Pressure Study of the Metal-Insulator Transition in TmSe

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High-pressure resistivity measurements on mixed-valence TmSe indicate a new electronic phase transition near 30 kbar at liquid-helium temperature. In the paramagnetic phase, the ρ-T curve shows unexpectedly small pressure dependence, in contrast with the predictions of a simple valence-change model. The onset of the aniferromagnetic ordering triggers a metal-insulator transition for pressures in the range 0–30 kbar. The new high-pressure phase is characterized by a steep decrease of the resistivity below 3.7 K at 32.5 kbar.

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Much of the experimental and theoretical work in mixed-valence systems has involved pressure-induced valence changes.[1] The most famous example is, of course, the semiconductor-to-metal transition in SmS, where the average valence of samarium changes precipitously from + 2 to about 2.8.[2] In the case of TmSe which is intermediate valence (IV) at $p=0$,[3] Guertin and coworkers have interpreted their magnetization results as a consequence of an increase in the trivalent character of thulium under pressure, and predicted completion of the $Tm^{2+} \rightarrow Tm^{3+} + 5d$ conversion near 20 kbar. In their picture, deviations from stoichiometry and external pressure produce similar effects which can roughly be scaled with the values of the lattice parameter a_0.

In this Letter we report the first experimental investigation of the low-temperature resistivity of TmSe under hydrostatic pressure up to 32 kbar. The resistivity is a crucial parameter particularly in mixed-valence systems where the intinerant electrons are directly related to the ratio of the valence states. Previous studies on Tm_xSe compounds with varying composition[4] have suggested that at $P=0$, the stoichiometric compound is insulating at 0 K. Since, for an integral number (n_e) of electron carriers per magnetic center,[5,6] the Kondo lattice model predicts a metal-insulator (MI) transition at 0 K, the crossing from an intermediate-valence state (IV) to the trivalent state appears particularly significant. Further comparisons can be made theoretically with the double-exchange model developed by Varma[7] and experimentally with the studies performed on nonstoichiometric samples.[4,8]

Our experiments were performed on a nearly stoichiometric sample (sample 1 of Ref. 4, $a_0 = 5.712$ Å; $T_N = 3.46$ K) down to 1.5 K in a pressure cell[9] working up to 32.5 kbar, then down to 30 mK using a clamp[10] ($P_{max} = 6$ kbar) screwed to the mixing chamber of a dilution refrigerator. The thermalization of the sample was checked down to 30 mK by comparing the zero-pressure data taken with the sample either in the clamp or immersed in the dilute ^3He-^4He phase inside the mixing chamber.

The room-temperature resistivity, in accord with earlier results of Batlogg *et al.*,[9] decreases with an initial rate of -1.26%/kbar. Figure 1 shows the variation of ρ between 100 K and T_N for several applied pressures. When the temperature decreases, the reduction of ρ under pressure is overcompensated by an enhanced negative temperature coefficient. As a consequence, the curves cross one another between 15 and 35 K. The slope $|d\rho/d\ln T|$ increases quasilinearly from 0.46 mΩ cm at $P=0$ to 0.63 mΩ cm at 20 kbar [Fig. 1, inset (b)]; at higher pressures, the variation becomes slower, most likely due to the approach to the 3+ state. The most surprising feature of these results is that, even at the maximum pressure of 32.5 kbar, the resistivity of TmSe differs drastically from that of normal trivalent ions in compounds such as $Gd^{3+}Se$.[11] This

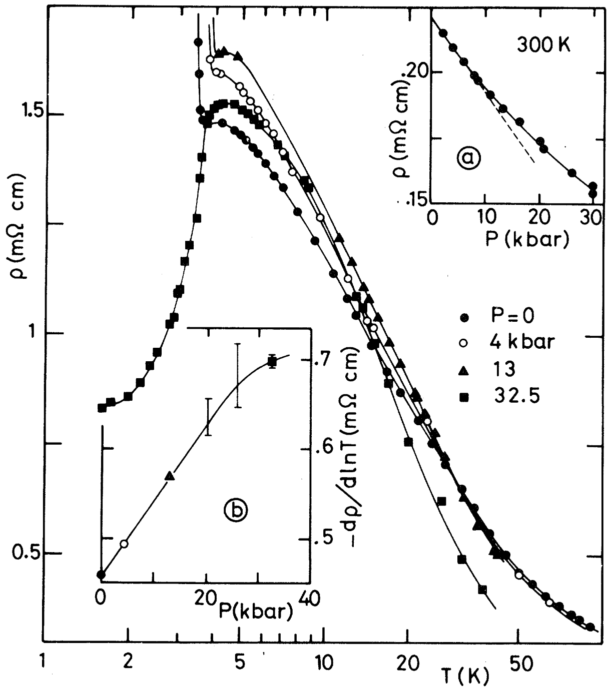

FIG. 1. Resistivity of TmSe under pressure in the paramagnetic phase. Inset (a): ρ(300 K) vs pressure. Inset (b): $\ln T$ slope vs pressure.

