

Valence changes in TmSe by alloying with TmTe and EuSe

B. Batlogg*

Laboratorium für Festkörperphysik der Eidgenössischen Technischen Hochschule, CH-8093 Zürich, Switzerland

(Received 2 July 1980)

The valence of the Tm ions in mixed-valent TmSe has been influenced by alloying with TmTe and EuSe in order to study the interaction between intermediate-valent rare-earth ions as a function of the degree of valence mixing. Magnetic, elastic, electrical, and optical properties have been measured on $\text{TmSe}_{1-x}\text{Te}_x$ crystals for seven distinct compositions. The degree of valence mixing is increased as Se is replaced by Te up to $\sim 20\%$ and the material remains metallic. Whereas TmSe orders metamagnetically ($T_N = 3$ K), the Te-containing samples are spontaneously magnetized below 3–5 K. This increasing strength of the ferromagnetic interactions, accompanying the increase of valence mixing, is consistent with the model of a double exchange coupling of mixed-valent Tm ions. $\text{TmSe}_{1-x}\text{Te}_x$ with $x \geq 0.5$ is semiconducting, the Tm ions are divalent and the overall electronic structure is similar to the ones of the Sm, Eu, and Yb monochalcogenides. The only peculiarities are the narrow energy gaps (0.2 to 0.35 eV) which require pressures of some 20 to 30 kbar to be closed. The magnetic properties are dominated by the crystal-field-split $^2F_{7/2}$ ground state, leading to ordering temperatures well below 1 K. As Eu replaces Tm in TmSe, it is divalent because of its highly stable $4f^7$ shell, whereas the $\text{Tm}^{2+} 4f^{13}$ and $\text{Tm}^{3+} 4f^{12} 5d$ configurations are nearly degenerate: in $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ they are separated by an energy gap of only 0.1 eV, which can be driven to zero with moderate external pressure (15 kbar). In the metallic $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$, the Tm ions are of predominantly inhomogeneously mixed-valent character since the Eu ions, being larger in volume, are thought to give rise to local deformations of the lattice.

I. INTRODUCTION

In the last decade particular attention has been attracted by the group of rare-earth (RE) "mixed-valent" compounds, where the two electronic configurations corresponding to the different valence states of each RE ion are degenerate in the sense that no energy is required to transfer an electron out of the $4f$ shell into the conduction band and vice versa. More precisely, this situation is labeled "homogeneous mixed valent" or "intermediate valent," in contrast to the "inhomogeneous valence mixing," where RE ions are in different, but integer-valent states. It is the coexistence of the highly correlated and localized $4f$ states of the itinerant $s-d$ states at the Fermi level that leads to a whole set of anomalous properties, but typical for intermediate-valent RE compounds.¹⁻³

One of the fundamental questions about intermediate-valent RE ions concerns their magnetic properties and the interactions among them. Therefore, it appears to be most useful to study the only magnetically ordering intermediate-valent compound,⁴⁻⁷ namely, TmSe. Besides its uniqueness, TmSe offers also the advantage to manipulate the degree of valence mixing by external means which is the relevant parameter in the problem.

TmSe crystallizes in the rocksalt structure like all

RE monochalcogenides and monpnictides, and all its physical properties are strongly influenced by the chemical composition.^{5,8-13} In a systematic study of TmSe with varying Tm-to-Se ratio Tm has been found to be close to $3+$ in $\text{Tm}_{0.87}\text{Se}$, $2.75+$ in stoichiometric TmSe and $2.72+$ in $\text{Tm}_{1.05}$.^{14,15} Here, the valence of Tm has been estimated from the lattice constant. The following short description relates to the ideal composition. Intraband absorption below 2-eV photon energy gives rise to the lustrous metallic brown-golden color. TmSe is a metamagnet with a Néel point of 3 K and an external field of ~ 5 kOe suffices to convert the antiferromagnetic type-I spin structure into a ferromagnetic one.⁷ Above ~ 40 K the magnetic susceptibility obeys a Curie-Weiss law ($\theta_p = -30$ K) and the effective magnetic moment is a weighted average of the divalent and trivalent free-ion value. The electrical resistance below room temperature increases continuously upon cooling from $\sim 220 \mu\Omega$ cm at 300 K to some $m\Omega$ cm in the millikelvin range, but drops by orders of magnitude in the ferromagnetic phase, i.e., by application of a magnetic field.^{4,10-15} The thermal expansion and the compressibility are higher than in comparable non-mixed-valent compounds like GdSe.¹⁵

Variations of the chemical composition lead to a variation of the Tm valence, but it is not possible to

increase the divalent character by adding more and more Tm to TmSe. Crystal chemical investigations indicate the occurrence of a new phase when the Tm-to-Se ratio exceeds ~ 1.05 .^{16,17} Therefore, alloying TmSe with either TmTe or EuSe promises an alternative way to further manipulate the Tm valence. Both in TmTe and in EuSe the RE ions are divalent and these compounds are semiconductors with energy gaps of 0.3 (Refs. 5 and 18) and 1.8 eV (Ref. 19), respectively.

The aim of the present work is to vary the Tm valence over a larger range than has been possible by only changing the stoichiometry of Tm_xSe . By introducing an anion with a larger ionic radius than Se it is expected that the valence of Tm becomes more mixed than by stoichiometry variation of Tm_xSe . A substitution of Tm with the integer divalent Eu should similarly pull the Tm valence closer to the divalent character. In addition we want to get a survey over the physical properties of the TmSe-TmTe and TmSe-EuSe alloy series with special attention to the RE-ion valence state and second, anticipating a major result of the first point, to study the magnetic interaction between Tm ions with a maximal degree of valence mixing. In particular, it will be possible for the first time to critically compare theoretical predictions concerning highly mixed-valent TmSe with the experiment. A variety of experimental techniques has been used [magnetization and electrical transport as a function of temperature (1.5–550 K) and/or pressure (< 20 kbar), and/or magnetic field (100 kOe), compressibility, optical spectroscopy]. It is neither intended nor possible from reasons of space limitation to explain and interpret every trifle detail of the results, but the key information will be extracted to construct a coherent picture.

II. TmSe-TmTe

A first general view of the TmSe-TmTe system is obtained by just looking at the electrical resistivity at ambient temperature and pressure (Fig. 1). At low Te concentration (x up to 20 at. %) the resistivity is nearly constant and the value of $\sim 200 \mu\Omega \text{ cm}$ is typical for the metallic RE selenides. Starting from TmTe on the other end, the resistivity drops from ~ 50 to $\sim 0.25 \Omega \text{ cm}$ for $TmSe_{0.5}Te_{0.5}$. Obviously a semiconductor-to-metal transition occurs in the range where ~ 20 to 50 at. % of Se is replaced by Te. The samples investigated in the present work were mostly single crystals or, in a few cases, well polycrystallized material. Crystal chemical aspects are discussed in Refs. 16 and 17, and it should be noted here that metallographic checks with an optical microscope revealed no obvious second phase.

The different questions in relation to the semiconducting and metallic properties require in the follow-

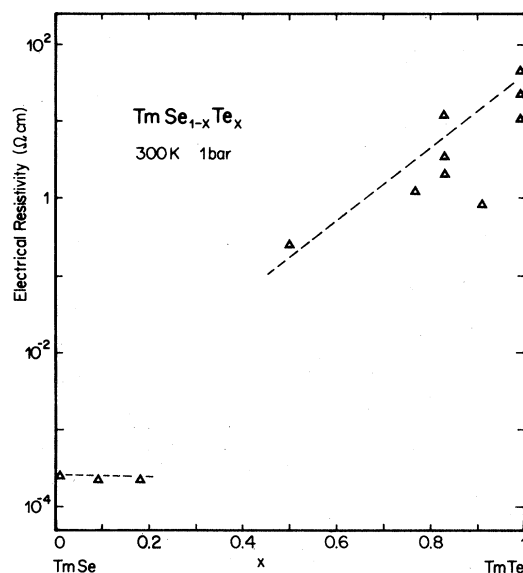


FIG. 1. Electrical resistivity of $TmSe_{1-x}Te_x$ at ambient temperature and pressure.

ing a separate discussion of the two subgroups of compounds.

