

Mixed valent magnetic TmSe alloys with TmTe and EuSe

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MIXED VALENT MAGNETIC TmSe:

A THE DIELECTRIC RESPONSE

B ALLOYS WITH TmTe AND EuSe

ABHANDLUNG

ZUR ERLANGUNG

DES TITELS EINES DOKTORS DER NATURWISSENSCHAFTEN

DER

EIDGENOESSISCHEN TECHNISCHEN

HOCHSCHULE ZUERICH

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PART A

THE DIELECTRIC RESPONSE

Abstract

The optical reflectivity of TmS and of TmSe with varying degree of valence mixing has been measured in the photon energy range from 30 meV (and partially from 1 meV) up to 12 eV. Intraband absorption below about 2 eV causes the metallic high reflectivity and the metallic lustrous colour.

The anomalous excitation spectrum of $\text{Tm}_{1.0}\text{Se}$ at low energy (<0.5 eV) is attributed to the intermediate valence character of this compound, and is consistent with the model of d electrons and holes scattered from partially occupied f states at the Fermi level.

The most striking result stems from the analysis of the collective mode of the conduction band plasma: those electrons, whose partial f-character is responsible for the intermediate valence features in TmSe, participate in the "d-electron" plasma oscillation as if they had no f character at all.

The one particle excitations above ~ 2 eV are well explained in terms of transitions from the p-valence band and from highly correlated 4f states into the double-structured 5d conduction band. A comparison with XPS spectra reveals an apparent difference for the value of the effective 4f Coulomb correlation energy as determined by the two experiments and points to different final state interactions.

Introduction

The enormously growing interest in the intermediate valent rare earth compounds is based on the challenging problems and features for both theorists and experimentalists. The crucial point is the degeneracy of two electronic configurations, say $4f^n$ and $4f^{n-1}5d$, representing two valence states of the rare earth ions because of the delocalized nature of the 5d wave functions. The occupation number of the 4f shell is no longer a stable integer (a good quantum number), and a high density of states at the Fermi level results from the interaction of localized f and delocalized d electrons¹⁻³⁾. The identity of the two constituting configurations may reappear in the experimental results in different ways: the experimental response either consists of a weighted average (e.g. lattice constant and Mössbauer isomershift) or a superposition (e.g. in photo electron and optical spectra for $h\nu < 0,1$ eV) of the typical $4f^n$ and $4f^{n-1}5d$ properties. Many results, however, unambiguously point to a qualitatively new ground state in the mixed valent situation: a lack of magnetic moments at low temperature, giant linear terms in the specific heat, softening of the lattice and anomalous transport properties, just to mention some.

Among all the intermediate valent (or homogeneously mixed valent) compounds TmSe is the unique exception in so far as it orders magnetically below $3K^{4-6)$. In contrast to intermetallic mixed valent compounds, but similarly to metallic-SmS and SmB_6 , in TmSe no other conduction electrons exist than those originally liberated from the 4f shell, with the consequence that all the peculiar effects due to the configuration degeneracy can be studied in an unadulterated situation.

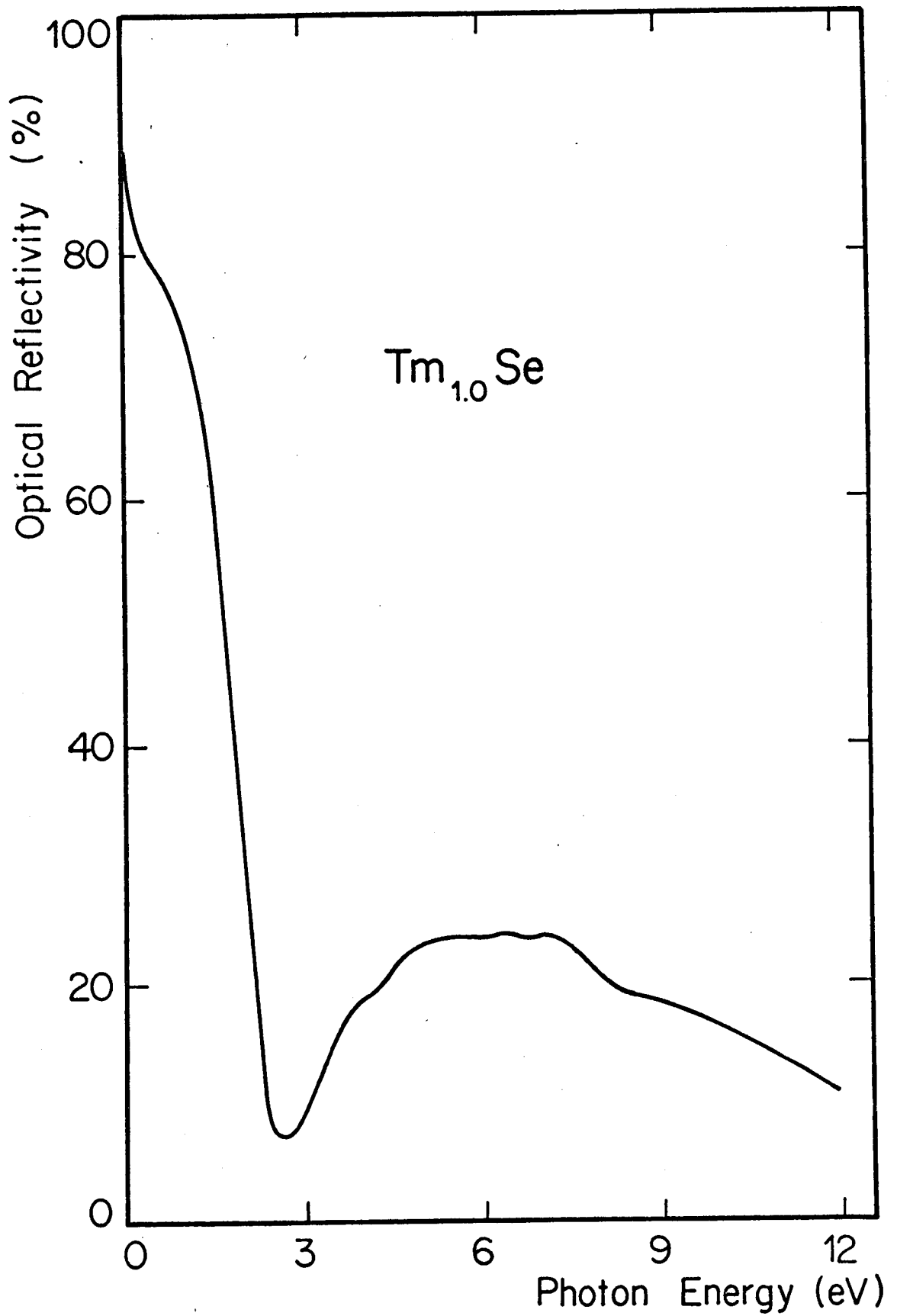
Experimentally TmSe has soon been recognized to be tricky in the sense that the chemical composition is hard to control and that the entire physical features sensitively depend upon it (7-14). After the extended and systematic study of various thermal, magnetic and transport properties the stoichiometry variation turned out to be a decisive tool to influence the Tm valence (13, 15). From the lattice constant the amount of divalent character has been found to increase from 0% in $\text{Tm}_{0.87}\text{Se}$ over 25 % in $\text{Tm}_{1.0}\text{Se}$ to 28 % in $\text{Tm}_{1.05}\text{Se}$, where the subscript indicates the molar ratio of Tm to Se. Within a given sample all Tm ions have been concluded to be in the same configuration and stoichiometric TmSe, therefore, being a homogeneously mixed valent compound with 25 % divalent and 75 % trivalent character in each Tm ion's groundstate (15). As main evidence for the homogeneous valence state in TmSe we have taken (1) the up to 4 times higher compressibility than in pure integer valent Tm and comparable RE compounds and (2) the magnetic susceptibility below $\sim 40\text{K}$ which we could not explain by an average of integer valent Tm contributions. This is supported by recent investigations of the $\text{Tm}_{1-x}\text{Y}_x\text{Se}$ alloy series where even in the single impurity limit the Tm ions have been found to be of mixed valent character (16). For stoichiometric TmSe the electrical resistivity increases steadily upon cooling from $200\mu\Omega\text{cm}$ at ambient temperature to $1.8\text{m}\Omega\text{cm}$ at 3K . Below $\sim 35\text{K}$ the magnetic susceptibility starts to deviate from its Curie-Weiss behaviour at higher temperature and indicates the growing importance of the interactions between the localized f and itinerant d electrons. This coupling is the stronger the higher the degree of valence mixing is. Finally, a metamagnetic ordering is established below 3K , and an applied field of some 5kOe induces a ferromagnetic transition. The concomitant changes of the resistance (by up to more than two orders of magni-

tude) again demonstrate the intimate connection between the f and the d electrons.

The aim of the present work is to investigate the optical excitation spectrum of an intermediate valent compound over a wide energy range. Of particular interest are (1) the behaviour at low photon energies (meV-range), (2) the collective mode of the 5 d conduction band plasma and (3) the interband excitations involving the 4f states. TmSe with varying chemical composition, together with trivalent TmS, is very well suited for this purpose because the valence of the Tm ions in these systems ranges from +3 to +2,7, allowing direct comparison between pure and mixed valent compounds.

Reflectivity measurements provide us with the dielectric response function. The depth of probing is given by the inverse absorption coefficient and typically amounts to 10^2 to 10^3 Å, meaning that the optical reflectivity measurements are not surface sensitive. The energy range used in this investigation covers electronic intraband and interband excitations and one can expect information about the position in energy of electronic states and about properties of the electron gas. The variation of the chemical composition of Tm_xSe , x being the molar ratio of Tm to Se, is the important experimental parameter also of the present work.

A first survey over the reflectivity spectra is obtained in fig. 1. Three distinct regions are obvious : metallic high reflectivity below ~ 1 eV, a steep edge between ~ 1 and $\sim 2,5$ eV and above the minimum at $\sim 2,7$ eV some less pronounced structures with a broad maximum of R between 5 and 7 eV. At a glance this spectrum is very suggestive of rare earth mono-



1 Optical reflectivity spectrum of $Tm_{1.0}Se$

chalcogenides with the cation in the trivalent state ¹⁷⁾. Because the chalcogen ion accepts only two electrons to fill the valence band derived from its p-states, a third electron remains in the conduction band and is responsible for the metallic character of these compounds. The conduction electrons form a solid state plasma giving rise to the high reflectivity at the lower photon energy range and the typical edge near the plasma resonance. At higher frequencies, the interband excitations start. The different energy ranges will be discussed separately in the following, because of the different type of information that can be deduced from them.

Interband excitations

Although the structure of the spectra is rather rich in the interband region, it would be difficult to explain it unambiguously without any experience with similar substances. Optical and photoelectron spectroscopy on semiconducting and metallic rare earth monochalcogenides, all crystallizing in the rocksalt structure, led to an universal energy level scheme of this class of compounds ¹⁸⁻²²⁾, which has been proposed originally for the semiconducting Europium chalcogenides ²³⁾. Accordingly, the valence band is derived predominantly from the Se 4p wave functions and the conduction band from the 5d and 6s rare earth states. Depending on the valency of the rare earth ion, the crystal is semiconducting if the rare earth ion supplies just the two electrons to fill up the valence band and it is an ionic metal with one conduction electron per formula unit when the rare earth ion is trivalent. Besides valence-conduction band excitations also electron promotion out of the $4f^n$ shell into

the empty conduction states is expected in the same energy range. The $n-1$ 4f electrons left behind can also be excited and the energy separations between these multiplets are characteristic and well known for each number n of 4f electrons²⁴⁾. This "fingerprint-like" uniqueness of the multiplet spectra makes it easy to determine the occupation number of the 4f shell.

Here we take the opportunity to clarify what kind of excitations involving 4f electrons are to be expected in homogeneously mixed valent compounds. Since we are dealing here with photon energies in the order of eV and the hybridization energies between 4f and 5d states are two or three orders of magnitude smaller, we are in the so called "high frequency" region²⁵⁾. This means, that two distinct sets of multiplets appear, corresponding to $4f^n$ and $4f^{n-1}$ initial configurations, as if two species of Tm ions were present in the sample. The spectra then consist of a superposition of integral-valent ion spectra with the intensities given by the amount of divalent and trivalent character in the intermediate valent ground state. Therefore, it has to be emphasized once again, that both photoelectron and optical (in the eV range) spectroscopy are indeed able to detect a valence mixing, but neither experiment can distinguish between a homogenous or an inhomogeneous mixing. For that purpose, experiments are needed involving measuring energies comparable or smaller than both the hybridization energy and the energy difference of the two electronic configurations under discussion. The 5d states, together with the 6s ones, form the conduction band but still experience the ligand field. In octahedral surroundings and in the simplifying framework of the point charge model the energy difference between the atomic triplet t_{2g} state at lower and the doublet e_g at higher

energy is proportional to the fourth power of the mean radial extension of the 5d wavefunctions and is inversely proportional to the fifth power of the distance to the surrounding point charges. Also in energy band calculations the density of the conduction band states is centered around two maxima²⁶⁻²⁸). And, indeed, the optical spectra of all the Sm, Eu, Gd and Yb monochalcogenides clearly reveal the double structure assigned to the 5d band splitting^{18-20, 29,30}). It is now quite surprising how well these experimentally found splittings can be parametrized by the point charge formula which would never be expected to apply so well for this case.

$$\Delta = d \frac{\langle r_d^4 \rangle}{R^5} \quad (1)$$

Taking the same value for the only parameter d (1.1×10^4 eVÅ) the calculated Δ agrees within better than 10 % with the observations. For the rare earth ion - chalcogen separation R it is obvious to take half of the lattice parameter a_0 . The appropriate choice, however, of the 5d shell radius r_d is less clear. Electron wave functions for the rare earths have been calculated from modified nonrelativistic Hartree-Fock and from relativistic Dirac-Slater equations and both methods lead to practically identical results³¹⁻³⁴). For our purpose it is important to note that the maximum of the 5d electron charge density and the empirical ionic radius coincide within a few percent. Therefore we replace the 5d shell radius by the ionic radius, which is experimentally given, applying a hard sphere model, by the lattice constant and the chalcogen ion radius. Numerically, this reads

$$\Delta (\text{eV}) = 1.1 \times 10^4 \frac{\left(\frac{a_0}{2} - r_x\right)^4}{a_0^5} \quad (2)$$

where a_0 and r_x are measured in Å. Optimal over-all agreement with the experiments is achieved, putting the chalcogen ion

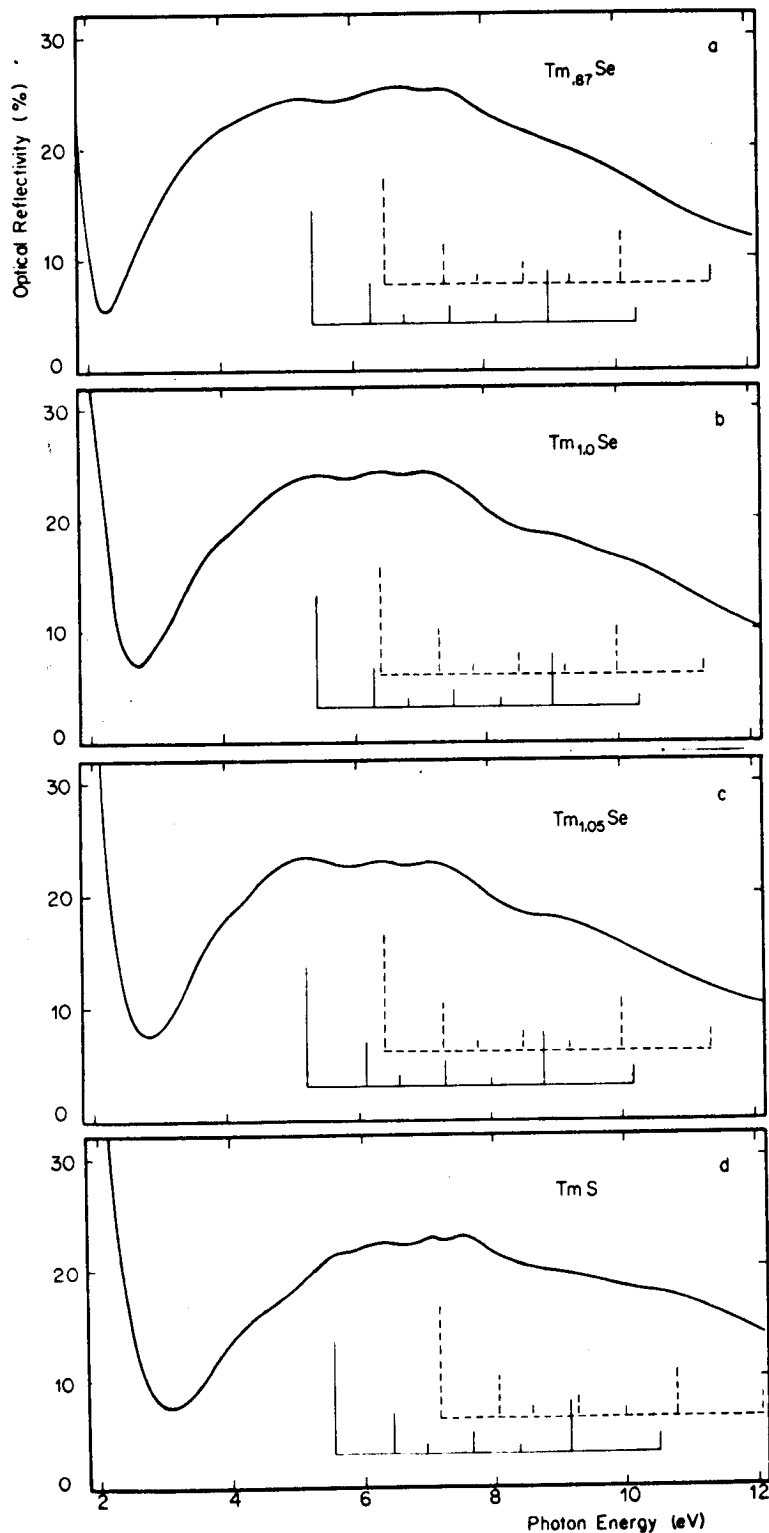
radius $r_X = 1.86 \text{ \AA}$, 1.98 \AA and 2.15 \AA for $X = S, Se$ and Te , respectively. As a manifestation of the growing covalent bonding character on passing from the sulfides to the tellurids the chalcogen ion radii used in (2) deviate very slightly (by less than 3 %) from the ones deduced from highly ionic compounds. (1.84 \AA , 1.98 \AA , 2.21 \AA). According to the above parametrization of the experiments (2), the splitting Δ for the Tm chalcogenides can be predicted to be $1.4, \sim 1.0, \sim 1.0$ and 1.2 eV for $TmS, Tm_{0.87}Se, Tm_{.98}Se$ and $Tm_{1.05}Se$, respectively.

Simultaneously with the removal of an electron out of the $4f^n$ shell by an optical absorption process, the remaining $n-1$ electrons can be excited giving rise to the typical $4f^{n-1}$ multiplet structures. Their energy separation is well known from optical absorption and luminescence studies ²⁴⁾. The probability to find the $4f^{n-1}$ final state in one of these excited multiplets is given by the coefficient of fractional parentage ³⁵⁾.

In the case of homogeneously mixed valent TmSe the electronic $4f^{13}$ and $4f^{12}5d$ configurations are equivalent in energy. In analogy to the results of the X ray photo electron spectroscopy ⁷⁾ in the optical excitation spectrum we expect $4f^{13} \rightarrow 4f^{12}5d$ and $4f^{12} \rightarrow 4f^{11}5d$ transitions which are separated by $\sim 6 \text{ eV}$ due to $4f$ Coulomb correlations. The former group of multiplets, however, hardly can be observed in the reflectivity spectrum since the conduction band electron plasma causes a very high reflectivity below $\sim 2.5 \text{ eV}$ and masks therefore these rather weak interband-type excitations. The separation in energy between the $4f^{11}$ final states is given by those of trivalent Er, having also 11 electrons in the $4f$ shell, but in order to account for the additional nuclear charge in Tm, the

energy scale is expanded by 10 %. Considering also the splitting of the 5d states by the ligand field into two subgroups, we expect all $4f^{12} \rightarrow 4f^{11}5d$ transitions to occur twice.

