

## Spontaneous Magnetization in a Mixed-Valent Rare-Earth Compound

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Clear experimental evidence is given for the first observation of a spontaneous magnetization in a mixed-valent rare-earth compound at low temperatures. The magnetic susceptibility, the magnetization, the magnetostriction, and the electrical conductivity of  $\text{TmSe}_{0.83}\text{Te}_{0.17}$  reveal a transition to a magnetically ordered state with a net magnetic moment below 5.5 K. This is in quantitative agreement with Varma's recent predictions based on a microscopic model for mixed-valent systems.

Many theoretical attempts to solve the problem of intermediate valency start by considering a single mixed-valent impurity in an otherwise normal background. Since in many mixed-valent rare-earth compounds, however, each rare-earth site is occupied by a mixed-valent ion (homogeneously mixed-valent compounds), the problem then arises to generalize this isolated-ion picture to the so-called concentrated case. There is no doubt that the mutual interactions among the mixed-valent ions play an important role, especially in the case of homogeneously mixed-valent compounds where the new ground state to a large extent is dictated by such interactions.

Mixed-valent rare-earth compounds usually show no magnetic ordering at low temperatures,<sup>1</sup> the only exception being  $\text{TmSe}$  which is metamagnetic below 3 K.<sup>2-5</sup> It is exactly this outstanding behavior of  $\text{TmSe}$  which might help us to shed some light on the nature of the above-mentioned interactions in mixed-valent compounds, which in most cases inhibit a magnetic ordering or even weaken the magnetic susceptibility of the material and, in one example so far, allow for a long-range magnetic ordering. One explanation for this distinctly different behavior was recently offered by Varma<sup>6</sup> who pointed to the fact that among all the rare-earth ions tending to mixed-valent behavior, only Tm has a magnetic ground state in both possible configurations, and that therefore a *double-exchange* mechanism involving the partly free  $4f$  electrons could provide the dominant magnetic coupling between the ions. This model at the same time predicts no magnetic ordering in all compounds where one of the possible configurations of the rare-earth ion has a ground state with  $J=0$ . A challenging result of this model is the prediction of ferromagnetic order in  $\text{TmSe}$  with a higher degree of mixing than observed up to now, where in the most favorable case an intermediate valency of +2.7 has been de-

duced from the lattice parameter.

A recent systematic study of  $\text{TmSe}$  with varying chemical composition revealed the possibility of an enhanced valence mixing by expansion of the lattice.<sup>7-10</sup> Such an enhancement of the divalent character of the Tm ions is offered by the partial replacement of Se by Te, keeping in mind that a mechanical and a chemical increase of the lattice constant are never quite the same.

Our low-field susceptibility measurements on a number of compounds of the type  $\text{TmSe}_{1-x}\text{Te}_x$  ( $0 < x < 1$ ) corroborate the above idea. The Curie-Weiss behavior reveals a decrease of the effective moment  $p_{\text{eff}}$  when  $x$  is increased, indicating the tendency towards divalency of the Tm ions. We recall that the free-ion moment is  $7.56\mu_B$  and  $4.54\mu_B$  for trivalent and divalent Tm, respectively. We also note that when more than half of the Se is replaced by Te ( $x \geq 0.5$ ), the compounds become narrow-gap semiconductors with Tm in its pure divalent state and that no single-phase and homogeneous material exists so far for  $0.2 < x < 0.5$ .<sup>11</sup>

Within the series  $\text{TmSe}_{1-x}\text{Te}_x$  the compound  $\text{TmSe}_{0.83}\text{Te}_{0.17}$  is outstanding in the sense that both the lattice constant and  $p_{\text{eff}}$  reveal an intermediate valence of +2.5, indicating the highest possible degree of mixing in Tm compounds. In view of a test of the above-mentioned predictions of the double-exchange model it seemed of interest to study this particular compound in some more detail and in this Letter we report measurements of the magnetic susceptibility, the magnetization, the electrical resistivity, the thermal expansion, and the magnetostriction of  $\text{TmSe}_{0.83}\text{Te}_{0.17}$ , unambiguously showing a *net spontaneous magnetization* below 5 K in zero magnetic field, quite in contrast to the antiferromagnetic ordering observed so far in  $\text{TmSe}$  for  $H=0$ . Within the same series, evidence for a spontaneous magnetization upon ordering has also been found in the compound  $\text{TmSe}_{0.91}\text{Te}_{0.09}$  although the anom-

alies in the properties investigated were much weaker in that case. The spontaneous magnetization, e.g., amounts to  $0.3\mu_B$  at 2 K, quite a bit smaller than that in  $\text{TmSe}_{0.83}\text{Te}_{0.17}$  (see below).

From the susceptibility measurements we deduce an effective moment of  $5.87\mu_B$  per Tm ion and a paramagnetic Curie temperature  $\Theta_p$  of  $-17$  K. This value for  $\Theta_p$  is quite different from the value deduced from stoichiometric TmSe where  $\Theta_p \sim -30$  K and indicates the enhanced ferromagnetic component of the exchange interactions.

