First Observation of a Magnetic-Exchange–Induced Valence Transition

W. Reim[a] and P. Wachter
Laboratorium für Festkörperphysik, Eidgenössisch Technische Hochschule Zürich, CH-8093 Zürich, Switzerland
(Received 15 March 1985)

A magnetic-exchange–induced valence transition has been observed for the first time for different compositions x of $Tm_{1-x}Eu_xSe$. This new effect is explained in terms of an exchange splitting $2\Delta E$ of the $5d$ conduction band which leads to a crossing of the lower $5d$ band edge with the Tm^{2+} $4f^{13}$ state at a certain temperature. The polar magneto-optical Kerr effect of the Eu^{2+} $4f^7 \rightarrow 4f^6 5d$ transition is used to study ΔE as a function of temperature via the magnetic red shift. Volume changes of more than 1% have been observed which correspond to an exchange-induced valence change of the Tm ions by 0.15.

PACS numbers: 78.20.Ls, 65.70.+y, 71.30.+h

Within the pseudobinary system $Tm_{1-x}Eu_xSe$, the replacement of the Eu ions by the smaller Tm ions leads to a reduction of the lattice constant. Compounds with $x > 0.25$ are semiconductors and at $x \approx 0.2$ a *compositionally induced* semiconductor-to-metal transition (SMT) has been observed.[1,2] For semiconducting compositions the energy gap is determined by the separation in energy of the Tm^{2+} $4f^{13}$ level and the $5d$ conduction band, while the Eu^{2+} $4f^7$ state is located about 1.85 eV below the conduction band.[3] The magnitude of the semiconducting gap has been determined from the behavior of the electrical resistivity under pressure showing a $\ln\rho$-ρ dependence up to the *pressure-induced SMT*.[4] The gap E_g is found to decrease linearly with composition x from ≈ 190 meV for $x = 0.85$ down to ≈ 40 meV at $x = 0.29$ near the compositionally induced SMT. In this Letter we report for the first time on a *magnetic-exchange–induced SMT*, which we found to occur in $Tm_{1-x}Eu_xSe$ for $0.25 < x \leq 0.85$. It will be shown that via the magnetic-exchange splitting of the $5d$ conduction band, which is studied by the polar magneto-optical Kerr effect, the semiconducting gap becomes closed followed by a valence change of the Tm ions from 2.0 up to 2.15. The transition into the intermediate-valent phase manifests itself in a volume collapse of 1%.

In the case of EuSe (and of course the other ferromagnetically ordering Eu chalcogenides), it is well known that the energy of the $4f^7 \rightarrow 4f^6 5d\ t_{2g}$ transition becomes reduced when the sample gets magnetized ("magnetic red-shift").[5] In a simple model which, however, describes the physics of this effect quite well, the magnetic red shift is explained by an exchange splitting of the $5d$ band[5] (for more complex models refer to Nolting[6]). The spin-polarized subbands are separated in energy by $2\Delta E = bJ_{df}\langle S_i S_j\rangle / S^2$ with the intra-atomic f-d exchange J_{df}, the spin-correlation function $\langle S_i S_j\rangle / S^2$, and b a scaling factor. For EuSe, $\Delta E \approx 160$ meV at $B = 4$ T which is of the same order of magnitude as E_g in $Tm_{1-x}Eu_xSe$ and hence it suggests a possible closing of the gap with temperature if ΔE is sufficiently large also in this system.

A direct study of the Tm^{2+} $4f^{13} \rightarrow 4f^{12}5d\ t_{2g}$ transition, however, is difficult because of substantial free-carrier absorption in this energy range. (Nevertheless, such an experiment has been performed and it is in quantitative agreement with conclusions drawn below.[7]) Therefore, we have used the Eu^{2+} $4f^7 \rightarrow 4f^6 5d\ t_{2g}$ excitation as a probe to study the energy and exchange splitting of the $5d$ band. A high-resolution measurement of the $4f^7$ excitation is achieved by the polar magneto-optical Kerr effect θ_K measured on cleaved single crystals. Figure 1 displays typical curves at temperatures above and below the magnetic ordering temperature of 13 K for $Tm_{0.15}Eu_{0.85}Se$ indicating $\Delta E \approx 190$ meV. The three peaks at energies between 1.8 and 2.5 eV all correspond to the Eu^{2+} $4f^7 \rightarrow 4f^6 5d\ t_{2g}$ transition and have been explained by a final-state splitting of the $4f^6$ configuration.[8]

