

## Magnetic mixed valent TmSe

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Various thermal, magnetic, and transport properties of single-phase Tm<sub>1-x</sub>Se crystals have been measured, partly as a function of temperature ( $0.04 \leq T \leq 300$  K), and/or magnetic field ( $H \leq 20$  kOe), and/or hydrostatic pressure ( $p \leq 20$  kbar). The Tm to Se ratio of the samples has been varied between 0.87 and 1.05. The valence state of the Tm ions is influenced by the chemical composition and the divalent character increases from  $\sim 0\%$  for Tm<sub>0.87</sub>Se to  $\sim 28\%$  for Tm<sub>1.05</sub>Se. The low-temperature magnetic susceptibility and the anomalously high compressibility are consistent with the model that the ground state of each Tm ion contains both divalent and trivalent character. In all crystals with this homogeneously mixed-valent character, the localized  $4f$  electrons and the itinerant  $5d$  electrons strongly interact below  $\sim 35$  K. Magnetic ordering occurs in all compounds investigated, but the type of ordering and the critical parameters of the magnetic phase diagram are again strongly influenced by the chemical composition.

### I. INTRODUCTION

Rare-earth ions in certain noninsulating compounds are labeled "mixed valent" in the sense, that their  $4f^n$  and  $4f^{n-1}5d$  configurations are energetically equivalent. In the  $4f^{n-1}5d$  configuration the  $5d$  electron is regarded as delocalized and therefore the two configurations correspond to two different valence states of the rare-earth (RE) ions. This degeneracy favors the hybridization of the localized  $4f$  and the extended  $5d$  wave functions. Consequently the average number of  $4f$  electrons on a given ion site is no longer an integer and the  $4f$  electron density has to be described in terms of a new ground state. Increasing experimental evidence suggests that the phenomenon of mixed-valent ions is a widespread feature of RE compounds [we do not consider the case of transition-metal mixed-valence compounds (MVC)] but a general and consistent theoretical description of such systems has not yet been elaborated.<sup>1</sup>

Experimentally it is obvious that mixed-valent compounds are rather complicated with respect to the electronic configuration. Either the mixed-valent state is only stabilized by inconvenient external parameters (high pressure, chemical alloying) or the materials exist in a wide homogeneity range of their chemical composition and their physical properties change quite drastically within this range. All these features are responsible for many uncertainties in the experimental results of studies on such materials.

In mixed-valent compounds of Ce, Sm, Eu, and Yb, one of the two possible configurations involved is nonmagnetic, i.e., the total angular momentum  $J=0$ . In such compounds, the magnetic moments seem to average to zero and no magnetic ordering is observed at low temperatures.<sup>1</sup> In compounds

with Pr, Tb, and Tm, both valence states of these ions are magnetic ( $J \neq 0$ ) and at least in one case, namely TmSe, long-range magnetic ordering has been observed in a mixed-valent material.<sup>2-5</sup> Apart from this unique feature, TmSe has the advantage of being a mixed-valent system already at normal pressure and without alloying. Moreover it is essential that the only possible itinerant electrons originally stem from the  $4f$  shell, a situation which is quite different from that in rare-earth intermetallic compounds with mixed-valence character, such as  $\text{EuCu}_2\text{Si}_2$ ,<sup>6</sup>  $\text{YbCuAl}$ ,<sup>7</sup> for instance.

Even the earliest investigations of TmSe revealed quite clearly that this material unfortunately is very difficult to prepare with reproducible composition and physical properties. Experimental results of various studies varied drastically from one sample to another.<sup>4,8-13</sup>

Since it has been realized that it is the *chemical composition* which decisively influences the behavior of TmSe, we started our investigation of TmSe by varying the Tm to Se ratio. The purpose was to obtain a first systematic and extended analysis of several physical properties.<sup>14</sup> Anticipating our results as a guideline for the reader we mention that *the valence of Tm* indeed strongly depends upon the chemical composition of TmSe. Therefore the variation of the stoichiometric ratio may be regarded to a certain extent as a tool to vary the Tm valence in TmSe. Special attention has been given to the characterization of the samples used in the experiments (see Sec. II). Whenever possible all the data have been taken on the very same single crystal. Thermal and transport properties, including their variation under the influence of external magnetic fields or pressure, reveal the special features of the magnetic-ion-

conduction-electron interaction and hence of the mixed valent state. In that respect it is of fundamental importance to distinguish between the case where each Tm ion has the same, but intermediate valence (homogeneous MVC) and the possibility of a static distribution of divalent and trivalent Tm ions within the compound (inhomogeneous MVC). The experimental results of our investigation are presented in Sec. III. In Sec. IV we discuss the implications of our data with special emphasis on the intermediate valence character of TmSe and in Sec. V we summarize the results of our investigation.

## II. SOLID-STATE CHEMISTRY OF $\text{Tm}_x\text{Se}$

From the chemical point of view the main purposes of this investigation were (i) to understand the phase relationship of Tm-Se and (ii) to find out if a valence instability is affecting the solid state chemistry of TmSe. Some of the results have been published elsewhere<sup>15</sup> and here, we present mainly the results concerning homogeneity. As the phase purity is of primary importance for valence instability problems, the phase diagram of TmSe was investigated up to 2300 °C in the composition range  $0.60 < x < 1.20$ . [ $x = (\text{mole Tm})/(\text{mole Se})$ ]. We used differential thermoanalysis (Mettler Thermoanalyzer) in small sealed W crucibles (diam = 4.5 mm), metallography, energy dispersive analysis of x rays, wet chemical analysis, density and microhardness measurements, as well as scanning electron microscopy. The lattice constant has been determined by a Debye-Scherrer technique and will be discussed in detail below. The results of these combined investigations not only show the existence of a gross homogeneity range at 300 K for  $\text{Tm}_x\text{Se}$  but also locate its Tm-rich phase boundary at  $1.03 < x < 1.05$  and its Se-rich phase boundary at  $x \sim 0.90$ . In addition, the homogeneity is also confirmed by single crystal Weissenberg photographs<sup>16</sup> and by electron diffraction.

The results of the phase diagram investigations can be used to optimize the crystal-growth conditions from the melt. Since two phase transitions of unknown nature have been observed at  $T \approx 1000$  and 1650 °C, long annealings should be performed at these temperatures. An alternative method is slow continuous cooling from the melting temperature the maximal value of which in the Tm-Se phase diagram is  $2032 \pm 10$  °C. Various cooling rates were used between 280 and 5.5 °C/min. Good results were achieved in the range of 40–50 °C/min with a reverse gradient position. At cooling rates near 5 °C/min the excess component was rejected from the slowly growing crystals due to constitu-

tional supercooling. Details of the general experimental methods, W crucibles, their sealing by electron bombardment, furnace design, etc., have been given previously.<sup>17</sup>

To obtain information on the incorporation of Tm and Se in the TmSe lattice, precision density measurements have been performed,<sup>18</sup> by the buoyancy method. It was found that the experimental densities were lower than the calculated ones. The results are consistent with a model assuming that all existing vacancies are the sum of Schottky pairs and of vacancies due to nonstoichiometry. The latter appear because the solution of Tm or Se in the TmSe lattice (in the homogeneity range) takes place by formation of vacancies in one sublattice. Therefore the lowest concentration of vacancies, approximately  $7.2 \times 10^{20} \text{ cm}^{-3}$  appears at the stoichiometric composition. The highest concentration of vacancies ( $4 \times 10^{21} \text{ cm}^{-3}$ ) appears at the composition with the maximal deviation from stoichiometry ( $x \approx 0.90$ ).

Very interesting conclusions about the vacancy distribution can be drawn from electron diffraction patterns recorded in a JEM 100 C electron microscope. For this purpose, fine crystal fragments were collected on holey carbon supporting films. The basic NaCl structure has been confirmed for samples of varying composition. The samples with Tm deficiency show bands of diffuse scattering, in addition to the reflections of the NaCl-type unit cell. The intensity decreases monotonically to zero as their composition approaches stoichiometry. The diffuse features, shown for a characteristic example in Fig. 1, are very similar to those observed by Kennett and Rudee<sup>19</sup> in Zr-deficient zirconium sulphide. They are thought to arise from short-range ordering of

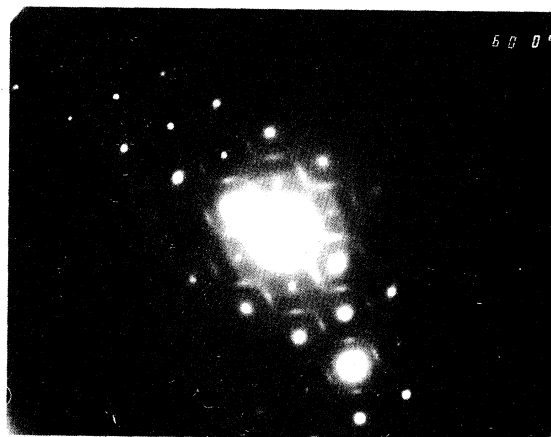


FIG. 1. Electron-diffraction pattern from  $\text{Tm}_{0.87}\text{Se}$ . The electron beam direction is [011].

