Divergence of the Very-Low-Temperature Residual Resistivity of Tm_xSe as $x \rightarrow 1$

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The resistivity of the intermediate-valence compounds Tm_xSe ($0.79 < x < 0.993$) has been measured down to 10 mK. The variation of the residual resistivity with composition (i.e., with the proportion of Tm^{2+}) suggests that a perfectly stoichiometric system might become insulating at 0 K. This divergence seems to take place when the two valence states are equal in concentration. A possible interpretation based on the recent developments of the Kondo-lattice models is discussed.

Since Bucher and co-workers first reported on the intermediate valence of TmSe,[1] one of the major advances has been the recognition that deviations from stoichiometry have a drastic effect on the physical properties of this compound.[2] In particular, the lattice constant a_0, which reflects the valence state of Tm, can be varied from about 5.71 Å in nearly stoichiometric samples, to about 5.62 Å in samples with the largest thulium deficiency.[3,4] These a_0's correspond, respectively, to an intermediate-valence state and a nearly 3+ state. The Curie constant exhibits a similar variation from 4.90 emu/mole (intermediate) to 6.95 emu/mole (almost that of Tm^{3+}).[4] In contrast with most intermediate-valence systems, TmSe orders antiferromagnetically at low temperatures.[1] Depending on a_0, the Néel temperature T_N varies from 1.7 to 3.5 K. No sizable valence change occurs at T_N as shown by the thermal expansion data.[3] The antiferromagnetic (AF) structure has been characterized by neutron diffraction measurements[5] to be type I in a sample with a large lattice constant. The application of a magnetic field converts this AF phase to a ferromagnetic (FM) phase, via a metamagnetic transition, at a critical-field H_c of a few kilo-oersteds[5]; a jump appears at H_c in the magnetization curve.[1,6,7] The transport properties of such nearly stoichiometric TmSe samples are very unusual.[8] Their electrical resistivities, which increase smoothly from room temperature (RT) down to T_N, exhibit a sudden rise below this temperature.[3,8] This effect is destroyed by the magnetic field and the resistivity in the FM phase then lies below the RT value.[3,9,10] In the past, these anomalous electrical properties of TmSe have been ascribed either to the Kondo effect of Tm^{2+} "impurities" in a matrix of Tm^{3+} (Refs. 7, 8, 9) or to a double-exchange mechanism involving $4f$ electrons moving between strongly coupled Hund's-rule atoms.[10,11] However, our previous measurements[8] had shown that the resistivity of a nearly stoichiometric TmSe saturates at a high value (4500 $\mu\Omega$ cm) at very low temperatures (10 mK) and, from the measurements of Batlogg *et al.*[3] (made down to 1.5 K),[3] one expects even higher residual resistivities in more stoichiometric samples. Therefore, to better understand this anomaly, we have undertaken a more systematic experimental study at very low temperatures.

We report here experiments performed on five Tm_xSe single crystals with lattice parameters ranging from 5.625 to 5.712 Å (see Table I). The preparation of the starting Tm_xSe ingot was described previously.[4] The Néel temperatures, deduced from the ac susceptibility peaks, are reported in Table I. The resistivity was then measured with a low-frequency ac brdige. The contacts consisted of four indium-soldered wires in the Van der Pauw geometry.[12] The very low-temperature measurements were performed in

TABLE I. Physical parameters of the Tm_xSe samples. The room-temperature lattice parameters (a_0) were determined by x-rays on adjacent parts of the samples.

Sample number	Batch reference	x	a_0 (Å)	ρ(RT) ($\mu\Omega$ cm)	T_N (K)
1	76-I-80	0.993	5.712	217±7	3.46
2	77-I-9	0.991	5.709	211±6	3.33
3	75-II-92	0.970	5.684	192±9	1.8
4	76-I-70	0.935	5.665	182±9	2.5
5	75-I-98	0.790	5.625	174±15	2.2

the mixing chamber of a dilution refrigerator. Particular attention was paid to the choice of the measuring currents so as to minimize Joule heating. With this restriction, the precision of measurements ranged from 10^{-3}–10^{-4} near 1 K to 10^{-2} at 8 mK.

The RT resistivities, which are given in Table I, are of the order of 200 $\mu\Omega$ cm, close to those reported by Batlogg *et al.*[3] On cooling from 300 to 4.2 K, the resistivities of samples 1 to 4 increase and exhibit a ln T variation between about 50 and 5 K; however, sample 5, which is nearly 3+, shows a decreasing resistivity. Our results, between 8 mK and 4.2 K, are shown in Fig. 1 as a function of ln T, in the same scale at the upper part and in expanded scales at the lower part. The resistivities of samples 1 and 2 have a jump at T_N (see detail in the inset). At 10 mK they reach residual resistivity values, ρ_0, of 5700 and 14 000 $\mu\Omega$ cm, respectively. Surprisingly, the resistivity varies almost linearly with the logarithm of temperature between 50 mk and 1 K. However, an activation-type law, $\sigma \propto e^{-E/kT}$, does not fit our data in any temperature range, even if a residual term σ_0 is added to account for the saturation at very low temperature. With decreasing Tm concentration, the anomaly at T_N disappears gradually; the total increase of the resistivity in the AF phase is only 20% in sample 3 and 10% in sample 4. Both of these still have a logarithmic term below T_N, but saturation occurs much sooner at low temperature. The most striking feature of the results in Fig. 1 is the drastic enhancement of the residual resistivity on approaching stoichiometry. This is better seen in Fig. 2, where ρ_0 is plotted as a function of the proportion c of Tm^{2+}. We obtained c from the RT Curie constant C_M, by assuming a linear relation between C_M and c rather than from the

