluctuations. Part of the tail could also be due to the combined effect of the pressure dependence of $T_C$ and a certain non-hydrostatic behavior of the pressure transmitting medium.

Let’s look now at the longitudinal magnetoresistance of TmSe$_{0.45}$Te$_{0.55}$ (see Sect. 3.2.1.). We have found the magnetoresistance to be predominantly negative, which we attribute to an enhancement of the carrier mobility. The alignment of the magnetic moments of the Tm ions by the field leads to a reduction of the magnetic scattering. Because in the metallic state the measurement was performed below the ordering temperature, the change of the degree of alignment by the field is larger than in the paramagnetic, semiconducting state. This could be an explanation for the larger magnitude of the relative resistance change observed in the metallic state. Under these conditions the magnetoresistance of TmSe$_{0.45}$Te$_{0.55}$ is of comparable magnitude as observed in metallic (at $p = 0$) TmSe$_{0.83}$Te$_{0.17}$ and TmSe$_{0.91}$Te$_{0.09}$ [18]. Astonishingly, we find in pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ at low fields ($H < 3$ kOe) a pronounced positive magnetoresistance. A similar effect has been reported [133] for TmSe ($\Delta \rho/\rho^0 = +5\%$ at $H = 1.2$ kOe and $T = 1.45$ K). In other investigations [18,66] of TmSe this phenomenon, however, is absent. The nature of the positive magnetoresistance remains to be unravelled.

We will close this chapter with a brief discussion of the question concerning the hybridization gap in pressure driven metallic TmSe$_{1-x}$Te$_x$. Antiferromagnetic TmSe is known to have such a gap [134] and accordingly the resistivity steeply increases with decreasing temperature below $T_N$ [66,67]. However, as the material is made ferromagnetic (magnetic field or substitution of Se by Te) the gap is absent for $T < T_C$ [134] and the resistivity decreases for $T \to 0$ [18,66,67]. Since in pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ we also observe a decrease of resistivity with decreasing temperature below 6 K (Fig. 3.1), we conclude that in the ferromagnetically ordered
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state no gap is present. The situation is different in the paramagnetic state. Point contact spectroscopy data [134] suggest a gap in TmSe$_{0.82}$Te$_{0.18}$ for $T > T_C$; this is compatible with $d\rho/dT < 0$ above $T_C$ [18]. Pressure driven metallic TmSe$_{0.45}$Te$_{0.55}$ shows also $d\rho/dT < 0$ in the paramagnetic state (Fig. 3.1), this might be the result of an energy gap.
4. TmSe–EuSe Alloys

4.1. Introduction

In the TmSe–EuSe system the rare earth ions are exchanged against each other. The substitution of the Eu\(^{+2}\) ions in EuSe by smaller Tm\(^{2+}\) ions leads to a reduction of the lattice constant [25]. For \(x > 0.25\) the Tm\(_{1-x}\)Eu\(_x\)Se compounds are semiconductors and at \(x \approx 0.2\) a compositionally induced semiconductor to metal transition (SMT) has been observed [25,96]. This transition is more complicated than in TmSe\(_{1-x}\)Te\(_x\), since there are at least three miscibility gaps for \(x < 0.2\) [97].

For the semiconducting compositions the energy gap \(E_g\) is determined by the separation in energy of the Tm\(^{2+}4f^{13}\) level and the 5d conduction band. The Eu\(^{2+}4f^7\) state is lying 1.8 eV below the \(4f^{13}\) level [18]. In Tm\(_{0.15}\)Eu\(_{0.85}\)Se optical absorption measurements revealed \(E_g \approx 0.2\) eV [98]. A continuous decrease of \(E_g\) with increasing Tm content was found [25,86,99] resulting in a very small gap of about 40 meV close to the SMT. The Tm and Eu ions in semiconducting Tm\(_{1-x}\)Eu\(_x\)Se \((x > 0.3)\) are in a divalent state [18,25,101]. In the metallic compounds \((0 < x < 0.2)\), on the other hand, the Tm ions are in a mixed valence state, whose character is predominantly inhomogeneous [18] since the Eu ions, being larger in volume, are thought to give rise to local deformations of the lattice.

Both EuSe \((T_N = 4.6\) K [4]) and TmSe \((T_N \approx 3\) K [54]) are metamagnets. The semiconducting Tm\(_{1-x}\)Eu\(_x\)Se samples reveal a remarkable enhancement of the ordering temperature up to 20.7 K [18]. Magnetization measurements on \(x = 0.5\) and 0.85 show the existence of a spontaneous moment [18,100]. Neutron diffraction on \(x = 0.5\) [101] proves the ordering to be long range ferromagnetic. It is speculated [18] that the enhancement of the ordering temperature as well as the type of the order in Tm\(_{1-x}\)Eu\(_x\)Se could be due to the few extrinsic carriers. Metallic Tm\(_{0.83}\)Eu\(_{0.17}\)Se orders antiferromagnetically \((T_N = 4.0\) K [18], 7.0 K [100]).

Like other magnetic semiconductors [4] Tm\(_{1-x}\)Eu\(_x\)Se compounds exhibit due to the exchange induced splitting of the conduction band a reduction of the energy gap as the sample gets magnetized (magnetic red shift). It has been found [98] that this red shift is so large in Tm\(_{1-x}\)Eu\(_x\)Se \((0.25 \leq x \leq 0.85)\) that the energy gap Tm\(^{4f^{13}}\)–5d closes spontaneously below the ordering point. This transition is accompanied by a valence change of the Tm ions.

The temperature dependence of resistivity at ambient pressure of semiconducting Tm\(_{1-x}\)Eu\(_x\)Se compounds has been measured for \(x = 0.5\) [18] and 0.85 [100]. A predominant feature of both \(\rho(T)\) measurements is a maximum near the magnetic
ordering point and a steep decrease with decreasing temperature in the ordered region. Spin disorder scattering and the magnetic red shift are thought to play an important role [98,100].

The semiconducting compounds can be transformed into a metallic state on the application of pressure [18,25,99]. An exponential decrease of resistivity is observed up to the SMT, which indicates a linear closing of the energy gap under pressure (Eq.(2.9)).

We have performed on semiconducting Tm0.5Eu0.5Se high pressure low temperature experiments in order to gain more insight into the transition to the metallic state. Is there also a pressure induced increase of resistivity present at low temperatures as we have found it in TmSe1−xTex? Another question of interest is the evolution of magnetism under pressure.