TABLE I. Physical properties of  $\text{Tm}_x\text{Se}$  derived in this work.

$x \equiv n_{\text{Tm}}/n_{\text{Se}}$	0.87	0.97	1.0	1.05
Lattice constant $a_0$ (Å)	5.628 <sub>5</sub>	5.663 <sub>5</sub>	5.705	5.715 <sub>5</sub>
Valence of Tm from $a_0$	+3	+2.89	+2.75	+2.72
Compressibility $\kappa$ at 300 K ( $10^{-6} \text{ bar}^{-1}$ )	1.5 ± 0.15	3.8 ± 0.2	4.2 ± 0.2	3.2 ± 0.2
Electrical resistivity at 300 K ( $\mu\Omega \text{ cm}$ )	210 ± 10	225 ± 15	235 ± 15	255 ± 20
Paramagnetic Curie temperature $\Theta_p$ (K)	-19.5	-24	-29	-31.5
Effective magnetic moment $p_{\text{eff}}$ ( $\mu_B/\text{Tm}$ )	7.29	6.77	6.39	6.02
Néel temperature $T_N$ (K)	~4.2	~3	2.9	3.5

Tm vacancies. The spatial extent of the streaks indicates that there may be vacancy correlation over 50–100 Å.

The measurements of the lattice constant alone provides some information concerning the valence state of the Tm ions. We again emphasize the  $x$  in  $\text{Tm}_x\text{Se}$  denotes the ratio (mole Tm)/(mole Se) and *not* the occupation number of either the cation or the anion sublattice. The lattice parameters  $a_0$  of  $\text{Tm}_x\text{Se}$  are given in Table I and have to be compared with the ones of other monochalcogenides of divalent and trivalent RE. A critical inspection of all data available in the literature leads to  $a_0^{3+} = 5.63$  Å and  $a_0^{2+} = 5.94$  Å for pure  $\text{Tm}^{3+}\text{Se}$  and a hypothetical  $\text{Tm}^{2+}\text{Se}$ , respectively. Divalent RE ions have a larger size because they have, compared with the trivalent ones, an additional electron occupying the highly localized  $4f$  shell which results in screening of the nuclear potential and consequently in a spreading out of the outer valence shells. The average valence of Tm in  $\text{Tm}_x\text{Se}$  may now be obtained, in the absence of a better way, by a linear interpolation of the measured lattice parameter between the two limiting values  $a_0^{3+}$  and  $a_0^{2+}$  (see Table I). The remarkable variation of  $a_0$  in  $\text{Tm}_x\text{Se}$ , which is an order of magnitude higher than in  $\text{Gd}_x\text{Se}$  with similar stoichiometry variations,<sup>20</sup> is a clear manifestation of the fact that the valence state of Tm in  $\text{TmSe}$  is mainly determined by the chemical composition. The amount of divalent Tm character therefore gradually increases from ~0% in  $\text{Tm}_{0.87}\text{Se}$  to ~28% in  $\text{Tm}_{1.05}\text{Se}$ . Thus the investigations described in the following part of this paper constitute a study of the physical properties of  $\text{TmSe}$  with respect to the varying valence state of Tm due to the controlled change of the chemical composition.

### III. EXPERIMENTAL RESULTS

#### A. Magnetic susceptibility

We have measured the magnetic susceptibility  $\chi = M/H$  in an external magnetic field of 500 Oe between 1.5 K and room temperature. In Fig. 2 we show  $\chi^{-1}$  as a function of temperature for all

compounds investigated. In each case a linear change of  $\chi^{-1}$  with temperature is observed for  $T > 50$  K. In terms of a Curie-Weiss law a systematic change of the effective moment  $p_{\text{eff}}$  and the paramagnetic Curie temperature  $\Theta_p$  is found (see Table I). With increasing  $x$ ,  $p_{\text{eff}}$  is decreasing and  $\Theta_p$  increases on the negative temperature axis. The decrease of the effective moment is in agreement with a systematic increase of the divalent character of the Tm ions as deduced from the lattice constant measurements because the free ion values of  $p_{\text{eff}}$  are  $7.56$  and  $4.58 \mu_B$  for  $\text{Tm}^{3+}$  and  $\text{Tm}^{2+}$ , respectively. The increase of the negative paramagnetic Curie temperature combined with the decreasing Curie constant indicates a

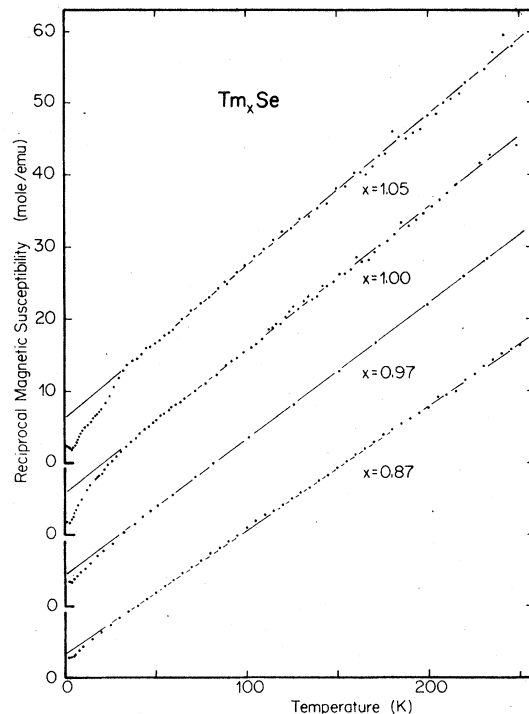


FIG. 2. Reciprocal magnetic susceptibility of  $\text{Tm}_x\text{Se}$ . Deviations from the linear temperature dependence below ~35 K increase as the divalent character of the Tm ions increases.

strong variation of the exchange interactions. In all the compounds we observe a drop of  $\chi^{-1}$  below the Curie-Weiss straight line at temperatures below about 35 K and the deviation grows with increasing Tm content. Since in our experiment we actually measure a magnetization we may also state that below 35 K the apparent magnetic moment of the Tm ions is enhanced above the value derived from the high-temperature behavior, contrary to what is usually observed in mixed valent compounds where the apparent magnetic moment usually decreases with decreasing temperature.

Previous authors<sup>5</sup> have applied molecular-field theory for the interpretation of the magnetic phase transitions. In the same approximation our experimental values of  $T_N$  and  $\Theta_p$  can be used to predict the type of ordering and compare it with the experimental results of neutron-diffraction studies, where a type-I antiferromagnetic order was found in zero magnetic field.<sup>5</sup> According to Smart<sup>21</sup> we may write in our case

$$-\frac{16}{3}J_1 + 8J_2 = T_N, \quad 16J_1 + 8J_2 = \Theta_p. \quad (1)$$

Here we assume the same effective spin  $S=1$  as has been used in Ref. 5. From these equations we obtain in the case of  $\text{Tm}_{1.0}\text{Se}$   $J_1 = -1.52$  K and  $J_2 = -0.64$  K, and therefore  $J_2/J_1 > 0$ . A type-I antiferromagnetic ordering, however, requires  $J_2/J_1 < 0$ , i.e., the next nearest-neighbor exchange  $J_2$  has to be ferromagnetic. In all our cases we find  $J_1 < 0$  and  $J_2/J_1 > 0$ . This is particularly due to the very large negative values of  $\Theta_p$  as derived from the temperature dependence of  $\chi$  well above 35 K. Since neutron-diffraction experiments<sup>5</sup> clearly revealed type-I ordering in zero field for samples exhibiting the same magnetic phase diagram as that shown in Fig. 12, we conclude that below 35 K the exchange interactions start to vary considerably with temperature. It appears that  $J_2$  becomes increasingly ferromagnetic with decreasing temperature and hence type-I antiferromagnetic order finally is stabilized below  $T_N$ . It is interesting to note that the compound  $\text{Tm}_{0.87}\text{Se}$ , where this variation of  $J_2$  is obviously very weak, does in fact not show type-I ordering. Type-II ordering consistent with our experimental values of  $T_N$  and  $\Theta_p$  for this compound has indeed been reported for Tm deficient samples.<sup>22</sup> In this case, additional complications arise, because the long-range ordering may be inhibited by the large amount of vacancies. Although the deviations from the Curie-Weiss law also set in at 35 K in this case, they are obviously not strong enough to change the type of ordering from that predicted by the high temperature behavior. We note that the stability criteria for the various magnetic phases based on

the molecular field approximation do not depend on the choice of  $S$  and the above discussion also holds for  $S \neq 1$ . The strong variation of  $\chi$  in  $\text{Tm}_x\text{Se}$  below 35 K (this temperature is independent of chemical composition) may be associated with the intermediate valence character of TmSe, because the abrupt change of the temperature dependence is not only observed for  $\chi$  but also for the electrical resistivity (see below).