A whole set of optical excitations with fixed relative energies is now predicted and ready to be compared with the experiments in fig. 2 a-d. Solid and broken lines correspond to final states with the d-electron being either in the lower and higher part of the 5d-band. The only free parameter is a shift on the absolute energy scale. A fair over-all agreement is obtained choosing the minimum $4f^{12} \rightarrow 4f^{11}5d$ excitation energy as given in Tab. I. For the sake of comparison and completeness the reflectivity spectrum of the non mixed valent TmS is shown in fig. 2d and the agreement between predictions and measurements is as satisfactory as for the Tm_xSe spectra. Besides these $4f$ $5d$ transitions also excitations from the p like bonding valence band into the conduction band occur and actually give rise to the rather steep increase of the reflectivity above the minimum which is in the different compounds located between 2 and 3 eV. Any determination of the valence band width from such a spectrum is ambiguous because it would reveal only a lower limit. From photo electron spectroscopy the width of the p valence band has been deduced to be about 8 eV in TmSe³⁶⁾ and 6 eV in TmTe³⁷⁾. Comparing other experimental findings on both semiconducting and metallic rare earth monochalcogenides^{38,39)} and considering the universality of the band structure of all NaCl structure compounds⁴⁰⁾ a valence band width of 5.5, 5 and 4 eV is expected, with about 1 eV uncertainty, for TmS, TmSe and TmTe, resp. The discrepancy of more than 50 % is surprisingly high and needs further clarifications, since there is no reason known why the valence bands just in the Tm chalcogenides should be extraordinary wide.



2 Part of the optical reflectivity spectrum of Tm_xSe ($x=0.87, 1.0, 1.05$) and TmS . The vertical bars indicate the calculated position and strengths of final state multiplets after $4f^{12} - 4f^{11}5d$ excitations. (Intensities should be compared only within each subgroup). Full and broken lines correspond to final states with the $5d$ electron either in the energetically lower or higher part of the conduction band.

The minimum energy necessary to promote an electron from the valence into the conduction band is given by the energy difference between the top of the valence band and the lowest unoccupied conduction states. Variation of the chemical composition of Tm_xSe is reflected not only in the degree of valence mixing but also in the density of the conduction band electrons. Similar effects occur also in GdS and $GdSe$ with varying stoichiometry and have been studied extensively¹⁷⁾. As a consequence of the different filling heights of the conduction band the $p \rightarrow d$ transitions start in $Tm_{0.87}Se$ by ~ 0.4 and ~ 0.5 eV lower in energy than in $Tm_{1.0}Se$ and $Tm_{1.05}Se$, resp. In TmS , however, it is the position of the p band that shifts the $p-d$ onset by $+ 0.7$ eV relative to $TmSe$.

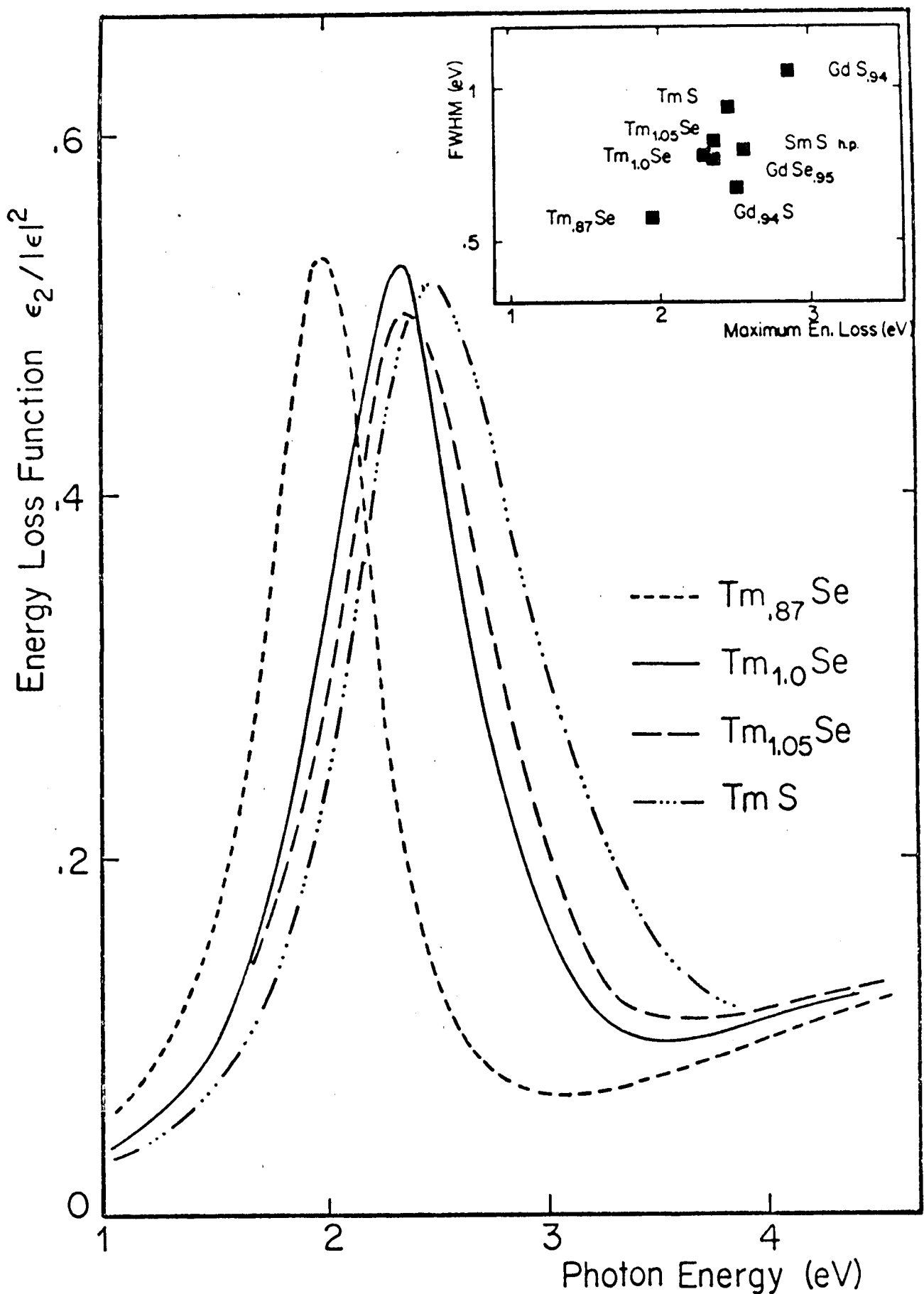
Conduction band plasma

The predominant structure of the TmS and $TmSe$ reflectivity spectra is the edge at 2 eV. This sudden drop from more than 70 % to less than 10 % within a narrow energy interval is characteristic for the metallic rare earth chalcogenides and is due to a plasma oscillation interfering with interband excitations. This plasma oscillation mode is not directly related to the "free 5d electron" behaviour. Its resonance character becomes obvious in the energy loss of electrons shot through the material. Although the energy loss function is closely related to the system's response to longitudinal perturbations, its wavevector-integral value can be calculated from the optically determined transverse zero-wavevector dielectric function

$$\epsilon(\omega, q=0) = \epsilon_1 + i\epsilon_2$$

From the measured reflectivity spectrum $\epsilon(\omega)$ has been evaluated

with the help of the Kramers-Kronig relation ⁴¹⁾ which connects real and imaginary part of a linear and causal response function. The imaginary part of the energy loss function is then obtained as $-\text{Im}(\epsilon^{-1})$ and shown in fig. 3. The energy of the conduction electron plasma resonance in the presence of the interband ($f \rightarrow d$, $p \rightarrow d$) excitations is given by $\epsilon_1(\omega) = 0$ and the peak maxima in fig. 3 are shifted only very little from this energy (by $\sim 0,05$ eV) due to damping effects. In the most simplified model to describe the free electron behaviour, the Drude model, only one frequency independent scattering parameter is used to describe both the collective mode damping and the zero frequency electrical conductivity. This assumption leads to a close relationship between these two experimentally accessible quantities, which, however, is not fulfilled in the metallic rare earth monochalcogenides. But there exists the general trend that the energy loss peak is the wider the higher in energy it occurs. That is exactly what one expects from a plasma excitation in the presence of interband transitions. Whereas the collective mode of a translationally invariant gas of electrons suffers no damping in the long wavelength limit ($q = 0$), its behaviour is markedly altered in the periodic crystal potential. If then the plasma resonance lies below the onset of the interband transitions, their pure real dielectric constant shields the electronic interactions and causes only a reduction of the resonance energy. If, however, the plasma mode and the interband excitations coincide in energy the collective mode is not only shifted in its energy but is also damped additionally. Accordingly, the plasma resonance width and the strength of the interband absorption are expected to be correlated.



3 Imaginary part of the energy loss function as deduced from optical data, demonstrating the resonance character of the coupled plasma-interband excitation. The insert correlates the energetic position of the maximum with the width for comparable metallic rare earth compounds, and indicates the decay of plasmons via one particle interband excitations.

As shown in the insert to fig. 3, this plasmon decay channel exists at least in the Gd- and Tm-sulfides and selenides since in these compounds the interband absorption steadily increases in the energy range under consideration.

It would be of basic interest to know the plasma resonance frequency ω_p in absence of interband excitations because it carries the important information about the electron gas density and the electron's effective mass. In a metal ω_p is generally given by the integral of the electron velocity over the Fermi surface. In the case of a spheric Fermi-surface it reduces to the well known formula

$$\omega_p = (Ne^2 4\pi) / m^*$$

where N and m^* denote the electron density and their effective mass respectively. Band structure calculations for the Eu- and Sm-monochalcogenides²⁶⁻²⁸⁾ agree in showing a parabolic minimum of the conduction band, about 1,5 to 2 eV deep and located at the X point in the Brillouin zone. One can estimate that the filling of the conduction band with one electron per cation results in an occupation of only the parabolic part, since photoelectron spectra indicate the conduction band to be filled up to $\sim 1,5$ eV³⁹⁾. This is some justification to treat the conduction electrons in the metallic rare earth monochalcogenides to a good approximation as quasi-free electrons with an effective mass m^* .

In the optical experiment we measure the response of a coupled system of interband and intraband excitations but now, only one component is of interest, namely that of the quasi-free electrons. Without any further information it would not be

possible to make a separation between both kind of excitations but the deep reflectivity minimum (fig. 1,2) allows to perform the decomposition in the present case. This minimum comes about because the quasi-free electrons at lower and the interband transitions at higher energies are only weakly absorbing in the overlapping energy region. The practical decoupling procedures are based on the additivity of the dielectric functions. A first method is to assume only quasi-free electron absorption at the lowest photon energies and to fit a model dielectric function to the experimentally determined $\epsilon(a)$. Usually, the simplest approach is the Drude model including two parameters: the plasmon frequency and an energy independent electron damping constant, the energy independence of the latter being a weak point. In a second procedure, one takes advantage of the negligible absorption of the quasi-free electrons compared to the interband transitions above a certain energy, which is given by the minimum in the absorptive part $\epsilon_2(\omega)$ provoked by the reflectivity minimum close to the edge.

Using the second decomposition method for $\epsilon(\omega)$ ¹⁷⁾ the plasma frequencies ω_p of the quasi-free electron system alone have been calculated and are given in Tab. I. The next step is to derive the electron density N provided the effective masse m^* is known. In the detailed study of LaS, GdS and GdSe the exactly same decoupling method has been applied and together with the carrier density as known from Hall-effect data the effective mass m^* in (3) has been determined to 1,3 and 1,65 times the free electron mass m_e for the sulfides and selenides, resp. ¹⁷⁾. The replacement of Gd by Tm in these compounds causes a lattice contraction of only less than 2 % and the band structure is expected to change only very little. Consequently

the same effective mass m^* as for the Gd compounds has been taken for the Tm compounds. The electron densities determined this way experimentally are listed in Tab. I and will now be compared with expected ones.

The main question to be answered is whether in mixed valent TmSe the number of electrons participating in the conduction band plasma oscillation is simply one per cation or whether it is given by the amount of trivalent character in the mixed valent ground state. The theoretical density can be calculated starting with the lattice constant and considering the actual occupation number of the cation sites, which is experimentally known by the density of the material and its chemical composition^{42, 43}). An other correction is necessary because of the variation of the Tm to Se ratio. Since two electrons per Se are needed to fill up the p-valence band, in Tm deficient samples two electrons per missing Tm are drawn away from the conduction band reducing the number of conduction electrons per present Tm. The reverse is expected to occur in the Se deficient samples ($x > 1$). Taking into account these corrections and postulating that the number of collective electrons coming from the Tm ions is given by the Tm valency as deduced from the lattice constant (Tab. I) the theoretically expected conduction band plasma density can be calculated and is given in Tab. I. A comparison with the experimental values reveals an excellent agreement for TmS and Tm_{0.87}Se, the two compounds with pure trivalent Tm ions. Although the few assumptions based on analogy to very similar substances are reasonable for themselves, they now appear to be justified again.

In the mixed valent counterparts, however, the experimental electron densities are up to 30 % higher than the expected ones.

These significant differences are immediately removed if, irrespective of the valence information from the lattice constant, a valence of +3 is used to calculate the densities. The new modified theoretical densities now are in best accordance with the experiments. This is the most important and striking result of the present investigation. It sheds new light on the nature of the "extra-electron" which plays the dominant part in forming the mixed valent ground state, symbolized as $4f^{13} \rightarrow 4f^{12}5d$. On the one side, its partial 4f character gives rise to all the typical mixed valence phenomena, such as for instance intermediate lattice constant, intermediate effective magnetic moment, enhanced compressibility and XPS spectra consisting of two sets of 4f final state multiplets. On the other hand, the extra electron seems to participate in the plasma oscillation as it had no 4f-character at all. At this point, a comparison with two similarly homogeneously mixed valent compounds is necessary. In metallic SmS, the analysis of the optical data revealed a density of 5d conduction electrons, participating in the plasma resonance, of 0.92 el/Sm and has been found to agree rather well with the Sm valence of 2.85 deduced from the lattice constant²⁰⁾. But now being aware of the present results on TmSe, the value of 0.92 might as well be interpreted to be close to 1 and therefore not to be in contradiction to the most recent findings. In the case of the other example, SmB₆, the plasma density has not been evaluated⁴⁴⁾, but a first comparison of its optical reflectivity spectrum with the one of LaB₆⁴⁵⁾ leads to the conclusion that the carrier density is within ~10 % the same in both compounds. The difference, however, is expected to be very pronounced, since an intermediate valence of 2.6 has been reported for Sm in

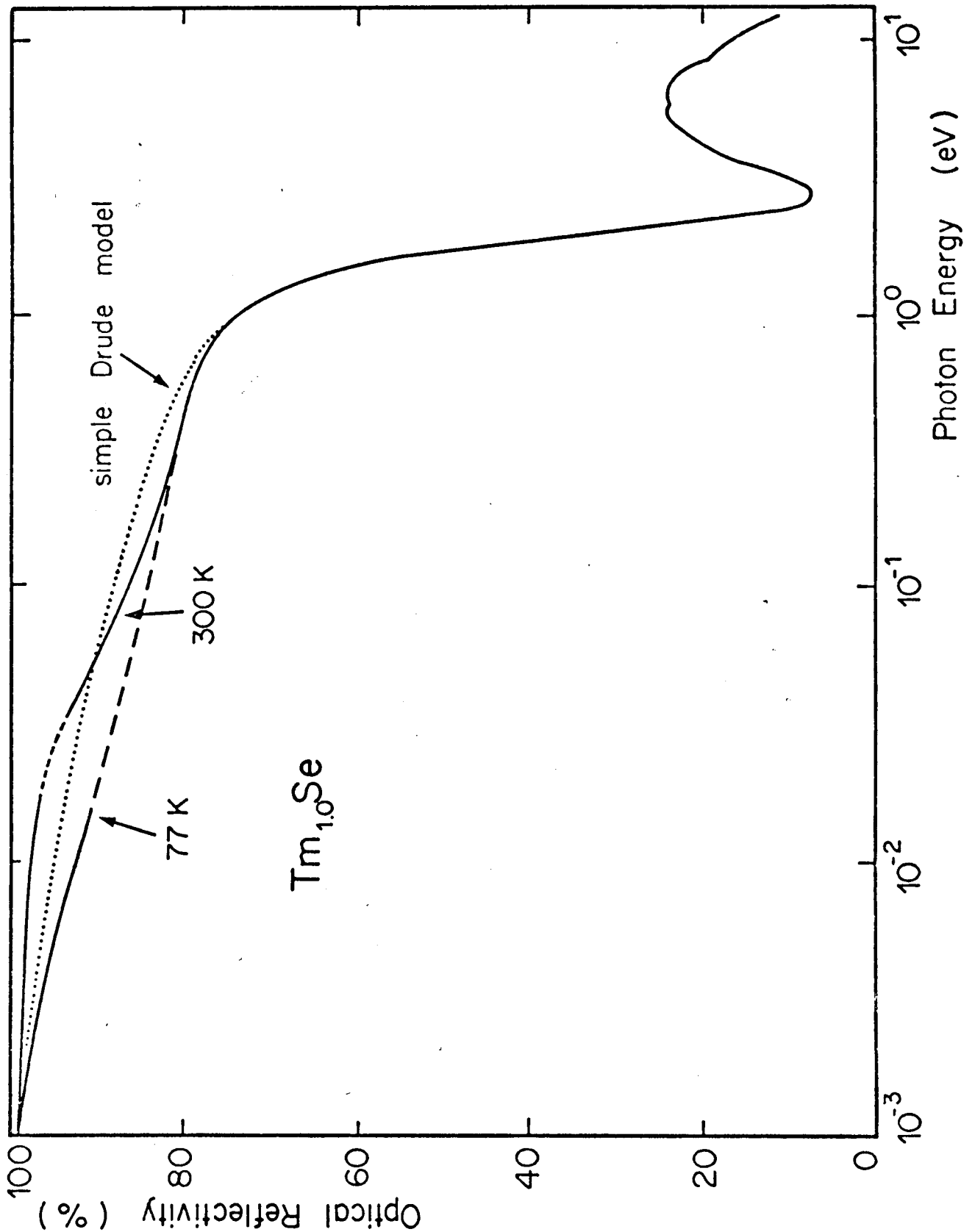
in SmB_6 (46-48), whereas La is integer trivalent in LaB_6 . In summary, the "extra" electrons appear to behave anomalously with respect to the conduction band plasma excitation not only in TmSe , but also in the two very closely related mixed valent compounds metallic SmS and SmB_6 .

In the above comparison, an other mixed valent compound, CeN , has not been taken into consideration on purpose, since several indications exist for an overlapping of the valence with the conduction band (49,50). This presence of a third kind of electronic states, in addition to f and d states, creates a totally different possibility of hybridization with so far not defined influence upon the valence mixing. At least the normal metallic temperature dependence of the electrical resistance (51), in contrast to the strong increase of ρ at low temperature in TmSe , SmS and SmB_6 , might be caused by the semimetallic character of CeN .

Low energy excitations

As mentioned above the optical reflectivity of TmSe is metallic high below about 1 eV photon energy, and in usual metals an interpretation in terms of only intraband absorption is appropriate. In the intermediate valent TmSe , however, it is worthwhile to investigate just the low energy range because only very little is known about the low lying excitations of a mixed valent compound.

In Fig. 4 the reflectivity of a polished $\text{Tm}_{1.0}\text{Se}$ sample is shown on a semilogarithmic scale for photon energies above 1meV (52).