4.2. Experimental Results

4.2.1. Electrical Resistivity

At room temperature we observe in Tm0.5Eu0.5Se under pressure a continuous SMT; the metallic state is achieved at 13.4 kbar (Fig. 4.1). Approximating log ρ(p) in the range 4 – 12 kbar by a straight line gives \( dE_g/dp = -8.9 \text{ meV/kbar} \). \( E_g(p = 0) = 120 \text{ meV} \) can be estimated. These values are in good agreement with earlier experiments [25,99]. At ambient pressure the resistance of Tm0.5Eu0.5Se is \( \rho(p = 0) = 19 \text{ mΩcm} \), this lies somewhat below \( \rho^*(p = 0) = 32 \text{ mΩcm} \), which can be deduced from the linear extrapolation of log ρ(p) in the range 4 – 12 kbar towards \( p = 0 \). This discrepancy can be interpreted that beside the thermally activated Tm 4f electrons (concentration \( n_{\text{act}} \)) also free electrons (concentration \( n_1 \)) due to impurities or non-stoichiometries are present. With the following calculation it is tried to give an estimate of the magnitudes of \( n_{\text{act}} \) and \( n_1 \). We assume for the the total carrier concentration

\[
n(p) = n_1 + n_{\text{act}}(p) \tag{4.1}
\]

with

\[
n_{\text{act}}(p) = n_0 e^{-E_g(p)/k_B T} \tag{4.2}
\]

\( n_{\text{act}} \) depends on pressure and becomes equal to \( n_0 \) when the gap is zero; \( n_1 \) is taken to be pressure independent. We assume that the above introduced \( \rho^*(p = 0) \) is the resistivity that the material would have in complete absence of impurity electrons, i.e. in the case \( n_1 = 0 \). When \( E_g = 0 \) the total number of carriers is \( n = n_1 + n_0 \), the experiment provides the corresponding resistivity: \( \rho_{\text{met}} = 320 \mu\Omega\text{cm} \). Tm0.5Eu0.5Se
Fig. 4.1. Pressure dependence of the electrical resistivity of Tm$_{0.5}$Eu$_{0.5}$Se at room temperature (solid line), at 150 K (squares) and at 50 K (triangles).

Has at ambient conditions the mobility $\mu = 23 \text{ cm}^2/\text{Vs}$ [86]. Following the experience with TmSe$_{0.32}$Te$_{0.68}$ [24] we take $\mu$ in first approximation as pressure independent. From

\[ \rho = \sigma^{-1} = (nq_e\mu)^{-1}, \]

(4.3)
where $q_e$ denotes the electronic charge, Eqs. (4.1) and (4.2), and experimental resistivities we estimate

$$n(p = 0) = 14.3 \times 10^{18} \text{ cm}^{-3}$$
$$n_1 = 5.7 \times 10^{18} \text{ cm}^{-3}$$
$$n_{\text{act}}(p = 0) = 8.6 \times 10^{18} \text{ cm}^{-3}.$$  

Under pressure the energy gap narrows, $n_{\text{act}}(p)$ increases and eventually becomes much larger than (the pressure independent) $n_1$. Under these circumstances the linear $E_g(p)$-relation leads to a linear log $\rho(p)$-relation which we observe for pressures above 4 kbar.

At ambient pressure we find for $\rho(T)$ (Fig. 4.2) qualitatively the same structure as was found by Batlogg [18] for the same nominal composition. Below 300 K $\rho$ increases slightly when the temperature is lowered. At 170 K there is a broad maximum. In this temperature range the resistivity seems to be influenced very much by extrinsic carriers. The behavior of $\rho(T)$ can be interpreted as the combined effect of thermally activated $4f$ electrons ($n_{\text{act}}$) with a negative temperature coefficient and free electrons ($n_1$) with a positive temperature coefficient. The predominant feature at low temperatures is a huge resistivity peak (at $T_{\text{max}} = 18$ K) near the magnetic ordering point (at $T_C = 16$ K (Sect. 4.2.2.)).

The temperature dependence of the resistivity of Tm$_{0.5}$Eu$_{0.5}$Se is dramatically influenced by pressure (Fig. 4.2). First, the situation for temperatures from 300 down to about 200 K shall be described. We see that the application of pressure leads to a more pronounced increase of resistivity with decreasing temperature. This can be understood in the following way. Pressure reduces the energy gap, thus the number of carriers which are thermally activated from the Tm $4f$ level is increased; but, since these are frozen out when the sample is cooled the change of resistivity becomes larger. At higher pressures ($p(300 \text{ K}) = 14.1$ and 15.9 kbar, Fig. 4.3) the sample is metallic, and we observe a decrease of the resistivity when the temperature is decreased. Being a common feature of normal metals, this contrasts the situation in pressure driven metallic TmSe$_{1-x}$Te$_x$ and SmS$_{1-x}$Se$_x$ where resistivity increases upon decreasing the temperature below room temperature.

Now we turn to the lower temperature regime. The resistivity peak (at $T_{\text{max}}$) shifts under pressure to higher temperatures and its height becomes reduced until at $p(300 \text{ K}) = 12.0$ kbar only a shoulder remains. At $p(300 \text{ K}) = 14.1$ kbar the $\rho(T)$ curve is quite complicated (Fig. 4.3). Just below room temperature the material behaves like a normal metall, but then close to 160 K there is a slight maximum which we believe is just due to the combined effect of pressure loss on lowering the temperature and pressure dependence of resistivity. At 19 K then there is another
peak structure, resembling the peak in \( \rho(T) \) of metallic \( \text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se} \) at 18 K [18]. The latter is somewhat broader, but both have at its maximum a resistance of 280 \( \mu\Omega \text{cm} \). At the highest applied pressure \( (p(300\text{ K}) = 15.9 \text{ kbar}) \), finally, the steady decrease of \( \rho \) with lowering \( T \) turns over at about 50 K to an increase with a shallow maximum around liquid helium temperature.
The measured log $\rho(T)$ curves for various pressures are transformed into a resistivity-pressure plot with temperature as a parameter. This has been done for temperatures far above the ordering temperature (Fig. 4.1). There is no peak structure present as we have found it in TmSe$_{1-x}$Te$_x$ (Figs. 3.3 and 3.4). Thus there is no evidence in Tm$_{0.5}$Eu$_{0.5}$Se for an excitonic insulator behavior. Due to extrinsic electrons the log $\rho(p)$-curves are more flat in the low pressure regime ($p < 6$ kbar) than at higher pressures. In contrast to TmSe$_{1-x}$Te$_x$ the transition into the metallic state occurs in Tm$_{0.5}$Eu$_{0.5}$Se at lower pressures when the temperature is decreased. This is the reason why we don't observe steplike $\rho(T)$ curves as we have seen in TmSe$_{0.45}$Te$_{0.55}$ (Fig. 3.5). Thermal expansion experiments [98] give evidence that the valence transition in Tm$_{0.5}$Eu$_{0.5}$Se is continuous also at low temperatures. Furthermore no Tm$_{1-x}$Eu$_x$Se compound showed a first-order pressure induced SMT at room temperature [18,25,99]. It is thought [25] that the lattice is stabilized by the Eu ions whose valency is not affected by the valence transition of the Tm ions.
4.2.2. Magnetic Susceptibility

Magnetic susceptibility has been measured on Tm\(_{0.5}\)Eu\(_{0.5}\)Se (Figs. 4.4 and 4.5). The shape of the ambient pressure \(\tilde{V}_{\text{ind}}(T)\) (susceptibility) curve of our sample looks very similar to a previous measurement on the same nominal composition [100] with the only difference that we find \(T_C = 16\) K (taking the peak temperature as \(T_C\)) lying somewhat below earlier measurements (\(T_C = 20.7\) K [18], 19.0 K [100] and 18.5 K [101]). At the ferromagnetic ordering point there is a relatively sharp peak followed on the low temperature side by a shoulder. This shoulder was absent in an earlier susceptibility measurement [18]. Up to \(p(20\text{ K}) = 11.1\) kbar we find an increase of \(T_C\) with the significant pressure coefficient \(dT_C/dp = 0.96\) K/kbar. This value is much larger than for example in EuO or EuS (\(dT_C/dp = 0.41\) K/kbar and 0.28 K/kbar [35], respectively). In this pressure regime we find a gradual change of the shape of \(\tilde{V}_{\text{ind}}(T)\) below \(T_C\) with increasing pressure. The shoulder first evolves to a maximum at 13 K for \(p(20\text{ K}) = 4.6\) kbar, then towards \(p(20\text{ K}) = 8.1\) kbar the dip between the two maxima vanishes. At \(T_C\) there is now a quite sharp kink present being typical for isotropic ferromagnets (e.g. EuO and EuS [35]). Increasing the pressure to \(p(20\text{ K}) = 9.3\) kbar doesn’t increase the ordering point any more but roundsen off the kink (Fig. 4.5). Then for \(p(20\text{ K}) = 12.0\) and 13.9 kbar we find completely different \(\tilde{V}_{\text{ind}}(T)\)-curves. Both the maximum susceptibility and the ordering point are considerably reduced. It is interesting to notice that the maximum occurs now at approximately the same temperature where the low temperature maximum at \(p(20\text{ K}) = 4.6\) kbar was present.