The calculation of the magnetic susceptibility is usually straightforward for RE compounds with ions of well defined valency. Calculating  $\chi$  on the basis of  $\text{Tm}^{3+}$  ions seems most justified for the case of  $\text{Tm}_{0.87}\text{Se}$  where we have several indications (lattice constant,  $p_{\text{eff}}$ ) that the Tm ions are close to trivalent. For  $\text{Tm}^{3+}$  ions in the NaCl structure we expect a singlet ground state of the crystal field-split Hund's-rule multiplet, and therefore a Van Vleck behavior of  $\chi$  at the lowest temperatures. The facts that (i) we do not observe the temperature-independent Van Vleck paramagnetism and (ii) that  $\chi^{-1}$  follows a Curie-Weiss law with virtually the full moment of free  $\text{Tm}^{3+}$  ions down to 35 K indicate that a possible crystal-field splitting of the  $4f$  electron energy levels would have to be very small and in addition, the ground state might not be a singlet state. Using the expression  $\chi^{-1} = \chi_{\text{CF}}^{-1} - \lambda$ , where  $\chi_{\text{CF}}$  is the crystal-field only susceptibility and  $\lambda$  is the molecular field constant, the experimental curve can, independent of the level sequence, be approximated by choosing the crystal field parameter  $B_4$  to be of the order of 1 mK, consistent with previous calculations,<sup>5</sup> and setting  $\lambda \sim -5$  mole/emu. It has to be mentioned, however, that the calculated susceptibility is not very sensitive to the choice of  $B_4$  and therefore not very well suited for a determination of the crystal field interaction. We also note that an estimate of  $\lambda$ , based on the assumption that  $\text{Tm}_{0.87}\text{Se}$  is a crystalline-electric-field induced-moment magnet (singlet ground state) and on the fact of the very small crystal-field splitting results in a value of  $\lambda \sim 0.2$  mole/emu. With previous authors<sup>5</sup> we therefore tend to the conclusion that singlet-ground-state behavior is not the essential ingredient in the magnetism of  $\text{Tm}_{0.87}\text{Se}$ .

## B. Electrical resistivity

The electrical resistivity  $\rho$  has been measured as a function of temperature ( $0.04 \leq T \leq 300$  K), magnetic field ( $H$  up to 20 kOe) and room-temperature external pressure up to 20 kbar. A four-probe dc technique has been used and both the current and the external magnetic field were parallel to [100],

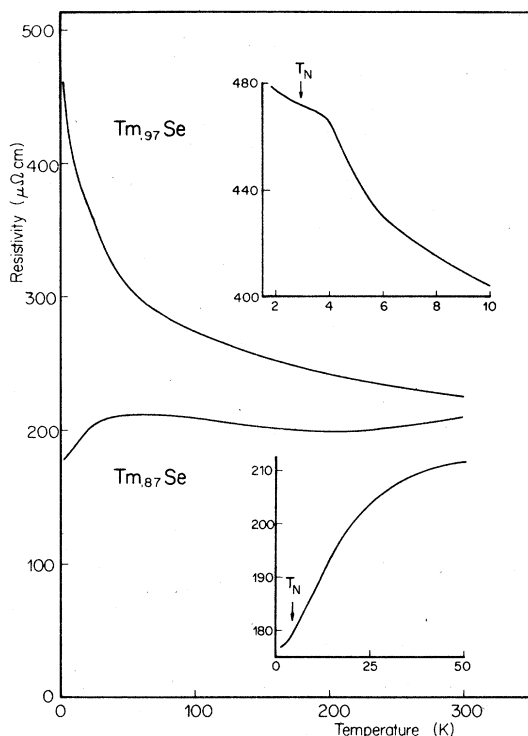


FIG. 3. Electrical resistivity of  $\text{Tm}_x\text{Se}$  ( $x=0.87, 0.97$ ) as function of temperature.  $T_N$  indicates the magnetic ordering temperatures.

### 1. Zero magnetic field

The room-temperature value of  $\rho$  increases from  $210 \mu\Omega \text{ cm}$  for  $\text{Tm}_{0.87}\text{Se}$  to  $255 \mu\Omega \text{ cm}$  for  $\text{Tm}_{1.05}\text{Se}$  (see Table I) and thus is only slightly higher than the one of  $\text{Gd}_x\text{Se}$ ,<sup>23</sup> containing only trivalent Gd. At lower temperatures the electrical resistivity is strongly affected by the chemical composition. Starting with  $\text{Tm}_{0.87}\text{Se}$ , the  $\rho$  vs  $T$  curve (Fig. 3) may be interpreted as a normal metallic background ( $\partial\rho/\partial T > 0$ ) with a broad peak superimposed, leading to a flat maximum around  $T=60 \text{ K}$  and an  $s$ -shaped decrease below this temperature (see insert Fig. 3). The point of inflection is at  $\sim 12 \text{ K}$ . The resistivity of crystals with a lattice constant indicating partial divalent Tm character steadily increases with decreasing temperature (Figs. 3 and 4, note the logarithmic temperature scale). The slope  $\partial\rho/\partial T$  becomes more and more negative when stoichiometry is approached and appears to be constant for  $x \geq 1$ . The linear dependence of  $\rho$  vs  $\log T$  between about 40 and 4 K is evident and resembles the resistivity anomalies provoked by magnetic ions in a metallic, nonmagnetic matrix (Kondo effect). The occurrence of long-range magnetic order is also reflected by the electrical resistivity. Whereas

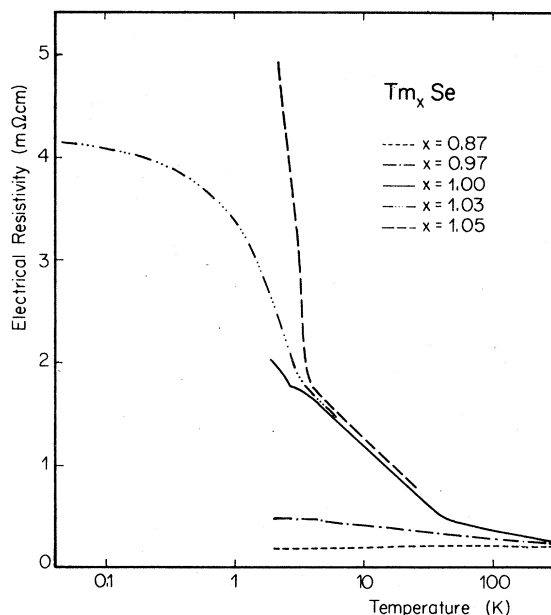


FIG. 4. Electrical resistivity of  $\text{Tm}_x\text{Se}$  below 300 K.

$\text{Tm}_{0.97}\text{Se}$  only shows a small additional shoulder just above  $T_N$  (insert Fig. 3) the resistivity of  $\text{Tm}_x\text{Se}$  with  $x > 1$  increases considerably below  $T_N$ , forming a pronounced kink of the  $\rho(T)$  curve at  $T_N$  and  $\partial\rho/\partial T$  actually remains negative down to 40 mK, in agreement with previously reported results<sup>10</sup> (Fig. 4).

### 2. Magnetoresistance

The zero-field measurements already indicate that the magnetic state strongly influences the electrical resistivity and previous authors have actually found a strong negative variation of  $\rho$  by applying external magnetic fields of moderate strength.<sup>11-13</sup> In  $\text{Tm}_x\text{Se}$  samples with  $x < 1$  the resistivity at  $T=2 \text{ K}$  is hardly affected by an external field and the relative change  $\Delta\rho/\rho$  is only about 1% at 20 kOe. The situation changes quite drastically when  $x \geq 1$ . A strong negative magnetoresistance is observed and a representative set of experimental curves is shown in Fig. 5 for the stoichiometric compound. Below  $T_N$ , two critical fields ( $\sim 2$  and  $\sim 5 \text{ kOe}$ , at 2 K) separate three different phases. We also note that the phase below  $\sim 2 \text{ kOe}$  does not reappear after a field sweep to  $H > 5 \text{ kOe}$ . No anomaly of  $\rho$  is then observed at  $T_N$  when the sample is subsequently heated above  $T_N$ . The drop of  $\rho$  at the higher critical field becomes sharper with decreasing temperature but no hysteresis could be detected. The resistivity of  $\text{Tm}_{1.0}\text{Se}$  at 20 kOe is still larger than at room temperature. Above  $T_N$ ,  $\rho$  decreases pro-

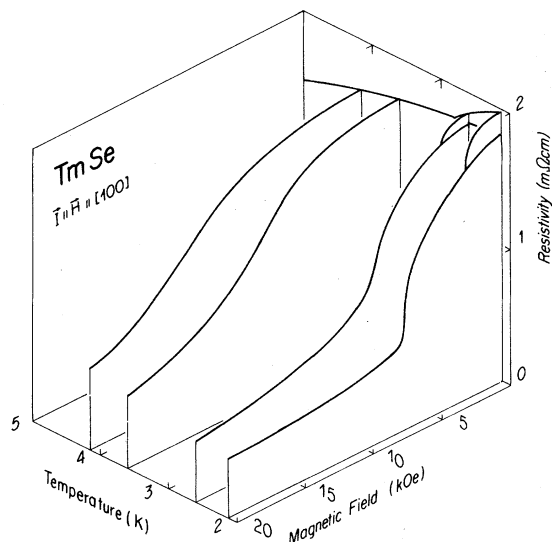


FIG. 5. Magnetoresistance curves of  $\text{Tm}_{1.0}\text{Se}$  at different temperatures. Below the magnetic ordering temperature  $T_N$ , the enhancement of  $\rho$  in fields lower than  $\sim 2$  kOe disappears after a first field sweep to  $H > 5$  kOe.

portional to  $H^2$  in low fields but tends to level off at the upper end of our field range.

