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To cite this version:

| B. Batlogg, E. Kaldis, P. Wachter. Valence changes and semiconductor-to-metal transitions in Tm$_{1-x}$EuxSe and TmSe$_{1-x}$Tex. Journal de Physique Colloques, 1979, 40 (C5), pp.C5-370-C5-371. <10.1051/jphyscol:19795131>. <jpa-00218917>

HAL Id: jpa-00218917

https://hal.archives-ouvertes.fr/jpa-00218917

Submitted on 1 Jan 1979

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Valence changes and semiconductor-to-metal transitions in Tm$_{1-x}$Eu$_x$Se and TmSe$_{1-x}$Te$_x$

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Résumé. — En alliant TmSe à EuSe ou TmTe il est possible de faire varier la valence de Tm entre environ 3+ et 2+. Les propriétés magnétiques, optiques et de transport mettent en évidence la transition métal-semiconducteur associée au changement de valence. Une pression hydrostatique permet d'inverser la situation en faisant passer Tm d'un état divalent à un état trivalent.

Abstract. — Alloying TmSe with either EuSe or TmTe results in a Tm valence varying from nearly 3+ to 2+. Optical, transport and magnetic properties show the concomittant metal-to-semiconductor transition. Hydrostatic pressure then converts Tm from divalent back to trivalent.

From investigations of TmSe with a systematically varying Tm to Se ratio an average Tm valence of ~ 2.75 has been deduced for the stoichiometric compound [1, 2]. The purpose of alloying TmSe with either TmTe or EuSe is twofold: first, to shift the Tm valence towards 2 and second, to prepare systems which contain only divalent rare earth ions but are so close to a valence crossover that even moderate changes of external parameters (temperature, pressure) are sufficient to induce drastic changes in the electronic structure.

It is the energy difference $\Delta E$ between the two configurations 4$f^{13}$(Tm$^{2+}$) and 4$f^{12}$5d(Tm$^{3+}$) which determines the valence state in any particular case. All the following considerations are based on the fact that this $\Delta E$ can be influenced externally. The 5d band states, derived from the RE 5d atomic states, are split by the crystal electric field of the octahedral surroundings and the energetically lower « 5d$^{2g}$ » part shifts to even lower energies as the interionic distances are reduced. Therefore $\Delta E$ depends sensitively upon variations of the lattice parameter.

TmSe-TmTe. — The partial replacement of Se ions by the larger Te ions offers the possibility of applying negative pressure through the anion lattice. TmTe is a semiconductor [3, 4] in which Tm is purely divalent. In the alloy system TmSe$_{1-x}$Te$_x$ with 0.5 $\leq$ x $\leq$ 1 the electrical resistivity at 300 K drops exponentially on going from TmTe ($\sim 10^5$ $\Omega$cm) to TmSe$_{0.5}$Te$_{0.5}$ ($\sim 0.3$ $\Omega$cm) and the temperature dependence shows typical semiconducting behaviour (see figure 1). As pointed out above, hydrostatic pressure is expected to close the energy gap and indeed we find an exponential decrease of the resistivity $\rho$ by 0.17 decades per kbar in all semiconducting samples. Assuming $\rho \sim \exp(\Delta E/kT)$, the value of $\Delta E$ can then be estimated using the measured change of $\rho$ under pressure and the measured $\rho$ for $\Delta E < 0$, corresponding for instance to the metallic TmSe$_{0.83}$Te$_{0.17}$ ($\sim 120$ $\mu\Omega$cm).

Accordingly $\Delta E$ decreases linearly within the experimental accuracy from 320 $\pm$ 30 meV for TmTe (in excellent agreement with ref. [4]) to 170 $\pm$ 30 meV for TmSe$_{0.5}$Te$_{0.5}$. The divalency of Tm for x $>$ 0.5 at normal pressure is also confirmed by the magnetic susceptibility and a representative example is shown in figure 2. The effective magnetic moment

$\mu_{eff} = 4.73$ $\mu_B$/Tm

is very close to the calculated free ion value of 4.58 for Tm$^{2+}$ (4$f^{13}$). Below $\sim 90$ K $\chi^{-1}$ starts to deviate from the Curie-Weiss straight line as expected from the crystal electric field effects on the 4f electrons.
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The paramagnetic Curie temperature ($\pm 0.5$ K) and the possible indication of magnetic ordering well below 1.5 K (see insert in figure 2) are very similar to the data of TmTe [5].

![Fig. 2. Reciprocal magnetic susceptibility of TmSe₀.₅Te₀.₅.](image)

For $x < 0.25$, Tm is intermediate valent. This follows from the resistivity at 300 K (100-200 $\mu\Omega$cm), which is typical for RE$^{5+}$ monochalcogenides, and from the high concentration of delocalized electrons giving rise to the high metallic reflectivity in the long wavelength part of the visible spectrum. Below 300 K the resistivity steadily increases on cooling and either stays constant below $\sim 3$ K ($x = 0.09$) or passes through a maximum at $\sim 5.5$ K ($x = 0.17$). The over-all behaviour (figure 3) strongly resembles that of Tm₀.₉₇Se. From the shape of the magnetoresistance curves the magnetic ordering temperatures can be estimated as $3 \pm 0.5$ K and $5.5 \pm 0.5$ K for $x = 0.09$ and 0.17, resp. Additional magnetization measurements on TmSe₀.₈₃Te₀.₁₇ show for the first time a spontaneous net magnetic moment ($T \lesssim 5$ K) in a mixed valent RE compound.

**References**