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Observation of the characteristics of Tm^{2+} and Tm^{3+} in homogeneous and inhomogeneous TmSe

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Résumé. — Nous présentons des mesures de susceptibilité faites sur le système Tm_ySe . Des mesures de susceptibilité sous pression montrent qu'il n'y a pas de conversion des ions 2^+ à 3^+ .

Abstract. — Susceptibility measurements on the Tm_ySe system ($0.79 < y < 1$) are presented. Susceptibility under pressure shows no conversion of 2^+ ions into 3^+ ions.

1. Introduction. — In the intermediate valence system Tm_ySe , the lattice parameter [1, 2] varies from 5.63 Å to 5.72 Å when y increases from 0.79 to unity. The high temperature Curie constant C_H varies with the thulium vacancy concentration and it attains — at the stoichiometry — the average value between the Tm^{2+} and Tm^{3+} Curie constants for the free ions. If we assume that the Tm^{2+} and Tm^{3+} states coexist in the sample, either statically on different sites or fluctuating on each site, then the Curie constant could be used to evaluate the relative fraction of each configuration, so $x = (C_3 - C_H)/(C_3 - C_2)$ (C_2 and C_3 are the free ion values for the Tm^{2+} and Tm^{3+} respectively; x is the Tm^{2+} concentration).

At the Rochester Conference [3] we have shown some evidence for the presence of these two configurations, and we analysed TmSe as $(\text{Tm}_x^{2+} \text{Tm}_{1-x}^{3+})\text{Se}$. In the simplest picture, a static mixing of these magnetic states implies that, at low temperatures, the $J = 7/2$ state of Tm^{2+} should give a magnetic Curie law corresponding to the magnetic doublet ground state of the crystal field, whereas the Tm^{3+} state is assumed to be a singlet state characterized by a temperature independent Van Vleck susceptibility. If both configurations are present we have to recognize these properties in the low temperature magnetization and susceptibility measurements.

2. Experimental results. — Figures 1 and 2 show the temperature dependence of the susceptibility at high and low T (lattice parameters a_0 are reported on figures; TmS is also shown for comparison). For the lowest lattice constants, the TmSe susceptibility is very similar to the TmS susceptibility, which is a Tm^{3+} singlet-ground-state compound with induced antiferromagnetism. Below 50 K, when x

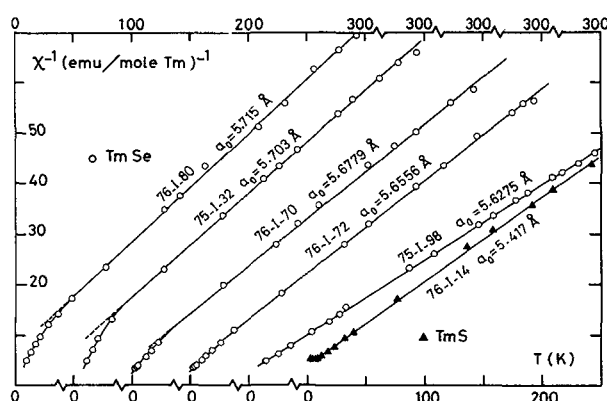


Fig. 1. — High temperature susceptibility of TmSe and TmS .

increases (a_0 increases) a Curie susceptibility due to Tm^{2+} is added to the Tm^{3+} Van Vleck susceptibility. With a doublet ground state, the Tm^{2+} magnetization should be written as $\sigma = Nx\mu_0 \tanh(\mu_0 h/k_B T)$ and therefore its Curie constant C_L at low temperature becomes $C_L = Nx\mu_0^2/k_B$ (μ_0 being the effective Tm^{2+} moment, x is the Tm^{2+} concentration), whereas the saturation magnetization is given by $\sigma_s = Nx\mu_0$. In this scheme, the ratio C_L/σ_s , independent of x ,

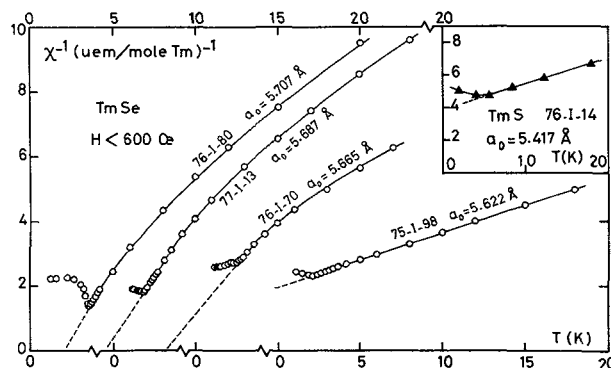


Fig. 2. — Low temperature susceptibility of TmSe and TmS .

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is related to the effective moment of the Tm^{2+} ions ; its deduced value (of the order of $3.5 \mu_B$) is greater than the magnetic moment of any possible ground state ($1.7 \mu_B/\text{Tm}^{2+}$) showing that the Tm^{2+} moment is enhanced by the Tm trivalent ions. We can then calculate the concentration of Tm^{2+} , in good agreement with the room temperature Curie constant determination [1]. For example, near stoichiometry we calculate $x = 0.53$ from the room temperature C_H , and $x = 0.54$ using the low temperature C_L/σ_S ratio.