4.3. Discussion

4.3.1. Low Temperature (\(T < 100\) K) Electrical Transport

The low temperature transport behavior of Tm\(_{0.5}\)Eu\(_{0.5}\)Se is dominated by magnetism. One important feature occurring in ferromagnetic semiconductors is the exchange induced splitting of the conduction band which leads to the so-called magnetic red shift \((\Delta E)\) of the absorption edge \(E_g\) [4]. The exchange splitting is described by (see e.g. [4])

\[
H_{\text{ex}} = -2 \sum_n J_n(r - R_n) s \cdot S_n,
\]

which is the interaction of a single electron (position \(r\) and spin \(s\)) and a set of spins \(S_n\) at positions \(R_n\), \(J_n(r - R_n)\) denoting the exchange constant. This leads to an energy separation of the spin polarized subbands of

\[
2\Delta E = b J_{fd} <S_i \cdot S_j> / S^2,
\]

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Fig. 4.4. Temperature dependence of the induced voltage $V_{\text{ind}}$ (magnetic susceptibility) of Tm$_{0.5}$Eu$_{0.5}$Se in the pressure range $p(20\text{K}) = 0 - 8.1$ kbar. Note the considerable increase of the ordering temperature.
Fig. 4.5. Temperature dependence of the induced voltage $V_{ind}$ (magnetic susceptibility) of Tm$_{0.5}$Eu$_{0.5}$Se in the pressure range $p(20K) = 9.3 - 13.9$ kbar. Note the significant reduction of both the ordering temperature and the magnitude of the induced voltage with increasing pressure. A transition from ferromagnetism to antiferromagnetism is suggested.
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with the intra-atomic $f-d$ exchange $J_{fd}$, the spin correlation function $\langle S_i \cdot S_j \rangle / S^2$ and $b$ a scaling factor [98]. It has been found [98] that in $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ and $\text{Tm}_{0.62}\text{Eu}_{0.38}\text{Se}$ this red shift ($\Delta E$) is even larger than the room temperature Tm $4f^{13} - 5d$ energy gap $E_g$ derived from $\rho(p)$ measurements [25]. Reflectivity and volume measurements on these compounds indicate indeed a magnetic exchange induced SMT and valence transition of the Tm ions [98]. Let’s look now at the resistivity curve of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ (Fig. 4.2) at ambient pressure. Below $T_{max}$ there is a decrease of almost three orders of magnitude. Several mechanisms can account for this decrease. First, the number of carriers is increased by the delocalization of Tm $4f$ electrons, second electrons which stem from localized impurity states (which are decoupled from the $5d$ band) can be delocalized by the magnetic red shift and third the mobility of carriers increases due to the reduction of spin disorder scattering (see below).

It is curious, however, that despite the magnetic exchange induced SMT and valence change the resistivity of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ at 1.5 K (1.4 m$\Omega$cm) is larger than in metallic $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ ($\rho(1.5 \text{ K}) = 0.26 \text{ m} \Omega \text{cm}$) or pressure induced metallic $\text{TmSe}_{0.45}\text{Te}_{0.55}$ ($\rho(1.5 \text{ K}) = 0.36 \text{ m} \Omega \text{cm}$). Only under pressure the resistivity of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ at our lowest temperature is reduced to comparable values ($\rho(1.5 \text{ K, p(300 K)}) = 15.9 \text{ kbar}) = 0.22 \text{ m} \Omega \text{cm}$).

We shall turn now to the resistivity peak at $T_{max}$ being most pronounced at $p = 0$. Such a behavior is well known in the doped magnetic Eu monochalcogenides (e.g. [4,102–104]). It is generally believed that spin disorder scattering plays an important role in an explanation of this resistivity peak. In this scheme the temperature dependence of resistivity is mainly determined by the temperature dependence of the mobility of carriers. To get an impression of the mechanism we present the qualitative description by DiMarzio et al [105]. Above $T_C$ due to short-range order there are local regions fluctuating into the ferromagnetic state with the surroundings being paramagnetic. The states of the bottom of the $5d$ band in this local region are pulled down by the magnetic red shift. Hence the low-lying conduction band states in this region have no equienergetic states in the surrounding paramagnetic region into which they could tunnel. The conduction electrons therefore tend to be bound within the fluctuation regions, i.e. they have their mobility reduced. As one approaches the ferromagnetic $T_C$, correlations between fluctuating ordered regions increase until ordered region $\rightarrow$ ordered region electron motion brings the resistivity rapidly down. Within this argument the temperature of the peak ($T_{max}$) should be correlated with the ferromagnetic ordering temperature $T_C$ on the high temperature side ($T_{max} > T_C$).

The quantitative treatment [106,107] of the scattering of the conduction elec-
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...trons by a disorder in the spin system is based on the same Hamiltonian (Eq.(4.5)) which is used for the theory of the magnetic red shift. Haas [107] evaluated the critical scattering within perturbation theory and obtained for a non-degenerate ferromagnetic semiconductor an expression for the mobility which is essentially influenced by the magnetic susceptibility $\chi$. This results in a mobility minimum at $T_C$ since $\chi$ becomes very large there. In a subsequent more rigorous theoretical study Alexander et al [92] have shown that in ferromagnetic semiconductors $T_C$ does not coincide with $T_{max}$ but it is at the inflection point $T_i$ of $\rho(T)$, with $T_C = T_i < T_{max}$. This theory is in accord with the experimental observations on CdCr$_2$Se$_4$ and EuO [92] and also with the above presented qualitative description. Our measurements give clear evidence that also in Tm$_{0.5}$Eu$_{0.5}$Se the ordering point $T_C$ is on the low temperature side of the resistivity peak and is correlated with $T_i$ (Fig. 4.6).

According to [104] the spin disorder scattering describes the physical situation correctly as long as the $d-f$ interaction is relatively small ($\mu \geq 1$ cm$^2$/Vs). Larger $d-f$ interaction may reduce the mobility to very small values. The electron then can become localized and form a magnetic polaron. From resistivity we can estimate the minimum mobility for Tm$_{0.5}$Eu$_{0.5}$Se at $p = 0$ and $T_{max}$. If we approximate the number of carriers under these circumstances by $n_1 = 5.7 \times 10^{18}$ cm$^{-3}$ (Eq.(4.4)), we derive $\mu \approx 1.5$ cm$^2$/Vs. This means that it is not a necessity to include magnetic polarons in a description of the low temperature transport behavior of Tm$_{0.5}$Eu$_{0.5}$Se.