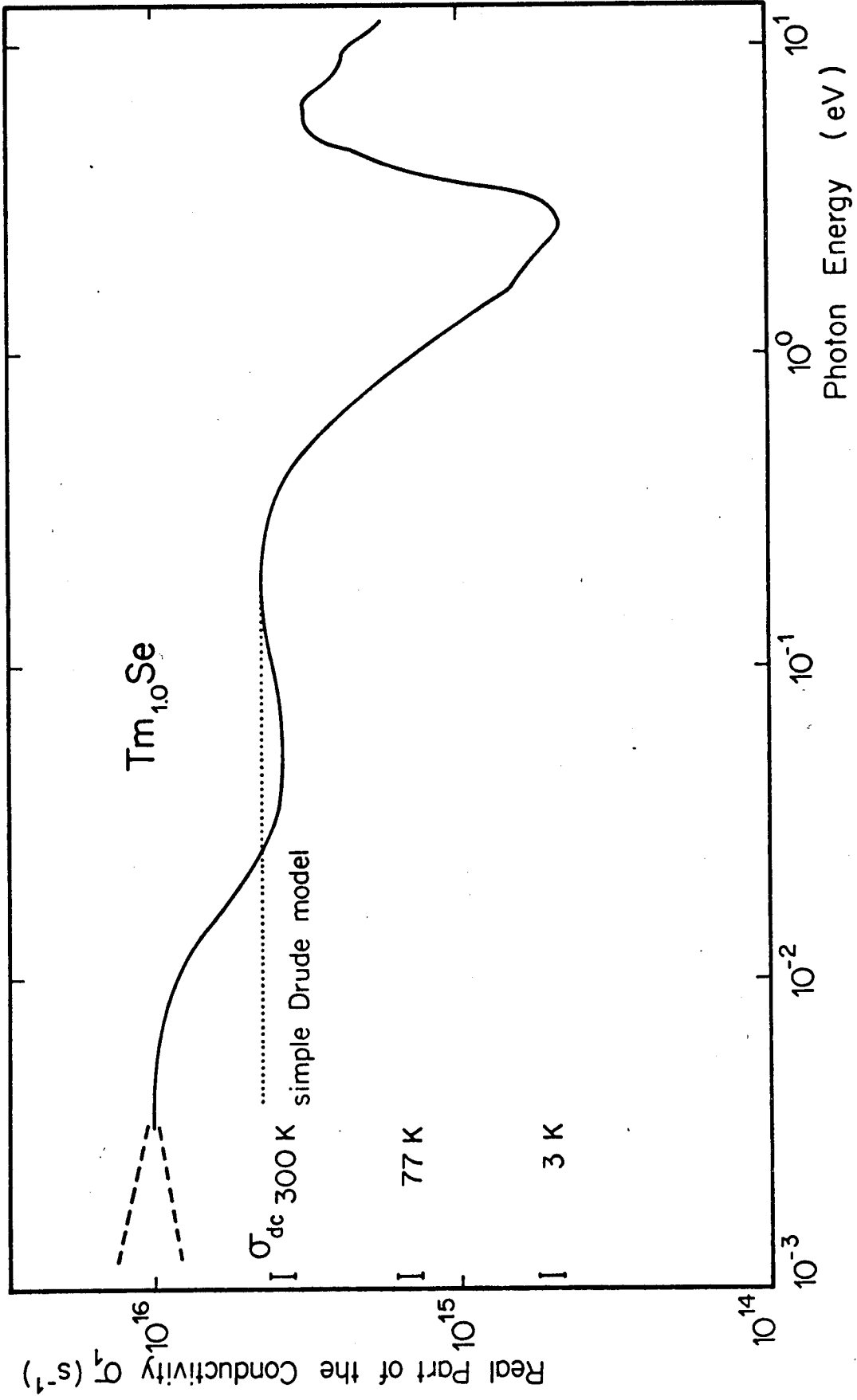
4 Optical reflectivity of intermediate valent $Tm_{1.0}Se$. The full curve represents the measurement and the broken lines are interpolations. The dots correspond to a simple Drude behaviour for an ordinary metal.

Polishing the crystal is indispensable since in the absolute measurements of the reflectivity any intensity loss due to surface scattering has to be avoided. The influence of this mechanical treatment has been checked in the eV-range and no qualitative changes other than a small shift of the reflectivity minimum at 2,7 eV by less than 0.1 eV could be detected.

For the sake of comparison the dotted line in fig. 4 represents the reflectivity spectrum of a model "Drude metal" whose parameters are obtained by fitting the behaviour close to the edge. The anomalies of TmSe are now obvious: whereas R of TmSe in the tenth eV range is lower than of the model metal, it exceeds the dashed curve below ~ 30 meV.

The quantitative discussion will be based on the frequency dependence of the conductivity, whose real part $\sigma_1(\omega)$ equals $[\omega \epsilon_2(\omega)]/4\pi$ and is displayed on a double logarithmic plot in fig. 5. Recall, that $\sigma_1(\omega)$ is just a measure of the absorption of the electromagnetic wave. The uncertainty at the low frequency limit in fig. 5 is caused by the different extrapolations of the reflectivity towards zero photon energy, a procedure necessary to perform the Kramers-Kronig analysis.

The minimum of σ_1 at ~ 2.6 eV separates the interband transitions, as discussed above, from the intraband excitations. In a well behaved metal, the conductivity below the minimum would increase towards lower frequency as it does also in TmSe and then tend to level off and would finally reach the d_c limit. Apparently, $\sigma_1(\omega)$ of TmSe markedly deviates twice from the simple



5 Real part of the frequency dependent conductivity. The dotted line indicate a simple Drude behaviour. The dc values of σ (taken from a 4-probe-measurement.....) are also given for various temperatures.

Drude model: σ_1 is too small around 0,05 eV but by a factor of 2 higher in the meV range. Experimentally known is also the dc-conductivity ($4,3 \times 10^3 \Omega^{-1} \text{cm}^{-1} \triangleq 3,9 \times 10^{15} \text{sec}^{-1}$), determined by a 4-probe technique and indicated in fig. 5. In order to join the dc value, σ_1 therefore has to drop again at still lower frequencies than covered in the present experiment. Besides the room temperature behaviour of the dielectric response, also its variation at lower temperature is of interest, because the dc resistivity continuously increases upon cooling. The interaction between the d- and f-electrons is presumed to be the reason and its strength is expected to be comparable with the photon energies used in the present work. In fig. 4 the optical reflectivity is indicated also for $T = 77 \text{ K}$. The following statements based on this 77 K curve are not to be taken quantitatively because of the experimental uncertainty in the intermediate energy range (0,02 to 0,6 eV) which had to be bridged by a smooth interpolation. The main conclusion, however, is not affected: the reflectivity at 0,02 eV and 77 K is by 7% lower than at 300 K and appreciably smaller than the one of a Drude model. As a consequence also the conductivity σ_1 at that frequency drops below the model behaviour and is therefore in agreement with the decrease of the dc conductivity. Obviously the dielectric response of homogeneously mixed valent TmSe deviates from the Drude model below the tenth-eV range and it is also worthwhile to note that the anomalous dc behaviour is reflected in the dielectric response at such high energies. Anomalies in the optical spectrum at low energies have been observed in two other well established mixed valent compounds: SmB_6 ⁵³⁾ and "metallic" SmS ⁵⁴⁾. Some peculiarities in the

EuB_6 spectrum have been interpreted with a small degree of valence mixing ⁵⁵⁾, but the sample preparation is a delicate problem and according to most recent results Eu now appears ⁵⁶⁾ to be pure divalent in EuB_6 .

The dielectric response spectrum of TmSe will be critically compared with some theoretical work explicitly dealing with intermediate valent compounds. In a first model T. Kaplan et al. ⁵⁷⁾ discuss the properties of the Sm-chalcogenides based on an "essentially excitonic" picture of most of the 5d-electrons in the high pressure ("metallic") phase of SmS. Whereas only ~ 0.1 5d electron per Sm occupy free-electron states, the other remain localized. The optical response will then consist of two ordinary Drude-type intraband contributions corresponding to the heavy 4f and to the light 5d electrons and an interband term resulting from transitions from the occupied narrow f-band. Additional low-energy intraatomic absorption between ground and excited mixed states are predicted in the range of tenth of an eV. Because the latter are not specified further, they can not be compared with the experiment and we will concentrate therefore on the 5d intraband excitation. In the model, the 5d plasma resonance should be much lower in energy than the observed one (4 to 5 eV) since only a fraction of a 5d electron is delocalized. To overcome this apparent discrepancy, f to d interband excitations had to be assumed to enhance the 5d-plasma frequency. This enhancement factor depends upon interband momentum matrix elements and the energy spectrum of the two band model and should finally give rise to a Drude behaviour, but nothing is said about the origin of the corresponding damping term. There is good reason to assume TmSe and metallic SmS

to be similar with respect to the band structure and the degree of valence mixing. The "essentially localized 5d" model in the case of TmSe is faced with the following problem: the stoichiometry variation of TmSe allowed to shift the amount of divalent character from 0% to $\sim 28\%$, furthermore TmS serves as non mixed valent standard. As discussed in detail in the preceding section, in all these compounds the 5d-electron intraband excitations and their plasmon energies are even quantitatively well explained assuming a completely delocalized 5d electron system. It is, on the other hand, an obvious problem to manage the interband enhancement factor in such a way that, irrespective of the valence mixing, the 5d intraband characteristics would agree with the experiments. In particular, it is not clear how the gradual transition from the non mixed valent $\text{Tm}_{0.87}\text{Se}$ to the mixed valent $\text{Tm}_{1.0}\text{Se}$ should be described and why the plasmon damping is comparable in all the compounds studied here. One is therefore left with the two possibilities that either all the parameters in the model (bandshapes, interband absorption damping, ..) by accident are such as to reproduce the measurements, which also can be quantitatively interpreted in terms of 5d intraband absorption in both mixed and non mixed valent compounds, or that the model just does not apply in the present case.

A second statement concerning anomalous low energy excitations is speculatively mentioned in the review article by Varma ²⁾. He points to the possibility of out-of-phase oscillations of the heavy f electrons against the much lighter d electrons, which is called the f-d acoustic mode. The ratio of the Fermi velocities of the two species of electrons determine the dispersion of this mode and its energy at the Brillouin zone boundary

can be estimated to be some tenth of an eV. Since it is not yet clarified how it contributes to the zero wavevector response of the system and whether it is at room temperature Landau-damped, due to the thermal motion of the f electrons, it can only be concluded that the existence of the f-d acoustic mode is not precluded by the experiment.

The optical properties of intermediate valent compounds are treated in a conventional picture by Suzuki et al.⁵⁵⁾ for $T=0$ and neglecting any new phenomena brought about by the valence mixing, such as f - d interaction, for instance. Accordingly only intra d, $f \rightarrow d$ and $d \rightarrow f$ transitions are of importance at low energies. Whereas the former are described by a simple Drude expression, the latter are determined by the position and the shape of the 4f density of states. In order to get some agreement with the experiments, the 4f states had to be assumed to be 0.4 to 0.5 eV wide in SmS and SmB₆, which is at least one order of magnitude wider than commonly inferred from the experiments and calculations²⁾. Due to the lack of any f-d interaction it is not possible to transfer this model to the present case of a strongly temperature dependent low energy absorption.

Last but not least, the most detailed treatment of this subject by Allen et al.⁴⁴⁾ has to be discussed. The f-d mixing is explicitly included in this description and causes the 4f levels to acquire a width Δ . They are located at the Fermi energy and because of their partial occupation (= intermediate valent situation) the 4f sites act for $kT \gg \Delta$ as non correlated resonant scattering centers for both d electrons and holes at the Fermi surface. The results for the dielectric function can be cast into a Drude-like expression but with a frequency and temperature dependent lifetime τ for the d electrons:

$$\epsilon(\omega, T) = 1 - \omega_p^2 / (\omega(\omega + i\tau(\omega, T)))$$

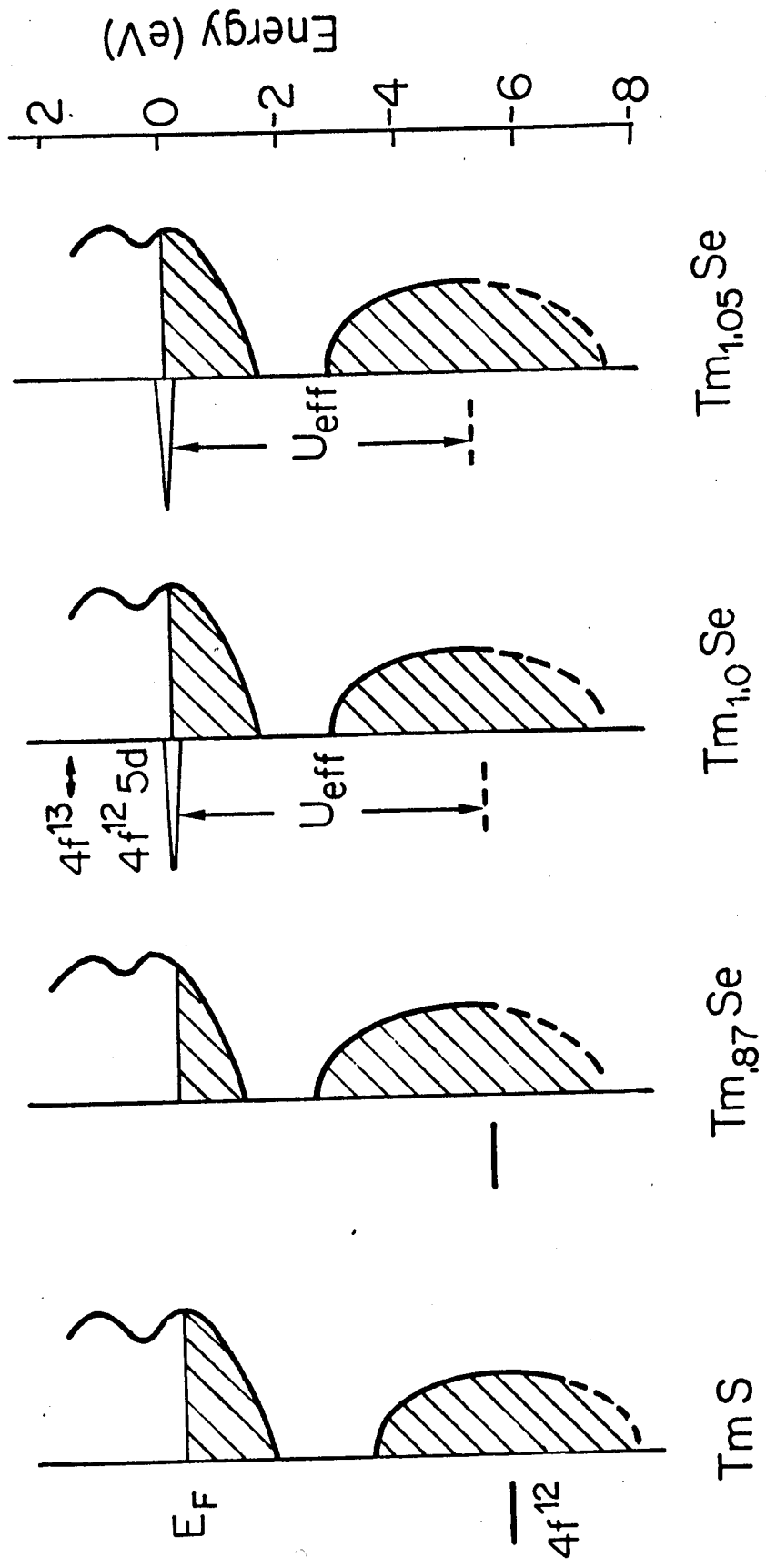
The explicit dependence of the complex τ upon ω and T is not possible to be given analytically, but has to be calculated numerically. The main features are the following: For photon energies well above the f-d matrix element (typically $\sim 0,1$ eV) the dielectric response at all temperatures is that of ordinary d electron intraband excitations. But it is markedly altered at lower energy: at sufficiently high temperatures ($kT \gg \Delta$) a plasmon like response is expected because electrons are thermally excited well above the states where they suffer strong scattering. At low temperatures, $\epsilon(\omega)$ decreases towards low frequency, dropping below the Drude behaviour as extrapolated from the unaffected d-intraband excitation range (at eV photon energy), and therefore reflects also the dc behaviour in the right way. In the framework of this f-d scattering theory it is possible to interpret the optical reflectivity of (intermediate valent) TmSe. It is not only the frequency dependence over the most extended range so far investigated in intermediate valent compounds, but also the low temperature behaviour that favours the description of the dielectric properties in terms of 5d electrons and holes strongly scattered at the partially occupied 4f states at the Fermi level.

Energy level diagram and discussion

All the information extracted from the optical spectra allows to compose a rough energy level diagram. It is, however, necessary to point to two peculiarities connected with such a task. First, in all the rare earth compounds, rather localized multi-electron states and common (usual) band states are involved in the optical excitations. Care must be taken when

these entirely different kind of states are represented on the same diagram, and from this reason they are drawn in Fig.6 on the left and right hand side of a vertical line. The second remark concerns the final state interactions. Whereas in photo electron spectroscopy the energy differences, say, with respect to the Fermi level refer to final states with an electron removed from the sample, in the optical experiment the excited electron and the hole left behind may interact considerably and make the energy difference to appear smaller (excitonic interaction).

In fig. 6, the energy level schemes of TmS and Tm_xSe are shown with the Fermi level as the common reference point. The top of the valence band is given by the onset of the $p \rightarrow d$ absorption and its width, although not being determined in the present experiment, is indicated with 4-5 eV, following the arguments presented in the preceding chapter. Not only in the $Tm-$, but also in all other metallic or semiconducting monochalcogenides and monpnictides of the rare earths., the optical transitions into the empty part of the conduction band lead to double structures in the spectra. Furthermore band structure calculations result in a density of conduction states with also two main maxima. Accordingly, a similar representation has been adapted in fig. 6 for TmS and Tm_xSe . The Fermi level lies the higher in the conduction band the more electrons have been found to participate in the plasma oscillation. Taking a height of ~ 1.5 eV for one electron per cation as is known from photo emission spectra, even the relative variations in the Tm_xSe series lead to very meaningful results, namely a rather constant gap between the bottom of the conduction- and the top of the valence band (~ 1.2 eV). The localized $4f^n$ states might be added to



6 Energy level schemes consistent with the optical data.

these schemes in locating them at an energy below E_F that is the minimum photon energy to promote one electron out of the 4f shell into a conduction band state. In the framework of this convention, the $4f^{12}$ states of pure trivalent TmS and $Tm_{0.87}Se$ lie 5.6 eV below the Fermi level.

For the intermediate valent $Tm_{1.0}Se$ and $Tm_{1.05}Se$ the energy level schemes need further explanation. The peak at E_F only symbolizes the high density of states due to the degeneracy in energy of the $4f^{13}$ and $4f^{12}5d$ configurations, but not the low lying excitations of the intermediate valent ground state. As discussed above, its excited states at high energy (eV) consist of ordinary $4f^{12} \rightarrow 4f^{11}5d$ and $4f^{13} \rightarrow 4f^{12}5d$ one electron transitions with an intensity factor corresponding to the amount of divalent and trivalent character in the ground state. The broken lines in the level scheme therefore indicate the photon energy, with respect to E_F at which the first $4f^{12} \rightarrow 4f^{11}5d$ type excitation of the mixed valent system occurs, and it equals the optically determined effective 4f Coulomb correlation energy U_{eff} (5.3 ± 0.2 eV). In X-ray photo electron spectra U_{eff} have been found to be 6.6 eV⁷⁾. The difference of 1.2 eV gives evidence that final state interactions cannot be neglected in either experiments. It would be worthwhile to study further the role of screening and excitonic interaction in these metallic rare earth compounds.