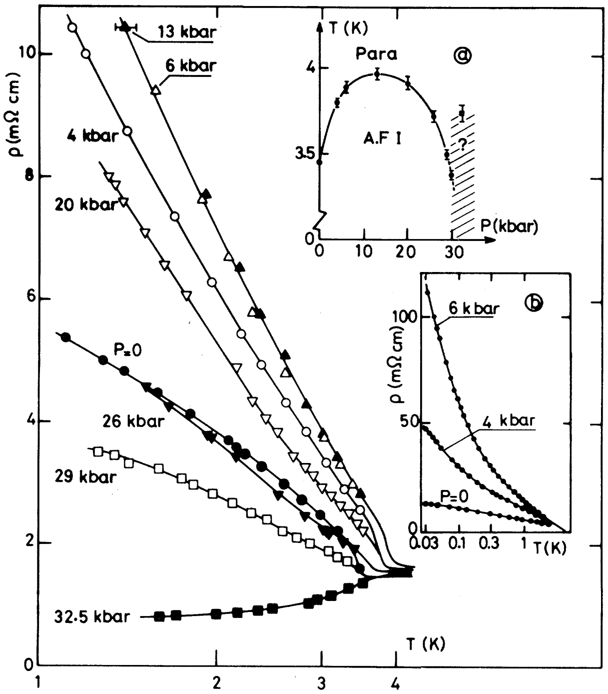

FIG. 2. Resistivity of TmSe under pressure in the antiferromagnetic phase. Inset (a): Magnetic phase diagram of TmSe under pressure; the new "metallic" region ($T < T^*$) is tentatively sketched by the hatched area. Inset (b): Very-low-temperature data.

is in contrast to the earlier magnetization work[12] from which thulium was predicted to become trivalent near 20 kbar. In particular, we want to emphasize the difference between the effects of pressure and deviations from stoichiometry.[4,8] In the latter case the decrease of the lattice parameter and then of the divalent admixture was accompanied by a strong reduction of the resistivity anomaly. Our results are in good accord with recent neutron diffraction experiments[13] which yield an anomalously large compressibility, characteristic of the IV state, even at 20 kbar. At all pressures ρ(4.2 K) roughly corresponds to the largest possible resistivity for 100% independent scattering centers in a metal assuming a maximum cross section (unitary limit). This would indicate that TmSe in all measured pressure ranges is near an electronic instability; the appearance of the antiferromagnetic ordering at T_N leads to an insulating phase as long as the IV character (the d-f mixing) is sufficiently strong ($P < 30$ kbar) and to a metallic phase for $P = 32$ kbar.

The results in the antiferromagnetic (AF) phase are shown in Fig. 2. Around T_N, all the data points are not shown but are represented by the full lines. In the following, the Néel temperature will be defined as at zero pressure by the position of the resistivity jump which coincides with the susceptibility peak (at zero pressure the difference in T_N defined by the peak in $\partial\rho/\partial T$ or the jump of ρ is less than − 0.05 K). The pressure dependence of T_N is in agreement with the preliminary results reported by Vettier *et al.*[13] from neutron diffraction experiments. The initial increase is followed by a turnover at the highest applied pressure of 20 kbar. Up to 13 kbar, T_N increases with pressure with an initial slope $dT_N/dP = +0.085 \pm 0.010$ K/kbar [Fig. 2, inset (a)] in accord with previous susceptibility[12] and neutron diffraction measurements. Simultaneously, the amplitude of the resistivity jump is enhanced, and on cooling to very low temperature, $\rho(T)$ rises much faster than at ambient pressure [Fig. 2, inset (b)]. It is important to realize the magnitude of this effect: At 30 mK, the resistivity at 6 kbar reaches 0.12 Ω cm, one order of magnitude larger than at $P = 0$, and nearly two orders of magnitude larger than $\rho(T_N)$ and than the residual resistivity reported for the nonstoichiometric sample[3] of Ref. 4 with the same lattice parameter. At higher pressures, 13 kbar $<P<$ 29 kbar, both T_N and the resistivity anomaly in the AF phase decrease gradually. At 20 kbar the data fall substantially below the curve at $P=0$. Finally, at 32.5 kbar, a sudden change occurs: the resistivity now decreases rapidly below 3.7 K from 1.4 to 0.8 mΩ cm near 1.5 K and the estimated ordering temperature, T^*, defined by the inflection point of $\partial\rho/\partial T$ is higher than at 30 kbar.