As a function of pressure, the position of the resistivity peak is closely related to the magnetic ordering temperature derived from susceptibility (Fig. 4.6). The degradation of the peak height with pressure is presumably linked to an increase of the carrier concentration by pressure and magnetic red shift induced closing of the energy gap. Such a decrease of the resistivity peak height has also been observed in EuO under pressure [105] or in EuX (X=O, S, Se) with doping [4,102-104]. At the highest pressure ($p(300K) = 15.9$ kbar) the sample is metallic over the whole temperature range. The magnetic susceptibility suggests antiferromagnetic order below $T_N \approx 10$ K (Sect. 4.3.2.). But there is no structure in $\rho(T)$ near this temperature.

4.3.2. Magnetism Under Pressure

Pure stoichiometric EuSe [108] and TmSe [54] exhibit complex magnetic phase diagrams. One common feature is that in both materials the antiferromagnetic phase below $T_N$ can be transformed to a ferromagnetic phase in the presence of a modest internal magnetic field $H_i$ ($H_i = 0.7$ kOe for EuSe at 4.6 K [108]; $H_i = 3$ kOe for TmSe at 3 K [54]). This indicates that both magnetic states have nearly the same energy.

It has been established that the magnetic properties of Eu monochalcogenides
Fig. 4.6. Pressure dependence of characteristic temperatures of resistivity (filled symbols: peak maximum $T_{\text{max}} = \square$; inflection point $T_i = \triangle$) and susceptibility (open symbols: peak maximum $= \square$; inflection points $= \triangle$ and $\diamond$). The indicated pressure is the value at 20 K. Up to 8.1 kbar the peak temperature of the susceptibility can be regarded as $T_C$. For $p = 12.0$ and 13.9 kbar the ordering point is suggested to occur at the inflection point on the low temperature side of the susceptibility peak (see text).
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are considerably influenced by the presence of additional electrons (see e.g. [109]). Generally, one observes already for very small concentrations of dopant (trivalent Gd, La, Tb, Dy, Lu or Y) a drastic increase of the paramagnetic Curie-Weiss temperature $\theta$ and the ferromagnetic ordering temperature $T_C$. There are several possibilities how additional electrons can affect magnetic order. If free they can mediate an indirect exchange between the magnetic ion spins (RKKY interaction) with the result that in the paramagnetic state $\chi$ and $\theta$ are increased [104,109]. If the material is ferromagnetic, the Curie temperature may increase. For an antiferromagnet below $T_N$, the conduction electrons may lead to the canting of the two sublattice magnetizations. If, on the other hand, the electrons with spin $s_i$ are bound to donors they can polarize the neighboring magnetic ions with spin $S_n$ forming ferromagnetic spin clusters which are surrounded by still paramagnetic regions. In a ferromagnet, this mechanism increases the Curie temperature. The “magnetic impurity” model of Kasuya and Yanase [135] (We follow here [4]) describes this situation; the electrons are assumed to be bound to shallow donors. The increase in Curie temperature comes to

$$k_B \Delta T_C = 2 \left( \sum_{i} j_{in} s_i \cdot S_n \right),$$

where $n$ is summed over the number of neighboring 4f spins and $i$ is summed over the number of impurity electrons. This equation can be approximately rewritten in the following form:

$$k_B \Delta T_C \approx \frac{n_{imp}}{n_{4f}} 2 \Delta E$$

where $n_{imp}$ and $n_{4f}$ are the numbers of impurity electrons and magnetic ions, respectively. $\Delta E$ is the magnetic red shift of the absorption edge. This relation could be well verified on Gd doped EuO crystals [110].

We discuss now the magnetism of Tm$_{0.5}$Eu$_{0.5}$Se at ambient pressure. The study of the low temperature neutron diffraction pattern of this compound [101] proved the existence of an ordered ferromagnetic moment component per rare earth ion. The measured moment of 2.12 $\mu_B$ per rare earth ion at saturation in zero external magnetic field was interpreted as due to approximately antiparallel alignment of Tm moment (4$\mu_B$) and Eu spin (7$\mu_B$) (mutual angle 134°). The absence of any long-range antiferromagnetic components in the diffraction pattern has been ascribed to the random distribution of Eu and Tm ions. We identify the susceptibility peak at 16 K of Tm$_{0.5}$Eu$_{0.5}$Se ($p = 0$) with the Curie temperature (Fig. 4.4). The reduction of

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7 It is worth mentioning here that all TmSe$_{1-x}$Te$_x$ compounds show a moment of this magnitude although only one type of rare earth ion is present in these compounds. Thus the above interpretation of the magnitude of the ordered moment of Tm$_{0.5}$Eu$_{0.5}$Se is not irrefutable.
4. TmSe–EuSe Alloys

$\chi$ for $T \to 0$ can be interpreted as due to a non-vanishing coercive force (Sect. 2.5.2.) or due to the antiferromagnetic short range order of the Tm and Eu moments. It has been speculated \[18\] that the few conduction band electrons are responsible not only for the high ordering point of Tm$_{0.5}$Eu$_{0.5}$Se with respect to EuSe and TmSe but also for the type of ordering and that the new additional exchange interaction is due to the conduction band electron polarization (RKKY) or bound magnetic polaron. A quantitative estimate of the enhancement of $T_C$ can be tried with the above discussed "magnetic impurity" model. If we introduce the values $n_{imp} = 5.7 \times 10^{18}$ cm$^{-3}$ ($n_1$ in Eq. (4.4)) and $n_{4f} = 1.8 \times 10^{22}$ cm$^{-3}$ and for the magnetic red shift $\Delta E = 0.24$ eV \[98\] into Eq. (4.8) we derive an increase $\Delta T_C$ of less than 2 K, which is too low to explain the high ordering temperature of Tm$_{0.5}$Eu$_{0.5}$Se. However, by the magnetic red shift induced valence change of the Tm ions \[98\] electrons from the 4f shell are liberated and could act as additional "impurity" electrons increasing $n_{imp}$ and hence $\Delta T_C$.

The following argument points also to an enhanced ordering temperature in Tm$_{0.5}$Eu$_{0.5}$Se. It is known that the nearest neighbor exchange constant $J_1$ in Eu monochalcogenides is ferromagnetic and is the stronger the smaller the energy difference Eu 4f$^7 - 5d_{2g}$ ($U$) is \[4\]:

$$J_1 \propto 1/U^2. \quad (4.9)$$

Now, in Tm$_{0.5}$Eu$_{0.5}$Se there are Tm 4f$^{13}$ electrons present which lie closely below the 5d conduction band. If we take the energy difference Tm 4f$^{13} - 5d_{2g}$ now as $U$, Eq. (4.9) indicates that the small value of $U$ will give a large $J_1$ which increases $T_C$. This argument, however, is weakened by the fact that the semiconducting TmSe$_{1-x}$Te$_x$ compounds are antiferromagnetic with a very low $T_N$ (see Sect. 3.1.) despite the presence of 4f electrons very close to the 5d band.

