Semiconductor-Metal Transition in Intermediate-Valence Tm Compounds: Novel Features

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$TmSe_{0.32}Te_{0.68}$ undergoes a continuous pressure-induced semiconductor-to-metal transition (at 1.4 GPa) in which the Tm ions change their valence. This has been studied by electrical-resistivity, Hall-effect, volume, elastic-constant, and magnetic-susceptibility measurements under pressure. Already in the semiconducting phase all the lattice-related properties indicate strong valence mixing, whereas the magnetic susceptibility remains typical of pure divalent Tm. These new results are discussed in terms of the pressure-induced $4f$-$5d$ hybridization and local correlation effects.

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For some time the intermediate-valence compounds of the rare earths have become a fascinating class of solids.[1-3] Their anomalous features have raised a great deal of interest: the lattice spacing with an intermediate value between the ones of the integer-valent compounds, the soft bulk modulus, the negative elastic constant c_{12}, and the absence of magnetic order in most intermediate-valent materials. For some of them an energy gap ($\Delta \sim 2$–6 meV) appears at the Fermi level at low temperatures as observed in SmB_6, TmSe, and the high-pressure phase of SmS.[4-7] The ground state of an intermediate-valent compound is a quantum mechanical mixture of both the $4f^n$ and the $4f^{n-1}5d$ configurations on each rare-earth ion. In some materials the intermediate-valent state is present under normal conditions; in others it can be reached by pressure or chemical variation starting with an ioniclike semiconducting compound. Here we study the pressure-induced transition from the *divalent* semiconducting into the *intermediate-valent* metallic state by a variety of measurements: electrical resistivity, Hall effect, specific volume, elastic constant, and magnetic susceptibility. The change from the stable atomiclike $4f^{13}$ (Tm^{2+}) configuration to the unstable intermediate-valent state is continuously traced by all these methods. Each of these methods probes a different aspect of the $4f$ shell. The most interesting and significant result is that the magnetic behavior does not mirror the lattice-related changes. These new results will be discussed in terms of the pressure-induced $4f$-$5d$ hybridization and local correlation effects.

In semiconducting $TmSe_{0.32}Te_{0.68}$ an energy gap (~ 200 meV) is formed between the localized $4f^{13}$ states and the $5d6s$ conduction-band states. An isostructural transition from the semiconducting to the metallic state takes place at 1.4 GPa (=14 kbar). The energy required for the excitation $4f^{13} \rightarrow 4f^{12}(5d6s)$ is reduced with pressure. This manifests itself in an exponential decrease of the electrical resistivity ρ by three orders of magnitude (Fig. 1). In the metallic range (> 1.4 GPa) the resistivity saturates around 4×10^{-4} Ω cm, a value observed in all metallic TmSe-TmTe compounds.[8] The measured Hall coefficient R_H under pressure (on the same single crystal) allowed us to calculate

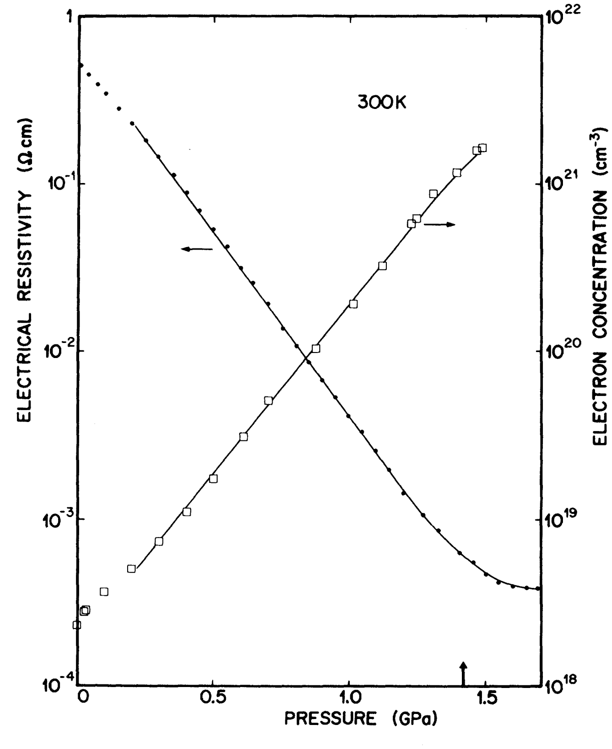

FIG. 1. Electrical resistivity and electron concentration of $TmSe_{0.32}Te_{0.68}$ under pressure. The semiconductor-metal transition is indicated by the arrow at 1.4 GPa.