At room temperature, the onset energy of the $4f^7 \rightarrow 4f^6 5d\ t_{2g}$ excitation in θ_K amounts to 2.08 eV in EuSe (somewhat larger than the gap of 1.85 eV as determined by optical absorption[5]) and decreases linearly with x down to 1.92 eV for $x = 0.38$. Subtraction of the respective magnitudes[4] of E_g from these energies yields the position of the Tm^{2+} $4f^{13}$ state relative to the Eu^{2+} $4f^7$ level, which comes out to be independent of composition x [Fig. 2(a)]. The onset energy at temperatures well below the magnetic ordering temperature, on the other hand, is reduced by the observed magnetic red shift ΔE [Fig. 2(b)]. It comes as a surprise that ΔE for $0.25 < x \leq 0.85$ is larger than in EuSe itself. Under the assumption of a temperature-independent separation in energy of the Tm^{2+} and Eu^{2+} $4f$ states, a crossing of the lower $5d$ band edge with the Tm^{2+} $4f^{13}$ level occurs for $0.25 < x \leq 0.85$. In other words, this low-temperature energy-level

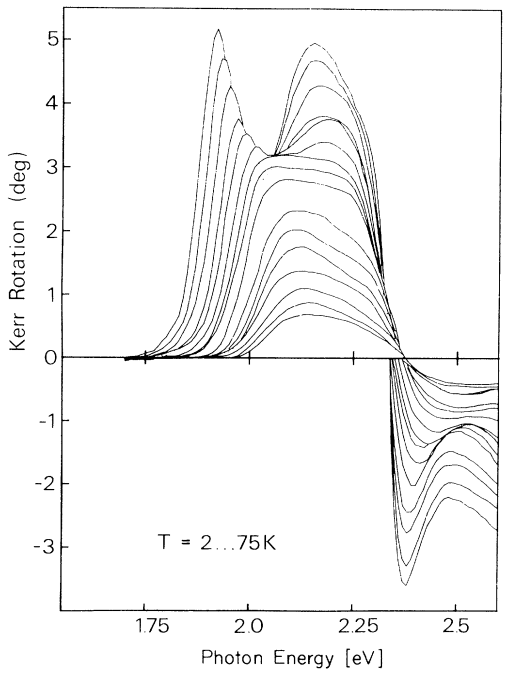

FIG. 1. Magneto-optical Kerr rotation θ_K of $Tm_{0.15}Eu_{0.85}$ at $B = 4$ T for temperatures above and below $T_N = 13$ K.

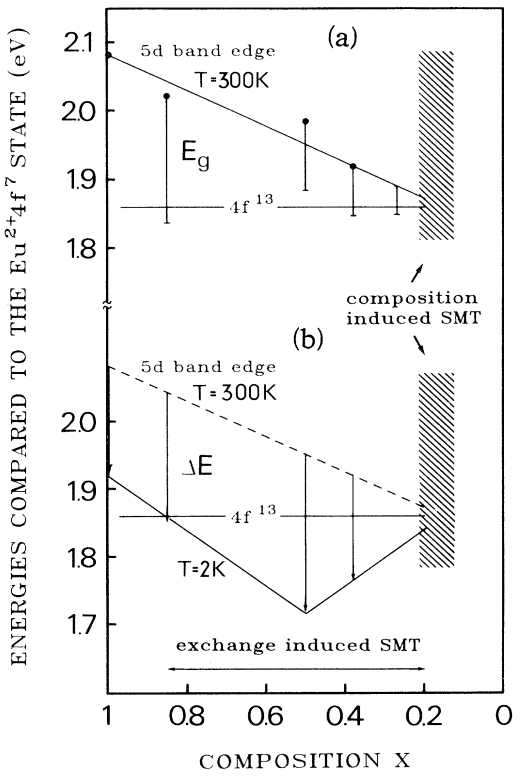

FIG. 2. (a) Onset energy of the Eu^{2+} $4f^7 \rightarrow 4f^6 5d\,t_{2g}$ transition in $Tm_{1-x}Eu_xSe$ at 300 K as a function of x from the polar Kerr effect. The subtraction of the respective semiconducting gap energy E_g (see text) yields the position of the Tm^{2+} $4f^{13}$ state relative to the Eu^{2+} $4f^7$ level. (b) Onset of the same Eu^{2+} excitation at 2 K. Compared to the value at 300 K, this energy is smaller by the size of the magnetic red shift ΔE. The energy separation of the Eu^{2+} and Tm^{2+} $4f$ states is kept constant.

scheme predicts an exchange-induced SMT in semiconducting $Tm_{1-x}Eu_xSe$ for $0.25 < x \leq 0.85$.

The SMT should go concomitantly with a transition to intermediate valency of the Tm ion. Figure 2(b) postulates the largest valence change for $x = 0.5$ with the bottom of the conduction band 140 meV below E_F at 2 K. A simple estimate of the magnitude of the valence change assuming a conduction electron density of states of 1 e^-/eV-spin gives a valence change of 0.15.