Concluding remarks

The dielectric response of homogeneously mixed valent TmSe for photon energies between 0.1 and 12 eV qualitatively resembles the trivalent rare earth chalcogenides. It is dominated by con-

duction electron absorption below some 2 eV and by interband ($p \rightarrow d$, $f \rightarrow d$) excitations above. The latter group of transitions agree fairly well in energy with predictions based on an empirical rule for related isostructural rare earth compounds. It is worth to note the minimum energy to induce optically the $4f^{12} \rightarrow 4f^{11}5d$ transition is by 1.2 eV smaller than the comparable energy in the X-ray photo electron spectra. Consequently, the values of the effective 4f Coulomb correlation energy as deduced from these two experiments are also different, and this is a manifestation of not negligible final state interactions such as screening and excitonic binding.

Below ~ 0.1 eV strongly frequency and temperature dependent deviations from a simple Drude metallic behaviour characterize the dielectric response. It is concluded that they are typical for the mixed valent situation and caused by the presence of 4f states at the Fermi level. The results are consistently explained in a framework of d electrons and holes resonantly scattered from not correlated f states at the Fermi surface.

A most important new aspect results from the analysis of the collective mode of the conduction band plasma in intermediate valent TmSe. The "extra" electron, that makes the difference between the pure ionic configurations $4f^{13}$ and $4f^{12}5d$, apparently fully participates in the plasma oscillation as it would have only delocalized 5d character. But simultaneously it is just its partial localized 4f character that has been thought to give rise to all the typical intermediate valence features like, e. g. the intermediate lattice constant, the two sets of 4f final states in XPS spectra, and the intermediate effective magnetic moment.

The answer to this obvious contradiction might be expected from a microscopic theory treating both the ground state properties and the excitation spectrum of a homogeneously mixed valent system like TmSe.

Table I

	τ_{M_S}	$\tau_{M_{0.87Se}}$	$\tau_{M_{1.0Se}}$	$\tau_{M_{1.05Se}}$
Lattice constant a_0 (Å)	5.42	5.63	5.69	5.715
τ_M valence, deduced from a_0	3.0	3.0	2.75	2.72
Reflectivity minimum (eV) (± 0.1 eV)	3.15	2.25	2.6	2.8
Onset of $4f^{12} \rightarrow 4f^{11}5d$ excitation (eV) (± 0.1)	5.5	5.4	5.4	5.2
Plasmon energy (eV)	5.3	3.6	4.35	4.5
Effective optical mass m^*/m_e	1.3	1.65	1.65	1.65
Electron density N_{el} exp. from p (10^{22} cm^{-3}) (± 0.1)	2.6	1.53	2.05	2.3
N_{el} theor. with τ_M -valence from a_0 (10^{22} cm^{-3})	2.5	1.5	1.5	1.65
N_{el} theor. assuming 1 el. per τ_M (10^{22} cm^{-3})	2.5	1.5	2.05	2.3

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PART A

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PART B

ALLOYS WITH TMTE AND EUSE

Abstract

The valence of the Tm ions in mixed valent TmSe has been influenced by alloying with TmTe in order to study the interaction between intermediate valent rare earth ions as 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 Tm valence is reduced from 2.75 ($x=0$) to 2.5 ($x=.17$) when Se is replaced by Te and the material remains metallic. Whereas TmSe orders metamagnetically ($T_N=3\text{K}$), the Te containing samples are spontaneously magnetized below 3-5K. 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 over-all 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 1K.

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 $\text{Tm}_{.5}\text{Eu}_{.5}\text{Se}$ they are separated by an energy gap of only 0.1 eV, which can be driven to zero with moderate external pressure (15kbar). In the metallic $\text{Tm}_{.83}\text{Eu}_{.17}\text{Se}$, 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.

Introduction

Some of the rare earth (RE) elements, those at the beginning (Ce, Pr), the middle (Sm, Eu) and at the end (Tm, Yb) of the series are well known to occur in more than one valence state. In the last decade particular attention has been attracted by the group of "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 and 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 compounds¹⁻³). Just to mention some: (1) the ionic radius, the effective magnetic moment as deduced from the high temperature susceptibility behaviour and the isomer shift in the Mössbauer spectra lie in between the values of pure integer valent RE ions. (2) photoelectron and optical spectra (in the visible and the UV range) are composed as if two distinct kinds of different but integer valent RE ions were present in the sample. (3) the crystal lattice is softened, the linear T-term in the specific heat is anomalously high and the optical excitation spectrum below some tenths of an eV deviates from the simple metallic behaviour.

In short terms, the 4f occupation number is not a good quantum number and the ground state of each RE ion contains a comparable amount of character corresponding to different valence states.

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 compound⁴⁻⁷⁾, namely TmSe. Besides of 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 -pnictides, 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 3+ in $\text{Tm}_{0.87}\text{Se}$, 2.75+ in stoichiometric TmSe and 2.72+ in $\text{Tm}_{1.05}\text{Se}$ ^{14,15)}. The following short description relates to the ideal composition. Intraband absorption below 2eV photon energy gives rise to the lustrous metallic brown-golden colour. TmSe is a metamagnet with a Néel point of 3K and an external field of $\sim 5\text{kOe}$ suffices to convert the anti-ferromagnetic typ I spin structure into a ferromagnetic one⁷⁾. Above $\sim 40\text{K}$ the magnetic susceptibility obeys a Curie-Weiss-law ($\theta_p = -30\text{K}$) 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 $\sim 220\mu\Omega\text{cm}$ at 300 K to some $\text{m}\Omega\text{cm}$ in the milli-Kelvin 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 GdSe¹⁵).

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 eV ^{5,18}) and 1.8 eV ¹⁹) respectively.

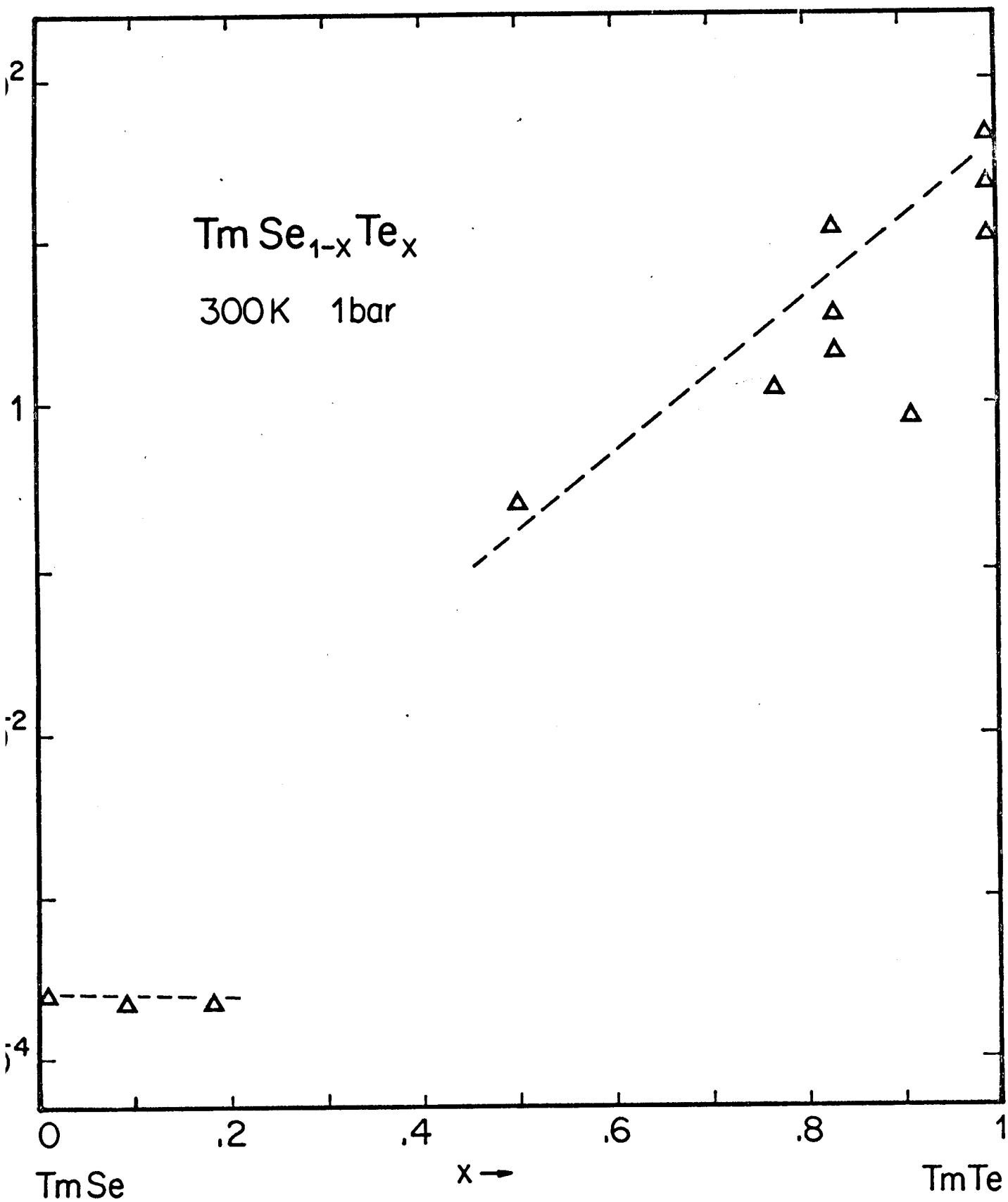
The aim of the present work is to vary the Tm valence over a larger range than has been possible by only changing the stoichiometry of Tm_xSe . By introducing an anion with a larger ionic radius than Se it is expected that the valency of Tm becomes less than 2.72, the optimal valence mixing obtained in the stoichiometry variation of Tm_xSe . A substitution of Tm with the integer divalent Eu in $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ should similarly pull the Tm valency closer to the divalent character. In addition we want to get a survey over the physical properties of the alloy series with special attention to the RE ion valence state and secondly anticipating a major result of the first point, to study the interaction between Tm ions with a maximal degree of valence mixing, that means when the Tm valence is just inbetween 2+ and 3+. In particular, it will

be possible for the first time to critically compare theoretical predictions concerning highly mixed valent $TmSe$ with the reality. A variety of experimental techniques has been used (magnetization and el. transport as 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.

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 concentrations (x up to 20 %) 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 $\sim 50 \Omega \text{cm}$ to $\sim 0.25 \Omega \text{cm}$ for TmSe_{0.5}Te_{0.5}. The fact, that TmSe_{1-x}Te_x crystals are hard to prepare^{16,17)} in the composition range from x=0.2 to 0.5 points to an instability region, which is also indicated in fig. 1 as discontinuity in the resistivity behaviour. The samples investigated in the present work were mostly single crystals or, in a few cases, well poly-crystallized material. Crystal chemical aspects are discussed in Ref. 16, 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 following a separate discussion of the two subgroups of compounds.



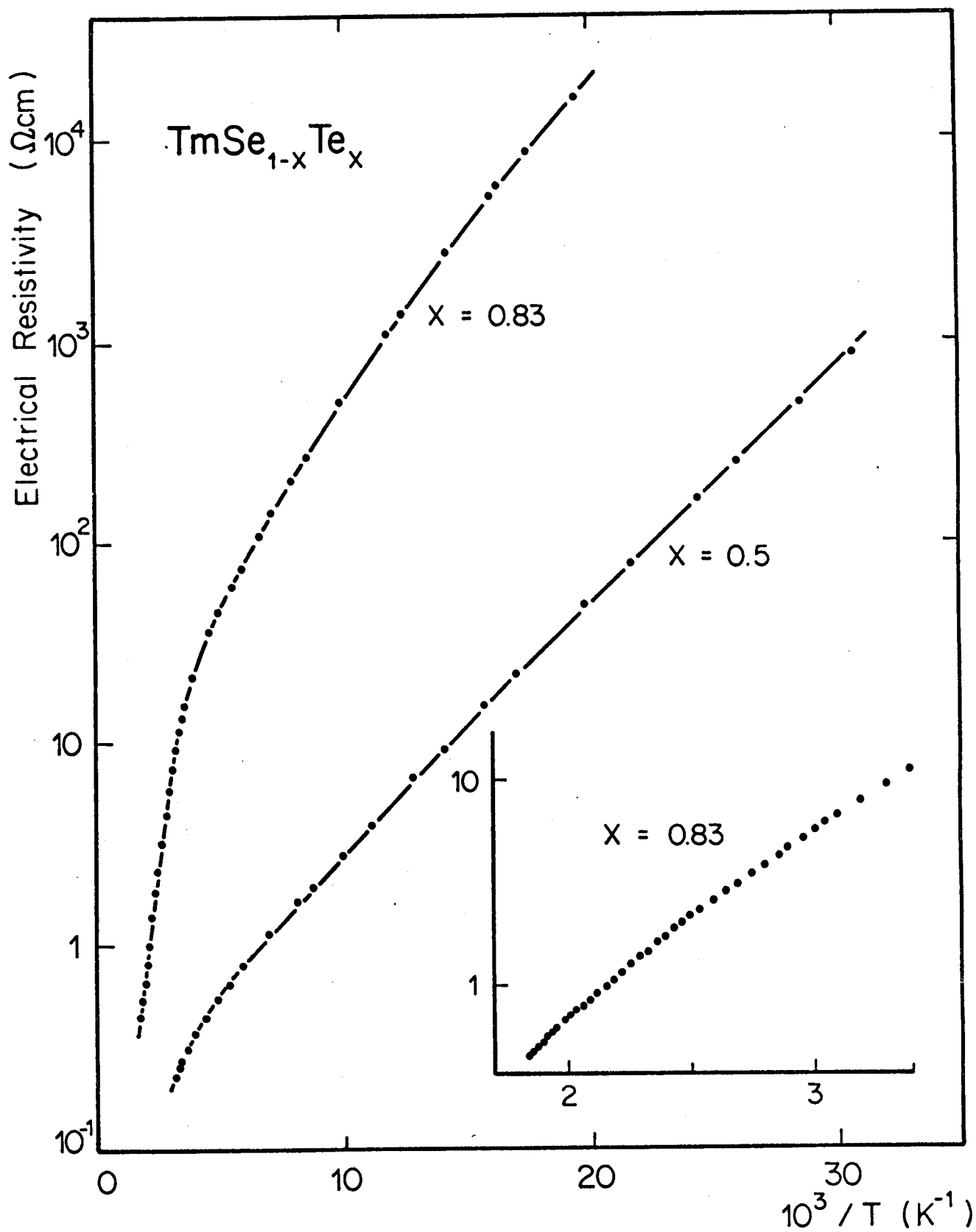
1 The electrical resistivity of $\text{TmSe}_{1-x}\text{Te}_x$ at ambient temperature and pressure.

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 $\text{TmSe}_{0.5}\text{Te}_{0.5}$ than for $\text{TmSe}_{0.17}\text{Te}_{0.83}$. In the insert to fig. 2 the resistivity of $\text{TmSe}_{0.17}\text{Te}_{0.83}$ is shown up to $T \sim 550$ K and from the shape 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 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 - 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 and 0.5 eV photon energy due to the onset of interband absorption and a very slow decrease towards lower photon energies because of the phonon absorption which, however, lies out of the frequency



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

$\text{TmSe}_{0.5}\text{Te}_{0.5}$

100

χ^{-1} (mole/emu)

50

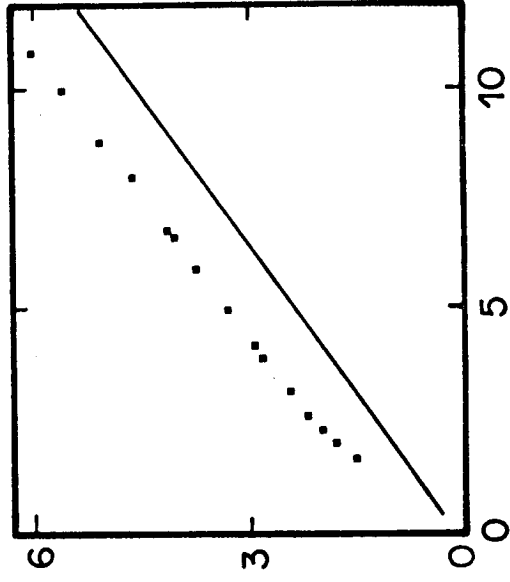
0

100

200

300

Temperature (K)



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

range investigated here. In crystals with more than $\sim 20\%$ Te replaced by Se ($0.5 \leq x \leq 0.8$) the few 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 raises 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 on going from TmTe to $\text{TmSe}_{0.5}\text{Te}_{0.5}$.

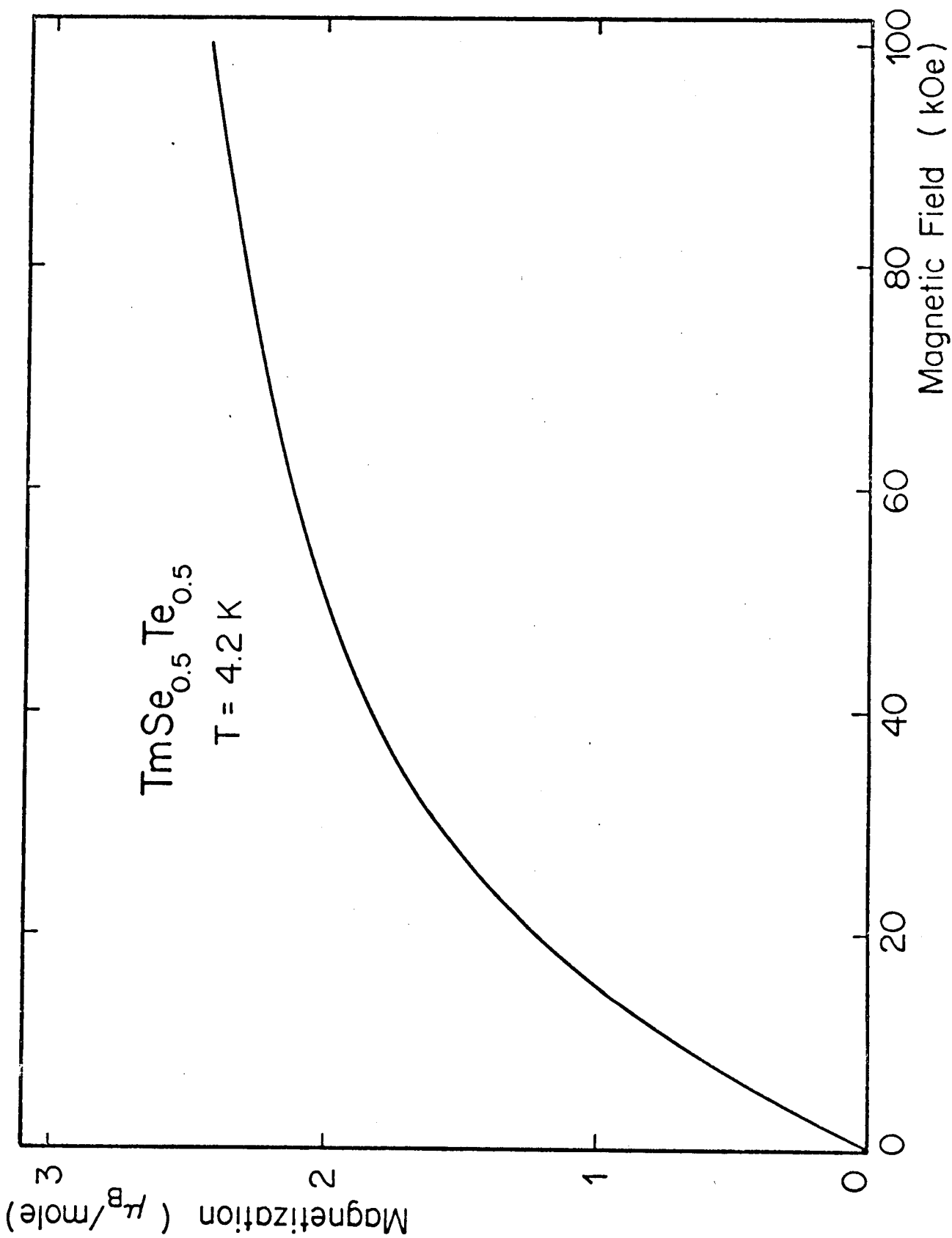
From these findings the divalency of Tm in $\text{TmSe}_{1-x}\text{Te}_x$ ($x \geq 0.5$) can be inferred and magnetic measurements will corroborate with it. In fig. 3 the inverse magnetic susceptibility χ^{-1} is shown for $\text{TmSe}_{0.5}\text{Te}_{0.5}$ as a function of temperature between 1.5 and 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 behaviour. 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 Tm^{2+} ($4f^{13}, {}^2F_{7/2}$) and Tm^{3+} ($4f^{12}, {}^3H_6$) the measured μ_{eff} therefore is the strongest evidence that Tm is divalent in $\text{TmSe}_{0.5}\text{Te}_{0.5}$. Since the same has been found in $\text{TmTe}^{5)}$, Tm can be concluded to be divalent in $\text{TmSe}_{1-x}\text{Te}_x$ with $x \geq 0.5$.