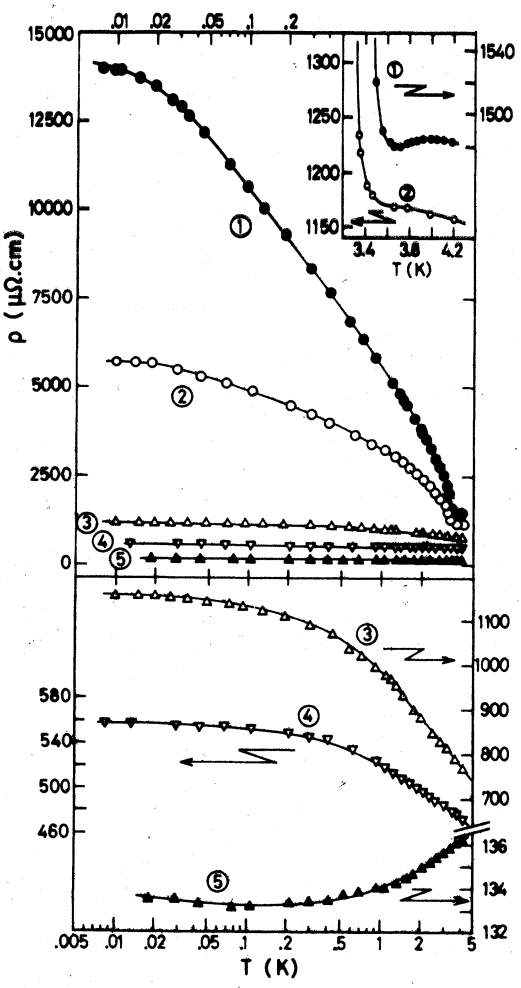

FIG. 1. Resistivities of the five Tm_xSe samples as function of ln T. Lower part: expanded scales. Inset: detail of the anomalies at T_N in samples 1 and 2 (note the linear temperature scale).

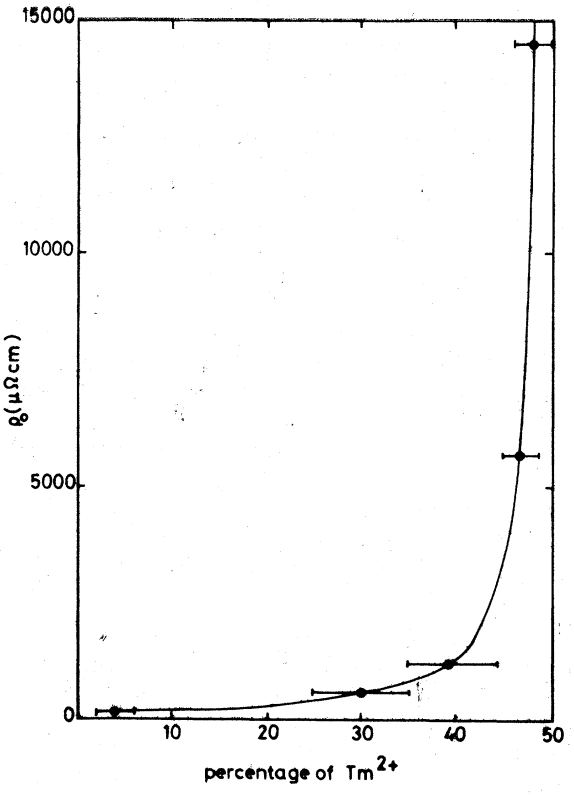

FIG. 2. Residual resistivities as function of the proportion of the 2+ state (deduced from the RT Curie constant).

classical Vegard's law (when C_M was not measured directly on the sample, its value was taken from the plot of a_0 vs C_M of Ref. 4). In contrast to Vegard's law which gives $c \approx 30\%$ of Tm^{2+}. C_M leads to $c \approx 50\%$ for a stoichiometric sample. This higher value for c is supported by the low-temperature magnetization[13] and by recent x-ray-absorption results.[14]

In Fig. 2, a divergence of ρ_0 appears near stoichiometry suggesting that a sample containing exactly 50% of Tm^{2+} might become insulating. We believe that this is a fundamental property of stoichiometric TmSe and that it can help us to understand what actually happens below T_N in these compounds. In particular, the interpretations proposed previously cannot account for this behavior. The residual resistivity seems to be much too large to be ascribed to an ordinary Kondo effect of Tm^{2+} "impurities" in a type-I AF matrix. On the other hand, the anisotropic conduction in the AF domains invoked in Ref. 10 cannot contribute more than a few percent to the low-temperature anomaly, since we observe only a small reduction of ρ when the system is prepared in the two domain state by cooling in an applied field. Moreover, the existence of some critical value for the proportion of 2^+ and 3^+, apparently very close to 50:50, where ρ_0 diverges, is not taken into account by this model.