A. Semiconducting TmSe-TmTe

Since TmTe is known to be a semiconductor, the exponential decrease of ρ on going towards $x = 0.5$ is very suggestive of a closing of an activation gap. This is confirmed by the temperature dependence of ρ as shown in Fig. 2 for two compositions. The slight curvature of the lines connecting data points on the Arrhenius plot appears to indicate the “extrinsic” origin of the charge carriers thermally activated into the conduction band. Donor levels are well expected to exist because the vacancy concentration in both the anion and cation sublattice is typically in the order of percents.¹⁶ Nevertheless the activation energy is smaller for $TmSe_{0.5}Te_{0.5}$ than for $TmSe_{0.17}Te_{0.83}$. In the insert to Fig. 2 the resistivity of $TmSe_{0.17}Te_{0.83}$ is shown up to $T \sim 550$ K and from the slope at the highest temperatures an activation energy of 0.23 eV is calculated using simple statistics

$$\rho(\Delta E, T) = \rho_0 \exp(+\Delta E/kT) \quad (1)$$

The factor $\frac{1}{2}$ has been omitted in the exponent following the experience with the Sm and Eu chalcogenides, and that reflects the apparent pinning of the Fermi level at the states forming the lower boundary of the gap. Furthermore, optical spectroscopy at 300 K in the infrared region (0.5 to 0.03 eV) strongly supports the semiconducting character of these compounds. The reflectivity for the Te-richest samples shows a relative maximum ($R = 24\%$) between 0.4-

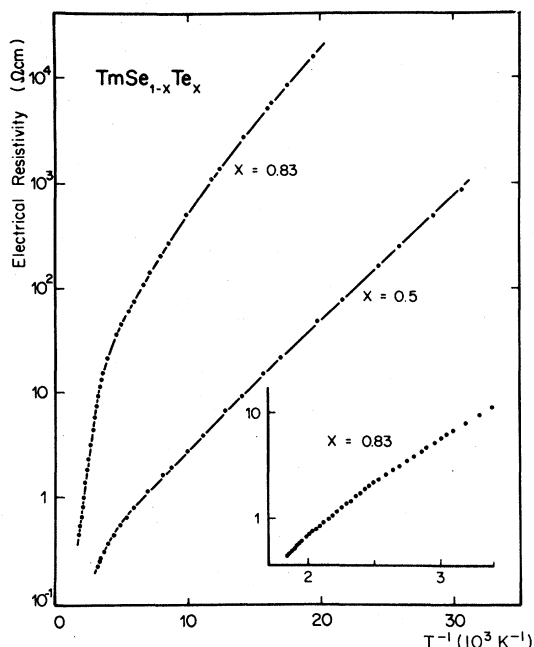


FIG. 2. Arrhenius plot of the electrical resistivity of semiconducting $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0.5$ and 0.83).

and 0.5-eV photon energy due to the onset of inter-band absorption and a very slow decrease towards lower photon energies because of the phonon absorption which, however, lies out of the frequency range investigated here. In crystals with more than ~ 20 at. % Te replaced by Se ($0.5 \leq x \leq 0.8$) the electrons thermally activated at room temperature form a conduction-band plasma with a plasmon energy in the order of a couple of tenths of eV. Thus, the reflectivity rises again below this typical energy. The optical spectrum in the infrared and the electrical resistivity are fully consistent with the conception of semiconductors with a gap that is narrowed ongoing from TmTe to $\text{TmSe}_{0.5}\text{Te}_{0.5}$.

From these findings the divalence of Tm in $\text{TmSe}_{1-x}\text{Te}_x$ ($x \geq 0.5$) can be inferred and magnetic measurements will corroborate with it. In Fig. 3 the inverse magnetic susceptibility χ^{-1} is shown for $\text{TmSe}_{0.5}\text{Te}_{0.5}$ as a function of temperature between 1.5 and 300 K. Above $T \sim 80$ K the data lie well on a straight line passing through the origin within ± 0.5 K and indicating a Curie paramagnetic behavior. The slope corresponds to an effective magnetic moment $\mu_{\text{eff}} = 4.74 \mu_B$ per mole. Comparing it with the free-ion values 4.58 and $7.56 \mu_B$ for $\text{Tm}^{2+}(4f^{13}, {}^2F_{7/2})$ and $\text{Tm}^{3+}(4f^{12}, {}^3H_6)$ the measured μ_{eff} therefore is another clear evidence that Tm is divalent in $\text{TmTe}_{0.5}\text{Te}_{0.5}$. Since the same has been found in TmTe ,⁵ Tm can be concluded to be divalent in $\text{TmSe}_{1-x}\text{Te}_x$ with $x \geq 0.5$.

Irrespective of the paramagnetic behavior of these compounds at higher temperature, the susceptibility

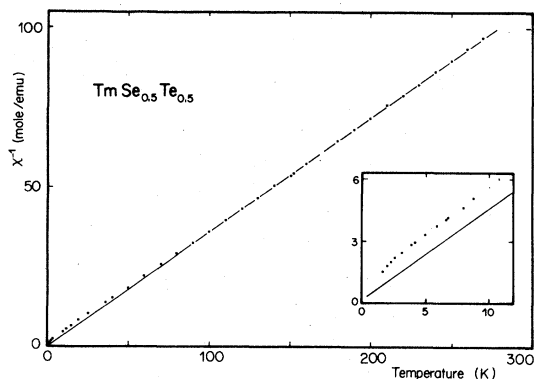


FIG. 3. Inverse magnetic susceptibility of $\text{TmSe}_{0.5}\text{Te}_{0.5}$ as a function of the temperature.

below ~ 80 K deviates markedly from the Curie line, which has to be taken as a manifestation of the crystal electric field partially raising the angular momentum degeneracy of the $J = \frac{7}{2}$ free-ion Hund's-rule ground state. Another evidence that $\text{TmSe}_{0.5}\text{Te}_{0.5}$ is not simply a paramagnet is revealed by the dependence of the magnetization on the applied field, as shown in Fig. 4 for $T = 4.2$ K and fields up to 100 kOe. If the $J = \frac{7}{2}$ ground state was not split by the crystal field the magnetization at 100 kOe would amount, according to a Brillouin function, to more than 90% of the saturation value of $4 \mu_B$ per molecule. The experimental results, however, lie far lower and cannot be represented by a Brillouin function.

The electronic structure of these semiconductors is expected to be the same as in the Sm, Eu, and Yb monochalcogenides, where it takes less energy to promote an electron out of the localized $4f$ states into the conduction band than out of the valence band.¹⁹ It is in this sense that the $4f$ level is the highest occupied state in energy and the energy gap therefore is given by the energy difference between initial and final states involving the strongly correlated $4f$ mul-

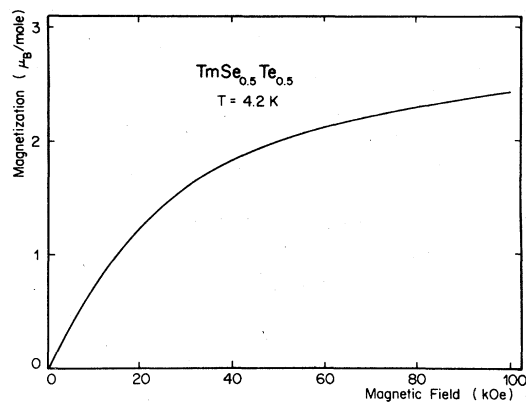


FIG. 4. Magnetization curve of $\text{TmSe}_{0.5}\text{Te}_{0.5}$ at $T = 4.2$ K.

tielectron system, and not simply between two band states. In general terms the gap E_g corresponds to $E(4f^{n-1}5d^1) - E(4f^n5d^0)$, where $5d^1$ means one electron in the conduction band, being derived primarily from the rare-earth $5d$ and $6s$ wave functions.

The crucial point for the principal understanding of many optical and electrical phenomena of these semiconductors is the fact, that the conduction band is subject to the ligand field and thus to variations of the interatomic distances. For instance, external pressure causes the upper branch of the band (in an oversimplified notation often designated " $5de_g$ ") to shift towards higher and the lower one (" $5dt_{2g}$ ") towards lower energies.²⁰ Consequently the gap E_g is narrowed when the lattice parameter is reduced either by pressure or, e.g., by anion substitution, whereby in the latter case the influence of the covalency on the band position is varied also.

This exactly applies to the replacement of Te by Se in TmTe. In the language of semiconductor physics the $4f$ states there act like donors of a density of one per cation site. When $E_g \leq 0$ each Tm $4f$ shell has lost one electron ($4f^{13} \rightarrow 4f^{12}5d^1$) and the material is metallic. The energy gap E_g may be roughly estimated from the electrical resistivity at room temperature following Eq. (1) and taking for $\rho_0 \equiv \rho(E_g = \Delta = 0)$ the measured value of $200 \mu\Omega \text{ cm}$ typically for the metallic $\text{TmSe}_{1-x}\text{Te}_x$ compounds (Fig. 1). The numerical results are given in Table I. A comparison for $\text{TmSe}_{0.17}\text{Te}_{0.83}$ with the activation energy deduced from $\rho(T)$ and for TmTe with more recent spectroscopic results¹⁸ (0.35 eV) reveals excellent agreement.

One of the reasons why the Sm monochalcogenides attracted so much interest is their pressure-induced semiconductor-to-metal transition.^{21,22} In particular the high-pressure phase of SmS is one of the earliest investigated intermediate-valent compounds. By measuring the resistivity change with pressure, the semiconducting $\text{TmSe}_{1-x}\text{Te}_x$ compounds are checked whether they are throughout similar to the other RE chalcogenides. The closing of the gap by pressure in these isostructural substances can be characterized by the difference of the deformation potentials of the states forming the gap ($4f^4$ and $5d6s$ conduction band). By definition the deformation potential Σ is

the variation in energy of an electronic state per unit lattice strain and $\Sigma' \equiv \Sigma(4f^{n-1}5d) - \Sigma(4f^n)$ has been found to be the same (~ 4.8 eV) for the Eu, Sm, and Yb chalcogenides.²¹ Experimentally Σ' is obtained by multiplying the pressure change of the gap (dE_g/dp) with the bulk modulus.

Using a piston-cylinder apparatus with ether as a transmitting fluid the resistivity has been measured in hydrostatic surroundings up to 20 kbars. The observed exponential decrease of ρ is exactly what is expected when the gap closes linearly under pressure and moreover the reduction can be evaluated quantitatively. Putting $E_g(p) = E_{g0} + (dE_g/dp) dp$ in Eq. (1) at constant temperature, dE_g/dp equals $(d \ln \rho / dp) kT$ and the numerical results are given in Table I for pressures below 10 kbar.