Irrespective of the paramagnetic behaviour of these compounds at higher temperature, the susceptibility 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 $J = 7/2$ free ion Hund's

rule ground state. An other 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 $J = 7/2$ ground state were 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 can not be represented by a Brillouin function.

So far it can safely be concluded that in TmSe the substitution of more than half of the Se ions by Te ions leads to semiconducting behaviour. The magnetic properties are very similar and are dominated by Tm ions in the divalent state.

But now, 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 band¹⁹⁾. 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 multielectron system, and not simply between two band states. In general terms the gap E_g corresponds to $E(4f^{n-1}5d^1) \rightarrow E(4f^n5d^0)$, where $5d^1$ means one electron in the conduction band, being derived primarily from the rare earth 5d and 6s wave functions.



4 Magnetization curve of $\text{TmSe}_{.5}\text{Te}_{.5}$ at $T = 4.2 \text{ K}$

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 "5d_g" designed) to shift towards higher and the lower one ("5d_{2g}") towards lower energies²⁰⁾. 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 (1) and taking for $\rho_0 \equiv \rho(E_g \equiv \Delta E = 0)$ 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 Tab. 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 inter-

mediate 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 ($4f^n$ and $5d6s$ conduction band). By definition the deformation potential $\bar{\Sigma}$ 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 multiplying the pressure change of the gap (dE_g/dp) with the bulk modulus.

Using a piston - cylinder apparatus with ether as the transmitting fluid the resistivity has been measured in hydrostatic surroundings up to 20 kbar. 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 eqn (1) at constant temperature dE_g/dp equals $(d \ln \rho / dp) \cdot kT$ and the numerical results are given in Tab. 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 $\sim 2/3$ as fast as at low pressure and (2) the lattice becomes markedly weaker ($\chi = 4 \times 10^{-6} \text{ bar}^{-1}$). 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 χ 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 chalcogenides ²¹) meaning that compressibility and specific volume per molecule are connected via a power law. Finally also the deformation potentials are listed in Tab. 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 4f electrons, the only

quantitative peculiarity is a small energy separation between the $Tm4f^{13}$ 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 band width, 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" 4f - level in relation to the 5d conduction band. This has been shown to hold even quantitatively for the Eu- and Sm-24), and now also for the Tm chalcogenides.

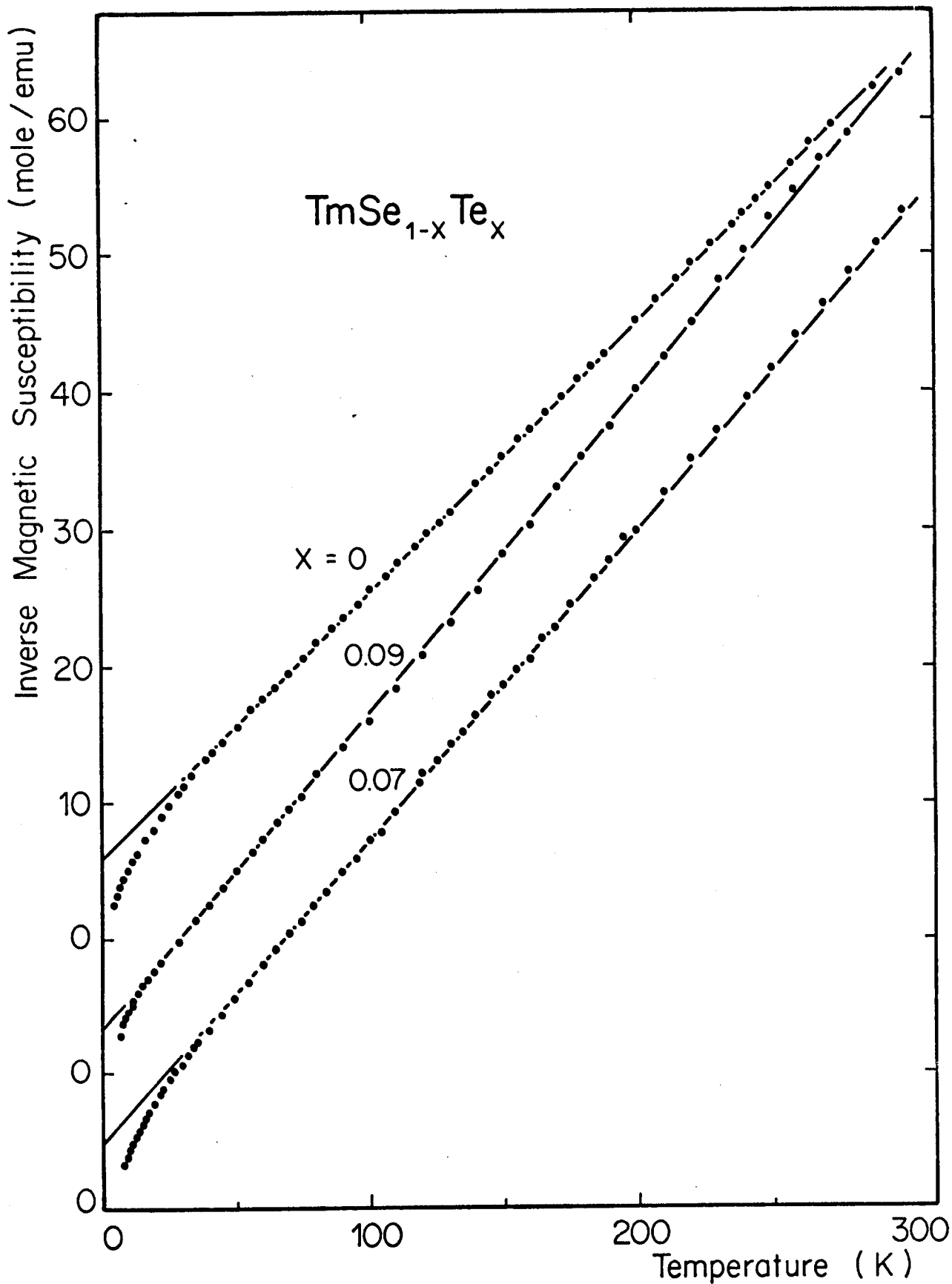
Metallic $\text{TmSe}_{1-x}\text{Te}_x$ ($0 \leq x \leq 0.2$)

This group of substances is of outstanding interest from the point of view of the mixed valence problem. The purpose is nothing less than to test a microscopic theory of the mixed valent ground state that predicts for the case of TmSe a ferromagnetic ordering if the degree of valence mixing exceeds a critical limit²⁵⁾. A verification of this challenging statement would be very important.

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 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 $5.87 \mu_B/\text{mole}$ for $\text{TmSe}_{1-x}\text{Te}_x$ with $x=0$, 0.09 and 0.17, resp.

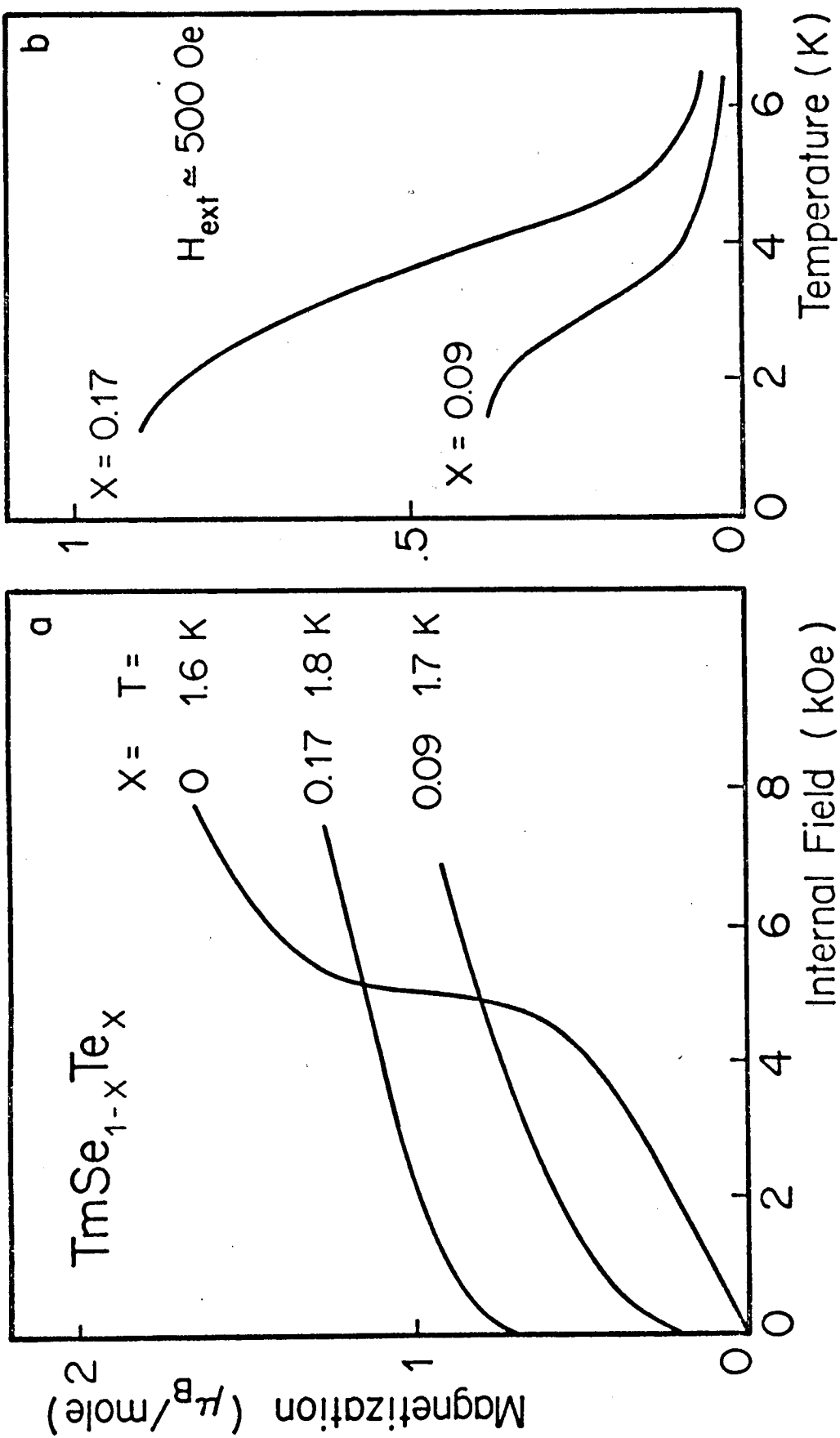
The free ion value amounts to 7.56 and $4.58 \mu_B$ / ion for trivalent and divalent Tm. Therefore, the divalent character increases when Se is replaced partially by Te, in agreement with the expectations. At the same time the paramagnetic Curie temperature Θ changes from -29 K for TmSe ¹⁵⁾ to -15 K and -17 K for the Te containing samples and thus indicates an overall enhancement of the ferromagnetic exchange interactions. From both the lattice constant (5.86 \AA) and the effective



5 Inverse magnetic susceptibility as function of the temperature for three metallic and intermediate valent $\text{TmSe}_{1-x}\text{Te}_x$ compounds. Note shifted zero for ordinate.

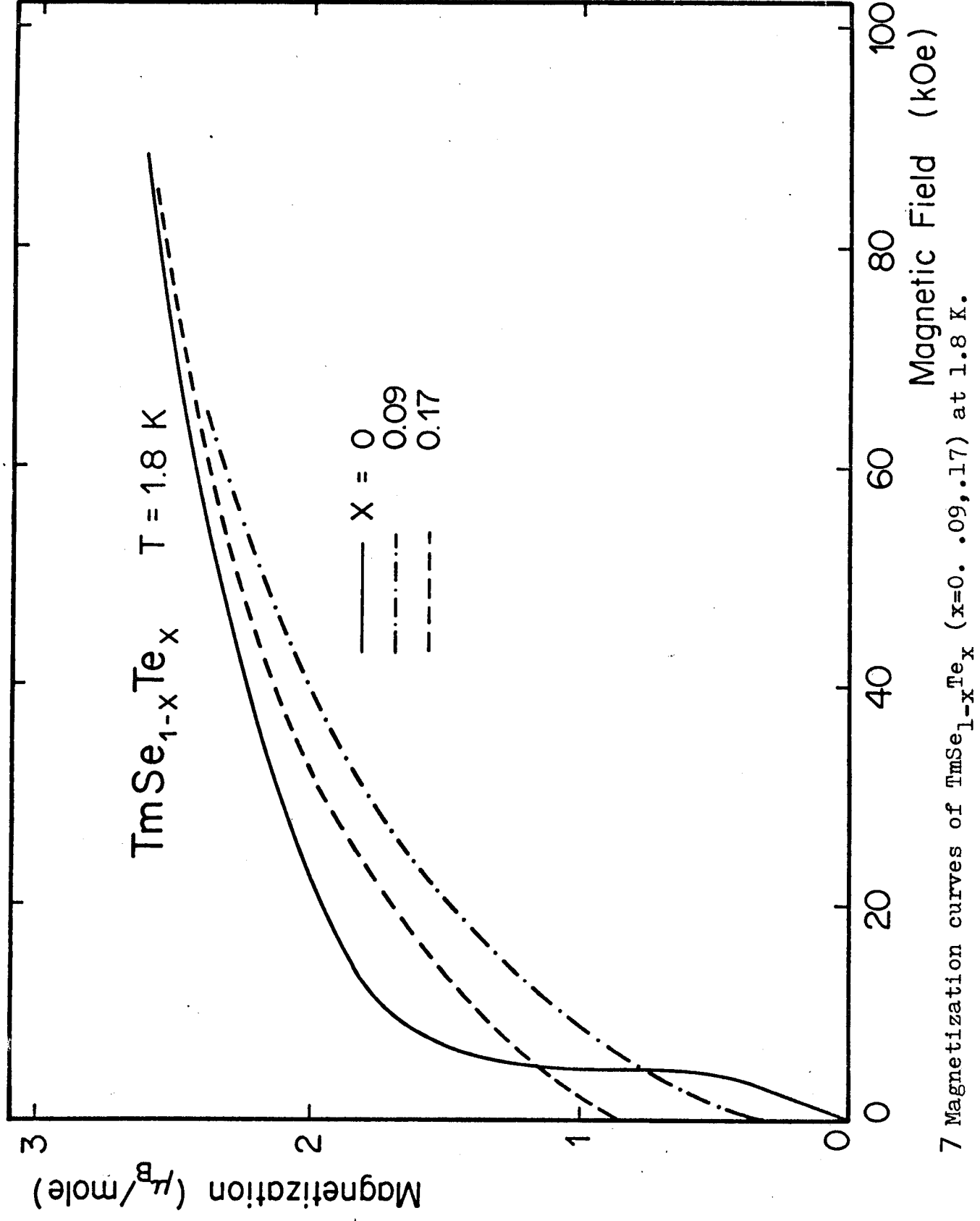
magnetic moment a valence of 2.5 can be deduced for Tm in $\text{TmSe}_{0.83}\text{Te}_{0.17}$. In this compound, therefore, the Tm ions are in a valence state with highest possible degree of mixing.

The differences between the three compounds become obvious in magnetization measurements at temperatures below 5 K (fig. 6a). While TmSe undergoes a metamagnetic transition at $H \sim 5\text{kOe}$ ($T_N = 3\text{ K}$), the magnetization of the alloys strongly raises within the first couple of hundred Oe up to $0.35\ \mu_B/\text{mole}$ for $x = 9\%$ and $0.8\ \mu_B/\text{mole}$ for $x = 17\%$. 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. 6b, showing the temperature dependence of the magnetization in an external field of $\sim 500\text{ Oe}$. 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 K 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 at all simple ferromagnets, as revealed by the magnetization in higher fields (fig. 7). It raises 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 $7\ \mu_B/\text{ion}$ for Tm^{2+} and Tm^{3+} , respectively.



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.



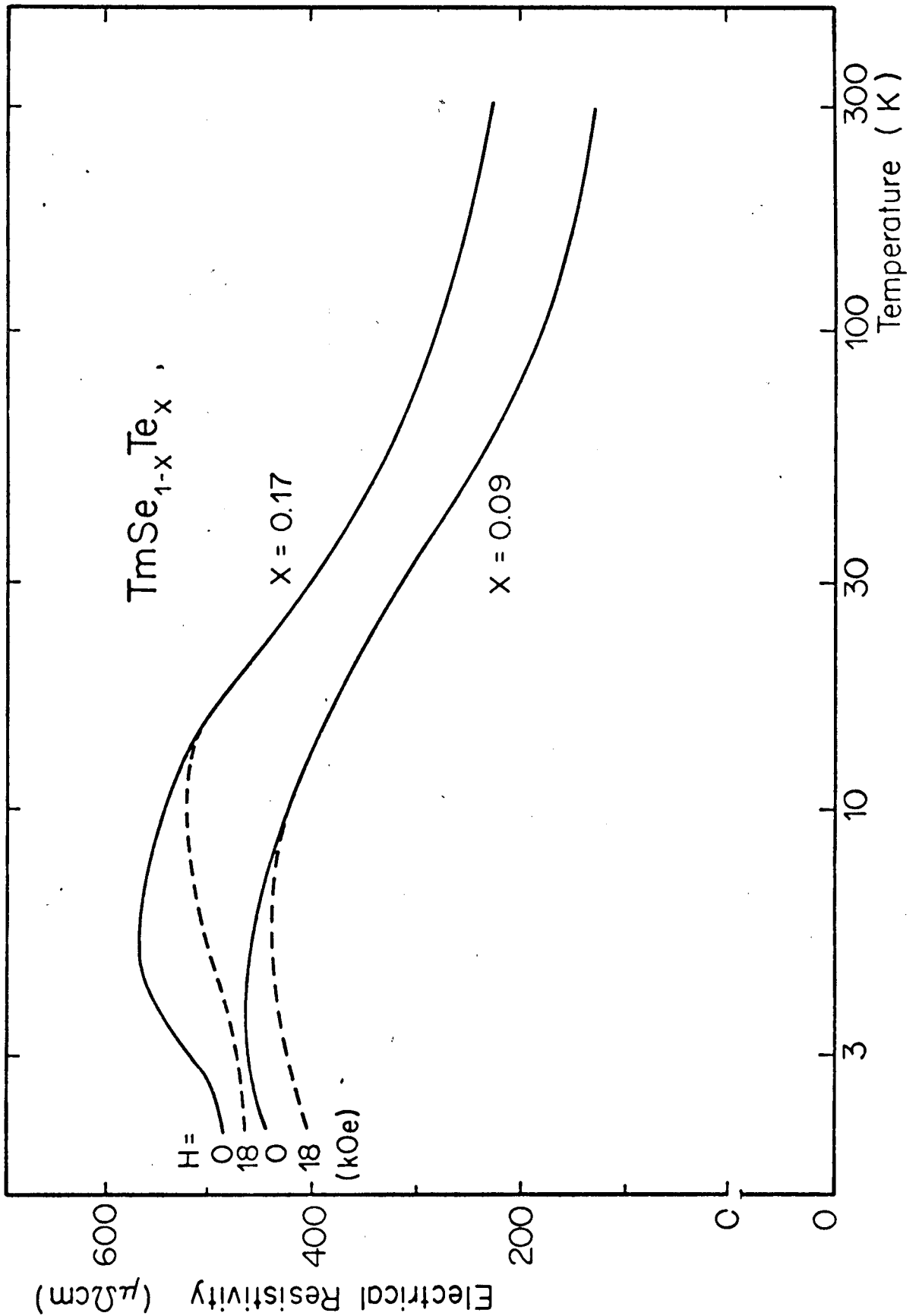
7 Magnetization curves of $\text{TmSe}_{1-x}\text{Te}_x$ ($x=0, .09, .17$) at 1.8 K.