Now we will look at the evolution of magnetism in Tm$_{0.5}$Eu$_{0.5}$Se under pressure. Up to $p(20K) = 8.1$ kbar we observe an increase of the Curie temperature with a remarkable pressure coefficient of $dT_C/dp = 0.96$ K/kbar. Several mechanisms lead to a $dT_C/dp > 0$. Pressure closes the energy gap and increases the number of carriers which increase $T_C$ via RKKY interaction or spin clusters (Eq. (4.7)). On the other hand it is known that the ferromagnetic interaction in Eu monochalcogenides gets enhanced when the lattice parameter is reduced either with pressure (EuO, EuS \[35\]) or in going through the chalcogenides from EuTe to EuO. If one adopts this experience on Tm$_{0.5}$Eu$_{0.5}$Se, then the pressure induced reduction of the lattice parameter, especially through the valence change of the Tm ions, gives an enhancement of $T_C$. It has to be kept in mind, however, that the situation is severely complicated by the occurrence of the magnetic red shift.
Concomitant with the pressure induced SMT a dramatic change of the magnetic behavior of Tm$_{0.5}$Eu$_{0.5}$Se occurs (Figs. 4.4 and 4.5). Both the ordering temperature and the magnitude of the susceptibility are considerably reduced as the pressure driven metallic state is achieved. We propose this to be the result of a pressure induced ferromagnetism to antiferromagnetism transition and speculate that the short range antiferromagnetic order (Tm-Eu) in Tm$_{0.5}$Eu$_{0.5}$Se at $p = 0$ has become now a long range antiferromagnetic order through the action of the delocalized Tm 4f electrons (RKKY). Taking the inflection point on the low temperature side of the susceptibility peak (Fig. 4.5) we determine $T_N = 10.3$ K for $p(20 \text{ K}) = 12.0$ and $13.9$ kbar. A change of the type of order under pressure could be expected since metallic ($p = 0$) Tm$_{0.83}$Eu$_{0.17}$Se is also antiferromagnetic ($T_N = 4.0$ K [18], 7.0 K [100]).

It would be very informative to perform high pressure neutron diffraction experiments on Tm$_{0.5}$Eu$_{0.5}$Se.
5. SmS–SmSe Alloys

5.1. Introduction

The Sm monochalcogenides SmX (X=S,Se,Te) are semiconductors. Sm is in the
divalent state. The energy gap $E_g$ is determined by the separation of the Sm$^{2+}$ 4$f^6$
state and the bottom of the 5d conduction band. Going through the series from
the telluride over the selenide to the sulfide, due to the shrinking size of the anion
the lattice constant decreases and hence the crystal field splitting of the 5d band is
enhanced [11]. It has been established [14] that the change of the width of the 5d
band does not influence the separation of its center of gravity from the 4$f^6$
level. However, $E_g$ is significantly reduced from 0.63 eV for SmTe [16] to 0.46 eV for SmSe
[12] and 0.1 – 0.2 eV for SmS [12,111].

The Sm monochalcogenides received great attention after the high pressure re¬
 sistivity studies by Jayaraman and coworkers in 1970 [16,12] who demonstrated that
these materials undergo a pressure induced semiconductor to metal transition (SMT)
which is accompanied by a valence change of the Sm ions. The transition was found
to be continuous for SmTe and SmSe, while discontinuous in the case of SmS. The
metallic state is achieved at 55, 45 and 6.5 kbar for SmTe, SmSe and SmS, respec¬
tively. In the intermediate valence state SmX exhibit a metallic reflectivity; collapsed
SmS, for example, appears golden to the human eye [12].

In 1972 Bucher and Maines [112] have studied SmSi$_{1-x}$Sex mixed crystals by
high pressure resistivity measurements at room temperature and have found that
the electronic transition goes from discontinuous ($x < 0.8$) to continuous ($x > 0.8$)
smoothly with composition. Further, the resistance drop associated with the tran¬
sition appears to diminish in magnitude progressively as $x$ is increased from 0 to
0.8.

Low temperature studies of the semiconducting state of SmS revealed a steady
decrease of resistivity with increasing pressure up to the SMT (1.8K: [113]; 4.2K:
[114]; 44 – 290 K: [115]). No peak structure similar to that of TmSe$_{1-x}$Tex ($x = 0.55$
0.68) (Figs. 3.3 and 3.4) is present.

The first low temperature resistivity measurements of collapsed SmS at high
pressure have been performed by Bader et al [114]. Instead of a positive temperature
coefficient, as is typical for a normal metal, their data revealed a continuous increase
of resistivity on cooling. At 10 kbar it increased from room temperature down to 4.2
K by a factor of ~ 6. This is in striking resemblance to SmB$_8$, which shows an even
larger increase in resistivity [8]. The explanation is thought to be the existence of a
tiny hybridization gap of the order of a few meV at the Fermi energy [8]. In the case
of SmS, however, the analysis of reflectivity measurements indicates a pseudogap [10], which means that the density of states has a dip at the Fermi level but does not vanish. High pressure experiments on SmS exceeding 20 kbar [116–118] revealed a dramatic change of the $\rho(T)$ curves at low temperatures. In this pressure regime the steep increase of $\rho$ towards $T = 0$ is absent. The resistivity rather shows a decrease for $T \rightarrow 0$. A similar change of $\rho(T \rightarrow 0)$ under pressure has been found for TmSe [119], SmSe [116] and SmB$_6$ [120]. This phenomenon can be interpreted as the pressure induced closing of the small hybridization gap.

The free ion ground state of Sm in the divalent state is nonmagnetic ($^7F_0$) whereas in the trivalent state it is magnetic ($^6H_{5/2}$) with a moment of $gJ = 0.71 \mu_B$. Susceptibility measurements ($p : 7.5 - 12$ kbar, $T : 1 - 300$ K) by Maple and Wohlleben [121] revealed that the ground state of the 4f shell in the metallic high-pressure collapsed phase of SmS is nonmagnetic. The same behavior was established later on for pressures up to 24 kbar ($T : 1.5 - 20$ K) [122]. These findings give evidence that Sm is not yet integer trivalent at these pressures. The nonmagnetic behavior is thought to be due to the demagnetizing tendency of the valence fluctuation [121]. It is estimated [122] that Sm reaches the purely trivalent state only at pressures of the order of 100 kbar.

Sm$_{1-x}$Se$_x$ is analogous to Tm$_{1-x}$Te$_x$ in the sense that in both cases a substitution of the anion is performed. The interesting question arises whether also in some Sm$_{1-x}$Se$_x$ compounds a peak structure in the $\rho(p)$ curves at low temperatures is present. Although not the case for pure SmS (0 – 6 kbar) this could nevertheless be possible for $x > 0$. The lattice of SmS remains stiff under pressure up to the first-order valence change [123], this contrasts the behavior of TmSe$_{0.60}$Te$_{0.40}$ where the bulk modulus becomes very soft before the first-order valence change occurs [2]. It is intriguing to study the volume-pressure relation of the SmS-SmSe mixed crystals. Does the lattice remain stiff up to the volume collapse like in SmS, or will there be a softening due the reduced strength of the first-order transition?

5.2. Experimental Results

5.2.1. Electrical Resistivity

Two stoichiometries of Sm$_{1-x}$Se$_x$ have been studied: $x = 0.11$ and 0.44. In Fig. 5.1 the pressure variation of the electrical resistivity of Sm$_{1-x}$Se$_x$ at ambient temperature is depicted. For Sm$_{0.56}$Se$_{0.44}$ the electrical contacts to the crystal were interrupted by the volume collapse (see Sect. 5.2.2) occurring at the SMT. Whereas for Sm$_{0.56}$Se$_{0.44}$ we find good agreement with the measurements of Bucher and
Maines [112], the log $\rho(p)$-curve of SmS$_{0.89}$Se$_{0.11}$ is rather flat at low pressures which is presumably due to extrinsic carriers. The first-order SMT occurs at 12.4 and 23.7$^8$ kbar for $x = 0.11$ and 0.44. These data compare well with values of other Sm$_{1-x}$Se$_x$ compounds (Fig. 5.2). We estimate the energy gap at ambient conditions to be $E_g = 165$ and 280 meV for $x = 0.11$ and 0.44, as deduced from Eq.(2.8) and the resistivities at $p = 0$ and in the metallic state. In the case of $x = 0.11$ the slope of log $\rho(p)$ for $p = 10 - 12.4$ kbar was extrapolated to zero pressure in order to get $\rho(p = 0)$ for the evaluation of $E_g$. There is a smooth variation of $E_g$ as a function of composition (Fig. 5.2).