In samples with Tm excess ( $x > 1$ ) the resistivity is similarly influenced by magnetic fields and different phases are observed below  $T_N$  as in  $\text{Tm}_{1.0}\text{Se}$ , but the effects are larger in magnitude. We note that at 2 K the ratio  $\rho(H=0)/\rho(H=20 \text{ kOe})$  exceeds 100 and the resistivity drops below its room temperature value with only a few kilo-oersteds, depending on the temperature. We also have to mention the occurrence of additional anomalies of unknown origin just above  $T_N$  in fields up to a few kilo-oersteds.

### 3. Resistivity at high pressures

The  $\text{TmSe}$  crystals give strong visual evidence of their metallic character. The long-wavelength part of the visible spectrum is strongly reflected by the plasma of the free charge carriers, leading to the metallic copper-brown color.<sup>24</sup> At high pressures we therefore do not expect similar spectacular changes of color and resistance as observed when Sm, Eu, and Yb monochalcogenides undergo a pressure induced semiconductor-to-metal transition.<sup>25</sup> On the other hand, the lattice constants of  $\text{Tm}_x\text{Se}$  reveal some divalent Tm character (25% on the stoichiometric compound) and thus the Tm ions are expected to be transformed under high pressures into the pure trivalent state. The electrical resistivity at ambient temperature under hydrostatic pressures up to 20 kbar has been measured in a piston-cylinder device with

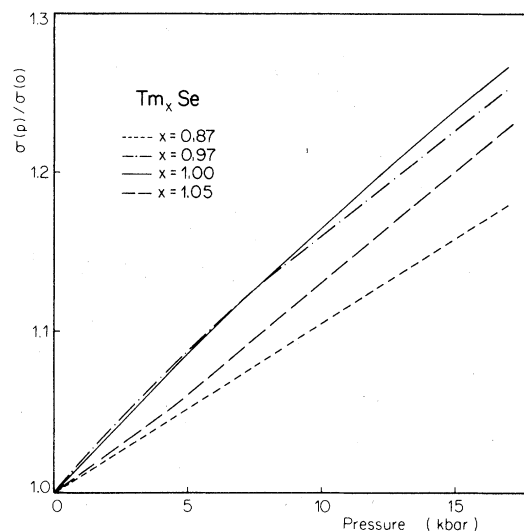


FIG. 6. Relative pressure dependence of the electrical conductivity  $\sigma$  at room temperature.

ether as the pressure transmitting medium.<sup>26</sup> The results for  $\text{Tm}_x\text{Se}$  are shown in Fig. 6 where the correction for the geometry factor due to sample compression has properly been taken into account. Generally the conductivity increases (the resistivity decreases) at high pressures. In the samples with a Tm content closest to stoichiometry the effect is maximal and their conductivity at  $p=20$  kbar is about 30% higher than at normal pressure. The relative change per kbar appears to decrease at higher pressures, but no discontinuity can be observed.

### C. Compressibility

As mentioned already, the  $4f$  occupation number, determining the valence, and the radius of the RE ions are closely related. Any instability of the electronic configuration involving the  $4f$  shell therefore gives rise to a change of the lattice properties such as lattice constant or bulk modulus. An illustrative example is the anomalous volume reduction accompanying the pressure induced valence change of Sm and Yb in their monochalcogenides.<sup>25</sup> The instability of the  $4f$  configuration in  $\text{Sm}_{1-x}\text{Y}_x\text{S}$ ,<sup>27</sup> and in  $\text{Ce}_{1-x}\text{Th}_x$ ,<sup>28</sup> is also reflected in a drastic softening of the lattice.

The volume-pressure relationships of  $\text{Tm}_x\text{Se}$  single crystals have been determined at room temperature using a strain gauge technique. From repeated measurements on different samples with the same composition an accuracy of 5% could be estimated. We have found that the compressibility  $\kappa = -(1/V)(\partial V/\partial p)$  of  $\text{Tm}_x\text{Se}$  is strongly varying with the chemical composition and reaches a maximum at stoichiometry (Table I). Whereas  $\kappa$  ap-

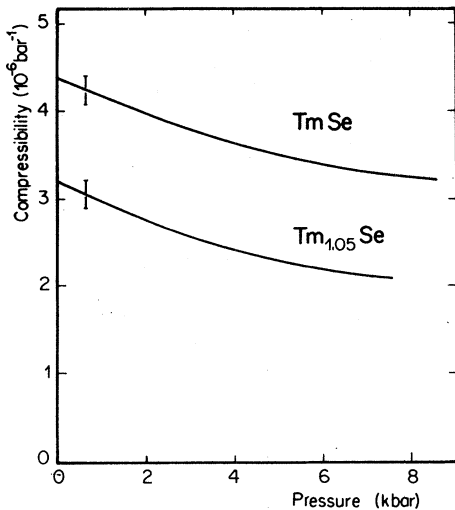


FIG. 7. Pressure dependence of the compressibility of  $\text{Tm}_x\text{Se}$  ( $x=1.0, 1.05$ ) at room temperature.

pears to be pressure independent up to 10 kbar for  $x=0.87$  and  $0.97$ , it decreases markedly with increasing pressure for samples with  $x \geq 1$  (Fig. 7).

From a comparison with other semiconducting and metallic RE monochalcogenides the "normal" compressibility of  $\text{TmSe}$  can be predicted.<sup>25,29,30</sup> Accordingly metallic  $\text{Tm}^{3+}\text{Se}$  and a hypothetical semiconducting  $\text{Tm}^{2+}\text{Se}$  should have a  $\kappa$  of  $\sim 0.95 \times 10^{-6}$  and  $\sim 1.6 \times 10^{-6} \text{ bar}^{-1}$ , respectively. The observed values, however, are up to a factor of 4 larger than the expected ones, and a detailed interpretation will be given in one of the following sections. In anticipation we note that these enhanced compressibilities will play an important part in the discussion about the valence state of Tm.

#### D. Thermal expansion and magnetostriction

The linear thermal expansion coefficient  $\alpha$  was measured along [100] between 1.5 and 15 K and in various external magnetic fields up to 15 kOe. We have already shown how the variation of  $x$  influences the temperature dependence of  $\alpha$  in this temperature range.<sup>31</sup> For  $x > 1$  we found a strong anomaly of  $\alpha$  at the magnetic phase transition in zero magnetic field, the strength of the anomaly (or the total strain) becoming larger with increasing  $x$ . For  $x < 1$  this anomaly is quenched by a factor of 10 for  $x=0.97$  and no similar anomaly is found for  $x=0.87$ . Complementary to previous publications<sup>14,31</sup> we show  $\alpha(T)$  in zero magnetic

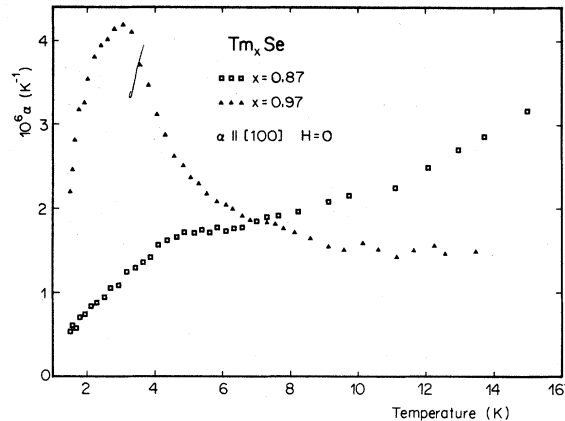


FIG. 8. Low-temperature linear thermal expansion coefficient  $\alpha$  of  $\text{Tm}_x\text{Se}$  ( $x=0.87, 0.97$ ).

field for  $\text{Tm}_{0.87}\text{Se}$  and for  $\text{Tm}_{0.97}\text{Se}$  in more detail in Fig. 8. It may be seen that the behavior is qualitatively different in these two compounds and we note that for  $\text{Tm}_{0.87}\text{Se}$ , in contrast to the rest of the series, no negative slope of  $\alpha(T)$  is observed.

As has been shown in earlier work<sup>3</sup> the low-temperature thermal expansion coefficient is strongly influenced by applying an external magnetic field. This is illustrated in Fig. 9 for  $\text{Tm}_{1.0}\text{Se}$  with the magnetic field direction parallel to [100]. For fields less than 3 kOe, the anomaly remains almost unchanged and is only slightly broadened on the low-temperature side. For fields stronger than 5 kOe, however, two distinct maxima appear, corresponding to phase boundaries III and IV in the magnetic phase diagram (see Fig. 12).