the carrier concentration n in a one-band model using $R_H = -1/ne$. The electron concentration is 2×10^{18} cm^{-3} at ambient pressure and increases exponentially to 2×10^{21} cm^{-3} at the transition to the metallic state. With use of a simple statistical model $n(p) = n_0 \exp[-\Delta E(p)/kT]$, the closing rate of the energy gap with pressure ($d\Delta E/dp = -122$ meV/GPa) can be calculated. The mobility $\mu = |R_H|/\rho$ increases only slightly from a value of ~ 6 cm^2/V·s, at ambient pressure, to ~ 10 cm^2/V·s at the transition. The conductivity in this type of a semiconductor is mainly determined by the thermal excitation of electrons from the localized $4f^{13}$ level into the $4f^{12}(5d6s)^1$ bandlike states.

In Fig. 2(a) the volume change of $TmSe_{0.32}Te_{0.68}$ (rocksalt structure) from the semiconducting to the metallic state is shown up to 3 GPa, as measured by the strain-gauge technique (solid line).[9] The dashed lines represent the theoretical volume variations of pure divalent and trivalent compounds as calculated by the Murnaghan equation of state. Already at ambient pressure the volume is less than that of a pure divalent compound of this composition. The bulk modulus versus pressure as a derivative of the volume-pressure curve is shown in Fig. 2(b) (solid line). The initial value of the isothermal bulk modulus is 33 ± 1 GPa and is also less than the typical values for divalent compounds (~ 50 GPa). An anomalous volume decrease is observed with increasing pressure: The crystal gets markedly softer in approaching the transition at 1.4 GPa, where the bulk modulus is only 6 GPa. Above the transition the crystal stiffens and the bulk modulus returns to its initial value at ~ 2.5 GPa. The minimum of the bulk modulus lies in the pressure region where the resistivity indicates the semiconductor-metal transition. The volume has appreciably decreased while still in the semiconducting phase. It is far below the expected volume of a divalent Tm compound. We calculated the corresponding volume decrease from the Hall-effect data [Fig. 2(a), dotted line] to show that the thermally induced process $4f^{13} \rightarrow 4f^{12} + e^-$ plays only a minor role in explaining the anomalous volume decrease in the semiconducting phase.

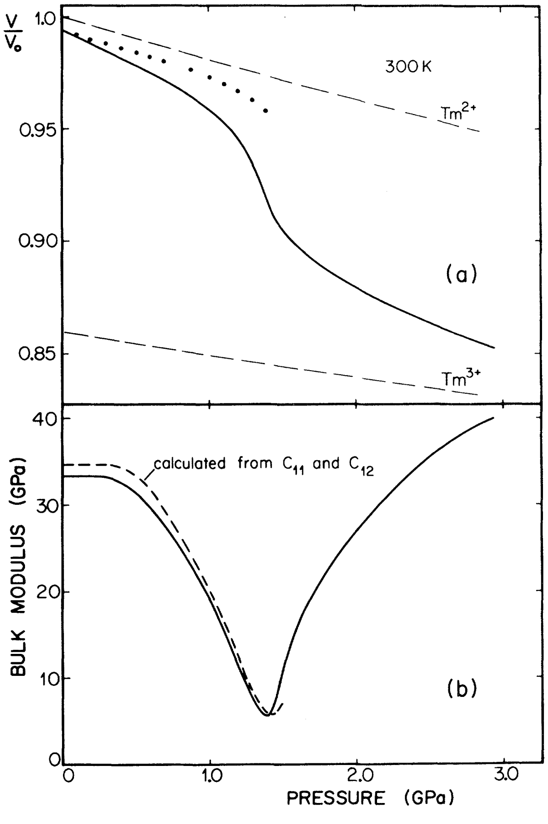

FIG. 2. Pressure dependence of (a) the specific volume and (b) the bulk modulus as a derivative of the specific volume (solid line) and as calculated from the elastic constants (dashed line) of $TmSe_{0.32}Te_{0.68}$.