It is known from volume-versus-pressure experiments[4] that the conversion of 15% Tm^{2+} into Tm^{3+} on the average is accompanied by a volume collapse of 1%. Thus in order to verify our interpretation of Fig. 2(b), we have performed length-change measurements using a capacitance dilatometer having a sensitivity of 10^{-8} and an accuracy of $\pm 2\%$. Figure 3 displays $\Delta L/L$ for different semiconducting ($x = 0.85$, 0.50, 0.38) and metallic ($x = 0.11$) compositions of $Tm_{1-x}Eu_xSe$ and shows for comparison the length change of EuS measured with the same apparatus. The magnetothermal striction was found to be isotropic. The indicated ordering temperatures have been determined from low-field susceptibility data on the identical samples.

For the reference material EuS, $\Delta L/L$ displays the expected behavior of a volume magnetostriction (exchange striction) with maximum slope of $\Delta L/L$ (or a peak in the expansion coefficient $\alpha = (1/L)(dL/dT)$ at the magnetic ordering temperature and a magnetic contraction of $\Delta V/V \approx 1.2 \times 10^{-3}$.[9] The most contrasting behavior is shown by $Tm_{0.5}Eu_{0.5}Se$, with clearly no relation between maximum slope and T_N. (The compounds $0.25 < x \leq 0.85$ are canted antiferromagnets with spontaneous magnetic moments.[4]) In addition, this compound shows the largest volume collapse of $\approx 1.1\%$, 10 times larger than for EuS. A similar behavior is found for $x = 0.38$, whereas the sample with the largest gap, $x = 0.85$, but also the compositionally induced intermediate-valent compound $x = 0.11$ display much smaller contractions by factors of 30 and 300, respectively.

The observed variation of $\Delta V/V$ with temperature in semiconducting $Tm_{1-x}Eu_xSe$ can hardly be related to exchange striction as in EuS. Apart from the missing relationship between T_N and maximum thermal expansion, this statement is supported by the variation of $\Delta V/V$ by a factor of 300 in this system although T_N changes only by a factor of 3. Since the magnitude of

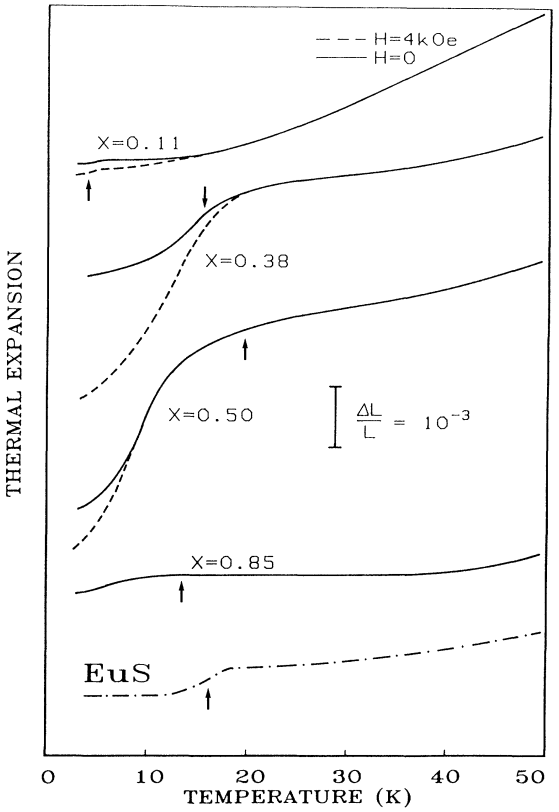

FIG. 3. Thermal expansion $\Delta L/L$ of semiconducting ($x=0.85$, 0.50, 0.38) and intermediate-valent ($x=0.11$) compositions of $Tm_{1-x}Eu_xSe$ in the temperature range near magnetic ordering. Arrows indicate the magnetic ordering temperatures determined with the same samples. EuS has been measured for comparison. The influence of an applied longitudinal magnetic field of 4 kG on $\Delta L/L$ is also shown for $x=0.5$, 0.38, and 0.11.

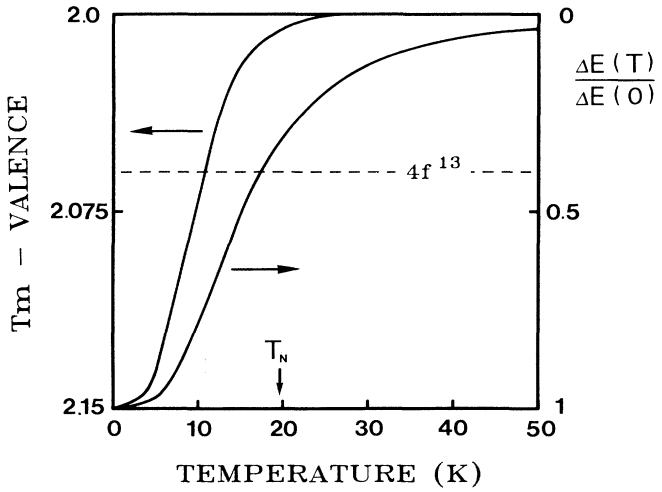

FIG. 4. Temperature dependence of the lower $5d$ band edge as derived from magneto-optics and magnetization measurements at 4 kG for $Tm_{0.5}Eu_{0.5}Se$. The temperature variation of the Tm valence is calculated from the measured volume change by Vegard's law.