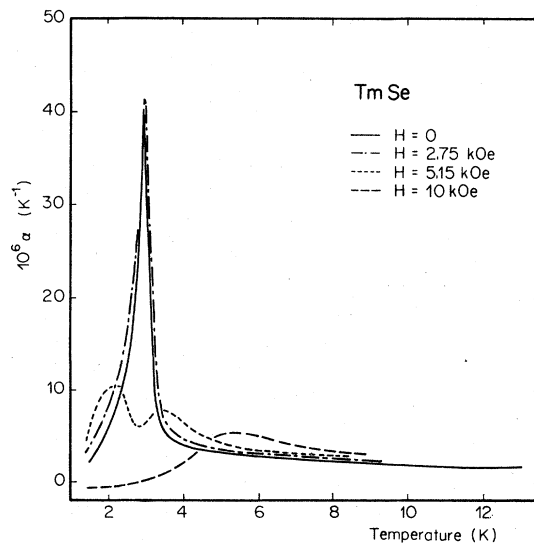


FIG. 9. Thermal expansion coefficient  $\alpha$  for  $\text{Tm}_{1.0}\text{Se}$  at different magnetic fields, between 1.5 and 12 K.

With still increasing magnetic field the lower anomaly disappears and  $\alpha$  even becomes negative. The upper anomaly is shifted to higher temperatures and gradually flattened out. Generally, the same behavior was observed in  $\text{Tm}_{1.05}\text{Se}$  and with much weaker anomalies in  $\text{Tm}_{0.97}\text{Se}$ . Magnetic fields have almost no influence on the thermal expansion of  $\text{Tm}_{0.87}\text{Se}$ , very similar to what has been found in the electrical resistivity experiments (see above).

In previous work the magnetostriction data have mainly been used to establish the magnetic phase diagram of these substances.<sup>3,12,14,31</sup> Here we also present the results of magnetostriction experiments in the paramagnetic region, where the strain  $\epsilon = [l(H) - l(0)]/l(0)$  varies quadratically with the magnetic field  $H$ . In Fig. 10 we show the temperature dependence of the total strain  $\epsilon$  in a magnetic field of 10 kOe. We immediately note that for the whole series investigated the strain is negative and increasing in magnitude with increasing Tm content. Magnetostriction data in the paramagnetic region have been presented before for  $\text{TmS}$ ,  $\text{Tm}_x\text{Se}$ , and  $\text{TmTe}$ .<sup>12</sup> It was shown that the magnetostriction of  $\text{TmTe}$  is positive and that this can be understood by considering the influence of the crystal electric field split ground state of the  $4f^{13}$  configuration of  $\text{Tm}^{2+}$  ions. In this case the sign of the magnetostriction is in agreement with the sign of the  $\alpha_J$  Stevens multiplicative factor, a feature that has been verified for several RE intermetallic compounds before.<sup>32</sup> This is, however, not the case for  $\text{TmS}$  and  $\text{TmSe}$ . Unfortunately,  $\text{TmS}$  is not a straightforward case because the magnetic field induced strain is, although negative, very small and several competing contributions may lead to this behavior. The crystal-field only magnetostriction is expected to be positive for  $\text{TmS}$  also. Comparing with these earlier results for  $\text{TmS}$  where the Tm ions are trivalent, we find almost the same magnetostriction for  $\text{Tm}_{0.87}\text{Se}$ , a further indication that in this compound the Tm ions are closest to being trivalent in the  $\text{Tm}_x\text{Se}$  series. We note however that the behavior of  $\text{TmS}$  and  $\text{Tm}_{0.87}\text{Se}$  differs considerably in the ordered region.

Figure 10 clearly reveals that the increasing divalent character of the Tm ions with increasing  $x$  obviously does not lead to a temperature dependence of  $\epsilon(H)$  as was observed for  $\text{TmTe}$ . Instead we measure an increasingly negative strain in the  $[100]$  direction. From low-temperature measurements of the magnetic susceptibility under hydrostatic pressure one expects a positive volume strain when applying an external magnetic field. Earlier work on  $\text{TmSe}$ ,<sup>3,33</sup> however, has shown that a magnetic field along  $[100]$  produces a tetrag-

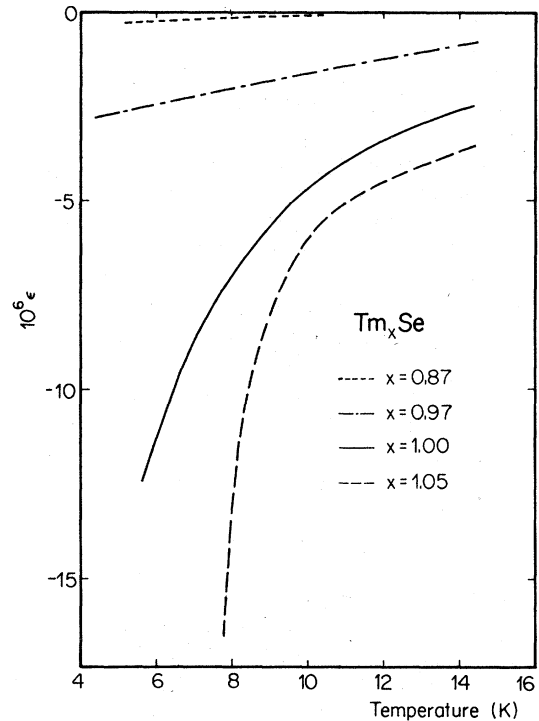


FIG. 10. Temperature dependence of the magnetostriction of  $\text{Tm}_x\text{Se}$  along  $[100]$  in an external magnetic field of 10 kOe.  $\epsilon = [l(H) - l(0)]/l(0)$ .

onal strain and the negative sign of  $\epsilon_{100}$  shows clearly that anisotropic interactions are important. The temperature dependence of  $\epsilon(H)$  still makes it tempting to ascribe the magnetostriction to the volume and field dependence of the crystal field energy levels of the  $4f$  electrons but CEF effects alone would predict  $\epsilon_{100} > 0$  and, far more important, no manifestation of any other crystal-field effect in  $\text{TmSe}$  has been found yet. We recall, however, that the temperature dependence of the magnetic susceptibility  $\chi$  also strongly deviates from a Curie-Weiss behavior at low temperatures (see above) and we therefore suggest that the anisotropic strain dependence of the exchange interactions  $\lambda$  is responsible for the magnetic field induced strains and that the strong temperature dependence of  $\epsilon(H)$  is then at least partly due to the temperature variation of  $\lambda$ . From Maxwell's relation  $\partial \epsilon_i / \partial H = \Omega (\partial M / \partial \sigma_i)$ , where  $\Omega$  is the molar volume,  $M$  the magnetization, and  $\sigma_i$  a stress in the  $i$  direction, we obtain  $\epsilon_i = \frac{1}{2} \kappa_i \chi H^2 (\partial \ln \chi / \partial \epsilon_i)$ , where  $\kappa_i$  is a uniaxial compressibility. For the volume strain  $\Delta V/V$  this formula also predicts a positive strain since  $\partial \ln \chi / \partial \ln V$  has been determined experimentally and found to be positive.<sup>33</sup>

High pressure work at low temperature<sup>33</sup> has shown quite clearly, however, that the magnetic



properties are very sensitive to anisotropic strains and from our experiments we conclude that a positive tetragonal strain along [100] results in a decrease of the susceptibility, at least in the paramagnetic region.

Results of magnetostriction experiments below  $T_N$ , the ordering temperature in zero magnetic field, have been given previously.<sup>31</sup> Here we should only like to mention that qualitatively the same behavior was found in  $\text{Tm}_{0.97}\text{Se}$ ,  $\text{Tm}_{1.0}\text{Se}$ , and  $\text{Tm}_{1.05}\text{Se}$ . The magnitude of the strain effects is, however, quite different in all three cases and also the values of the critical fields associated with the boundaries of the magnetic phase diagram differ appreciably. According to our magnetostriction measurements the phase boundary IV appears to have a negative slope in  $\text{Tm}_{0.97}\text{Se}$ .

#### IV. DISCUSSION

First it must be made clear whether the mixed valence state of  $\text{Tm}_x\text{Se}$  has to be interpreted in terms of a static distribution of divalent and trivalent Tm ions (similar to, e.g., Eu in  $\text{Eu}_3\text{S}_4$ ) or whether all Tm ions, in a quantum mechanical sense, combine the divalent and the trivalent character and, in their ground state show mixed valence behavior. These two possibilities are usually labeled as inhomogeneous and homogeneous mixed valence, respectively. In general, measurements of the isomer shift in the Mössbauer spectra allow an unambiguous distinction between these two cases. This most direct method cannot be applied to  $\text{TmSe}$  because the isomer shift in Tm corresponding to the different valence states is much smaller than the line width itself. The combination of all our measurements, however, gives strong evidence that the Tm ions in  $\text{Tm}_x\text{Se}$  ( $x=0.97, 1.0, 1.05$ ) are in a homogeneously mixed valence state, as will be discussed in the following.