The behavior of TmSe is similar to the pressure-induced metallic state of $TmSe_{0.32}Te_{0.68}$; both show an intermediate lattice constant and a soft bulk modulus. This analogy suggests a measurement of the elastic constants in $TmSe_{0.32}Te_{0.68}$ under pressure, since TmSe has a negative elastic constant c_{12}.[10] We expect c_{12} to become negative in the transition from the semiconducting to the metallic state. The most striking feature is that c_{12} is positive at ambient pressure, but becomes negative at about 0.5 GPa (well below the transition at 1.4 GPa). The soft bulk modulus B in both the semiconducting and the metallic states is mainly caused by the negative c_{12} because in $B\,[=(c_{11}+2c_{12})/3]$ c_{11} becomes almost equal to $-2c_{12}$ in approaching the transition. The dashed line in Fig. 2(b) represents the adiabatic bulk modulus as calculated from the elastic constants c_{11} and c_{12}. Both curves are in good agreement and the differences lie within the experimental uncertainties.

Another signature of the state of the $4f$ shell is the molar Curie constant C_M (C_M is related to the effective magnetic moment p_{eff} by $p_{\mathrm{eff}}^2 \simeq 8C_M$ in emu). The C_M values for the free ions Tm^{2+} ($4f^{13}$) and Tm^{3+} ($4f^{12}$) are 2.58 and 7.14, respectively. A *divalent* character of Tm in all semiconducting $TmSe_{1-x}Te_x$ compounds has to be inferred from C_M![8] The divalency of these compounds comes as a surprise since all lattice-related properties point to an intermediate valence. We therefore measured the magnetic susceptibility of $TmSe_{0.32}Te_{0.68}$ under pressure up to 1.7 GPa to see where the change of the molar Curie constant in the semiconductor-metal transition sets in. The results show unambiguously a divalent state up to the transition at 1.4 GPa and the intermediate Tm valence occurring only in the metallic phase. The same behavior was qualitatively observed in a similar investigation on TmTe under pressure[11] but a precise comparison with the lattice constant was not possible at that time.

As a new result, all lattice-related properties indicate an intermediate-valent Tm state already in the semiconducting phase whereas the magnetic susceptibility points to a divalent state of the Tm ions. To elucidate this basic difference we compare the valences as determined either by the lattice constants or by the molar Curie constants (by linear interpolation between the values for the divalent and trivalent states) of different compounds from the series TmSe-TmTe and Tm_xSe (Fig. 3). The solid line would correspond to valence values the same for both methods. The solid dots in Fig. 3 represent the Tm valences in the system $TmSe_{1-x}Te_x$. The triangles show the results of the pressure variation in $TmSe_{0.32}Te_{0.68}$ All the other points are results from investigations of various authors[12–15] and are in good agreement with each other. The dashed line of Fig. 3 is a guide to the eye. We now realize that there is a clear discrepancy in determining the valence from the lattice constant a_0 or from the molar Curie constant C_M. This incompatibility does not only exist for the strongly f-d-mixed semiconductors but also for the metallic Tm_xSe[14] and $TmSe_{1-x}Te_x$ compositions. For TmSe, the lattice-constant interpolation yields a Tm valence of ~2.75; from the C_M data a valence of ~2.55 can be deduced. The latter value can also be extracted from x-ray photoemission[16] as well as from the L-edge x-ray absorption spectroscopies.[17] The recently published M-edge measurements[18] yield a valence of ~2.8, which is more in agreement with the lattice-constant valence values.