It is noteworthy that the resistivity decreases continuously within the observed range. Crystals, however, with the composition $\text{TmSe}_{0.5}\text{Te}_{0.5}$ crumbled above 10–12 kbar, possibly due to high internal stress, but the resistivity of the fragments turned back to the starting value at ambient pressure. The minimum pressures necessary to complete the semiconductor-to-metal transitions, as following from the gap width and its closing rate below 10 kbar, lie between ~ 20 kbar for $\text{TmSe}_{0.5}\text{Te}_{0.5}$ and ~ 35 kbar for TmTe. And indeed, this estimate is in best agreement with experiments on TmTe.²³

For the sake of completeness, some observations indicating a slightly modified closing mechanism above 10 kbar should be added: (1) the resistivity continues to drop exponentially with increasing pressure, but only \sim two-thirds as fast as at low pressure; and (2) the lattice becomes markedly weaker ($\kappa = 4 \times 10^{-6} \text{ bar}^{-1}$). This could be explained by an energy gap that is not of the same magnitude for each Tm site, being aware of the fact that the bottom of the conduction band is expected to be "warped" because different anion surroundings cause a locally variable ligand-field splitting. Further studies of this interesting problem are in progress and detailed results will be published later.

In addition the compressibility κ has been determined in the same pressure equipment by a strain gauge technique. The results (see Table I) fit into an Anderson-Nafe plot of the Sm, Eu, and Yb chal-

TABLE I. Semiconducting $\text{TmSe}_{1-x}\text{Te}_x$ ($x \geq 0.5$).

$x =$	0.5	0.77	0.83	1
Lattice constant (\AA)	6.07	6.245	6.28	6.34
Energy gap E_g (meV)	180 ± 20	240 ± 30	250 ± 30	320 ± 40
$d \log \rho / dp$ (decades/kbar)	0.16	0.18	0.21	
dE_g / dp (meV/kbar)	-10 ± 1	-11 ± 1	-12.5 ± 1	-10^a
Compressibility κ ($10^{-6}/\text{bar}$)	2.2^b	2.3 ± 0.1	2.4 ± 0.05	2.65^c
Deformation potential Σ' (eV)	4.5 ± 0.5	4.8 ± 0.6	5.2 ± 0.5	

^aFrom Ref. 21.

^bFrom extrapolation.

^cFrom Ref. 10.

cogenides²¹ meaning that compressibility and specific volume per molecule are connected via a power law. Finally also the deformation potentials are listed in Table I. The agreement with the "universal" value of 4.8 eV is the most conclusive evidence that the semiconducting $\text{TmSe}_{1-x}\text{Te}_x$ ($x \geq 0.5$) compounds are qualitatively identical with the Sm, Eu, and Yb chalcogenides. Apart from the number of 4*f* electrons, the only quantitative peculiarity is a small energy separation between the Tm 4*f*¹³ level and the bottom of the conduction band leading to energy gaps of at most 0.35 eV. The main reason for these differences, apart from the influence of the ligand field upon the conduction bandwidth, can be seen already in the atomic properties of the RE ions, namely, in their third ionization energy: the higher it is, the deeper in energy lies the "divalent" 4*f* level in relation to the 5*d* conduction band. This has been shown to hold even quantitatively for the Eu and Sm,²⁴ and now also for the Tm chalcogenides.

B. Metallic $\text{TmSe}_{1-x}\text{Te}_x$ ($0 \leq x \leq 0.2$)

This group of substances is of outstanding interest from the point of view of the mixed-valence problem. The purpose is to test a microscopic theory of the mixed-valent ground state that predicts for the case of TmSe a ferromagnetic ordering if the degree

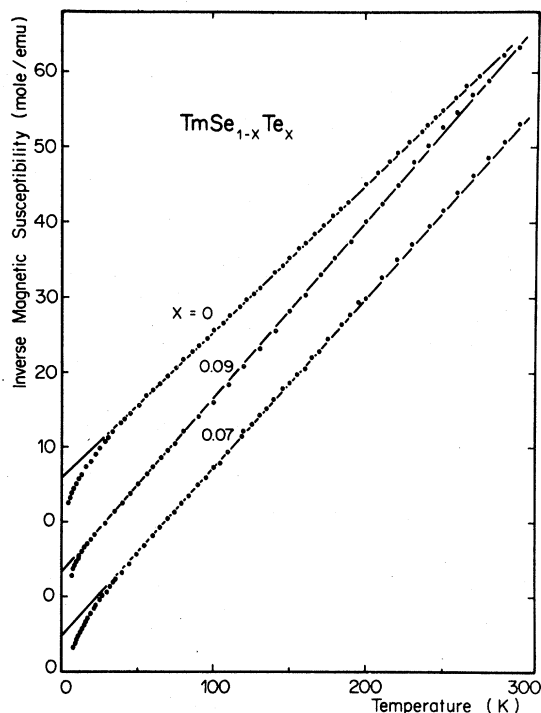


FIG. 5. Inverse magnetic susceptibility as a function of the temperature for three metallic and intermediate-valent $\text{TmSe}_{1-x}\text{Te}_x$ compounds. Note shifted zero for ordinate. (The lowest curve is for $x = 0.17$, not 0.07.)

of valence mixing exceeds a critical limit.²⁵ A verification of this challenging statement would be very important.

1. Magnetic properties

Although not only geometrical effects are to be expected when the lattice is expanded by anion substitution, the magnetic-susceptibility measurements confirm that the main purpose is served, namely, to increase the degree of valence mixing. In Fig. 5 the inverse susceptibility χ^{-1} is shown as a function of temperature for three compositions. Above ~ 40 K, a Curie-Weiss law is obeyed and from the slope of the straight line the effective magnetic moments are calculated to be 6.39, 5.85, and 5.87 μ_B /mole for $\text{TmSe}_{1-x}\text{Te}_x$ with $x = 0, 0.09$, and 0.17, respectively. The divalent character increases when Se is replaced partially by Te, in agreement with the expectations. At the same time the paramagnetic Curie temperature Θ changes from -29 K for TmSe (Ref. 15) to -15 and -17 K for the Te-containing samples and thus indicates an overall enhancement of the ferromagnetic exchange interactions at least at high temperatures. From both the lattice constant (5.86 Å) and the effective magnetic moment a valence of 2.5 can be deduced for Tm in $\text{TmSe}_{0.83}\text{Te}_{0.17}$. In this compound, therefore, the Tm ions are in a valence state with the highest possible degree of mixing.

The differences between the three compounds become obvious in magnetization measurements at temperatures below 5 K [Fig. 6(a)]. While TmSe undergoes a metamagnetic transition at $H \sim 5$ kOe ($T_N = 3$ K), the magnetization of the alloys strongly rises within the first couple of hundreds Oe up to 0.35 μ_B /mole for $x = 9$ at. % and 0.8 μ_B /mole for $x = 1$ at. %. Considering also the demagnetizing field, a spontaneous magnetization results for the two mixed-valent compounds,²⁶ the similarity of which is also reflected in Fig. 6(b), showing the temperature dependence of the magnetization in an external field

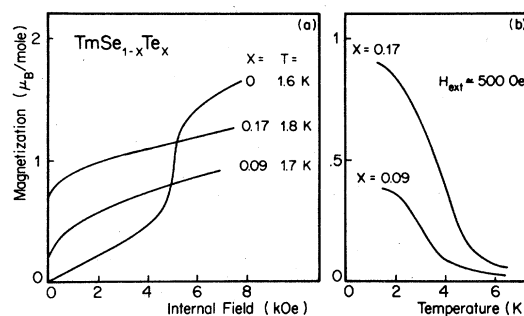


FIG. 6. (a) Magnetization curves for intermediate-valent $\text{TmSe}_{1-x}\text{Te}_x$. The two Te-containing samples are spontaneously magnetized at the given temperatures. (b) Temperature dependence of the magnetization of the spontaneously magnetized samples in an external field of 500 Oe.

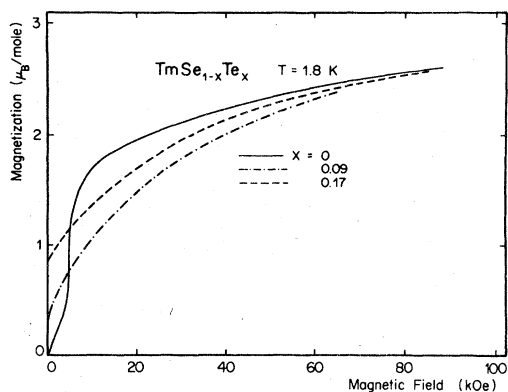


FIG. 7. Magnetization curves of $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0, 0.09, \text{ and } 0.17$) at 1.8 K.

of ~ 500 Oe. Generally these curves are suggestive of a material exhibiting spontaneous magnetization. A precise definition, however, of the ordering point is difficult because of the pronounced high-temperature tails, but 3.5 and 5 K are upper limits for $\text{TmSe}_{0.91}\text{Te}_{0.09}$ and $\text{TmSe}_{0.83}\text{Te}_{0.17}$, respectively. The lower spontaneous moment and the shift of the $M(T)$ curve towards lower temperatures demonstrate that the same mechanism as in $\text{TmSe}_{0.83}\text{Te}_{0.17}$ is also dominant in $\text{TmSe}_{0.91}\text{Te}_{0.09}$, but with a reduced magnitude. The two compounds are not simple ferromagnets, as revealed by the magnetization in higher fields (Fig. 7). It rises only slowly, does not show any trend to saturate and is even at the highest applied field in this experiment far below the free-ion maximum value of 4 and $7\mu_B$ ion for Tm^{2+} and Tm^{3+} , respectively.