We have performed low temperature high pressure resistivity measurements on SmS$_{0.89}$Se$_{0.11}$ (Fig. 5.3). Clear semiconducting behavior is found for $p(300 K) = 0$, 8.5, 10.4 and 11.6 kbar. At ambient pressure the slope of log $\rho(1/T)$ at 300 K using Eq.(2.8) gives only 36 meV. This is much smaller than the above stated value for $E_g$, being another indication for the presence of impurity electrons. In the temperature range 10−120 K we find that log $\rho$ varies linearly with $T^{-1/4}$ (Fig. 5.4) which expresses that the conductivity under these conditions is mainly determined by hopping processes [124]. Within this concept electrons sit in localized traps, but they acquire a finite mobility through thermally activated tunneling to close lying free traps.

The collapsed phase ($p(300 K) = 12.5$ and 15.3 kbar) is not a simple metal as revealed by the fact that the resistivity increases when the temperature is lowered below 300 K. At 20.3 K and 17.4 K a shallow maximum is discernible for the pressure runs $p(300 K) = 12.5$ and 15.3 kbar, respectively (Fig. 5.5). Such a feature has been reported for non-stoichiometric SmS (5% excess Sm in the starting material) by Konczykowski et al [125] and has been interpreted as due to scattering of carriers by extrinsic Sm$^{3+}$ ions.

In Fig. 5.6 we present the log $\rho(p)$-plot for various temperatures. We do not observe a similar peak structure as there was present in TmSe$_{1-x}$Te$_x$ ($x = 0.55$ and 0.68) (Figs. 3.3 and 3.4). It is important, however, to realize that an appreciable part of the log $\rho(p)$ curve just before the collapse to the metallic state is not accessible with our technique at low temperatures. This shall be briefly explained now. If we apply at room temperature a pressure of slightly below 12.4 kbar (the pressure where the SMT occurs) we end up at 5 K with about 9.3 kbar (see Sect. 2.1.1.). Let’s assume that the transition pressure will increase by 5 kbar to 17.4 kbar, if $T$ is reduced to 5 K (this is approximately found for SmS [111,126]). Hence the occurrence of a hysteresis (5.1 kbar at room temperature) makes it impossible to study $\rho(p)$ at 5 K in the range of 9.3 < $p$ < 17.4 kbar! Some structure in $\rho(p)$ might be hidden in

$^8$ This value has been determined from the $V(p)/V_0$ measurement quoted in Sect. 5.2.2.
Fig. 5.1. Pressure dependence of the electrical resistivity of Sm$S_{1-x}Se_x$ at room temperature. The solid lines represent our measurements, whereas the dash-dotted lines are data from [112]. In the case of Sm$S_{0.56}Se_{0.44}$ the measurement could be performed only up to the SMT; the dashed line gives the expected behavior.
5. SmS-SmSe Alloys

Fig. 5.2. Variation of the transition pressure $p_{SMT}$ (upper part) and the energy gap (lower part) of SmS$_{1-x}$Se$_x$ with stoichiometry $x$. The asterisks are our data, the dots are from [112] (the energy gaps have been determined with Eqs. (2.8) and (2.9)), the triangles from [12] and the cross is from [111]. The straight lines are guides to the eye.
5. SmS–SmSe Alloys

Fig. 5.3. Temperature dependence of the electrical resistivity of SmS$_{0.89}$Se$_{0.11}$ for various pressures. The pressures indicated are values at room temperature.

This pressure range.

$\rho(p)$ could be measured very well with increasing pressure, also through the SMT and in the metallic state, but as the SMT was reversed with decreasing the pressure, the single crystal was destroyed, presumably due to the large sudden increase in volume. This makes it impossible to reproduce the original resistivity.
5. SmS–SmSe Alloys

Fig. 5.4. Temperature dependence of the electrical resistivity of SmS$_{0.89}$Se$_{0.11}$ at ambient pressure in a log $\rho$ vs. $T^{-1/4}$ plot. The dots represent the measurement; for clarity only few data points are shown. The straight line fits the data very well.

![Graph showing temperature dependence of resistivity](image)

after cycling. On examination after release of pressure the single crystals exhibited numerous cracks which run parallel to the cubic directions. The same has been reported for SmS [12].

5.2.2. Volume

We have measured at room temperature the pressure dependence of the volume $V(p)/V_0$ of SmS$_{0.56}$Se$_{0.44}$ (Fig. 5.7, upper part). $V_0$ denotes the volume at $p = 0$. The first-order collapse is clearly visible at 23.7 kbar. The large sudden change in volume ($\Delta V/V = -7\%$, $V$: volume just before the transition) affected negatively the characteristics of the strain gauges glued onto the crystal. The measurement in the collapsed phase is only qualitatively correct. Upon lowering the pressure the transition is reversed at 21.4 kbar. As in the case of the resistivity, the volume can be measured only once due to the destruction of the crystal by the first-order volume expansion. In the lower part of Fig. 5.7 we present the bulk modulus which
5. SmS–SmSe Alloys

Fig. 5.5. Temperature dependence of the electrical resistivity of SmS$_{0.89}$Se$_{0.11}$ in the pressure driven metallic state. The pressures indicated are values at room temperature. Note the linear scale for the resistivity.

is defined as

$$B(p) = -V\frac{dp}{dV} = -(V/V_0)\frac{dp}{d(V/V_0)}. \quad (5.1)$$

Up to 15 kbar SmS$_{0.56}$Se$_{0.44}$ reveals the usual linear increase of $B$ with pressure which is written as

$$B(p) = B_0 + B_0'p \quad (5.2)$$

with the definitions

$$B_0 \equiv B(p = 0)$$

$$B_0' \equiv \frac{dB}{dp} \bigg|_{p=0}. \quad (5.3)$$

We find for SmS$_{0.56}$Se$_{0.44}$ $B_0 = 440$ kbar and $B_0' = 2$. The bulk modulus $B_0$ is
Fig. 5.6. Pressure dependence of the electrical resistivity of SmS\textsubscript{0.89}Se\textsubscript{0.11} for various temperatures. Note the large hysteresis measured at room temperature.

comparable to the values determined for the pure Sm monochalcogenides (Table 5.1).