The appearance of a spontaneous magnetization is reflected in a magnetization curve measured at 1.8 K and shown in Fig. 1. Taking into account the demagnetization factor of our samples we find that the magnetization amounts to  $\sim 0.8\mu_B$  per Tm ion at zero field and then gradually reaches  $2.5\mu_B$  per Tm ion at 80 kOe without really showing saturation. Since our crystals are expected to consist of more than one magnetic domain, the spontaneous moment might well be higher than observed in this macroscopic measurement. In order to evaluate the magnetic ordering temperature, the low-field magnetization ( $H_{\text{ext}} \sim 100$  Oe) is displayed in Fig. 2(a). It rises steeply below 5 K and tends to saturate below 2 K.

As an important experimental detail we note that identical curves result from several measurements when the sample is warmed up to far above the ordering temperature and cooled again. These rather direct evidences for the appearance of a net magnetization in the ordered state of  $\text{TmSe}_{0.83}\text{Te}_{0.17}$  are supported by the low-temperature behavior of the electrical resistance, the thermal expansion, and the magnetostriction.

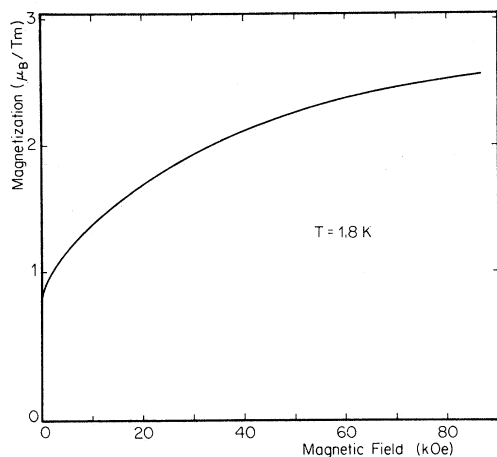


FIG. 1. Field dependence of the magnetization  $M(H)$ .  $H$  was parallel to [100] and demagnetization corrections were taken into account.

The electrical resistivity steadily increases from its room-temperature value of  $220 \mu\Omega \text{ cm}$  to approximately  $570 \mu\Omega \text{ cm}$  at 5 K, quite reminiscent of the behavior of Tm-deficient TmSe without, however, the clear logarithmic temperature dependence. The most striking difference from TmSe is, of course, the decrease of  $\rho$  below 5 K [see Fig. 2(c)]. In mixed-valent TmSe such a decrease was only observed in an external magnetic field of sufficient strength to induce the ferromagnetic phase.<sup>7-9, 12-14</sup> The magnetic ordering is also reflected in the magnetoresistance. An external field always reduces  $\rho$  (by  $\sim 11\%$  at  $T = 4$  K and  $H = 18$  kOe) and the curvature of  $\rho(H)$  gradually changes the sign upon passing through  $T = 5$  K. The temperature dependence of  $\rho$  taken in a field of 18 kOe again shows the onset of magnetic order.

The magnetic phase transition is also very distinctly revealed by thermal expansion and magnetostriction measurements. The zero-field linear thermal expansion coefficient along [100]

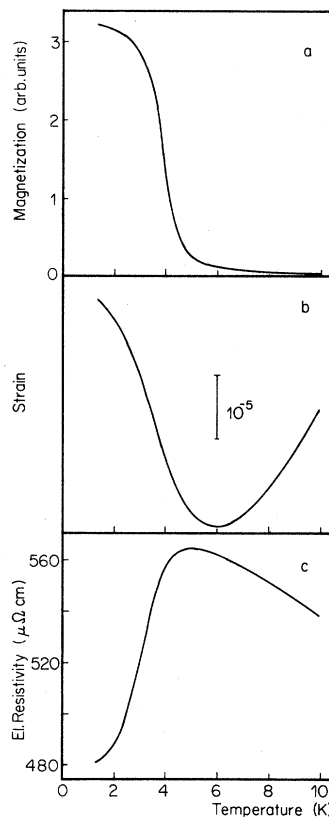


FIG. 2. Temperature dependence of (a) the magnetization in an external field  $H = 100$  Oe; (b) the total strain along [100] in zero external field; and (c) the zero field electrical resistivity; between 1.5 and 10 K.

shows a pronounced negative anomaly with a peak value of  $\alpha = -13 \times 10^{-6} \text{ K}^{-1}$  at 3.8 K. This temperature coincides with that where  $\partial M/\partial T$  in small fields has its maximum value. The shape of the anomaly is unusual in the sense that it does not show mean-field behavior but is quite symmetric around the peak temperature instead. This peak temperature is substantially lower than what is found for the onset of magnetic order,  $T_c$ . The total strain amounts to about  $3 \times 10^{-5}$  and is opposite in sign to that observed<sup>7-9,12</sup> in TmSe [see Fig. 2(b)]. Well above  $T_c$  a magnetic field causes a lattice expansion with a normal paramagnetic  $H^2$  dependence of the strain  $\epsilon$ . At 5.6 K the initial slope  $(\partial \epsilon/\partial H)_{H=0}$  changes sign, thus indicating the onset of magnetic ordering. In the ordered phase the magnetostriction is negative and we note that an external field of 14 kOe completely quenches the anomaly of the expansion coefficient found in zero field.