Penney and Melcher<sup>34</sup> have worked out a model describing successfully the electronic configuration crossover and the lattice collapse in  $\text{SmS}$  and related compounds. They have considered both elastic and electronic energies and find that the mixed valence state is, in general, characterized by a compressibility which is higher than in the pure integer valence states. The increase of the compressibility of  $\text{Tm}_x\text{Se}$  with increasing  $x$  and the positive pressure dependence of the electrical conductivity are consistent with this model and hence are the strongest indications that the Tm ions are in a homogeneously mixed valence state. This is further supported by measurements of the far-infrared reflectivity as a function of temperature. As in metallic  $\text{SmS}$  and  $\text{SmB}_6$ ,<sup>35-37</sup> two well estab-

lished homogeneously MVC, the excitation spectrum reveals anomalies at low photon energies which have to be attributed to strong absorption mechanisms, due to a high density of states at the Fermi energy, typical for homogeneously mixed valent compounds.<sup>38</sup>

In combination with the measurements of the compressibility it is quite interesting to note that the total thermal contraction from room temperature to 4.2 K is about twice as large for the Tm-rich samples as for the Tm deficient specimens. Thus the increase of the compressibility is accompanied by an increase of the thermal expansion coefficient indicating the growing contribution of the anharmonic terms of the lattice potential in crystals with mixed valence character.

The magnetic ordering at low temperature would be much easier to explain for an inhomogeneously mixed valence state. In this case it should be possible to describe the magnetic susceptibility by adding up the respective contributions from divalent and trivalent Tm ions, but we find that this is not possible within reasonable limits. For an inhomogeneously mixed valent state we would also expect that at least indications of crystal-field effects on thermal properties should be observed but previous work has shown that this is not the case. Based on all these facts we conclude that in  $\text{Tm}_x\text{Se}$  ( $x=0.97, 1.0, 1.05$ ) the Tm ions are all in a homogeneously mixed valent state. Only for the sake of completeness do we not exclude the possibility of small amounts, (of the order of a few percents) of divalent and trivalent Tm ions to be present in our samples. Such "impurities" could arise mainly from crystal imperfections other than vacancies.

From all our experiments it follows consistently that the divalent character of the Tm ions increases with increasing  $x$ . Since this increase of divalency is accompanied by an increase of the lattice constant it should be possible to suppress the divalent character by applying external hydrostatic pressure. Guertin and co-workers<sup>33</sup> concluded from their low-temperature measurements of the magnetization of  $\text{Tm}_x\text{Se}$ , under external pressure that with increasing pressure the Tm ions gradually lose their partial divalent character and they estimated, in combination with compressibility data from ultrasonic experiments,<sup>12</sup> that above approximately 20 kbars, the Tm ions should be purely trivalent. It may be expected that the difference between the mixed valent and the trivalent state manifests itself in the electrical resistivity. From our resistivity and volume measurements under pressure we have calculated the electrical conductivity  $\sigma = \rho^{-1}$  as a function of the lattice parameter and the result is

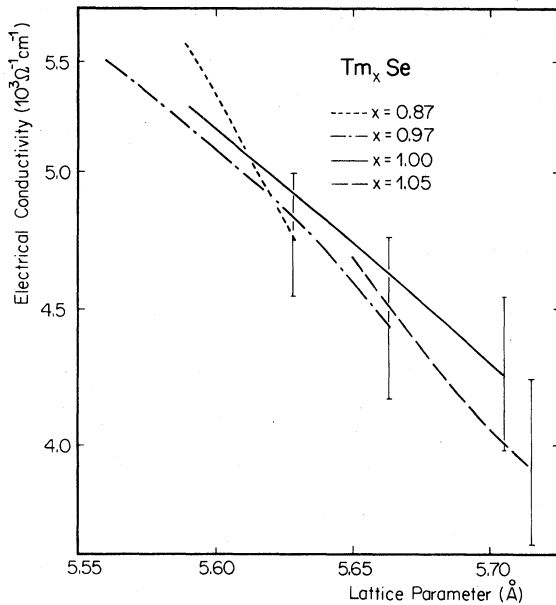


FIG. 11. Electrical conductivity  $\sigma$  of  $\text{Tm}_x\text{Se}$  as function of the lattice parameter at room temperature. The bars indicate the uncertainty of the absolute value due to the geometry factor.

shown in Fig. 11. For all samples the curves lie surprisingly close together and reflect a common behavior. The applied pressure is sufficient to reduce the lattice constant of  $\text{Tm}_{0.97}\text{Se}$  and  $\text{Tm}_{1.0}\text{Se}$  below the one expected for purely trivalent  $\text{TmSe}$  ( $a \sim 5.63 \text{ \AA}$ ). Evidently we do not observe any distinct discontinuity of  $\sigma(a)$  around that value but at least for  $x=0.97$  and  $1.0$  the slope appears to change. We recall that the resistivity of  $\text{SmS}$  does not show any anomaly when going from the intermediate valence range to the pure trivalent one either.<sup>39</sup> If we consider that both the charge carrier concentration and the mobility determine the conductivity it is difficult to analyze the results of Fig. 11 in a straightforward way. As indicated above, however, the volume reduction energetically favors the  $4f^{12}5d$  configuration of the Tm ions rather than  $4f^{13}$  and hence electrons are more likely occupying conduction-band states than localized  $4f$  orbitals. As a consequence the average charge carrier concentration  $n_e$  increases. This increase should also show up in a positive shift of the plasma resonance energy  $h\omega_p$  since  $\omega_p$  is proportional to  $n_e^{1/2}$ . Preliminary reflectivity measurements at high pressures indeed reveal a shift of  $\omega_p$  towards higher frequencies and we therefore conclude that the increase of the conductivity with decreasing lattice parameter is at least partly due to an increase of the carrier concentration. The smooth curves in Fig. 11 are consistent with a gradual valence change of the Tm

ions and the further increase of  $\sigma$  with decreasing lattice parameter below  $5.63 \text{ \AA}$ , in the trivalent state can probably be traced back to the influence of pressure on the energy bands which is obviously quite considerable as well. Of course, the pressure required to reduce the lattice parameter below the "pure trivalent" value of  $\sim 5.63 \text{ \AA}$ , strongly depends on the compressibility and the zero pressure lattice constant. For  $\text{Tm}_{0.97}\text{Se}$  and  $\text{Tm}_{1.0}\text{Se}$  these pressures are 6 and 10 kbars, respectively, therefore considerably lower than estimated in Ref. 33.

The volume dependence of the conductivity is more pronounced in  $\text{Tm}_{0.87}\text{Se}$ . It seems quite likely that in this case the vacant RE sites are trapping electrons and hence reducing the free-carrier concentration. As a visible consequence the color of  $\text{Tm}_{0.87}\text{Se}$  is purple, in contrast to the usual copper-brown color of all the other compounds with higher Tm contents. The rather large pressure dependence of  $\sigma$  may then be explained by a large volume dependence of the binding energy of the trapped electrons. Similar effects have been observed before in metal deficient Gd chalcogenides. The fact that  $\text{Tm}_{0.87}\text{Se}$  still has the lowest room temperature resistivity of the series shows that one obviously has to consider mobility effects as well. Estimates using optical data<sup>9,38</sup> actually indicate that the mobility decreases appreciably with increasing divalent Tm character from  $\sim 1.9 \text{ cm}^2/\text{V sec}$  for  $\text{Tm}_{0.87}\text{Se}$  to  $\sim 1$  for  $\text{Tm}_{1.05}\text{Se}$ . This is exactly what one expects in the homogeneously mixed valent situation where both  $4f$  and  $5d$  states are present at the Fermi energy.

Turning to the temperature dependence of the resistivity we find again a quite different behavior in  $\text{Tm}_{0.87}\text{Se}$  compared to the rest of the series (Fig. 3). Such a temperature dependence of  $\rho$  might possibly be explained by taking into account crystal-field effects caused by the splitting of the  $J=6$  ground state of the  $\text{Tm}^{3+}$  ions. It would, however, require an energy splitting much larger than that observed in corresponding Tm mononictides but recent estimates based on neutron diffraction experiments resulted in rather small crystal-field interactions in  $\text{Tm}_x\text{Se}$ .