The detailed pressure dependence of the bulk modulus of SmS has been determined with ultrasound measurements under hydrostatic pressure up to 6 kbar [123]. These data give $B'_0 = 2.4$ being close to our value for SmS\textsubscript{0.56}Se\textsubscript{0.44}. In SmS the bulk
5. SmS-SmSe Alloys

Table 5.1 Bulk modulus data of the Sm monochalcogenides.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Bulk modulus $B_0$ [kbar]</th>
<th>Method</th>
<th>Pressure range [kbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmS</td>
<td>476 ± 50(^a)</td>
<td>X-rays $V/V_0(p)$</td>
<td>0 – 4</td>
</tr>
<tr>
<td></td>
<td>420 ± 30(^b)</td>
<td>X-rays $V/V_0(p)$</td>
<td>0 – 6.5</td>
</tr>
<tr>
<td></td>
<td>475(^c)</td>
<td>Ultrasound</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>503(^d)</td>
<td>Ultrasound</td>
<td>0</td>
</tr>
<tr>
<td>SmSe</td>
<td>400(^e)</td>
<td>X-rays $V/V_0(p)$</td>
<td>1 – 10</td>
</tr>
<tr>
<td>SmTe</td>
<td>400(^e)</td>
<td>X-rays $V/V_0(p)$</td>
<td>1 – 10</td>
</tr>
</tbody>
</table>

\(^a\)Ref. [127], \(^b\)Ref. [122], \(^c\)Ref. [128], \(^d\)Ref. [123], \(^e\)Ref. [17].

The bulk modulus begins to decrease for pressures above 3 kbar. The subsequent softening of the lattice towards the valence instability, however, is relatively small and amounts to a reduction of $B$ in the pressure range $3 – 6$ kbar by 10%. The mixed crystal SmS$_{0.56}$Se$_{0.44}$ exhibits a much more pronounced softening, $B$ is reduced by nearly 80%, reaching a minimum value of $B_{\text{min}} = 100$ kbar just before the transition at 23.7 kbar. This behavior is reminiscent of TmSe$_{0.60}$Te$_{0.40}$ which also undergoes a first-order transition and shows a reduction of $B$ of the same order of magnitude before the transition [2].

5.3. Discussion

Falicov and Kimball [129], and Ramirez et al [130] (FKR) have proposed a model for a temperature driven SMT involving a localized state and a conduction band separated by an energy gap. The electron-hole interaction is taken into account. Within their model bound excitons are formed only if the attractive electron-hole interaction exceeds a critical value. The authors explicitly restrict the parameters to take on only those values which do not lead to the formation of an exciton. The electronic states are assumed to be basically unchanged in their character. These assumptions put the model in clear-cut contrast to the excitonic insulator or intermediate valence models. According to the FKR model, the SMT can be continuous or discontinuous depending on the strength of the electron-hole interaction energy in relation to the gap energy. Bucher and Maines [112] have modified this model using the volume rather than the temperature as the free variable and have found that it explains their data on SmS$_{1-x}$Se$_x$ reasonably well: change from discontinuous to continuous SMT and decrease of transition strength with increasing Se content.

In TmSe$_{1-x}$Te$_x$, on the other hand, the change from discontinuous to continuous SMT is discussed [61] within the electron-hole liquid theory. We think that this could
5. SmS–SmSe Alloys

Fig. 5.7. Pressure dependence of the specific volume (upper part) and the corresponding bulk modulus (lower part) of SmS$_{0.56}$Se$_{0.44}$ at room temperature. Note the considerable softening of the lattice above 15 kbar.
5. SmS–SmSe Alloys

also be done for the Sm$_{1-x}$Se$_x$ compounds.

The present available low temperature high pressure resistivity data on SmS [113-115] and SmS$_{0.89}$Se$_{0.11}$ (this work) do not give any evidence for a possible transition to the excitonic insulator state in SmS$_{1-x}$Se$_x$ as we have found for TmSe$_{1-x}$Te$_x$ ($x = 0.55$ and 0.68) (see Sect. 3.3.1.1.). Nevertheless SmS$_{1-x}$Se$_x$ appears to be a promising candidate system for such a transition. Like in TmSe$_{1-x}$Te$_x$ each Sm ion has a statistically different anion surrounding giving rise to a warped bottom of the conduction band. Hence the same arguments in favor of the transition to the excitonic insulator hold which were presented in Sect. 3.3.1.1. for TmSe$_{1-x}$Te$_x$. Similar to the measurements of Bucher and Maines [112] we find a change in slope of the log $\rho(p)$ curve of SmS$_{0.56}$Se$_{0.44}$ at 13 kbar (Fig. 5.1). In SmS$_{0.89}$Se$_{0.11}$ such a behavior is not seen but it could be masked by the presence of extrinsic carriers. Since Se rich SmS$_{1-x}$Se$_x$ compounds reveal either a reduced strength of the first-order SMT or a continuous SMT they seem to be best for a further search for a transition to the excitonic insulator state.

The semiconducting nature of SmS at $p = 0$ is expressed by the enormous increase of resistivity when the temperature is decreased below room temperature (in the range $290 > T > 44$ K $\rho$ increases by four orders of magnitude [115]). Above $2-3$ kbar, however, the temperature dependence of the resistivity is reversed, exhibiting a normal metallic behavior. At 4 kbar there is a clear-cut decrease when the temperature is lowered from 300 K to 100 K [115]. At these pressures Hall effect data indicate that the number of carriers is essentially temperature independent ($301 > T > 78$ K: [115]; $130 > T > 50$ K: [113]), hence the variation of $\rho(T)$ is due to the temperature dependence of mobility. The chemical potential crosses the conduction band already near 2 kbar [113], i.e. at a pressure where the Sm$^{2+}$ $4f^6$ level is still significantly below the conduction band. In SmS$_{0.89}$Se$_{0.11}$ we don’t find such a metallic behavior before the collapse, this indicates that the chemical potential lies more closely at the $4f^6$ level and that it does not cross the conduction band before the valence transition.

In the collapsed phase of SmS$_{0.89}$Se$_{0.11}$ (Fig. 5.5) we observe a steep increase of resistivity below 10 K which we ascribe to be due to the existence of a hybridization gap at the Fermi energy. Like in collapsed SmS [10] it is probably only a pseudo gap.

The elastic behavior of SmS [123] has been found to be in some contrast to the TmSe$_{1-x}$Te$_x$ compounds [2]. SmS remains rather stiff up to the valence transition. Poisson’s ratio, although considerably reduced under pressure, stays positive [123]. In TmSe$_{0.32}$Te$_{0.68}$, on the other hand, the lattice becomes very soft and Poisson’s ratio becomes negative much earlier than the metallic state is achieved [2,51]. The difference is ascribed [123] to the strongly first-order character of the transition in
5. **SmS-SmSe Alloys**

SmS, as distinct from the continuous nature of that in TmSe$_{0.32}$Te$_{0.68}$. SmS$_{0.56}$Se$_{0.44}$ looks different. The lattice becomes very soft before the transition (Fig. 5.7). We think that this is connected to the reduced strength of the first-order transition ($\Delta V/V = -7\%$) with respect to SmS ($\Delta V/V = -11\%$ [131], $-13\%$ [122]). The occurrence of the significant decrease of the bulk modulus $B$ leads us to the speculation that also in the case of SmS$_{0.56}$Se$_{0.44}$ Poisson's ratio becomes negative already in the semiconducting state. This could be tested with ultrasound measurements under pressure.

Finally, it would be interesting to extend the volume-pressure measurements on SmS$_{1-x}$Se$_x$ with stoichiometries near $x = 0.8$, where the character of the transition changes from discontinuous to continuous. There will be a second order phase transition, whose $p-V$ curve can be analysed near the transition ($p_c, V_c$) by the relation

$$|p - p_c| \propto |V - V_c|^\delta.$$  

(5.4)

$\delta$ denotes the critical exponent. In the alloy system TmSe$_{1-x}$Te$_x$ for the critical composition with $x = 0.5$ values of $\delta = 2.72$ for $p < p_c$ and $\delta = 3.1$ for $p > p_c$ have been determined [2,24] which are very close to the value of $\delta = 3$ predicted by mean-field theory. The FRK model is a mean field theory [129,130]. Because of its successful application to the SmS$_{1-x}$Se$_x$ system [112] it is tempting to expect $\delta \approx 3$ for $x \approx 0.8$. 