We mention that a negative Curie temperature together with a spontaneous magnetization is observed in ferrimagnets. In the present case, the negative sign of Θ stems for the high-temperature behavior of the susceptibility. As has been discussed in detail for TmSe, in Ref. 15, it is an additional magnetic interaction becoming effective below 40 K, that leads to the actually observed long-range magnetic ordering.⁷ This conclusion has been drawn from the fact that exchange parameters, within the framework of a mean-field theory, could be derived consistently only if exclusively low-temperature data (various parameters of the magnetic phase diagram) have been taken into account. Any attempt, however, to include Θ as a "high-temperature" property led to contradictions.

2. Electrical transport

The electrical transport properties in homogeneously mixed-valent compounds attract special attention because they are dominated by the electronic structure in the energy region of kT around the Fermi surface, and typical anomalies are expected because of the presence of $4f$ states at E_F .

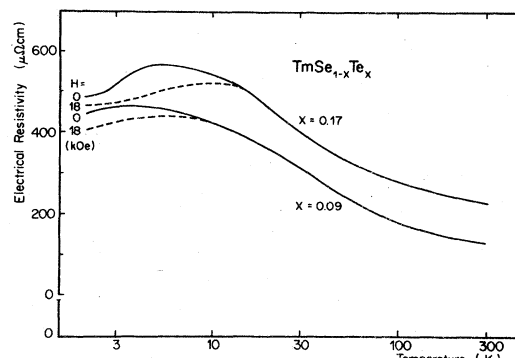


FIG. 8. Temperature dependence of the electrical resistivity for $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0.09$ and 0.17) in external fields of 0 and 18 kOe. The field and current directions are parallel to [100]. Upper and lower curves correspond to the upper and lower zero of the ordinate.

For all these metallic $\text{TmSe}_{1-x}\text{Te}_x$ compounds the absolute value of the resistivity at room temperature is about the same, lying between 200 and $250 \mu\Omega \text{ cm}$. On going to lower temperatures, it increases continuously and below 10 K some tendency occurs to level off (see Fig. 8). In TmSe the resistivity steeply rises further at and below the Néel point and becomes constant only in the mK region at as high values as some $m\Omega \text{ cm}$.^{11, 12, 15} In contrast, in samples with a partial replacement of Se by Te, ρ even decreases below the temperature where an indication

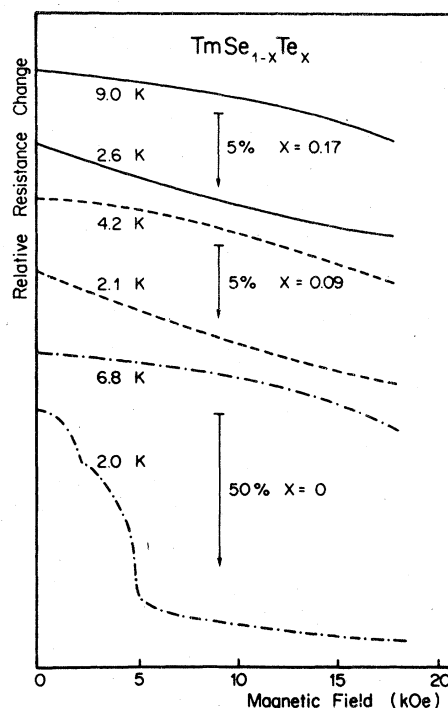


FIG. 9. Magnetic field dependence of the electrical resistivity in $\text{TmSe}_{1-x}\text{Te}_x$. Note the change in scale for TmSe. ($\vec{T} \parallel \vec{H} \parallel [100]$).

of magnetic ordering exists [Fig. 6(b)]. It is also noteworthy that the resistance of these compounds do not show the logarithmic dependence with temperature between 40 and 4 K, as it does for TmSe.

To demonstrate the magnetic origin of at least part of the resistance rise, some magnetoresistivity curves are shown in Fig. 9. For the sake of clearness only two curves are given for each compound. In the paramagnetic state the resistivity drops proportional to the square of the applied field. At the metamagnetic transition in TmSe, where the magnetic moments change from a canted antiparallel to a parallel ordering,⁷ ρ decreases considerably.^{10, 12-15} Depending on the exact chemical composition of TmSe, a reduction of ρ by more than two orders of magnitude between $H = 0$ and ~ 20 kOe has been found. The different magnetic phases in TmSe are also reflected in the curvature of the $\rho(H)$ curves. Therefore, it can be inferred also from the magnetoresistance that TmSe_{0.83}Te_{0.17} in zero field is in a similar magnetic phase as TmSe above the metamagnetic transition.

3. Discussion

A basic question to be answered at the beginning is whether TmSe_{1-x}Te_x with $x \leq 0.2$ belongs to the so-called homogeneously or inhomogeneously mixed-valent compounds. That they are mixed valent at all has to be concluded from both the intermediate value of the effective magnetic moment and the intermediate lattice constant.

A straightforward method would be to measure the isomer shift in Mössbauer spectra but this powerful method is doomed to failure in the case of Tm because the isomer shift corresponding to different valence states is much smaller than the linewidth itself.²⁷ From the whole set of the present and most recent investigations,¹⁵ however, we are supplied by strong arguments favoring an interpretation in terms of a homogeneous mixed valence.

A first one stems from the volume-pressure relation. In a semiempirical model, Penney and Melcher²⁸ described rare-earth systems with unstable configuration taking into account both elastic and electronic energies. They find a characteristic softening of the lattice in the (mixed) intermediate-valence phase due to the presence of $4f$ states at the Fermi surface, their density being much higher than the one of the $5d$ conduction band. Experimentally this has been found to be true until now for SmS-SmAs, SmS-YS,²⁹ and TmSe with variation of the chemical composition.¹⁵ The pressure dependence of the volume and hence the compressibility of TmSe_{1-x}Te_x ($x = 0$ and 0.17) has been measured using a strain gauge technique under truly hydrostatic conditions. The results are given in Fig. 10 and two features are remarkable. First, the absolute values at ambient pressures are up to 5 times higher than one would

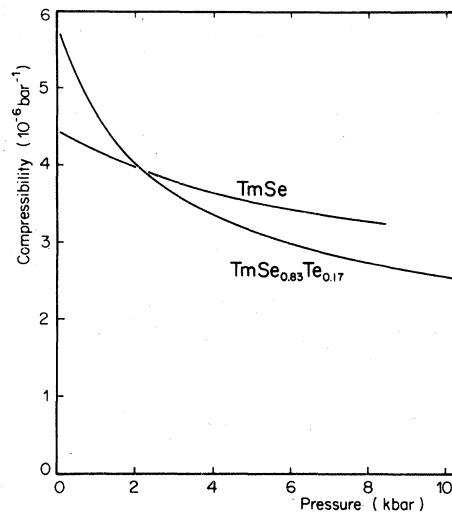


FIG. 10. Pressure dependence of the isothermal compressibility of TmSe and TmSe_{0.83}Te_{0.17} at $T = 300$ K.

expect for the same compounds containing Tm ions in pure integral-valence states. Second, a distinct decrease of κ occurs at higher pressures (it has to be noted that this behavior does not change after several pressure cycles). These facts are consistent with the assumption of homogeneously mixed-valent Tm in these compounds and a pressure-induced transition towards an integer-trivalent state. It should be recalled that a volume reduction favors the $4f^{12}5d$ (Tm³⁺) configuration rather than $4f^{13}$ (Tm²⁺).

Another indication of homogeneous valence mixing is the magnetic susceptibility. In the case of an inhomogeneous mixing of valencies it would be possible to calculate the susceptibility simply by a weighted average of the known contributions of the integer-valent ions. But it is the low-temperature part of χ ($T < 40$ K) (see Fig. 5) that cannot be reproduced by such an adding, within reasonable limits, because of its qualitatively different feature. Therefore, the anomalously high compressibility and the magnetic susceptibility indicate the Tm ions being in a *homogeneously mixed-valent state* not only in TmSe (Ref. 15) but also in the metallic TmSe_{1-x}Te_x compounds. It has to be admitted that the presence of a very small fraction of integer-valent Tm ions in the order of percent and caused by crystal imperfections cannot be excluded.