Magnetic properties are correlated with the Tm^{2+} concentrations, as shown in figures 2 and 3. The antiferromagnetic Neel temperature, the magnetization jump, the paramagnetic Curie temperature, the susceptibility at the transition temperature and the residual resistivity are strongly x dependent. For instance, on figure 3, we show the magnetization jump characteristic of a metamagnetic transition ; it is clearly observed for the almost stoichiometric samples ($a_0 = 5.71 \text{ \AA}$), but it disappears completely for the samples with higher vacancies ($a_0 = 5.622 \text{ \AA}$). This shows that the metamagnetic transition appears when the Tm^{2+} character is strong.

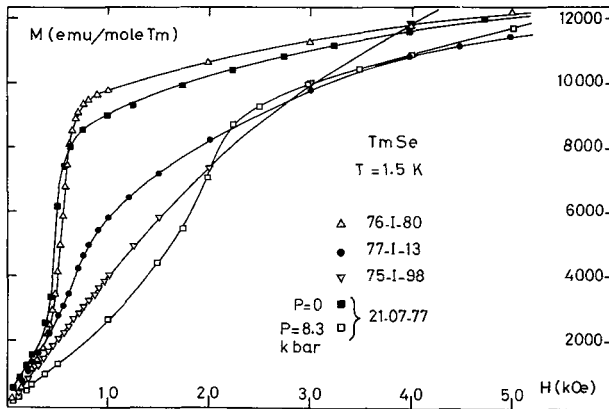


Fig. 3. — Low temperature magnetization of TmSe.

We will also describe some results obtained under pressure on a nearly stoichiometric sample. As reported on figure 4, above 50 K, the paramagnetic Curie Weiss susceptibility is exactly the same at both pressures ($p = 0$ and $p = 8.3 \text{ kbar}$). Below 50 K, the susceptibility under pressure is lower ; at T_N , the ratio between the 8 kbar and zero pressure susceptibilities is about 1/3. The striking points are the similar temperature dependence of the susceptibility and the same approximate values of the saturation magnetization (Fig. 3). The similar ratio C_L/σ_S at low T , and the same value of C_H at high T , for both pressures, support clearly that the Tm^{2+} concentration does not change : in contradiction with the reference [4] there is no conversion of Tm^{2+} into Tm^{3+} ions. The increase

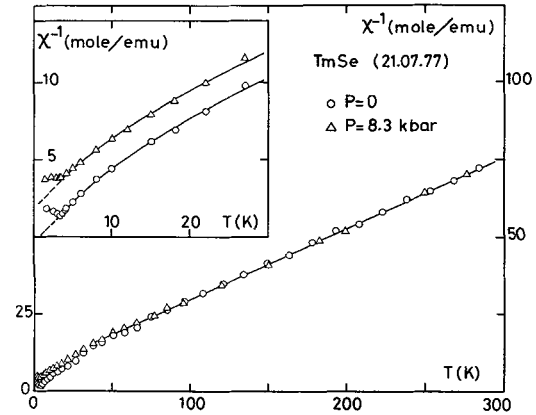


Fig. 4. — Magnetic susceptibility of TmSe under pressure.

under pressure of the critical field H_C can be correlated to the corresponding decrease of χ at T_N : the product $\chi(T_N) H_C$ is almost a constant, as in some metamagnetic transitions. The strong pressure dependence of χ at T_N is analogous to effects observed in Kondo lattices such as CeAl_2 and CeAl_3 [5]. In these compounds, the Kondo parameter of the Ce^{3+} ions is strongly pressure dependent ; in TmSe, the parameter describing the Kondo effect of Tm^{2+} in the TmSe matrix is also strongly pressure dependent but not the fraction of one configuration. An extrapolation of the metamagnetic theory [6] using a phenomenological law for the local induced moments (a Kondo-like behaviour), could be fruitful in the interpretation of such properties : an interesting question will be the change of the order of the field induced transition as a function of the Kondo temperature.

In conclusion, the TmSe study suggests the simultaneous presence of Tm^{2+} and Tm^{3+} configurations in the same sample above T_N . This effect exists not only in samples with thulium vacancies but in the stoichiometric samples also. This behaviour in a homogeneous environment for each Tm supports the idea of the presence of Tm^{2+} and Tm^{3+} characteristics on the same site. Below T_N the analysis in terms of two distinct configurations may no longer be valid, specially for samples near stoichiometry. The large increase [3] of the resistivity below T_N suggests some localization of the conduction electrons in a new state. Strong evidence of this effect has been recently observed by Haen *et al.* [7] : the residual resistivity at 10 mK versus x , diverges for $x = 0.5$, which surprisingly corresponds to the stoichiometric TmSe. This suggests that this phenomenon can arrive when the fraction of Tm^{2+} is equal to the number of conduction electrons with which they interact to give Kondo effects above T_N and a new ground state below T_N , as treated by Jullien [8] for a Kondo lattice.

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