An accurate determination of  $T_c$  is difficult because in all physical properties we find pronounced tails in their temperature dependence close to but above  $T_c$ . These high-temperature tails are probably due to fluctuations although their extension is actually too large to be solely due to critical behavior in the usual sense. We have to admit, however, that not much is known about the mechanisms involved in phase transitions of mixed-valent systems.

In the present case the magnetization is very similar to that observed<sup>15</sup> in TmSe except for the metamagnetic behavior at low fields found in the binary compound. This supports the view that the same magnetic phase that was found between phase boundaries III and IV in TmSe, i.e., in fields above the metamagnetic transition, already appears in zero external field in  $\text{TmSe}_{0.83}\text{Te}_{0.17}$ . Such a behavior is, in fact, to be expected from the results of our previous work<sup>7-9</sup> in TmSe where it was established that the degree of valence mixing can be influenced by means of a variations of the chemical composition. The resulting changes of the magnetic properties lead to the conclusion that a decrease of the intermediate valence of the Tm ions from +3 to +2.5 causes an increase of the Néel temperature and a reduction of the metamagnetic transition field (phase boundary III). Our previous data suggest that this critical field should be zero for an intermediate valence lower than +2.4 and the corresponding Curie temperature  $T_c$  is predicted to be in the vicinity of 5 K. We should like to mention here that similar conclusions have been drawn in the

work of Andres *et al.*<sup>16</sup> The surprising agreement between these estimates and the data presented above reveal that in TmSe competing exchange interactions determine the low-temperature magnetic behavior. The relative importance of these interactions strongly depends on the degree of valence mixing, and the increasing importance of the ferromagnetic exchange then finally leads to a transition from an antiferromagnetic type of ordering to an order with net magnetization.

It is tempting to ascribe the small magnetic moment and the lack of saturation of  $M$  to crystal-field-split energy levels of the  $4f$  electrons and their magnetic field dependence. In the context of mixed-valent compounds with the hybridization of  $4f$  and  $5d$  states, however, the usual concept of crystal electric fields is not applicable. Indeed, all other experiments in homogeneously mixed-valence compounds have failed so far to demonstrate crystal-field effects as they are usually observed in metallic rare-earth materials. It may very well be that other demagnetizing mechanisms typical for mixed-valence compounds are also effective in this case.

Considering another possibility for the striking moment reduction we note that the features of the magnetization (see Fig. 2) are compatible with the concept of *double-exchange* interaction. As de Gennes<sup>17</sup> pointed out, the ferromagnetic double exchange always competes with other exchange mechanisms. This may lead to complicated spin arrangements and therefore to magnetization curves as we observe in our experiment.

As mentioned above the idea to invoke the double-exchange interaction to describe the unusual physical properties of TmSe has recently been brought up by Varma.<sup>6</sup> Basically, double exchange is provided by real motion of electrons between unfilled shells obeying Hund's rules and is significant when the bandwidth is not large compared to the intra-atomic exchange integrals. The strength of this ferromagnetic coupling is to lowest order proportional to the number of these itinerant electrons. In the homogeneous mixed-valent compounds, the rather localized  $4f$  states hybridize with the  $5d$  band states and acquire a width of the order of  $10^{-2}$ – $10^{-3}$  eV. The motion of the "double-exchange electrons" is particularly favored when the moments of the individual ions are parallel and a decrease of the electrical resistivity in a ferromagnetically ordered state is anticipated. This is what is actually observed in TmSe and now in chemically expanded TmSe

( $\text{TmSe}_{0.83}\text{Te}_{0.17}$ ) with a high degree of valence mixing. As mentioned above, a direct consequence of this double-exchange theory is the prediction of ferromagnetism in strongly mixed-valent  $\text{TmSe}$  and our observation of a net magnetic moment in a substance prepared accordingly gives strong support for these ideas.

From earlier and the present work we note that in mixed-valent  $\text{TmSe}$  compounds  $\chi$  deviates from the high-temperature Curie-Weiss behavior below 40 K and this is true for all samples investigated. The enhancement of  $\chi$  is growing with increasing mixed-valent character and this again is in qualitative agreement with expectations using the double-exchange theory. It needs, however, to be clarified why at the same temperature and parallel to the increase of  $\chi$  the electrical resistivity rises considerably with decreasing temperature.

In conclusion, we believe that our present investigation provides new results to clarify the nature of interactions in homogeneously mixed-valent compounds, which are, without doubt, an essential ingredient to understand the behavior of such materials. In that sense it is encouraging to note that predictions of a microscopic theory are in agreement with our experimental findings.

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