There exists no straightforward explanation for the resistance behavior of homogeneously mixed-valent compounds. For the case of TmSe, Andres *et al.*³⁰ invoked a scattering of thermally excited d electrons, from the $4f^{12}5d$ ground configuration to a virtual-bound $4f^{13}$ state, overlapping the Fermi level of the $5d$ electrons. A different explanation has been proposed by Berger *et al.*¹¹ arguing that the low-temperature resistivity of TmSe is dominated by the

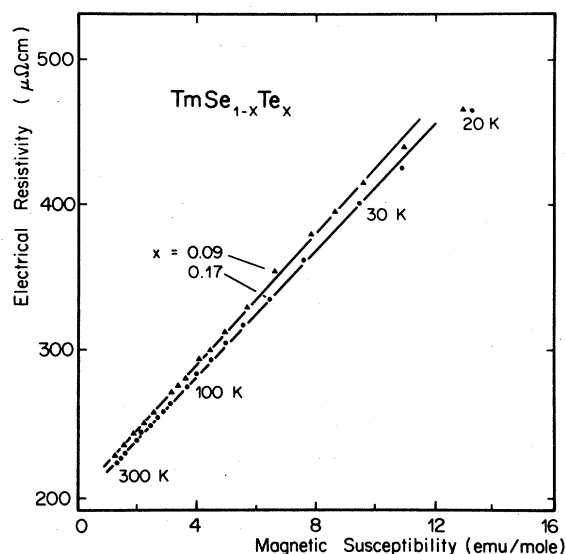


FIG. 11. Relationship between the electrical resistivity and the magnetic susceptibility of $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0.09$ and 0.17). The numbers indicate the temperature in K.

Kondo resistivities of both Tm^{2+} impurities and the Tm^{3+} host, but the assumption of an inhomogeneous valence mixing has been called in question seriously because more recent results³¹ show that the Tm ions in $\text{Tm}_x\text{Y}_{1-x}\text{Se}$ have both divalent and trivalent character even in the single-impurity limit. The negative temperature coefficient of the resistance observed (generally) below room temperature in homogeneously mixed-valent compounds has been treated by Chui.³² His model is based on the plausible assumption that both d and f states are present at the Fermi level. An attractive Coulomb force then exists between the rather mobile d electrons and the very heavy $4f$ holes that causes an excitonic interaction. The probability for this d - f electron-hole pair to be bound together increases as the temperature is lowered and diverges theoretically in a power-law manner when $T = 0$ is approached, finally leading to an excitonic insulator. To account for the reality impurities and phonons have been considered and the theory predicts at the end a straight $\log\rho$ - $\log T$ curve at intermediate temperatures which is rounded off at lowest and highest temperatures. Although this mechanism most probably plays an important part in all mixed-valent compounds at temperatures above the region where collective ground-state properties are dominant, the resistivity of $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0, 0.09$, and 0.17) is not well reproduced in its temperature behavior by the f - d electron-hole pair theory.

There is a most remarkable experimental relation between the electrical resistance and the magnetic susceptibility of the two $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0.09$ and 0.17) samples. In both substances a linear depen-

dence of ρ upon χ is established in Fig. 11 for temperatures above ~ 30 K. As follows from Fig. 5 this limit of 30 K just coincides with the beginning of the deviation of χ from the Curie-Weiss law.

C. Double-exchange model

A main purpose of the present work was to get more insight into the microscopic mechanism leading to magnetic ordering in TmSe, and in general, into the interactions between mixed-valent ions. The magnetic collective state in TmSe is outstanding among all other mixed-valent compounds because, historically seen, it was just the constant value of the magnetic susceptibility at low temperatures and the absence of a magnetic cooperative phase, that did initiate the subsequent run in mixed-valent rare-earth compound (see, e.g., Ref. 1).

Phenomenologically Tm has been recognized to be different from the other rare earths forming mixed-valent compounds because only in Tm the two integer-valent ground states ($4f^{13}3H$ and $4f^{12}2F$) carry a magnetic moment. In the others, one of the $4f$ configurations has a total angular momentum $J = 0$. This fact, now and a theoretical treatment of the interaction between two mixed-valent impurities, led Varma to the speculation that the double-exchange (DE) mechanism was responsible for the magnetic ordering in TmSe.²⁵ The concept of DE had been elaborated in connection with Ca-substituted La-manganite, a prototype of a transition-metal mixed-valent compound.³³⁻³⁶ Here, only a short outline of the basic ideas is necessary. DE is provided by a real transfer of electrons between not completely filled shells. If only the Hund's-rule (intra-atomic exchange) energy within the shell exceeds the bandwidth of the "exchanged" (Zener) electrons, a ferromagnetic coupling is established between the ionic moments. Two points are to be noted: the strength of DE increases, to first order, proportional to the number of these Zener electrons and second, double exchange is absent if the ground state of one of the valence states is nonmagnetic, or at least separated from an excited magnetic state by an energy large compared to the Zener-carrier bandwidth.²⁵

For the rare-earth mixed-valent compounds, Varma treated the following modified DE Hamiltonian (replacing the total spin by the total angular momentum)

$$H_{ij} = t_{ij} (|\vec{J}_i + \vec{J}_j + \vec{s} + \frac{1}{2}|) / (2J + 1) ,$$

where t_{ij} is the transfer integral of the extra f electron with spin \vec{s} from site i with total angular momentum \vec{J}_i to site j with \vec{J}_j . This Hamiltonian can be transformed into an equivalent finite power series in $\vec{J}_i \vec{J}_j$ (Ref. 37) and in this notation it is obvious why both \vec{J}_i and \vec{J}_j have to be different from

zero in order to become coupled via the DE.²⁵

Varma pointed out that the conditions for DE are fulfilled in the case of TmSe. The 4*f* electrons, obeying Hund's rule, acquire some mobility via the *f-d* hybridization and the resulting *f*-transfer integral (typically less than 10⁻² eV) is small compared to the intra-atomic coupling energy (~1 eV). Since the number of the 4*f* electrons that play the part of the Zener carriers is given by the degree of valence mixing and is maximal for a valence of 2.5, the relative importance of the ferromagnetic DE in TmSe is expected to be influenced by valence manipulations. In a semiempirical model, it has been predicted that TmSe would order ferromagnetically if the valence of Tm could be reduced from its value of 2.75 in stoichiometric TmSe below 2.6.²⁵ Similar conclusions have been drawn also from the experimentally found variation of the magnetic phase diagram upon variation of the valence.^{13,15} The partial replacement of Se by Te evidently allowed to drive the Tm valence even to the highest possible mixed value of 2.5 and the theoretical model can be critically compared with the experiments now.

The low-field magnetization curves [Fig. 6 (a)] showing the transition from metamagnetism (with a critical field of 5 kOe) to spin arrangements with net spontaneous magnetization, clearly demonstrate the growing importance of ferromagnetic coupling, in agreement with the expectations based on the DE model. Also another peculiar detail appears to be confirmed in the experiments: the parallel orientation of the local ionic moments is accompanied by an optimal mobility of the Zener electrons. This is exactly what is observed in TmSe_{1-x}Te_x ($x \leq 0.2$) where the electrical resistance decreases upon magnetization of the sample (Fig. 8). This happens either spontaneously (in Te-substituted compounds) or by application of an external field.

And finally, the absence of a saturation of the magnetization at high fields is also consistent with the DE picture because, as de Gennes³⁶ pointed out, the interplay of the ferromagnetic DE and other exchange mechanisms may generally lead to complicated spin structures and magnetization curves as observed in the present cases. A similar high-field magnetization behavior is also typical for other, not ordered mixed-valent compounds and therefore may well be a common feature of all these systems and not specifically related to DE. The argument, however, that this is due to the crystal-field effect acting on the 4*f*-level scheme is not convincing, since all experiments failed so far to reveal any trace of crystal-field effects as they are known from usual rare-earth compounds.¹⁰

In conclusion, all experiments on TmSe_{1-x}Te_x ($x \leq 0.2$) give strong evidence of the mixed-valent character of each of the Tm ions. In these compounds, which all order magnetically, the relative

strength of the ferromagnetic exchange interactions increases as the degree of valence mixing is increased also and it becomes dominant when the valence approaches 2.5. All this, together with the resistance behavior, is in best accordance with the hypothesis of the double-exchange mechanism as the dominant magnetic coupling between mixed-valent ions. This is the first time that a microscopic theory of the interactions in intermediate-valent rare-earth compounds appears to be supported by the experiment.

III. TmSe-EuSe

The peculiarity of this alloy system is that the rare-earth ion is exchanged and the purpose of this study is to investigate the valence state of the two kinds of cations in the mixed crystals, because in principle, both Tm and Eu can occur divalent and trivalent. In particular, we are interested in (1) the relative position in energy of the Tm and Eu 4*f* levels, (2) the valence of the Tm and Eu ions, and (3) the conduction band which is derived from the RE 5*d* and 6*s* wave functions.

EuSe is a semiconductor with an energy gap of 1.8 eV, the Eu ions are divalent and their moments order metamagnetically below $T_N = 4.6$ K.³⁸ Starting from the Tm-rich end, the Tm_{1-x}Eu_xSe crystals are still metallic at $x = 0.2$, but they become semiconducting when more Eu than Tm occupies the cation sublattice. Two illustrative examples, one of each group, will be discussed in the following.

A. Semiconducting Tm_{0.5}Eu_{0.5}Se

A first information about the valence states of Tm and Eu is revealed by the magnetic susceptibility χ .