A possible explanation, somewhat speculative at present, is based on the "Kondo-lattice" Hamiltonian considered by Jullien *et al.*[15] This model treats the $4f$ electrons as localized spins, with an exchange coupling to the conduction electrons described by the parameter J. The main property of this Hamiltonian is the existence of a critical value of J, above which a gap is opened in the conduction band at 0 K. As a consequence, the system is an insulator at 0 K if there is exactly one conduction electron per localized spin, and it remains metallic otherwise. Application of a magnetic field destroys the insulating state and restores the metallic conductivity. In TmSe, the instant state of the system can be regarded as a mixture of cN Tm^{2+} and $(1-c)N$ Tm^{3+}, with $(1-c)N$ carriers in the conduction band. If the Kondo coupling takes place only in the divalent state (because the crystal-field ground state of Tm^{3+} is a singlet), the critical condition of the model of Jullien *et al.* is fulfilled when the valence states are in the proportion 50:50. We have seen above that this is nearly the case in the most stoichiometric samples. This interpretation is more relevant to the case of a heterogeneous mixed valence. However, the resistivity measurement probes the microscopic state of the system with a characteristic time, which can be shorter than that of the valence fluctuation. A similar argument has been proposed[16] to explain the spin fluctuation contribution to the resistivity in actinide compounds. The properties of the model have not yet been derived for $T \neq 0$, but it is to be expected that the gap will disappear at some temperature. Although the occurrence of AF order, which obviously plays an important role in TmSe, is not predicted, it is not definitely excluded by the model. On the other hand, the justification for using this Kondo-lattice Hamiltonian is certainly open to question since the large values of J required for the opening of a gap are probably beyond the limit of validity of the Schrieffer-Wolff transformation,[17] which allows one to derive the Kondo Hamiltonian from the Anderson Hamiltonian. In a recent paper,[18] the Kondo problem for concentrated systems is treated as an extension of the dilute case. When the concentration approaches unity, the authors obtain a gap of width T_K at the Fermi level. Accordingly, the residual resistivity per impurity increases drastically and diverges when the concentration reaches 100%.[19] Thus we believe that the Kondo-lattice model might contain some of the physical ingredients necessary to describe the transport properties of TmSe, provided the parameters entering the starting Hamiltonian are not taken too literally.

In conclusion, the new results reported in this paper show that the residual resistivity of Tm_xSe diverges when x tends to unity. They strongly suggest that perfectly stoichiometric TmSe might become insulating at $T = 0$. Whether this phenomenon is due to a Kondo-lattice insulating state, or to some other mechanism, is still open to discussion and we hope these new results will stimulate further theoretical work on the low-temperature transport properties of TmSe.

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Spin-Flip Scattering and the Dynamics of the Superconducting Order Parameter

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Pair-field susceptibilities of Al films doped with the magnetic impurity Er have been measured. The spin-flip scattering time determined from studies above T_c is consistent with the results of electron spin resonance measurements. Below T_c the transverse mode of the order parameter propagates only when there is a gap in the excitation spectrum.

The simplest and most complete technique for studying the dynamical properties of the superconducting order parameter is to measure the wave-vector- and frequency-dependent pair-field susceptibility.[1] This method was first applied in the normal state where the order parameter is described by a time-dependent Ginzburg-Landau equation.[2] When the technique was extended below T_c, a propagating mode was found.[3] This mode has been interpreted as an oscillation in the phase of the order parameter and is the high-frequency limit of what is known as the "transverse" mode or T mode.[4] There is also a "longitudinal" mode or L mode, which is diffusive, associated with the amplitude of the order parameter. Branch imbalance experiments[5] have been used to determine the relaxation of the T mode in a nonpropagating regime. The relaxation of the "longitudinal" mode has been studied in a number of ways including laser excitation.[6]

The detailed character of the dynamics of the order parameter is determined by the "anomalous" term in the self-consistency equation of the Eliashberg theory.[7] This term describes the deviations from equilibrium of the order parameter and the quasiparticle distribution function. As magnetic impurities, which break pairs, alter the "anomalous" term, the nature of this term may be inferred from the magnetic-impurity concentration dependence of the pair-field susceptibility.[8]

Here we report measurements of the pair-field susceptibility of dirty-limit Al films doped with Er. Measurements above T_c have been used to determine the spin-flip scattering time τ_s, which along with the transition temperature and the diffusion constant D serve to fully parametrize theories proposed for the regime below T_c. For Al, the phonon inelastic scattering time τ_E is such that $\omega\tau_E \gg 1$ is always satisfied and thus τ_E is