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6. Concluding Remarks

In this study we have investigated the pseudo-binary alloy systems TmSe$_{1-x}$Te$_x$, Tm$_{1-x}$Eu$_x$Se, and SmS$_{1-x}$Se$_x$. They have in common that they all exhibit a pressure induced semiconductor to metal transition (SMT) coupled with a valence change, but otherwise they reveal quite different phenomena. The SMT is well known in rare earth monochalcogenides and experimentally one observes in these compounds a steady, exponential decrease of resistivity under pressure. We find the same behavior in our materials at room temperature. It came to a surprise, when we studied this transition in TmSe$_{0.45}$Te$_{0.55}$ and TmSe$_{0.32}$Te$_{0.68}$ at low temperatures, that these compounds reveal a peak structure in their log $\rho(p)$ curves. We think that the proposed interpretation involving the concept of the excitonic insulator is very promising and should be further pursued. However, stressing the similarity [61] to the band structure of expanded ScN, a transition of semiconducting TmSe$_{1-x}$Te$_x$ to the excitonic insulator state should not occur. This argument is essentially based on the existence of three degenerate conduction band minima. In TmSe$_{1-x}$Te$_x$, however, each Tm ion has a statistically different anion surrounding. We think that this deviation from full translational symmetry of the crystal might lift the degeneracy, leading to a single non-degenerate conduction band minimum. In this case the excitonic instability is not ruled out any more. It is an intriguing question, whether other compounds reveal a similar peak structure. We did neither in Tm$_{0.5}$Eu$_{0.5}$Se nor in SmS$_{0.99}$Se$_{0.11}$ find evidence for this. We believe, however, that the SmS$_{1-x}$Se$_x$ alloys are very promising candidates. One should investigate there especially the Se rich stoichiometries, since they have a SMT which is first-order of reduced strength or is continuous. Under these conditions the transition to the excitonic insulator phase appears to be more probable [77]. The theory of the excitonic insulator has been developed predominantly for simple band structures with Mott-Wannier excitons. Our materials are much more complicated, however. In TmSe$_{1-x}$Te$_x$ the valence "band" is formed by localized 4f states and the excitons are probably of the Frenkel type; a new theory for the excitonic insulator taking into account these characteristica would be very desirable.

Magnetic order exists in TmSe$_{1-x}$Te$_x$ and Tm$_{1-x}$Eu$_x$Se, but is absent in SmS and SmSe. It remains an unresolved question, why the semiconducting TmSe$_{1-x}$Te$_x$ compounds have such a low ordering point ($T_N < 0.4\, \text{K}$), although the Tm ions have an appreciable ordered moment (TmTe: $2.3\, \mu_B$ [58]). In the metallic state (achieved by pressure or stoichiometry) ferromagnetism with $T_C$ up to 6 K occurs. We suspect the RKKY interaction and the double exchange mechanism to play an important role in the enhancement of the ordering temperature.
6. Concluding Remarks

Both, transport and magnetic behavior of semiconducting Tm$_{1-x}$Eu$_x$Se mixed crystals are essentially influenced by the presence of magnetic Eu$^{2+}$ ions and free carriers from impurities or non-stoichiometries. Tm$_{0.5}$Eu$_{0.5}$Se is a ferromagnetic semiconductor with $T_C = 16$ K. Near the magnetic ordering point an extraordinary peak is present in $\rho(T)$ and in the magnetically ordered state the resistivity is considerably reduced. It is suggested that the temperature dependence of the electrical resistivity below $\sim 100$ K is dominated by spin disorder scattering (mobility) and magnetic red shift (number of carriers). Under pressure very interesting but also complicated processes are observed. Magnetism and resistivity are strongly influenced by the narrowing of the energy gap leading to the SMT and the valence transition of the Tm ions. The susceptibility measurements indicate a concomitant ferromagnetism to antiferromagnetism transition. We would like to emphasize once more that the situation is further complicated through the fact that the energy gap gets not only reduced by pressure but also by the magnetic red shift. It would be of great value to perform additional low temperature high pressure investigations on semiconducting Tm$_{1-x}$Eu$_x$Se such as neutron scattering (to study magnetism), and accurate volume measurements with strain gauges (to study the valence transition).

The high pressure study of the bulk modulus of SmS$_{0.56}$Se$_{0.44}$ has established a certain similarity of this compound to semiconducting TmSe$_{1-x}$Te$_x$: before the SMT and valence transition occurs, the lattice gets markedly softer. We speculate that also in SmS$_{0.56}$Se$_{0.44}$ Poisson's ratio becomes negative already in the semiconducting state.
7. References

7. References

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Curriculum Vitae

1958, April 24  Born at Chur (GR).
1965 - 1971  Primary school at Bad Ragaz (SG).
1973 - 1977  Gymnasium at Sargans (SG); maturity type C.
1978 - 1983  Study of mathematics and physics at the Swiss Federal Institute of Technology (ETH) in Zürich, Switzerland. Special emphasis on courses in solid state physics and optics.
1983  Diploma work in experimental physics on “Volume-Pressure Measurements on Rare Earth Compounds and Uranium Monochalcogenides” under the supervision of Prof. Dr. P. Wachter and Dr. H. Boppart.
October 1983  Diploma of the ETH in physics.
Since January 1984  Teaching assistant in the group of Prof. Dr. P. Wachter at the Institute for Solid State Physics of the ETH Zürich.

1982, March 29  Marriage with Barbara Jakob.
1983, November 12  Birth of our son Ueli.
1986, July 2  Birth of our daughter Linda.
Publications


Oral Presentations

1. “Das Verhalten von Tm$_{1-x}$Eu$_x$Se unter Druck”, Spring Meeting of the Swiss Physical Society, April 6, 1984, Bern, Switzerland.


5. “Elektrischer Widerstand von TmSe$_{1-x}$Te$_x$ in Funktion von Druck und Temperatur”, Fall Meeting of the Swiss Physical Society, October 9, 1986, Bern, Switzerland.

6. “Magnetische Ordnung in TmSe$_{0.45}$Te$_{0.55}$ unter Druck”, Spring Meeting of the Swiss Physical Society, March 19, 1987, Zürich, Switzerland.

7. “The Behavior of TmSe$_{1-x}$Te$_x$ under High Pressure at Low Temperatures”, seminary talk, November 6, 1987, AT&T Bell Laboratories, Murray Hill, USA.


9. “The Behavior of TmSe$_{1-x}$Te$_x$ under High Pressure at Low Temperatures”, seminary talk, November 16, 1987, University of California, Davis, USA.

10. “The Behavior of TmSe$_{1-x}$Te$_x$ under High Pressure at Low Temperatures”, seminary talk, November 19, 1987, University of California, San Diego, USA.


12. “Vom Halbleiter zum Metall: Untersuchungen an TmSe-TmTe Verbindungen unter Druck bei tiefen Temperaturen”, seminary talk, May 5, 1988, Laboratorium für Festkörperphysik, ETH Zürich, Zürich, Switzerland.
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