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 from the high temperature behaviour 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.

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 .

For all these metallic $\text{TmSe}_{1-x}\text{Te}_x$ compounds the absolute value of the resistivity at room temperature is quite 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 raises further at and below the Néel point and becomes constant only in the mK - region at as high values as some $\text{m}\Omega\text{cm}$ ^{11, 12, 15)}. In contrast, in samples with a partial



8 Temperature dependence of the electrical resistivity for $\text{TmSe}_{1-x}\text{Te}_x$ ($x=.09, .17$) 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.

replacement of Se by Te, ρ even decrease below the temperature where an indication of magnetic order exists (fig. 6b). It is also noteworthy that the resistance of these compounds do not show the logarithmic dependence with temperature between 40K and 4K, as it does for TmSe.

To demonstrate the magnetic origin of at least part of the resistance raise, 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 2 orders of magnitude between $H = 0$ and $H \sim 20$ kOe has been found. The different magnetic phases in TmSe are also reflected in the curvature of the $\rho(H)$ curves, being negative in the ferromagnetic and positive in the others. 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. Further, a comparison of $\rho(H)$ in fig. 9 and $M(H)$ in fig. 6 confirms the speculation that the relative decrease of the resistance is related to the absolute value of the magnetization.

Discussion

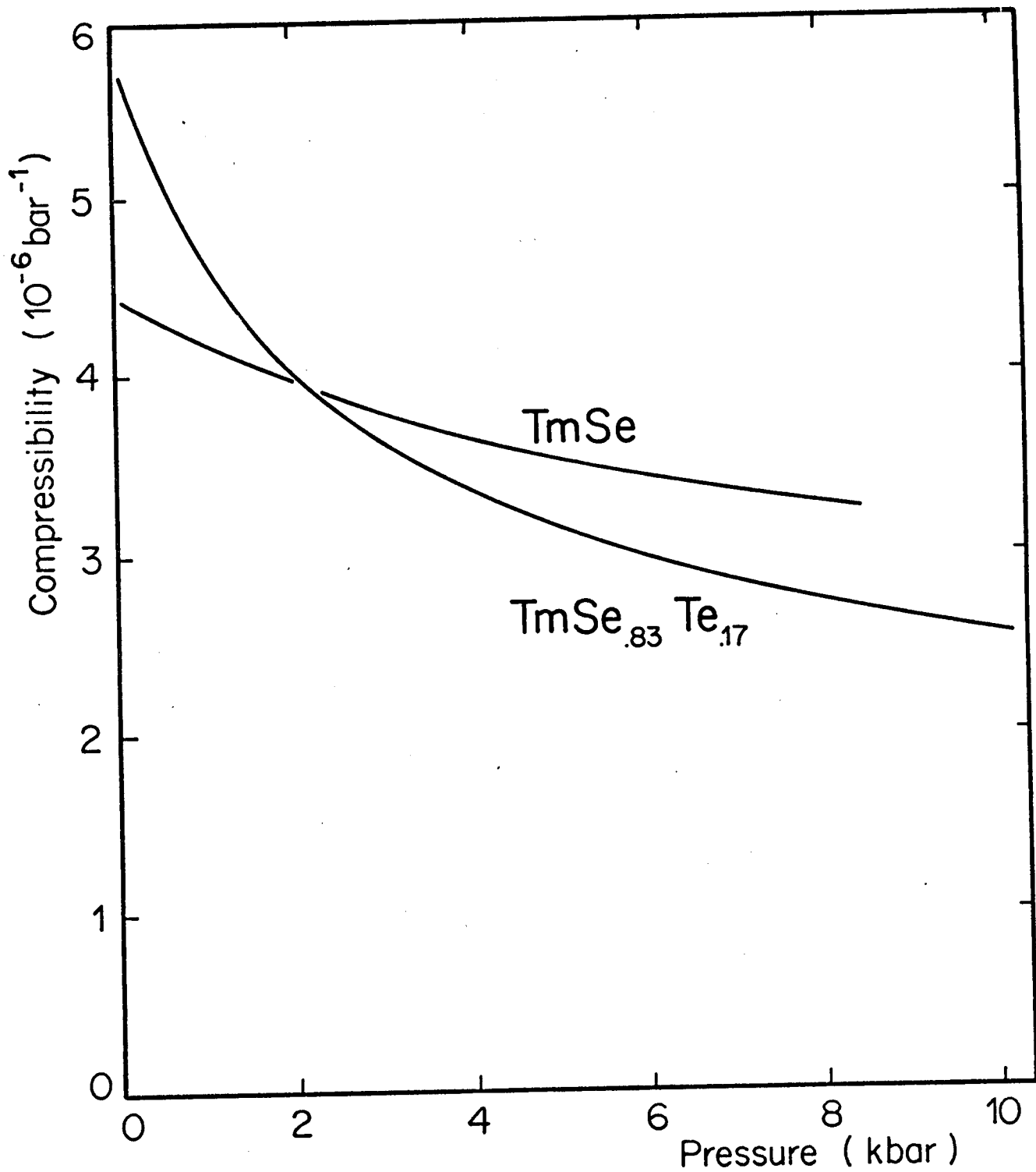
A basic question to be answered at the beginning is whether $\text{TmSe}_{1-x}\text{Te}_x$ with $x \leq 0.2$ belongs to the so called homogeneously or inhomogeneously mixed valent compounds. That they are mixed valent at all has to be concluded from both the intermediate value of the effective magnetic moment and the intermediate lattice constant. To put it differently, are the divalent and trivalent characteristics ingredients to the groundstate of each Tm ion or is the cation sublattice occupied by purely di- and trivalent species with their conventional properties?

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 line width itself²⁷⁾. From the whole set of the present and most recent investigations¹⁵⁾, 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 semi-empirical 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 till

now for SmS-SmAs, SmS-YS²⁹⁾ and for TmSe with variation of the chemical composition ¹⁵⁾. The pressure dependence of the volume and hence the compressibility $\chi = -(\partial V/\partial p)/V$ of $\text{TmSe}_{1-x}\text{Te}_x$ ($x = 0.09, 0.17$) 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 pressure are up to 5 times higher than one would expect for the same compounds containing Tm ions in pure integral valence states. Secondly a distinct decrease of χ occurs at higher pressures (it has to be noted that this behaviour does not change after several pressure cycles). These facts now are fully 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 favours the $4f^{12}5d$ (Tm^{3+}) configuration rather than $4f^{13}$ (Tm^{2+}).

An other 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 can not be reproduced by such an adding, within reasonable limits, because of its qualitative different feature. Therefore, the anomalously high compressibility and the magnetic susceptibility strongly indicate that the Tm ions are in a homogeneously mixed valent state not only in TmSe ¹⁵⁾ but also in the metallic $\text{TmSe}_{1-x}\text{Te}_x$ compounds. It has to be admitted that the presence of a very small fraction of



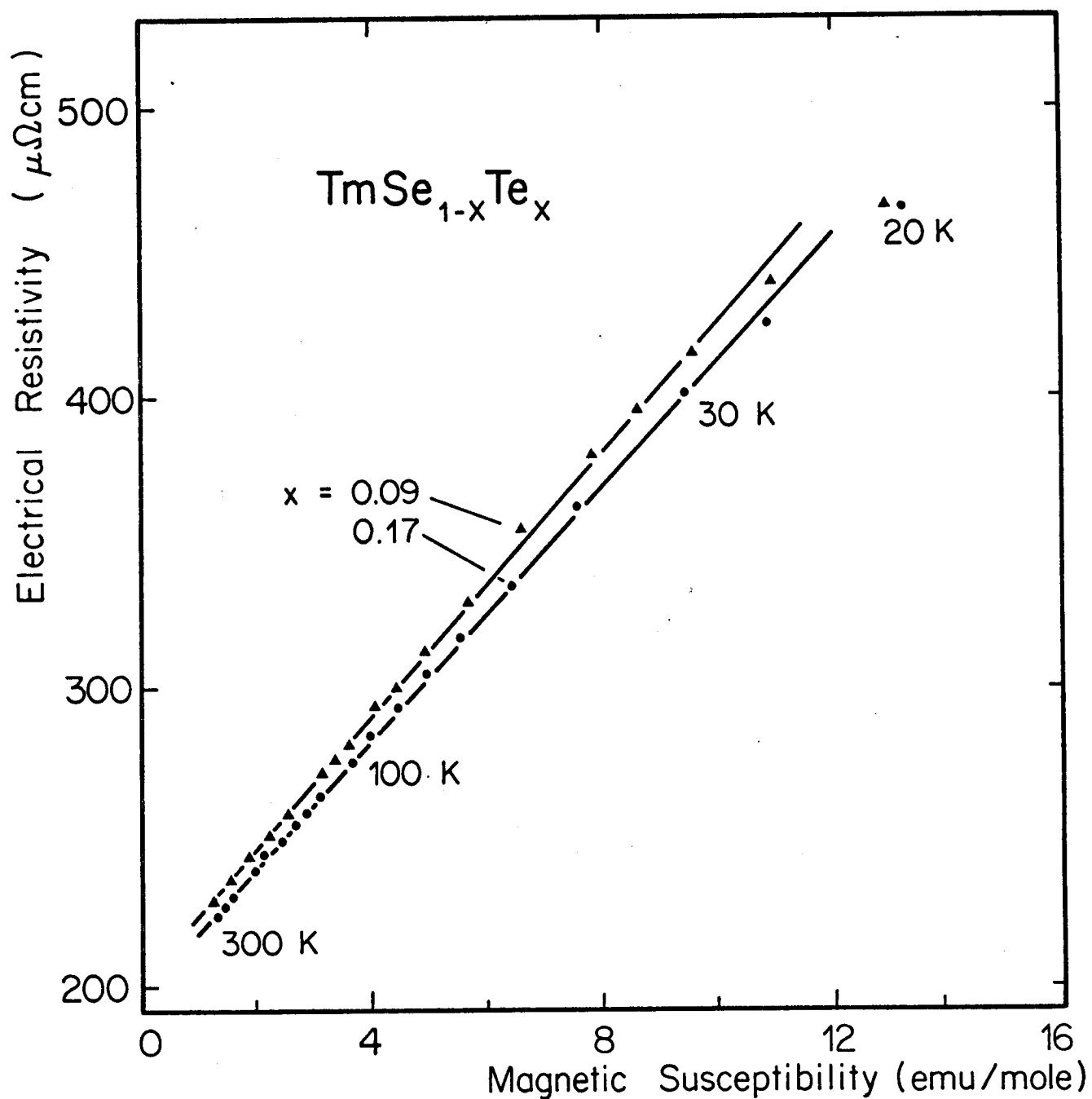
10 Pressure dependence of the isothermal compressibility of TmSe and TmSe_{.83}Te_{.17} at T = 300 K

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 behaviour 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 by 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 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 $Tm_xY_{1-x}Se$ have both di- 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 Chui³²⁾. 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 by Chui and his 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 $\text{TmSe}_{1-x}\text{Te}_x$ ($x=0, 0.09, 0.17$) is not well reproduced in its temperature behaviour by the fd 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 dependence 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. This experimental fact is left as a challenge for theorists.



11 Relationship between the electrical resistivity and the magnetic susceptibility of $\text{TmSe}_{1-x}\text{Te}_x$ ($x = .09$ and $.17$). The numbers indicate the temperature in K.

The 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 TmSe²⁵⁾. The concept of DE had been elaborated in connection with Ca-substituted La-manganit, a prototype of a transition metal mixed valent compound³³⁻³⁶⁾. Here, only a short outline of the basic ideas is necessary. DE is provided by real transfer of electrons between not completely filled shells. If only the Hund's rule (intraatomic exchange) energy within the shell exceeds the band width 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 secondly, double exchange is absent if the ground state of one of the valence states is non-magnetic, or at least separated from an excited magnetic state by an energy large compared to the Zener-carrier band width.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 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 $\vec{J}_i \vec{J}_j$ 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 $4f$ 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 intraatomic coupling energy (~ 1 eV). Since the number of the $4f$ -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 2.6²⁵⁾. 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 deviations of the susceptibility below ~ 40 K (fig. 5) and the paramagnetic Curie temperatures are the first hint to a increasing ferromagnetic coupling with reduced Tm valence. In particular, the low field magnetization curves (fig. 6a) 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 a ferromagnetic exchange mechanism, in agreement with the expectations based on the DE model. Also an other 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 $\text{TmSe}_{1-x}\text{Te}_x$ ($x \leq 0.2$) 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 behaviour 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 4f 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 compounds¹⁰).

In conclusion, all experiments on $\text{TmSe}_{1-x}\text{Te}_x$ ($x \leq 0.2$) give strong evidence of the mixed valent character of each of the Tm ions. In these homogeneously mixed valent 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 behaviour, 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.

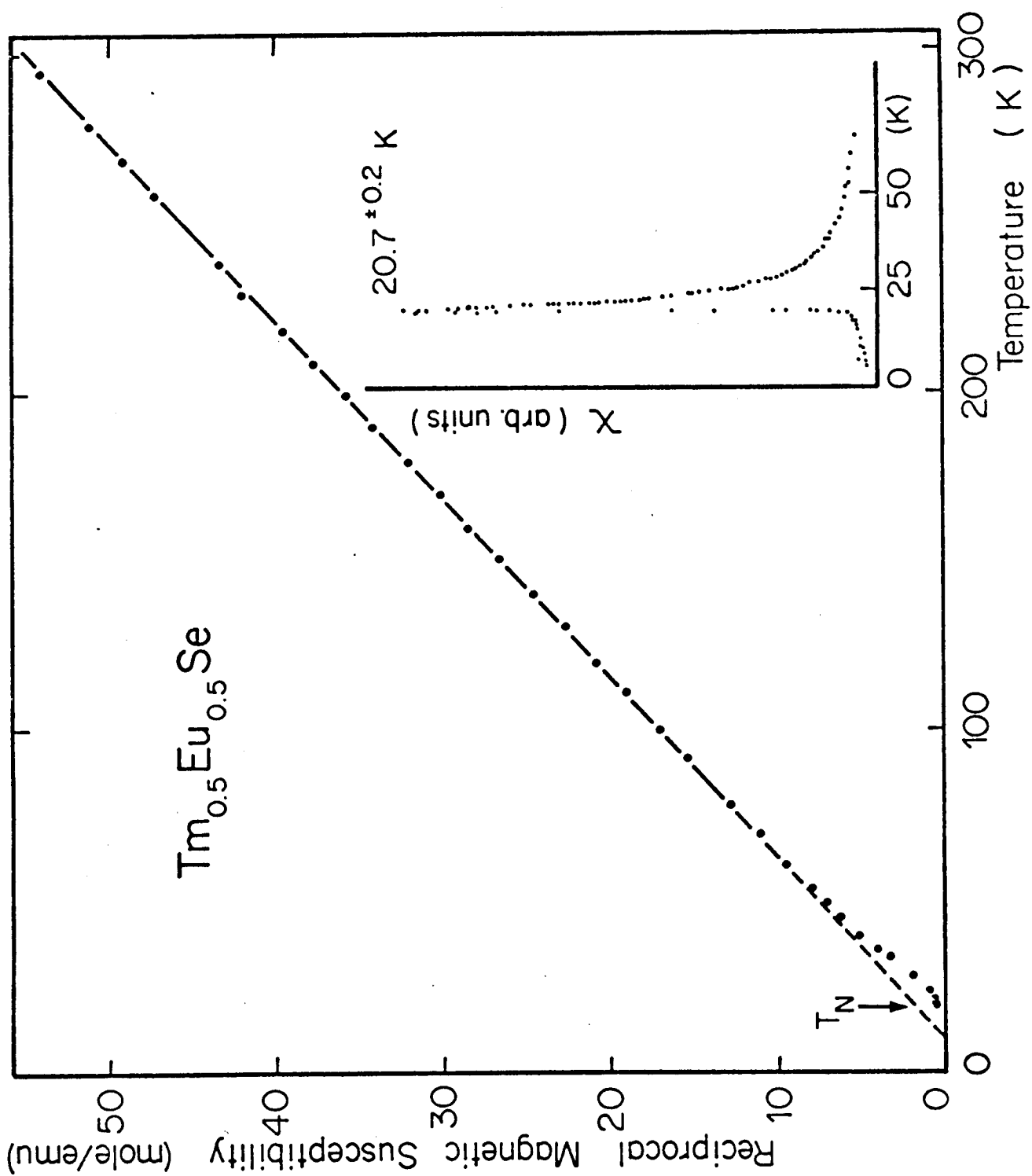
TmSe- EuSe

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 4f levels (2) the valence of Tm and Eu ion and (3) the conduction band which is derived from the RE 5d and 6s wave functions.

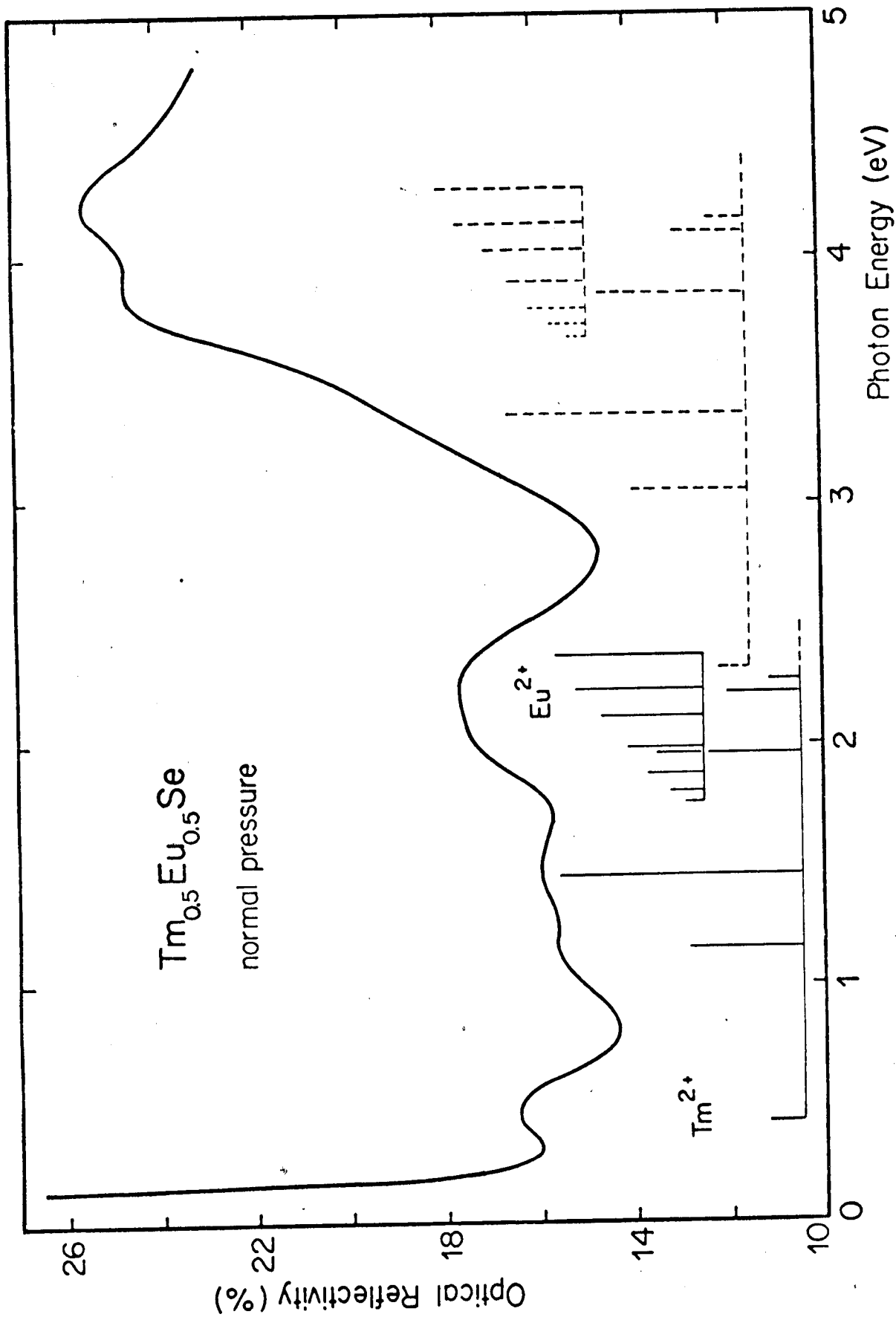
EuSe is a semiconductor with an energy gap of 1.8 eV, the Eu ions are divalent and their moments order metamagnetically below $T_N = 4.6 \text{ K}$ ³⁸⁾. Starting from the Tm rich end, the $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ crystals are still metallic at $x = 0.2$, but they become semiconducting when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

Semi-conducting $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$

A first information about the valence states of Tm and Eu is revealed by the magnetic susceptibility χ . Fig. 12 shows the temperature dependence of χ^{-1} between 25 K 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 divalency of both type 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 important statement 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 multiplets ³⁹⁾ and their relative position in energy ⁴⁰⁾ are indicated by the sets of bars also included in the Figure. Similarly as 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 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.