the exchange striction is proportional to the internal magnetic energy U_m, which in turn can be calculated from the magnetic coupling parameter J_{12}, the exchange striction is proportional to T_N.[10]

However, the observed volume reductions are in excellent agreement with Fig. 2(b). For $x=0.15$, the exchange splitting of the conduction band just equals E_g. Because ΔE follows the spin-correlation function,[5] the bottom of the $5d$ band approaches the Tm^{2+} $4f^{13}$ state only at $T \ll T_N$ which leads to minor changes in $\Delta V/V$ below $T_N/2$ corresponding to a valence change of $\leq 2\%$. In the case of $Tm_{0.5}Eu_{0.5}Se$, on the other hand, $\Delta E(T)$ equals E_g already at higher temperatures, but still well below T_N, while for $x=0.38$ the gap becomes closed near T_N because of the reduced magnitude of the semiconducting gap. Figure 4 displays the energy of the bottom of the $5d$ t_{2g}-band relative to the Tm^{2+} $4f^{13}$ level as determined from the temperature dependence of the magnetic red shift $\Delta E(T)$. In addition, the valence of the Tm ions is shown, calculated from $\Delta V/V$. It is remarkable that the valence changes only by 0.01 until the gap is closed, although the magnetization has risen already to half of its saturation value. However, as soon as the gap is closed, the Tm valence alters rapidly with temperature.

For the compositionally induced intermediate-valent compound $x=0.11$, the Tm valence at room temperature is estimated from lattice-constant data to be ≈ 2.6. Both spin-polarized $5d$ subbands are now partly occupied already at room temperature, which result can be extracted from the conduction electron spin polarization of TmSe of 30%.[11] However, if both $5d$ subbands are partly occupied, the temperature variation of $2\Delta E$ only induces a change in the occupation numbers of these subbands, but the number of conduction electrons and hence the valence of Tm is practically independent of temperature. The observed $\Delta V/V \approx 10^{-4}$ is attributed to a pure magnetostrictive effect similar to that for TmSe, which displays a volume magnetoelastic effect of the same order of magnitude.[12] It should be mentioned that the spontaneous magnetization decreases with $1-x$ and becomes zero at the compositionally induced SMT. Therefore the influence of an applied magnetic field on ΔE increases with $1-x$ which in fact has been observed (Fig. 3) (longitudinal magnetostriction).

We have shown that a magnetic-exchange–induced SMT occurs in semiconducting $Tm_{1-x}Eu_xSe$ for $0.25 < x \leq 0.85$. It could be demonstrated that the

mixing of d and f wave functions is negligible as long as the semiconducting gap is present. This behavior contrasts with the observation of substantial valence mixing in $TmSe_{1-x}Te_x$ already for semiconducting compositions x,[13] and points out the different mechanisms which force the Tm ions to enter the intermediate-valent state in these two systems.

The authors are grateful to E. Kaldis for the growth and chemical characterization of the single crystals and to J. Schoenes for some critical discussions. We acknowledge the expert technical assistance of H. P. Staub and K. Mattenberger in part of the experiment and the financial support of the Swiss National Foundation.

---

[a]Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598.

[1]B. Batlogg, E. Kaldis, and P. Wachter, J. Phys. (Paris), Colloq. **40**, C5-370 (1979).

[2]E. Kaldis and B. Fritzler, J. Phys. (Paris), Colloq. **41**, C5-135 (1980).

[3]B. Batlogg, Phys. Rev. B **23**, 650 (1981).

[4]H. Boppart and P. Wachter, in *Physics of Solids under High Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 301, and to be published.

[5]P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 509.

[6]W. Nolting, Phys. Status Solidi (b) **79**, 573 (1977).

[7]W. Reim, H. Boppart, and P. Wachter, J. Magn. Magn. Mater. (to be published).

[8]J. Schoenes, Z. Phys. B **20**, 345 (1975).

[9]F. Lévy, Phys. Konden. Mater. **10**, 71 (1969).

[10]B. E. Argyle, N. Miyata, and T. D. Schultz, Phys. Rev. **160**, 413 (1967).

[11]W. Reim, O. E. Hüsser, J. Schoenes, E. Kaldis, and P. Wachter, J. Appl. Phys. **52**, 2155 (1984).

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

[13]H. Boppart and P. Wachter, Phys. Rev. Lett. **53**, 1759 (1984).