In all other compounds  $\rho$  steadily increases with decreasing temperature. Volume effects due to thermal expansion hardly change the average number of charge carriers and if anything  $n_e$  should slightly increase and hence decrease the resistivity. The increasing negative slope  $\partial\rho/\partial T$  with increasing mixed valence character of the compounds indicate the gradual onset of a scattering mechanism which strongly depends on temperature. It is very tempting to ascribe the logarithmic increase of  $\rho$  with decreasing temperature (see

Fig. 4) to a Kondo-type scattering but again the temperature dependence of  $\chi^{-1}$  (see Fig. 2) is not in agreement with such an explanation. Further arguments against explaining the resistivity behavior on the grounds of a Kondo effect arise from a comparison of the characteristic "Kondo temperature",  $T_K$  of approximately 15–20 K, as deduced from  $\rho(T)$ , with the rather weak magnetic fields of about 10 kOe ( $\sim 1$  K) necessary to compensate the enhanced resistivity. It should also be kept in mind that the Kondo concept applies strictly only for the case of very dilute systems (non interacting magnetic impurities) and this is certainly not the case for TmSe and Tm<sub>1.05</sub>Se where the divalency of the Tm ions amounts to 25%–30%. Although theoretical attempts have been made to generalize the dilute case towards the concentrated limit,<sup>40,41</sup> we feel that these calculations are not yet at the state for comparison with experimental results of real systems. Another mechanism to be considered probably in every explanation of the low-temperature raise of the resistivity is based on the homogeneously mixed valent situation itself. Since the density of excitation states is very high in a small energy range  $\Delta$  around the Fermi energy due to the hybridization of the 4*f* and the 5*d* states, the transport properties are expected to change if the thermal excitation energy becomes comparable or even lower than  $\Delta$ .

At this point we think it is essential to mention what we believe is one of the major unsolved problems concerning the interpretation of the physical properties of Tm<sub>x</sub>Se, namely the construction of an electronic ground state exhibiting mixed valence properties including a nonzero magnetic moment. Several attempts have been made to construct a mixed valent ground state but they are all related to the case where one of the possible ionic configurations is nonmagnetic and it appears that with this condition one observes a weakening of the magnetization with decreasing temperature.<sup>42</sup> In the case of Tm<sub>x</sub>Se one has to find a mechanism which with decreasing temperature not only enhances the electrical resistivity but also the magnetic moment. It is quite obvious from Figs. 2 and 4 that for Tm<sub>1.05</sub>Se and Tm<sub>1.0</sub>Se both  $\partial\rho/\partial T$  and  $\partial\chi/\partial T$  change considerably around 35 K. The same features, although much weaker, are discernible in the case of Tm<sub>0.97</sub>Se. As pointed out above a distinctly different behavior is observed in Tm<sub>0.87</sub>Se. That the change of slope of a transport property ( $\rho$ ) and a static thermodynamic quantity ( $\chi$ ) appears at the same temperature again gives strong evidence for an intimate interplay of localized and itinerant electron states. It has been suggested that double exchange interactions might be relevant to the behavior of Tm<sub>x</sub>Se.<sup>43</sup> The double

exchange mechanism might lead to an increase of the electrical resistance assuming an increasing antiferromagnetic correlation in the ion lattice and the antiferromagnetic ordering would be accompanied by a sudden enhancement of the resistivity as observed experimentally. It has, however, to be considered that the temperature dependence of  $\chi$  shows a contradictory behavior in as much as we observe an increasing ferromagnetic contribution with decreasing temperature.

The magnetic ordering of TmSe is up to now a unique feature among the well established mixed valent compounds. The type of ordering, the anomalies in the physical properties associated with the ordering and the influence of external magnetic fields on critical values connected with the ordered phases are clearly very much dependent on  $x$ . Again Tm<sub>0.87</sub>Se does not show the characteristic features of all the other compounds. Although, mostly from magnetostriction measurements, we conclude that Tm<sub>0.87</sub>Se is in some sort of an ordered state below 4.2 K, there are hardly any anomalies to be observed in all the properties investigated. With such a large amount of RE vacancies it is even doubtful whether a long-range order can be established. And indeed we find it extremely important to compare our electron diffraction results on Tm<sub>0.87</sub>Se (Fig. 1) with the neutron-diffraction results obtained on similar colored Tm deficient samples.<sup>22</sup> The correlation length of both the vacancies and of the magnetic moments are in the order of 100 Å. Thus the interaction between the magnetic moments appears to be strongly moderated by a high vacancy concentration.

The properties in the ordered regime are best discussed on the basis of the magnetic phase diagram, first established in Ref. 3 and later confirmed in further investigations<sup>5,33</sup> (see Fig. 12). The phase boundaries I, II, and III are characterized by discontinuities appearing in several physical properties when studied in varying external magnetic fields (volume, magnetoresistance, magnetization). Line IV is probably not a phase boundary in the usual sense but roughly divides two regions of quite different magnetic behavior, namely paramagnetism at temperatures above IV and ferromagnetic features at temperatures below line IV.

The most pronounced effects in both the magnetostriction and the magnetoresistance are observed at phase boundary III. The positive length change along [100] nearly compensates the contraction occurring at  $T_N$  in zero field and the slope  $\partial\rho/\partial H$  reaches its maximum across boundary III. With still increasing magnetic field above phase boundary III again both magnetostriction and mag-

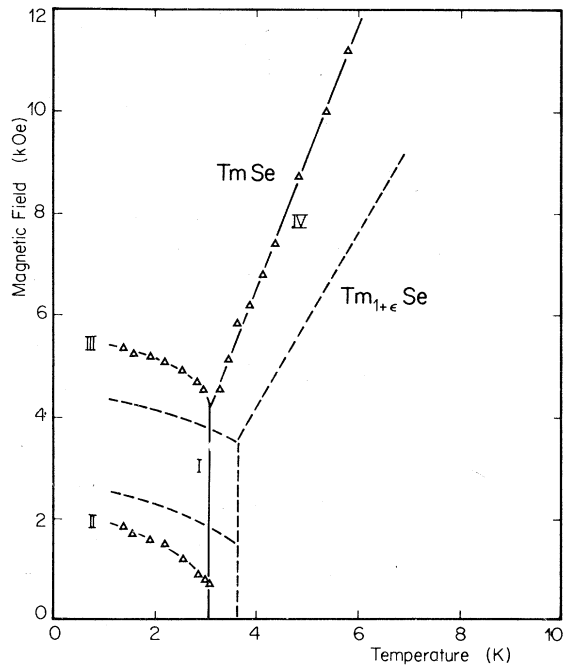


FIG. 12. Low-temperature magnetic phase diagram for  $Tm_{1-x}Se$  and  $Tm_{1+x}Se$ .

netoresistance show typical ferromagnetic saturation. The sign of the slope of the magnetostriction is opposite ( $\partial\epsilon/\partial H > 0$ ) to that observed in the paramagnetic phase, where  $\partial\epsilon/\partial H < 0$ . This is one of the features to identify line IV of the diagram. Further indications for the existence of IV are the sign change of  $\partial\rho/\partial T$  when measured in external fields  $H > 5$  kOe and, for a rather limited field range, the appearance of a double peak in  $\alpha(T)$  as shown in Fig. 9.

A very puzzling effect is the sudden increase of  $\rho$  at  $T_N$  when measured in zero external magnetic field. The negative slope  $\partial\rho/\partial T$  actually persists to the lowest temperatures in the millidegrees Kelvin region (see Fig. 4 and also Ref. 10). This behavior is closely related to the special features of the phase below phase boundary II. All experimental facts indicate that one is dealing with an ordered phase but split up in many tiny domains and it appears that at least part of the additional resistivity is due to a strong scattering at the domain walls. This phase can be suppressed with rather moderate fields (boundary II) and it does not reappear after removal of the magnetic field. Evidence for this hysteretic behavior was recently given by results of magnetostriction and netoresistance<sup>31</sup> experiments and the same features were observed in neutron diffraction experiments<sup>5</sup> as well. It is still not quite clear why the zero field type-I antiferromagnetic ordering is accom-

panied by this appearance of microdomains, a feature usually not seen in other magnetically ordering RE materials. It may, in our case, have to do with the enhanced compressibility and the obviously very small anisotropy energy. We ought to mention here, that very similar effects in  $\rho(T)$  and  $\rho(H)$  have been observed before in impure EuTe.<sup>44</sup> The magnitude of the resistivities were, however, larger than in our case by a factor of 1000, indicating that doped EuTe is a degenerate magnetic semiconductor.

The influences of  $x$  on the magnetic phase boundaries have already been shown in Ref. 31 and we mention them here for completeness. Increasing  $x$  leads to a slight increase of  $T_N$  and to a lowering of the phase boundaries III and IV. Phase boundary II is shifted towards III. Thus the strength of the magnetic interactions seems to increase with the increasing mixed valent character of the Tm ions. This holds for the antiferromagnetic nearest neighbor exchange  $J_1$ , as calculated from Eqs. (1), just as well as for the ferromagnetic next nearest-neighbor exchange  $J_2$  as indicated by the lowering of phase boundary III. This is rather surprising since one might expect a weakening of the magnetic interactions in the mixed valent state.

## V. SUMMARY

The purpose of the present investigations was to study for the first time in a systematic and extended manner the properties of the magnetically ordering mixed valent compound TmSe on well characterized samples. Special attention has been given to the problems: (i) is TmSe an inhomogeneous or a homogeneous MVC, (ii) what is the interaction between localized and itinerant electrons and (iii) to what extent are the physical properties influenced by the chemical composition?