12 Temperature dependence of the magnetic susceptibility of $Tm_{.5}Eu_{.5}Se$. In the insert, the ordering point is located at 20.7 ± 0.3 K.

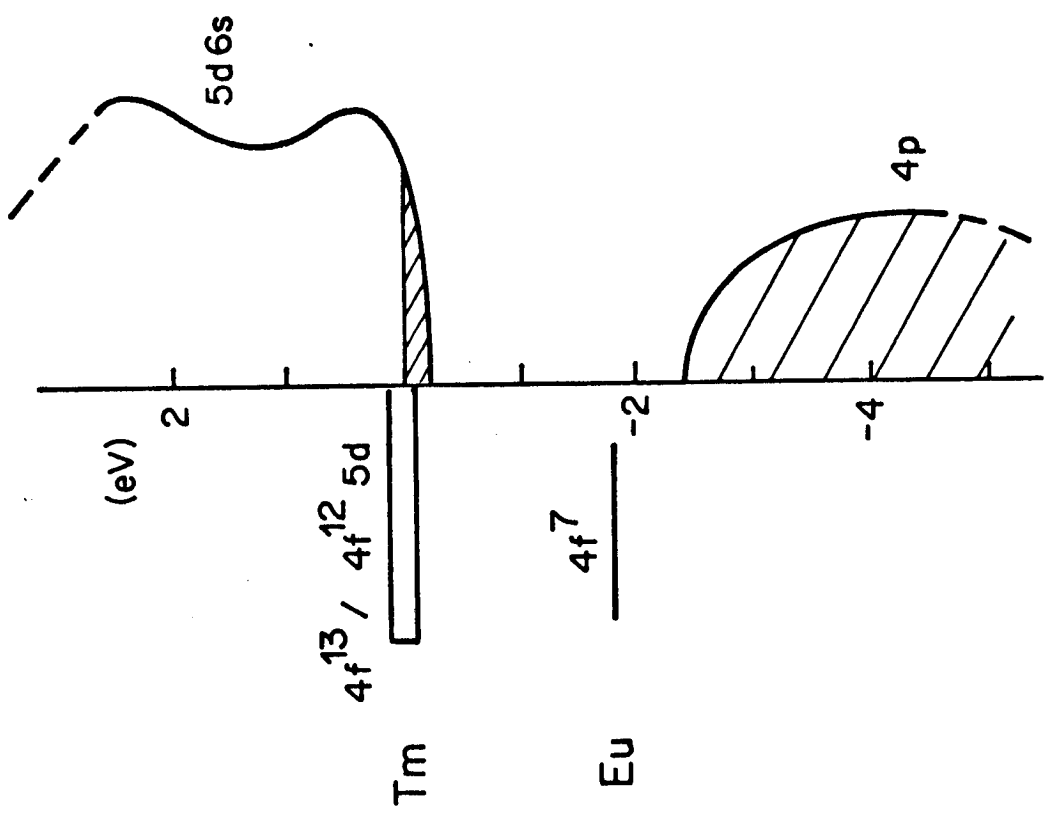
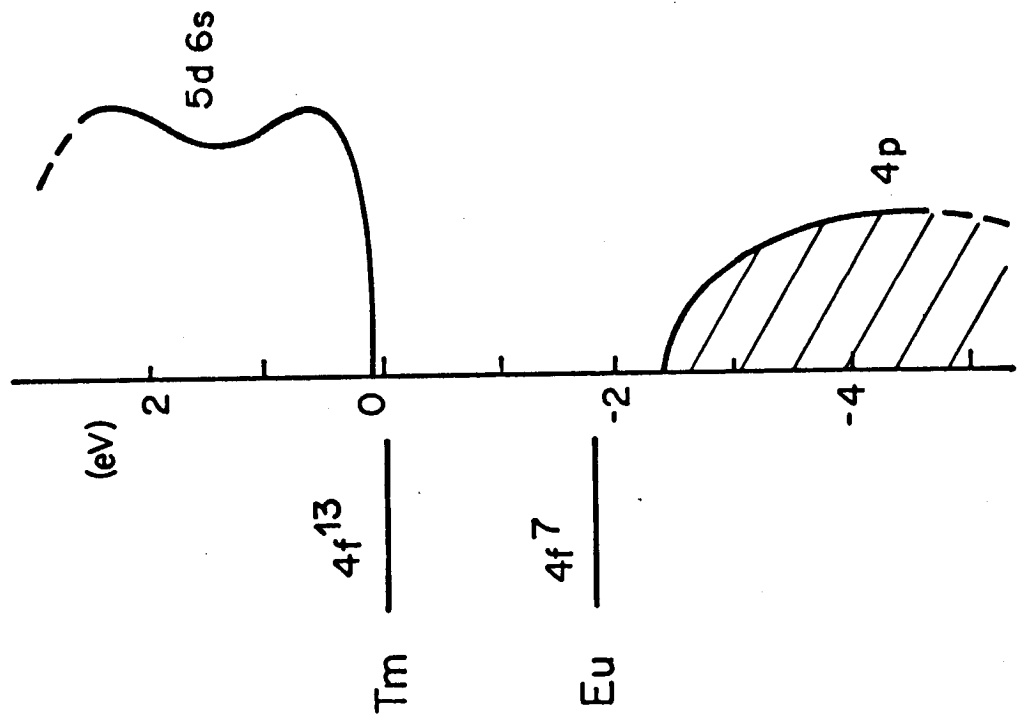


13 a Optical reflectivity spectrum of $Tm_{0.5}Eu_{0.5}Se$ at 300 K. The bars indicate the calculated intensities of the final state multiplets after excitations of 4f electrons.

The energy gap, therefore, between the $4f^{13}$ level and the bottom of the conduction band is as narrow as to allow some electrons to be thermally excited across it. The intra-conduction band absorption of these carriers is responsible for the steep reflectivity raise 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 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

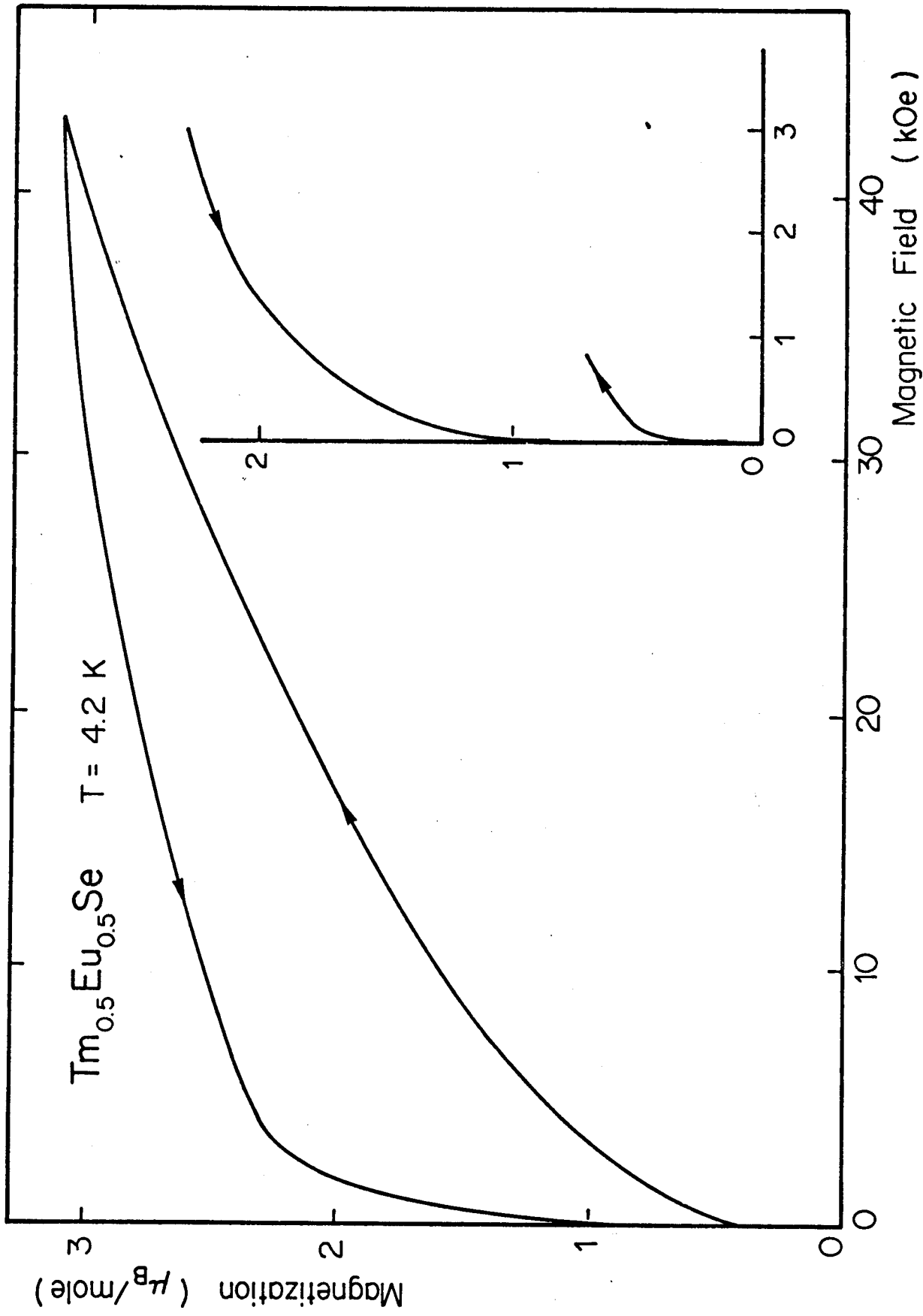


Tm_{0.5}Eu_{0.5}Se

14 Energy level schemes for semiconducting and metallic Tm_{0.5}Eu_{0.5}Se.

to 23.89 eV for Tm and 25.13 eV for Eu ⁴²⁾. A comparison reveals that by 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.

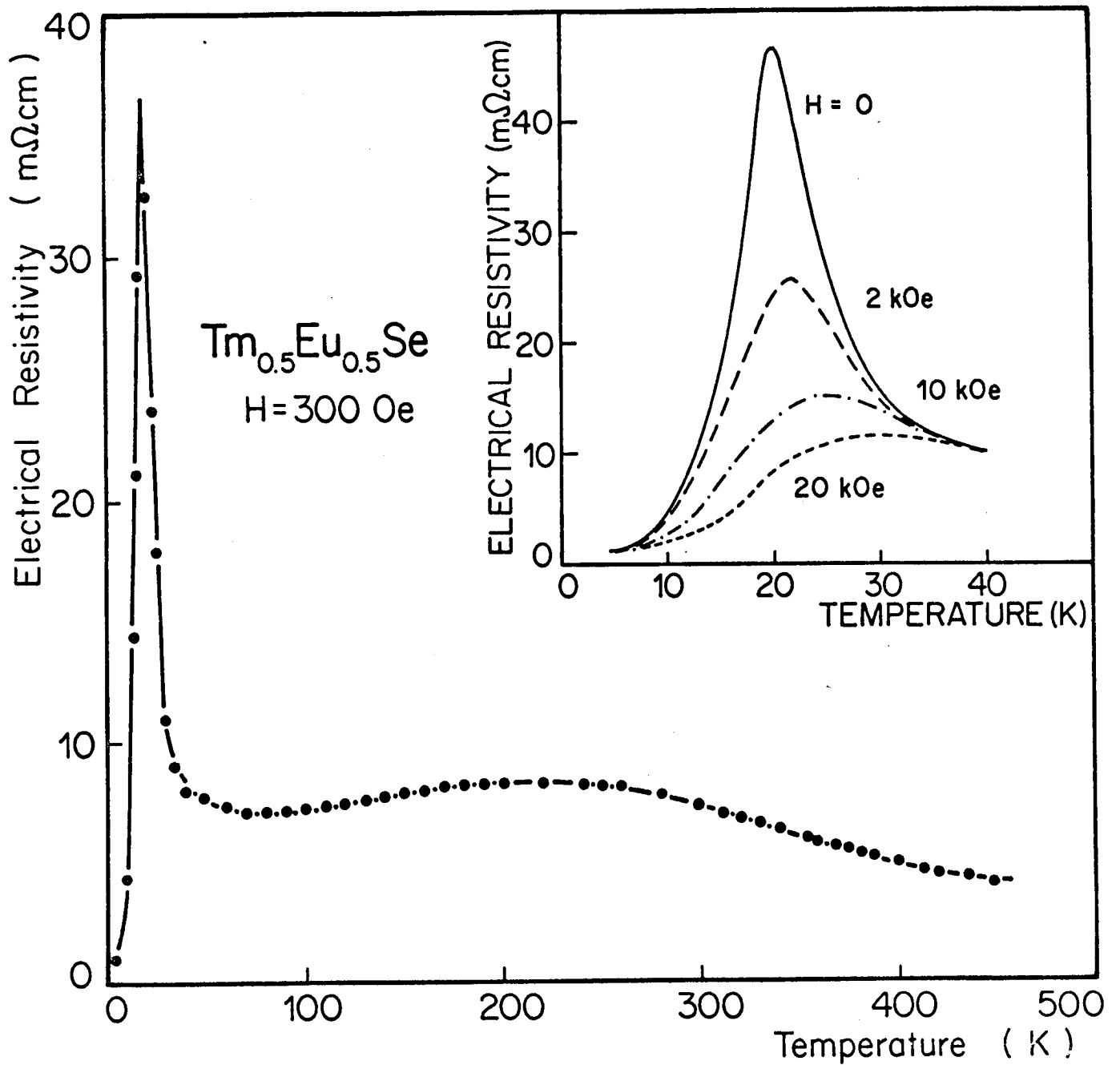
The magnetic properties and the electrical resistivity are of interest for themselves and will be discussed now. In the insert to fig. 12, the sharp peak of the magnetization, measured in an external field of 100 Oe, marks the ordering point. The temperature of 20.7 ± 0.2 K is remarkable for $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$, because firstly T_N in pure EuSe equals 4.6K ³⁸⁾, and secondly the density of the strongly magnetic Eu moments is only about half the one of EuSe. A magnetization curve of $\text{Tm}_{0.5}\text{Eu}_{0.5}\text{Se}$ is given in fig. 15. 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 these field strengths, a complicated spin arrangement has to be inferred, recalling that a saturation at $(7 + 4)/2 = 5.5\mu_B/\text{mole}$ 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 (RKKY) or bound magnetic polaron. A similar raise of the ordering temperatures has been observed for instance in doped Eu chalcogenides ⁴³⁾ and more recently in the GdP - GdS alloy system ⁴⁴⁾ (RKKY).



15 Magnetization curve of $Tm_{.5}Eu_{.5}Se$ at $T = 4.2$ K.

The electrical resistivity at room temperature 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. 16. A predominant feature is the maximum at the magnetic ordering point and the decrease in the ordered region. A nearly identical behaviour is also shown by Gd doped EuS ⁴⁵⁾ and has been ascribed to critical scattering of electrons by correlated spins^{45, 46)}.