We have shown that in TmSe, the onset of the type-I AF structure is always accompanied by an electronic transition into a semiconducting state for pressures between 0 and 30 kbar. The presence of a maximum in the variation of T_N with pressure is a very singular feature: in the microscopic model of TmSe proposed by Varma,[7] one would rather expect a steady increase of T_N, due to the gradual weakening of the ferromagnetic double-exchange interactions as the concentration of divalent admixture decreases. We believe that the maximum of T_N is the consequence of the interplay between two phenomena: (i) the magnetic coupling among the thulium moments and (ii) a hybridization mechanism which favors the emergence of a nonmagnetic ground state: Similar situations are encountered in the magnetically ordered "Kondo-lattice" compounds,[6] and in antiferromagnetic Mott insulators.[14]

Furthermore, the amplitude of the very-low-temperature resistivity anomaly appears to be strongly correlated with the variation of the ordering temperature under pressure. For example, the values of the resistivity at 1.6 K (Fig. 2) go through a maximum at approximately the same pressure as T_N. Quantitatively, the resistivity in the ordered phase at any pressure cannot be described by a simple activation law $\rho=\rho_0\exp(\Delta/k_BT)$. However, if we introduce explicitly the magnetic character of the transition by taking $\Delta=\Delta(T)$ proportional to the intensity of the (100) magnetic line observed in Ref. 13: $\Delta(T)=\Delta(0)I(T)/I(0)$, we obtain a good fit for the resistivity between T_N and $0.5T_N$ with $\Delta(0)=2.3$, 3.2, and 2.5 K for $P=0$, 6, and 20 kbar, respectively. These values for the energy of the gap reflect the occurrence of a maximum in the insulating character of AF TmSe at about 10 kbar. Below $0.5\times T_N$, such an analysis fails, but a $\ln\rho$ vs $\ln T$ plot shows a power-law dependence of $T^{-\alpha}$ with $\alpha=0.2$, 0.4, and 0.6 for $P=0$, 4, and 6 kbar, respectively. The physical origin could be related to the presence of disordered centers (vacancies, impurities) in an insulating state.[15] The possibility of an intrinsic number of self-trapped defects may be an open question.

The metal-insulator transition cannot be regarded as an example of a Slater-type insulator.[16,17] The opening of a very small gap in all directions of k space seems very unlikely here.[18] The IV character emphasizes the role of d-f hybridization and in the case of TmSe of magnetic correlations.

The magnetic behavior of TmSe is characterized at low temperature by a Curie law, Korringa relaxation, and a $\ln T$ increase of the resistivity in the paramagnetic regime just above T_N. All these properties seem to correspond to the picture of a localized moment interacting with the conduction electrons via a Kondo-type exchange Hamiltonian. The relevance of Kondo-lattice models[5,6] is therefore an appealing possibility for the gap opening. However, its disappearance when the validity of such a model is apparently fulfilled ($n_e=1$) raises questions of the microscopic basis of the Kondo-lattice approach or of a change in the magnetic structure which must be checked by neutron diffraction experiments. We point out the difficulty of extrapolating the Kondo effect of a single impurity to the lattice case without including the IV phenomena. The Kondo effect for a single impurity is due to the combined spin and orbit resonant scattering produced by the impurity center; extrapolation to a lattice involves the coupling between $4f$ localized and $4f$ delocalized states, i.e., the IV phenomena. Further theoretical investigation must prove the microscopic basis of the Kondo lattice and its range of applicability.[19]

Our observation of the disappearance of the MI transition at 32.5 kbar in the vicinity of the pressure change to the trivalent state emphasizes the central role of the d-f hybridization. The occurrence of a gap due to such a mechanism, first suggested by Coqblin and Blandin[20] and discussed by Mott,[21] has been studied recently in more detail by Martin and Allen[22] for the special case of SmB_6 where the gap opening appears now well established.[23,24] In agreement with the prediction of Martin and Allen,[22] a gap does not occur for the rocksalt crystals of TmSe in its paramagnetic and induced ferromagnetic phases[4]; it occurs in the AF state because of the symmetry breaking.[22] In contrast, the compound TmS is close to the 3+ state and is metallic.[3] It must be pointed out that the order of magnitudes of the quasilogarithmic increase of the paramagnetic resistivity observed for TmSe and for the collapsed phase of SmS at low pressure below 50 K are similar.[25] The recent conclusion of Stevens[26] that low excited states of IV SmS form a continuum must be confirmed by further experiments.

In summary, our results indicate that the valence change in TmSe is less sensitive to pressure than previously assumed, and quantitatively different from the effect of nonstoichiometry. They do not support the double-exchange picture and the Kondo-lattice model. They suggest a strong competition between magnetic interactions and hybridization processes in the vicinity of T_N. They are in agreement with the conclusions of Martin and Allen[22] and Coqblin *et al.*[27] that a gap is unlikely in a ferromagnetic IV state and may not be precluded in an AF phase. Finally, they provide the first experimental evidence for a new metallic ground state above 30 kbar which should stimulate further investigation of the field phase diagram of TmSe under pressure and of the pressure change of the crystal field.

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