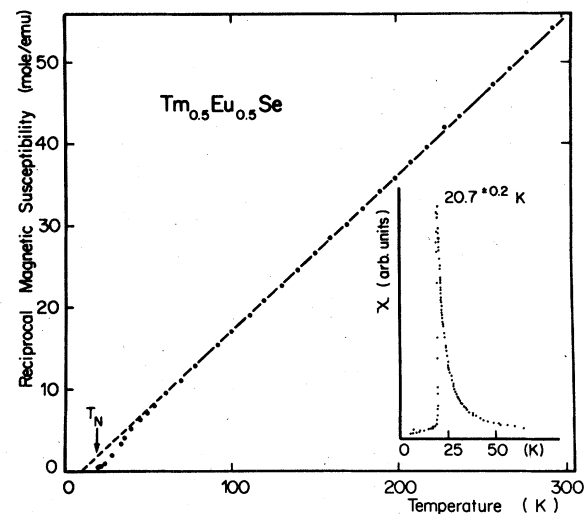


FIG. 12. Temperature dependence of the magnetic susceptibility of Tm_{0.5}Eu_{0.5}Se. In the inset, the ordering point is located at 20.7 ± 0.3 K.

Figure 12 shows the temperature dependence of χ^{-1} between 25 and 300 K. Above ~ 50 K, the susceptibility obeys a Curie-Weiss law with a positive paramagnetic Curie temperature of 9.9 ± 0.3 K and an effective moment of $6.53\mu_B$ per mole. Comparing this value with the expected one for a 1:1 mixture of pure divalent-free Tm and Eu ions ($6.35\mu_B/\text{ion}$), the divalence of both types of cations in $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ can be inferred. The same conclusion has to be drawn also from the lattice constant ($a_0 = 6.04 \text{ \AA}$). In order to test this and to locate the $4f$ levels energetically, the optical reflectivity of a cleaved face has been measured between 0.03 and 5 eV photon energy at ambient temperature. The spectrum [Fig. 13(a)] consists of a variety of peaks and they can all be assigned unambiguously to $4f^{13} \rightarrow 4f^{12}5d$ and $4f^7 \rightarrow 4f^65d$ excitations. The calculated intensities of the $4f$ final-state multiplets³⁹ and their relative position in energy⁴⁰ are indicated by the sets of bars also included in the figure. Similar to all RE monochalcogenides, the transitions into the $5d$ conduction band occur twice^{18,24,41} because it is subject to the ligand field and its density of states is grouped around two maxima. The broad peak centered at 4

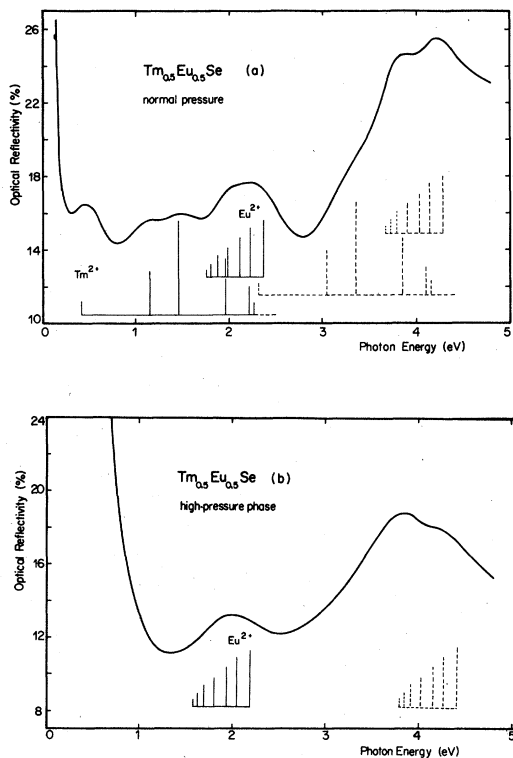


FIG. 13. (a), (b) Optical reflectivity spectrum of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ at 300 K. The bars indicate the calculated intensities of the final-state multiplets after excitations of $4f$ electrons.

eV reflects p valence-to-conduction-band excitations. The first absorption maximum, involving an electron of the $\text{Tm}^{2+} 4f^{13}$ shell, lies at 0.45 eV and as a consequence, the minimum energy to induce an electronic transition of the form $4f^{13} \rightarrow 4f^{12}5d$ does not exceed 0.2 eV. The energy gap, therefore, between the $4f^{13}$ level and the bottom of the conduction band is narrow enough to allow some electrons to be thermally excited across it. The intraconduction-band absorption of these carriers is responsible for the steep reflectivity rise at the lowest photon energies in Fig. 13(a), their density can be estimated to be a few percent per cation. Donor levels due to crystal imperfections (vacancies) might well be also a source of the conduction electrons. The $4f^7$ states of Eu^{2+} are by 1.8 eV lower in energy than the $4f^{13}$ of Tm^{2+} . Thus, it is to be expected that moderate external pressure (10–20 kbar), which lowers the bottom of the conduction band via the enhanced strength of the ligand field, closes the energy gap and leads to a valence transformation of *only* the Tm ions. The valence state of Eu, however, would remain the same unless additional pressure (~ 200 kbar) is applied to close the 1.8-eV gap.

A rough sketch of the electronic structure, as it follows from the above analysis for semiconducting $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$, is given on the left-hand side of Fig. 14.

The gross features of the electronic-level scheme are explained in the following model: in the crystalline arrangement the $5d$ and $6s$ orbitals of the Tm and Eu ions overlap and form a common conduction band of some eV width. The rather localized $4f$ shells are either occupied by 7 (Eu) or 13 (Tm) electrons and their distance in energy to the conduction band is closely related to the third ionization energy, which is of characteristic magnitude for each sort of RE ions and amounts to 23.89 eV for Tm and 25.13

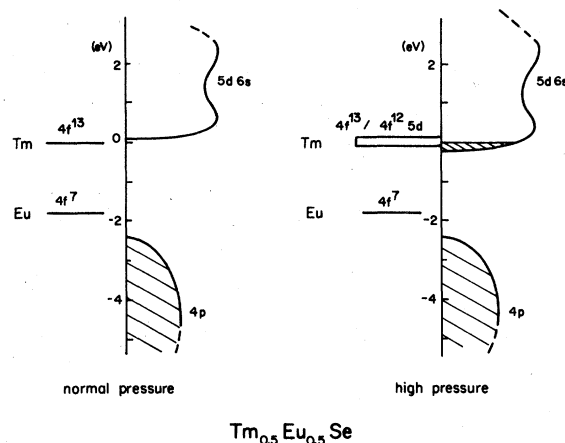


FIG. 14. Energy-level schemes for semiconducting and metallic $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$.

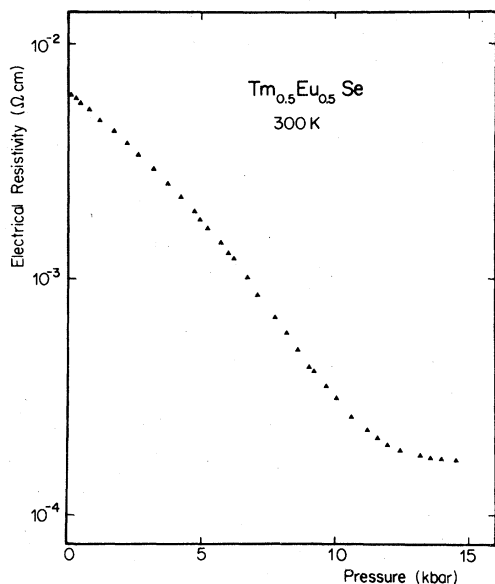


FIG. 15. Pressure dependence of the electrical resistivity of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$.

eV for Eu.⁴² A comparison reveals that 1.24 eV less energy has to be paid to remove the third electron from Tm than from Eu atoms. It is in principle this energy difference now that has been found in the optical spectrum for electron excitation from the $4f^7$ and $4f^{13}$ level, respectively, into the common $5d$ conduction band.

The small energy gap is expected to become closed by external pressure. This has been verified by measuring the electrical resistivity at 300 K as a function of hydrostatic pressure up to 15 kbar (Fig. 15). The resistance decreases continuously up to 12 kbar and tends to level off at a value of $180 \mu\Omega \text{ cm}$ at higher pressures. It is clear from the energy-level scheme that the resistance drop can only be caused by a, at least partial, conversion of the Tm ions towards trivalency. Indeed, this can be proved spectroscopically taking advantage of the fact that the high-pressure phase of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ is also stabilized at ambient conditions after mechanical polishing. A detailed report of this phenomenon will appear later,⁴³ but we note here only, that the reasons are not exactly identical with those allowing to obtain the famous golden surface of SmS. In $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ it is the large number of loading and unloading cycles that induces even in a bulk sample and under truly hydrostatic conditions a remanent volume reduction. In Fig. 13(b), the reflectivity curve of such a high-pressure surface (after polishing) is given and the comparison with Fig. 13(a) immediately reveals the important differences: (1) All the excitations involving the $\text{Tm}^{2+} 4f^{13}$ states are missing, whereas the Eu $4f^7$ excitations are still present, and (2) the sharp re-

flectivity edge at low photon energy is shifted by +0.6 eV. This is a clear spectroscopic evidence that only the Tm $4f$ states are involved in the pressure-induced phase transition. In addition volume measurements show that the Tm ions are not fully converted to the trivalent state at 15 kbar and it remains to be clarified whether they are homogeneously or inhomogeneously mixed valent. Nevertheless, the electronic structure of the high-pressure phase is schematized on the right-hand side of Fig. 14. This way to represent the Tm $4f$ states should only indicate that they lie close to the Fermi level.

The magnetic properties and the electrical resistivity are of interest for themselves and will be discussed now. In the inset to Fig. 12, the sharp peak of the magnetization, measured in an external field of 100 Oe, marks the ordering point. The temperature of 20.7 ± 0.2 K is remarkable for $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$, because firstly T_N in pure EuSe equals 4.6 K,³⁸ and secondly the density of the strong magnetic Eu moments is only about one-half the one of EuSe. A magnetization curve of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ is given in Fig. 16.