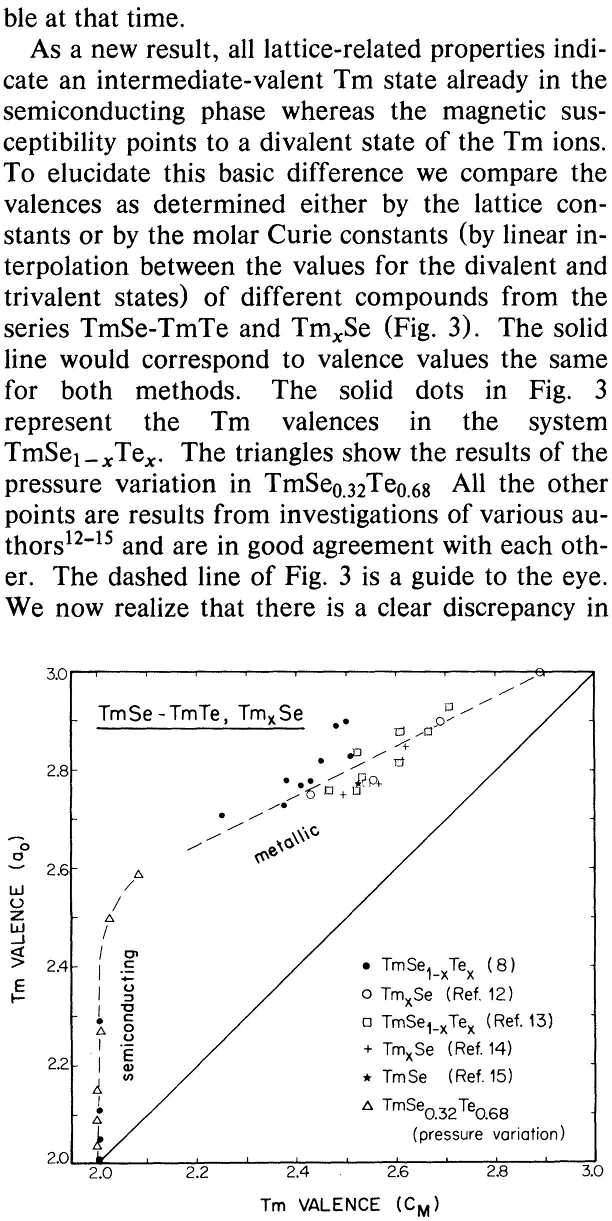

FIG. 3. The comparison between the Tm valences as deduced from the lattice constants (a_0) on the one side and the molar Curie constants (C_M) on the other side. The full line would correspond to Tm valences the same for both methods.

This qualitative behavior is not restricted to the compound $TmSe_{0.32}Te_{0.68}$. Similar effects can also be observed in the other semiconducting TmSe-TmTe crystals[8]; however, we performed most of the measurements on $TmSe_{0.32}Te_{0.68}$ because of the availability of large single crystals and its modest transition pressure. From the lattice-dynamical point of view the minimum of the bulk modulus and the elastic constant c_{12} at the semiconductor-metal transition point to the very unstable state of the Tm $4f$ shell. It is surprising that the magnetic susceptibility is not influenced by this instability; moreover, the quantum numbers L, S, and J corresponding to a stable atomiclike $4f^{13}$ (Tm^{2+}) configuration remain unaltered until the transition to the metallic state takes place, as deduced from the effective magnetic moment.

In the ioniclike semiconducting state the $4f$ electrons are highly localized and possess well-defined moments obeying Hund's rules. The separation in energy between localized $4f$ states and the $5d$ conduction band decreases under pressure and as a result of the increasing f-d hybridization the overlap of the f and (ds) orbitals at neighboring sites increases. Thus, the probability for the f electron to be outside the $5s,5p$ shell is increased. This reduces the screening of the outer electrons from the core charge; consequently the volume of the Tm ion decreases. This electron-lattice interaction leads to the characteristic features of intermediate-valent compounds: the intermediate lattice constant, the anomalously soft bulk modulus, the negative elastic constant c_{12}, and phonon softening. While still in the semiconducting phase, the energy gap is between a localized $4f$ state with $5d$ admixture and a $5d$ bandlike state with $4f$ admixture. With the narrowing of the gap the effect of local correlations between f holes and d electrons (i.e., excitonic effects) becomes more important. These strongly correlated states retain the quantum numbers L, S, and J of the original $4f$ configuration, as inferred from magnetic measurements. In approaching the transition these states begin to overlap more and more. We speculate that at the semiconductor-metal transition these states do not delocalize in the sense of a Mott transition. Moreover, we believe that the observed gap in the intermediate-valent metallic phase is due to local correlations and *f-d* hybridization effects and thus we would expect a continuous transition from the semiconducting gap into a "hybridization-correlation" gap.

In conclusion, we have show that the *f-d* hybridization and the correlation between the *f* hole and the *d* electron play an important role in the mechanism of the semiconductor-metal transition in Tm compounds. It is the increasing hybridization with pressure which causes the anomalous lattice-related properties in the semiconducting phase. The strong *f-d* correlation keeps the localized character of the 4*f* state with its original quantum numbers until the semiconductor-metal transition takes place. Consequently basic differences between lattice-related and magnetic measurements result.

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