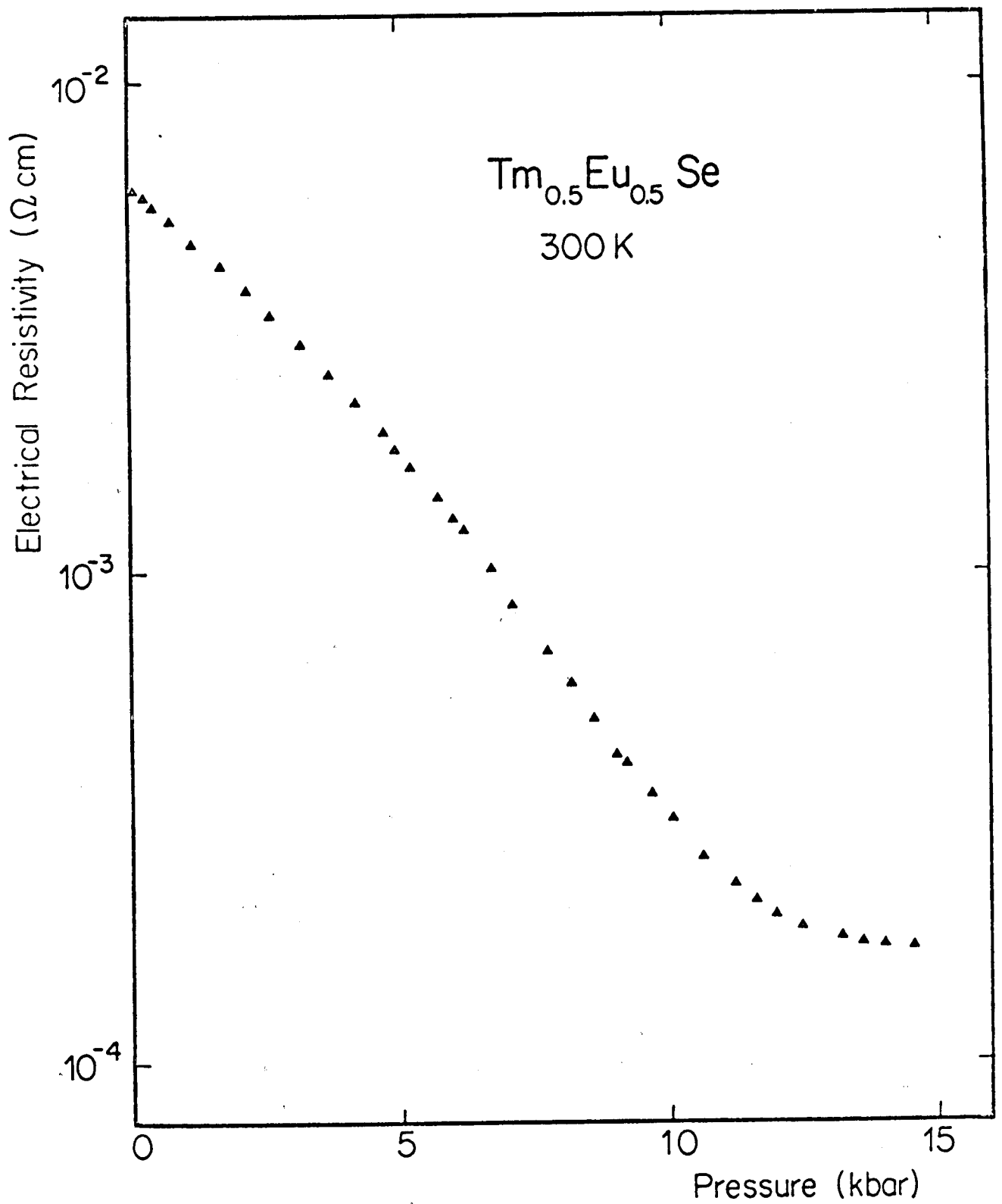
The magnetic origin of this anomaly becomes apparent when the resistance is measured in an external field (insert fig. 16): the peak is reduced to one half for $H = 2 \text{ kOe}$ and totally quenched in a field of 20 kOe . At higher temperature ρ first increases linearly up to 200 K , passes through 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 by 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 $\text{Tm}^{2+4f^{13}}$ 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 well known to be band like 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



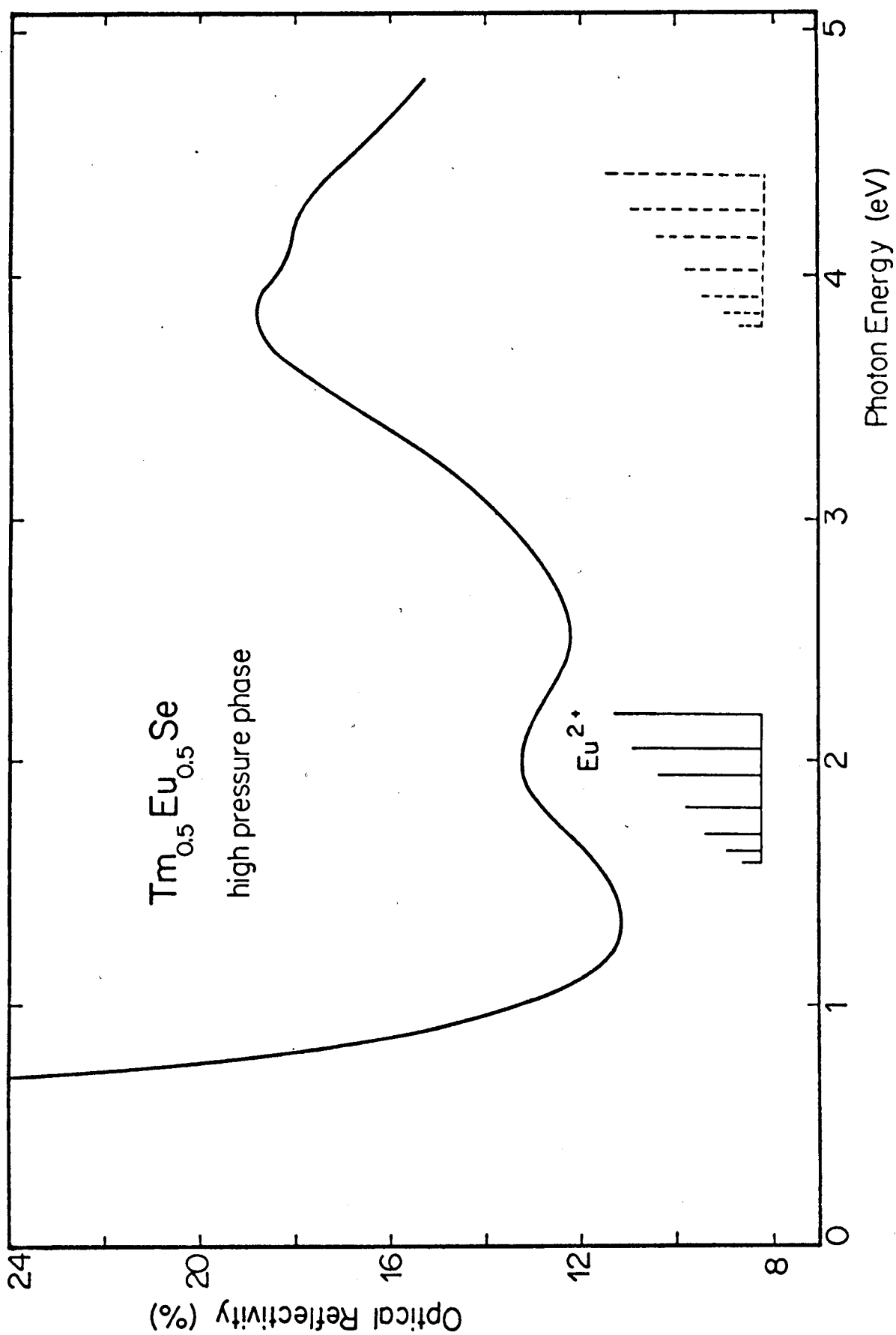
16 Temperature dependence of the electrical resistivity of $\text{Tm}_{.5}\text{Eu}_{.5}\text{Se}$ at normal pressure. The strong influence of the magnetic field on the anomaly at the ordering temperature is given in the insert.

~ 100 meV. In a traditional polaron picture of electrons coupled to phonons, this would mean a not realistic 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).

As mentioned above, the small energy gap is expected to become closed by external pressure. This has been verified measuring the electrical resistivity at 300 K as function of hydrostatic pressure up to 15 kbar (fig. 17). 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 an, 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 phenomena will appear later ⁴⁷⁾, 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 deloading 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 $\text{Eu } 4f^7$ excitations are still present and (2) the sharp



17 Pressure dependence of the electrical resistivity of $Tm_{.5}Eu_{.5}Se$.



13b 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.

reflectivity 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.

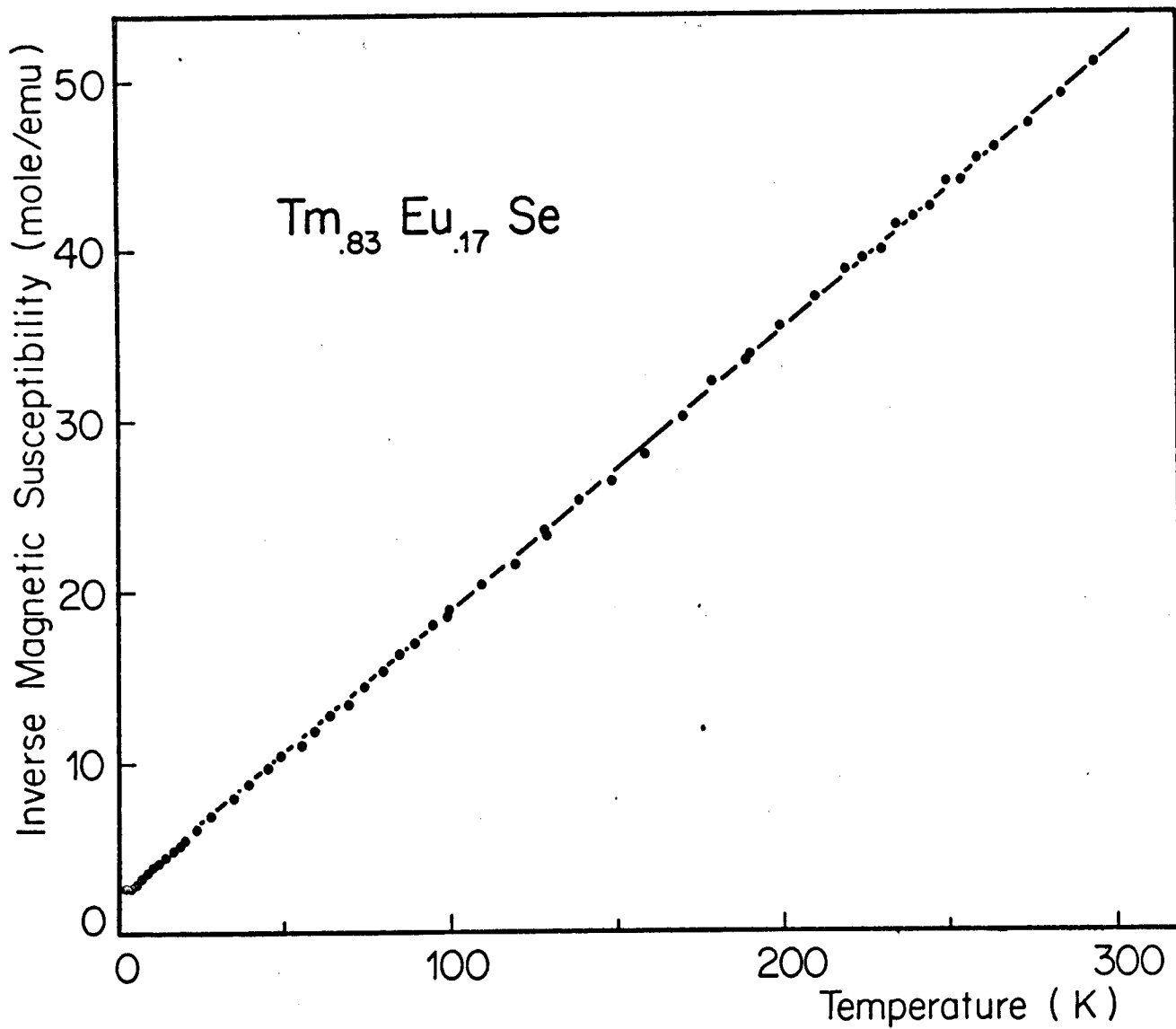
In conclusion, the semiconducting example of the $\text{Tm}_{1-x}\text{Eu}_x\text{Se}$ lead to an understanding what happens when two different RE ions, both tending to form mixed valent compounds, occupy the same cation sublattice in the same anion surroundings: the 4f level of Tm and Eu are separated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

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 possible as in the semi-conducting 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 2 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.

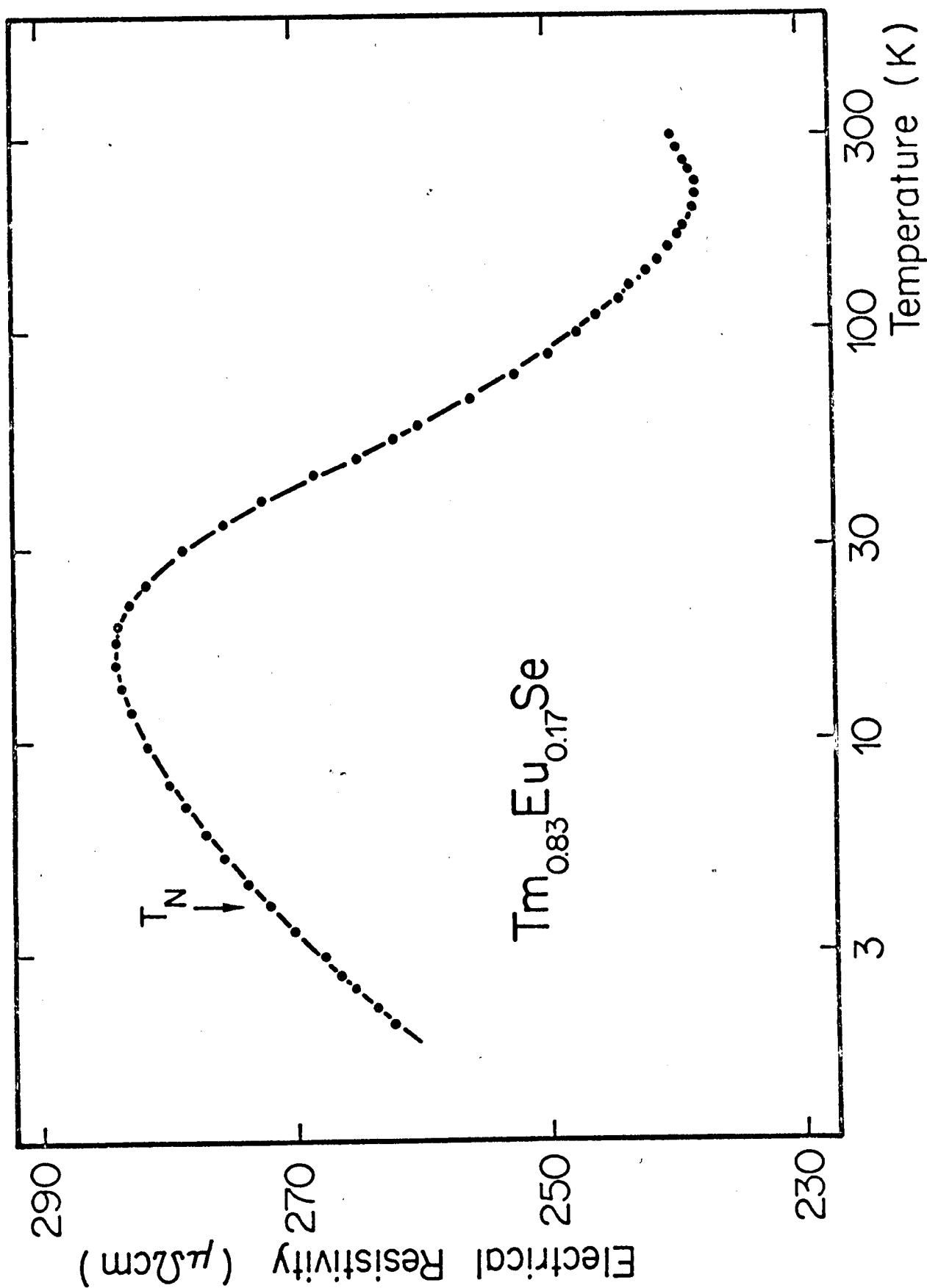
In all Tm selenides and related compounds with intermediate valent Tm ions the electrical resistance raises considerably (by factors of 2 to >10) at low temperature and only decreases in the magnetically ordered phase with net magnetization. The resistivity of metallic $\text{Tm}_{.87}\text{Eu}_{.17}\text{Se}$ as function of T is



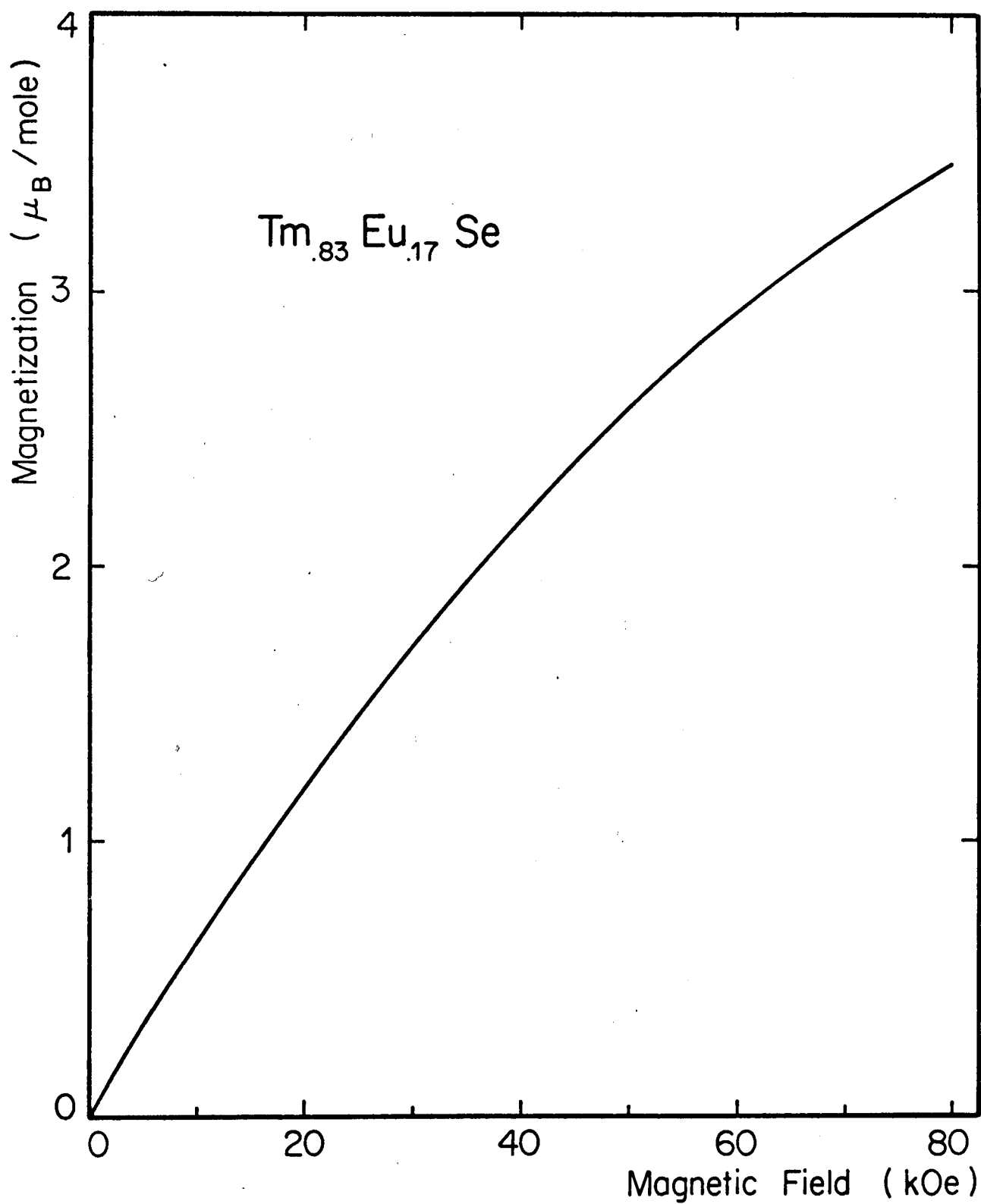
18 The inverse magnetic susceptibility of $\text{Tm}_{.83}\text{Eu}_{.17}\text{Se}$ as function of the temperature ($T_N = 4 \pm 0.3$ K)

given in Fig. 19 and the behaviour 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 K 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 to accept the same electronic structure for $Tm_{.83}Eu_{.17}Se$ 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 , $Tm_{11,30}Se_6$ and $Tm_{0.87}Se_{15}$, three compounds where the Tm ions are just at the border to 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 Eu 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 $Tm_{0.83}Eu_{0.17}Se$ 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,



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



20 Magnetization curve of $\text{Tm}_{.83}\text{Eu}_{.17}\text{Se}$ at $T = 1.8\text{ K}$.

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 on the borderline of being either divalent and/or trivalent: in $\text{Tm}_{.5}\text{Eu}_{.5}\text{Se}$ Tm is divalent but external pressure of only ~ 15 kbar suffices to induce a conversion of the valence towards triple plus. In the metallic $\text{Tm}_{.83}\text{Eu}_{.17}\text{Se}$ 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.

Concluding remarks

A summary of the results and their discussion are given at the end of each chapter and need not to be repeated here again. 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 to vary the intermediate Tm valence from 3 to 2.5. Among all RE mixed valent compound TmSe is of predominant importance because (1) both integer valent states of Tm have a not vanishing 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 concentratest 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.

Semiconducting $\text{TmSe}_{1-x}\text{Te}_x$

X =	0.5	0.77	0.83	1
Lattice constant (Å)	6.07	6.245	6.28	6.34
Energy gap E_g (meV)	180 \pm 20	240 \pm 30	250 \pm 30	320 \pm 40
d log ρ / dp (decades/kbar)	0.16	0.18	0.21	a)
d E_g / dp (meV/kbar)	-10 \pm 1	-11 \pm 1	-13.2 \pm 0.3	-10
Compressibility χ (10^{-6} /bar)	2,2 ^{c)}	2.3 \pm 0.1	2.4 \pm 0.05	2.65 ^{b)}
Deformation potential Σ' (eV)		4.5	5.5	

Notes:

- a. from Ref. 21
- b. from Ref. 10
- c. from extrapolation

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

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PART B

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