Correcting for the demagnetizing field, a spontaneous moment of $0.5-1 \mu_B/\text{mole}$ exists at 4.2 K. From the absolute value of the magnetization ($3.1 \mu_B/\text{mole}$ at 40 kOe) and its slow and sublinear increase at this field strengths, a complicated spin arrangement has to be inferred, recalling that a saturation at $\frac{1}{2}(7+4) = 5.5 \mu_B/\text{mole}$ is expected. We are left with the speculation that the few conduction-band electrons are responsible not only for the high ordering point but also for the type of ordering and that the new additional exchange interaction is due to the conduction-band electron polarization [Rudderman Kittel Kasuya Yosida (RKKY)] or bound magnetic polaron. A similar rise of the ordering temperatures has been observed for instance in doped-Eu chalcogenides⁴⁴ and more recently in the GdP-GdS alloy system⁴⁵ (RKKY).

The electrical resistivity at room temperature

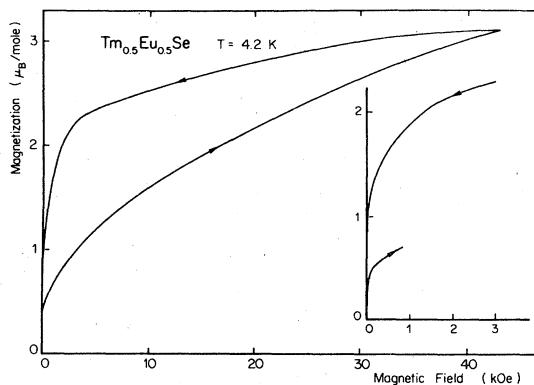


FIG. 16. Magnetization curve of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ at $T = 4.2$ K.

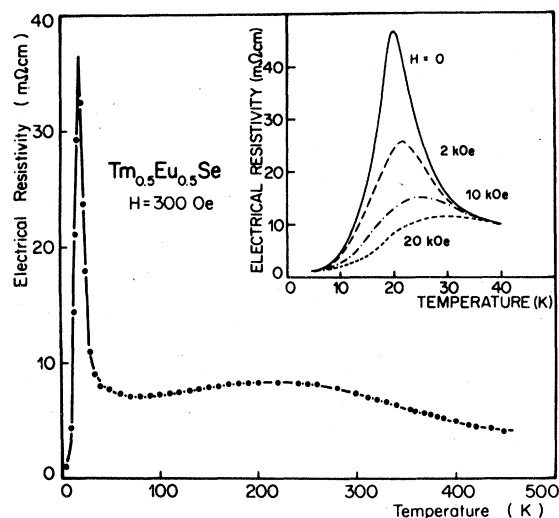


FIG. 17. Temperature dependence of the electrical resistivity of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ at normal pressure. The strong influence of the magnetic field on the anomaly at the ordering temperature is given in the inset.

amounts to $7 \text{ m}\Omega \text{ cm}$, a typical value for a semiconductor at the border to degeneracy. Its temperature dependence between 4 and 450 K is given in Fig. 17. A predominant feature is the maximum at the magnetic ordering point and the decrease in the ordered region. A nearly identical behavior is also shown by Gd-doped EuS (Ref. 46) and has been ascribed to critical scattering of electrons by correlated spins.^{46,47}

The magnetic origin of this anomaly becomes apparent when the resistance is measured in an external field (inset Fig. 17): the peak is reduced to one-half for $H = 2 \text{ kOe}$ and totally quenched in a field of 20 kOe. At higher temperature ρ first increases linearly up to 200 K, passes through a maximum and finally decreases exponentially above $\sim 300 \text{ K}$, the activation energy of this drop being $50 \pm 5 \text{ meV}$. This might be explained in principle in two different ways: (1) at low T ($T < 200 \text{ K}$), extrinsic carriers of constant concentration make normal band conduction with a positive temperature coefficient of ρ due to phonon scattering. At higher T , additional "intrinsic" electrons are thermally activated from the Tm^{2+} , $4f^{13}$ level, which is close ($\sim 0.1 \text{ eV}$) to the conduction band, and the resistivity decreases exponentially because of the increasing number of carriers. (2) The whole temperature dependence is ascribed to the motion of small polarons, which is bandlike at low T and of hopping type at higher temperatures. In the framework of this idea, the binding energy of the polaron turned out to be twice the activation energy, in the present case a rather high value of $\sim 100 \text{ meV}$. In a traditional polaron picture of electrons coupled to phonons, this would mean an unrealistic coupling constant α in the order of 100. No final distinction

between the two versions can be made at this point because further measurements, such as Hall effect, are necessary (and have been started).

In conclusion, the semiconducting example of the $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ lead to an understanding of what happens when two different RE ions, both tending to form mixed-valent compounds, occupy the same cation sublattice in the same anion surroundings: the $4f$ level of Tm and Eu is separated by 1.8 eV in energy. Even if the Tm ions undergo an electronic phase transition involving the $4f$ states, the Eu $4f^7$ level remains unaffected. A similar behavior of Yb in $\text{Sm}_{1-x}\text{Yb}_x\text{S}$ has been observed in the meantime.⁴⁸

B. Metallic $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$

In this mixed system the evaluation of the valence states of Tm and Eu is not as straightforward as in the semiconducting counterpart. The lattice constant ($a_0 = 5.76 \text{ \AA}$) and the effective magnetic moment ($7.07 \mu_B/\text{mole}$ calculated from the Curie-Weiss law of the temperature-dependent susceptibility (Fig. 18) represent intermediate values. Since the spectroscopic study of the preceding chapter revealed the $4f^7$ level of Eu^{2+} to lie 1.8 eV below the corresponding $4f^{13} \text{Tm}^{2+}$ states, a shift of the Fermi energy by $\sim 2 \text{ eV}$ relative to the $4f^7$ states would be necessary to change the valence of Eu.

Such a variation of the electronic energies is, however, not to be expected even when all Tm ions become trivalent. Therefore, we postulate that Eu is divalent also in metallic $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$. After this restriction is made, the fraction of divalent Tm character is estimated from the lattice constant and the effective moment to be $25 \pm 5\%$ and the question is still open, whether all Tm ions are in an intermediate-valence state or whether some ions are divalent and others trivalent.

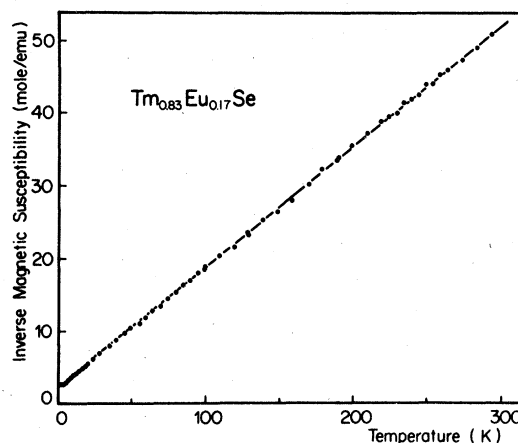


FIG. 18. Inverse magnetic susceptibility of $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ as a function of the temperature ($T_N = 4 \pm 0.3 \text{ K}$).

In all Tm selenides and related compounds with intermediate-valent Tm ions the electrical resistance rises considerably (by factors of 2 to > 10) at low temperature and only decreases in the magnetically ordered phase with net magnetization. The resistivity of metallic $\text{Tm}_{0.87}\text{Eu}_{0.17}\text{Se}$ as a function of T is given in Fig. 19 and the behavior is quite different from the described one. Above 220 K, a normal positive temperature coefficient is observed. The resistance ρ increases upon cooling between 200 and 18 K by 20% and decreases again towards lower temperature. It is just this drop of ρ below 18 K, which cannot be related to magnetic ordering ($T_N = 4$ K), and that rules out the acceptance of the same electronic structure for $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ as for homogeneously mixed-valent TmSe, namely, the presence of f states and holes at the Fermi energy. Instead, the broad hump in the resistance curve is reminiscent of TmS, Tm_5Se_6 ,^{11,30} and $\text{Tm}_{0.87}\text{Se}$,¹⁵ three compounds where the Tm ions are just at the border of valence mixing, but still trivalent. The resistance maximum has been attributed to d -electron scattering (from the $4f^{12}5d$ configuration) into the $4f^{13}$ state (of trivalent Tm) lying close to, but in the order of meV above the Fermi level. We adopt this explanation also in the present case and have to admit that some additional $4f^{13}$ states, belonging to a small fraction of divalent Tm ions, are occupied also. The divalent and therefore larger Ee ions are thought to induce a local lattice deformation and to cause therefore the inhomogeneous valence state of the Tm ions.

The magnetic susceptibility of $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ is constant below $T_N = 4.0 \pm 0.3$ K ($\theta_p = -13$ K) and from the field dependence of the magnetization at 1.8 K (see Fig. 20) an antiferromagnetic ordering can be deduced. Any attempt, however, to determine the particular type of ordering by applying a two-exchange-parameter mean-field theory is not meaningful, although formally possible, since more than one kind of magnetic ions are present in the sample.