To obtain this information we have measured various physical properties, partly as a function of temperature, magnetic field or external pressure, and we have varied the chemical composition of the single phase crystals of  $Tm_xSe$  (where  $x$  denotes the Tm to Se ratio) from  $x = 0.87$  to  $x = 1.05$ .

From all our data we are lead to the conclusion that the variation of the chemical composition results in a shift of the valence of the Tm ions from +3 in  $Tm_{0.87}Se$  to +2.72 in  $Tm_{1.05}Se$ . The high compressibility and the magnetic susceptibility, which, within reasonable limits, we cannot explain by a weighted superposition of pure divalent and trivalent ion contributions, indicate the *homogeneously* mixed valent character of TmSe.

Independent of the chemical composition, a change of the temperature dependence of the mag-

netic susceptibility  $\chi$  and the electrical resistivity  $\rho$  is observed at 35 K. Compared to the behavior between 35 K and room temperature we note an enhanced increase of both the apparent magnetic moment and  $\rho$  with decreasing temperature below 35 K. The strong interaction of the  $4f$  shell with the itinerant electrons is also apparent in the magnetic field dependence of the magnetostriiction and the magnetoresistance at low temperatures. In order to explain this interaction a double exchange mechanism has been discussed<sup>45</sup> but we argue that this picture is not consistently applicable, at least if the double exchange model is

taken in its traditional meaning.

In conclusion we may state that this systematic study was necessary to establish a profound experimental background for the theoretical understanding of the magnetically ordering MVC TmSe.

#### ACKNOWLEDGMENTS

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- <sup>1</sup>*Proceedings of the International Conference on Valence Instabilities and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).
- <sup>2</sup>E. Bucher, K. Andres, F. J. di Salvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Jr., *Phys. Rev. B* **11**, 500 (1975).
- <sup>3</sup>H. R. Ott, K. Andres, and E. Bucher, *AIP Conf. Proc.* **24**, 40 (1974).
- <sup>4</sup>B. B. Triplett, N. S. Dixon, P. Boolchand, S. S. Hanna, and E. Bucher, *J. Physique, Colloq.* **35**, C6-653 (1974).
- <sup>5</sup>H. Bjerrum Møller, S. M. Shapiro, and R. J. Birgeneau, *Phys. Rev. Lett.* **39**, 1021 (1977).
- <sup>6</sup>E. R. Bauminger, D. Froindlich, I. Novik, S. Ofer, I. Felner, and I. Mayer, *Phys. Rev. Lett.* **30**, 1053 (1973).
- <sup>7</sup>W. C. M. Matteno, R. A. Elenbaas, and F. R. de Boer, *Commun. Phys.* **2**, 147 (1977).
- <sup>8</sup>M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, *Phys. Rev. Lett.* **32**, 885 (1974).
- <sup>9</sup>B. Batlogg, A. Schlegel, and P. Wachter, *Physica B* **86-88**, 229 (1977).
- <sup>10</sup>A. Berger, E. Bucher, P. Haen, F. Holtzberg, F. Lapierre, T. Penney, and R. Tournier, in Ref. 1, p. 491ff.
- <sup>11</sup>W. M. Walsh, Jr., K. Andres, L. W. Rupp, Jr., L. D. Longinotti, in Ref. 1, p. 499ff.
- <sup>12</sup>H. R. Ott, B. Lüthi, and P. S. Wang, in Ref. 1, p. 289ff.
- <sup>13</sup>P. Haen, F. Holtzberg, F. Lapierre, T. Penney, and R. Tournier, in Ref. 1, p. 495ff.
- <sup>14</sup>B. Batlogg, E. Kaldis, and H. R. Ott, *Phys. Lett. A* **62**, 270 (1977).
- <sup>15</sup>E. Kaldis, B. Fritzlér, and W. Peteler, *Zeitschrift für Naturforschung* (to be published).
- <sup>16</sup>G. Chapuis, University of Lausanne (private communication).
- <sup>17</sup>E. Kaldis, *Principles of the Vapour Growth of Single Crystals in Crystal Growth Theory and Techniques*, edited by C. H. L. Goodman (Plenum, New York, 1974), Vol. I.
- <sup>18</sup>B. Fritzlér, thesis, Laboratorium für Festkörperphysik ETH, 1978 (unpublished).
- <sup>19</sup>H. M. Kennett and M. L. Rudee, *Philos. Mag.* **35**, 129 (1977).
- <sup>20</sup>W. Beckenbaugh, J. Evers, G. Güntherodt, E. Kaldis, and P. Wachter, *J. Phys. Chem. Solids* **36**, 239 (1975).
- <sup>21</sup>J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, 1966).
- <sup>22</sup>S. M. Shapiro, H. B. Møller, J. D. Axe, R. J. Birgeneau, and E. Bucher, *J. Appl. Phys.* **49**, 2101 (1978).
- <sup>23</sup>R. Hauger, E. Kaldis, G. von Schulthess, P. Wachter, and C. Zürcher, *J. Magn. Magn. Mat.* **3**, 103 (1976).
- <sup>24</sup>B. Batlogg, A. Schlegel, and P. Wachter, *J. Phys. Colloq.* **37**, C4-267 (1976).
- <sup>25</sup>A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, *Phys. Rev. B* **9**, 2513 (1974).
- <sup>26</sup>One of the authors (B.B.) is indebted to Dr. M. Brouha, Philips Research Laboratories, Eindhoven, for helpful discussions about the high-pressure apparatus.
- <sup>27</sup>T. Penney, R. L. Melcher, F. Holtzberg, and G. Güntherodt, *AIP Conf. Proc.* **29**, 392 (1976).
- <sup>28</sup>M. C. Croft and R. D. Parks, in Ref. 1, p. 455ff.
- <sup>29</sup>F. Lévy, P. Wachter, *Solid State Commun.* **8**, 183 (1970).
- <sup>30</sup>S. von Molnar, T. Penney, and F. Holtzberg, *J. Phys. Colloq.* **37**, C4-241 (1976).
- <sup>31</sup>H. R. Ott, B. Batlogg, E. Kaldis, and P. Wachter, *J. Appl. Phys.* **39**, 2118 (1978).
- <sup>32</sup>B. Lüthi, P. S. Wang, Y. H. Wong, H. R. Ott, and E. Bucher, *Proceedings of the Second International Conference on Crystal Field Effects in Metals and Alloys* (Plenum, New York, 1977).
- <sup>33</sup>R. P. Guertin, S. Foner, and F. P. Missell, *Phys. Rev. Lett.* **37**, 529 (1976).
- <sup>34</sup>T. Penney and R. L. Melcher, *J. Phys. Colloq.* **37**, C4-275 (1976).
- <sup>35</sup>B. Batlogg and P. Wachter, in Ref. 1, p. 537.
- <sup>36</sup>F. W. Allen, in Ref. 1, p. 533.
- <sup>37</sup>J. W. Allen, Richard M. Martin, B. Batlogg, and P. Wachter, *J. Appl. Phys.* **49**, 2078 (1978).
- <sup>38</sup>B. Batlogg (unpublished).
- <sup>39</sup>T. Kaneko, H. Yoshida, S. Abe, and M. Okashi, *J. Appl. Phys.* **49**, 2100 (1978).
- <sup>40</sup>S. Doniach, in Ref. 1, p. 169ff; *Physica B* **91**, 231 (1977).
- <sup>41</sup>F. D. M. Haldane, *Phys. Rev. B* **15**, 2477 (1977).
- <sup>42</sup>D. K. Wohlleben and B. R. Coles, *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. V.
- <sup>43</sup>C. M. Varma, U. S.-Japan Seminar, on Physical Properties of Rare-Earth Magnetic Semiconductors (unpublished).
- <sup>44</sup>Y. Shapira, S. Foner, N. F. Oliveira, Jr., and T. B. Reed, *Phys. Rev. B* **5**, 2647 (1972).
- <sup>45</sup>C. M. Varma and R. J. Birgeneau, *Bull. Am. Phys. Soc.* **23**, 232 (1978).

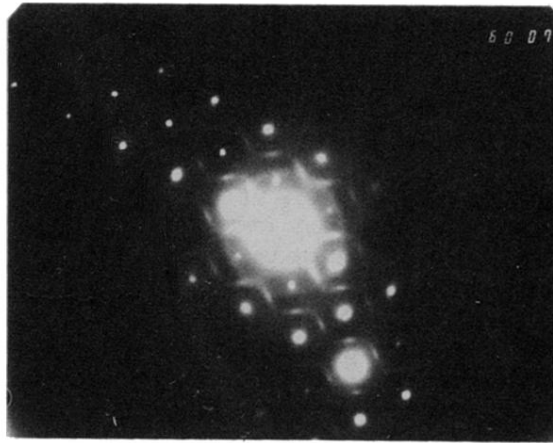


FIG. 1. Electron-diffraction pattern from  $\text{Tm}_{0.87}\text{Se}$ . The electron beam direction is [011].