In summary, the Tm ions in $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ are just

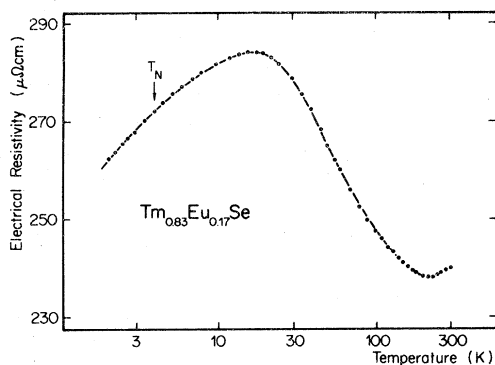


FIG. 19. Temperature dependence of the electrical resistivity of $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ on an expanded scale.

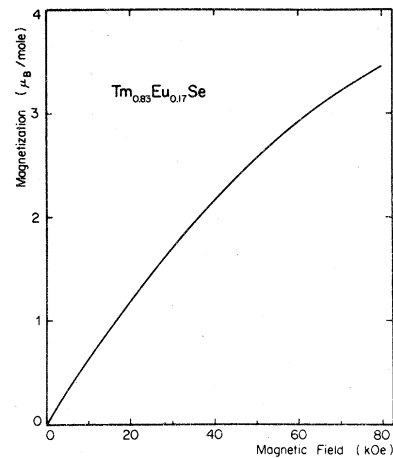


FIG. 20. Magnetization curve of $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ at $T = 1.8$ K.

on the borderline of being either divalent and/or trivalent: in $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ Tm is divalent but external pressure of only ~ 15 kbar suffices to induce a conversion of the valence towards triple plus. In the metallic $\text{Tm}_{0.83}\text{Eu}_{0.17}\text{Se}$ the Tm ions have been concluded to be predominantly in an inhomogeneously mixed-valence state because the Eu ions locally distort the lattice. On the other hand, Eu is divalent in $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ due to the high stability of its $4f^7$ configuration, being situated 1.8 eV lower in energy than the Tm $4f^{13}$ level.

III. CONCLUDING REMARKS

A summary of the results and their discussion are given at the end of each chapter and need not be repeated here. The reader is also referred to the abstract.

It is, however, worthwhile to note that new and fundamental insight into the properties of intermediate-valent RE ions and in particular their magnetic interaction could be gained, thanks to the systematic study of a specifically chosen alloy series starting out with TmSe, and permitting us to vary the intermediate Tm valence from 3 to 2.5. Among all RE mixed-valent compounds TmSe is of predominant importance because (1) both integer-valent states of Tm have a nonvanishing magnetic moment, and (2) it is not an intermetallic compound with the advantage that the only conduction electrons are the extra electrons freed from the $4f$ shell. The intermediate-valent situation can therefore be studied in its purest and most concentrated version. Although an encouraging agreement with the double-exchange model describing some magnetic properties has been found in the experiment, a coherent and universal theory of the mixed-valence state appears to be as difficult as desirable.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor P. Wachter for continuous interest, advice, and generous support of this investigation. He is also very

grateful to Dr. E. Kaldis and B. Fritzier for growing and characterizing the crystals and to H. Boppart and Dr. H. R. Ott for valuable discussions. The technical assistance of K. Mattenberger, H. J. Müller, and H. P. Staub, and the financial support of the Schweizerischer Nationalfonds is gratefully acknowledged.

*Present address: Bell Laboratories, Murray Hill, N.J. 07974.

¹Proceedings of the International Conference on Valence Instabilities and Related Narrow Band Phenomena, edited by R. D. Parks (Plenum, New York, 1977).

²C. M. Varma, Rev. Mod. Phys. **48**, 219 (1975).

³J. H. Jefferson and K. W. H. Stevens, J. Phys. C **11**, 3919 (1978).

⁴H. R. Ott, K. Andres, and E. Bucher, in *Magnetism and Magnetic Materials—1974 (San Francisco)* edited by C. D. Graham, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1974), p. 40.

⁵E. Bucher, K. Andres, F. J. DiSalvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Jr., Phys. Rev. B **11**, 500 (1975).

⁶B. B. Triplett, N. S. Dixon, P. Boolchand, S. S. Hanna, and E. Bucher, J. Phys. (Paris) **35**, C6-653 (1974).

⁷H. Bjerrum Møller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. **39**, 1021 (1977).

⁸M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. **32**, 885 (1974).

⁹B. Batlogg, A. Schlegel, and P. Wachter, Physica (Utrecht) **86–88B**, 229 (1977).

¹⁰H. R. Ott, B. Lüthi, and P. S. Wang, Ref. 1 p. 289 ff.

¹¹A. Berger, E. Bucher, P. Haen, F. Holtzberg, F. Lapierre, T. Penney, and R. Tournier, in Ref. 1, p. 491 ff.

¹²P. Haen, F. Holtzberg, F. Lapierre, T. Penney, and R. Tournier, in Ref. 1, p. 495 ff; F. Holtzberg, T. Penney, and R. Tournier, J. Phys. (Paris) **40**, C5-315 (1979).

¹³W. M. Walsh, Jr., K. Andres, L. W. Rupp, Jr., and L. D. Longinotti, in Ref. 1, p. 499 ff.

¹⁴B. Batlogg, E. Kaldis, and H. R. Ott, Phys. Lett. A **62**, 270 (1977).

¹⁵B. Batlogg, H. R. Ott, E. Kaldis, W. Thöni, and P. Wachter, Phys. Rev. B **19**, 247 (1979).

¹⁶E. Kaldis, B. Fritzier, and W. Peteler, Z. Naturforsch. A **34**, 55 (1979).

¹⁷E. Kaldis, B. Fritzier, E. Jilek, and A. Wisard, J. Phys. (in press).

¹⁸R. Suryanarayanan, G. Güntherodt, J. L. Freeouf, and F. Holtzberg, Phys. Rev. B **12**, 4215 (1975).

¹⁹P. Wachter, Rev. Solid State Sci. **3**, 189 (1972).

²⁰B. Batlogg, J. Schoenes, and P. Wachter, Phys. Rev. Lett. A **49**, 13 (1974).

²¹A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B **9**, 2513 (1974); E. Bucher, V. Narayanamurti, and A. Jayaraman, J. Appl. Phys. **42**, 1741 (1971).

²²A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. **25**, 368, 1430 (1970).

²³A. Jayaraman, E. Bucher, and D. B. McWhan, in *Proceed-*

ings of the Eighth Rare Earth Research Conference, edited by T. H. Henrie and R. E. Lindstrom (U.S. GPO, Washington, D.C., 1970), p. 333.

²⁴B. Batlogg, E. Kaldis, A. Schlegel, and P. Wachter, Phys. Rev. B **14**, 5503 (1976).

²⁵C. M. Varma, US-Japan Seminar on Physical Properties of RE Magnetic Semiconductors, Sendai, October 5–7, 1977 (unpublished) and in Ref. 1, p. 201; Solid State Commun. **30**, 537 (1979).

²⁶B. Batlogg, H. R. Ott, and P. Wachter, Phys. Rev. Lett. **42**, 278 (1979).

²⁷J. M. D. Coey and O. Massenet, in Ref. 1, p. 211.

²⁸T. Penney and R. L. Melcher, J. Phys. (Paris) **37**, C4-275 (1976).

²⁹S. von Molnar, T. Penney, and F. Holtzberg, J. Phys. (Paris) **37**, C4-241 (1976).

³⁰K. Andres, W. M. Walsh, Jr., S. Darack, L. W. Rupp, Jr., and L. D. Longinotti, Solid State Commun. **27**, 825 (1978).

³¹A. Berger, P. Haen, F. Holtzberg, F. Lapierre, J. M. Mignot, T. Penney, O. Pena, and E. Tournier, J. Phys. (Paris) **40**, C5-364 (1979).

³²S. T. Chui, Phys. Rev. B **13**, 2066 (1976).

³³G. H. Jonker and J. H. Van Santen, Physica (Utrecht) **16**, 337 (1950).

³⁴C. Zener, Phys. Rev. **82**, 403 (1951); **81**, 440 (1951).

³⁵P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

³⁶P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

³⁷M. Cieplak (unpublished).

³⁸A most recent review of the physical data on the Eu chalcogenides: P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 3.

³⁹P. A. Cox, *Structure and Bonding*, edited by J. D. Dunitz et al. (Springer, Berlin, 1975), Vol. 24.

⁴⁰G. H. Dieke, in *Spectra and Energy Levels of Rare Earth Ions in Crystals*, edited by H. H. & H. Crosswhite (Interscience, New York, 1968).

⁴¹G. Güntherodt, Phys. Condens. Matter **18**, 37 (1974).

⁴²L. R. Moss, J. Phys. Chem. **75**, 393 (1971).

⁴³B. Batlogg, H. Boppart, and P. Wachter (unpublished).

⁴⁴F. Holtzberg, T. F. McGuire, S. Methfessel, and J. S. Suits, J. Appl. Phys. **35**, 1033 (1964).

⁴⁵P. Wachter, E. Kaldis, and R. Hauger, Phys. Rev. Lett. **40**, 1404 (1978).

⁴⁶S. von Molnar and M. W. Shafer, J. Appl. Phys. **41**, 1093 (1970).

⁴⁷P.-G. de Gennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).

⁴⁸A. Jayaraman and R. G. Maines, Phys. Rev. B **19**, 4154 (1979).