

## Pressure Induced Semiconductor to Metal Transition in TmTe

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(Received 8 August 1996)

The pressure induced semiconductor to metal transition in the rare earth compound TmTe has been investigated with electrical resistivity measurements under high pressure. At room temperature, the resistivity showed an exponential decrease up to 2 GPa, indicating a linear closing of the energy gap, followed by an almost pressure independent metallic regime. The resistivity in the metallic regime showed a logarithmic temperature dependence reminiscent of a Kondo effect and a TmSe-like anomaly appeared at low temperature and above 5 GPa. At 5.7 GPa the resistivity showed an abrupt decrease that corresponded to the structural phase transition. [S0031-9007(97)02350-8]

PACS numbers: 75.20.Hr, 75.30.Mb

Electrons move in solids interacting with each other by the Coulomb force. To know the electronic state in a solid is fundamentally a many body problem. Band theory, a mean field theory to treat this problem, has been successful for many kinds of materials, but it is not able to explain the properties of *d* or *f* electron systems in which the interactions among the electrons are strong. A wide variety of magnetic and transport properties arise from the correlations among *d* or *f* electrons: metal-insulator transition, itinerant magnetism, valence fluctuation, Kondo effect, heavy fermions and superconductivity, and so on. These are now called strongly correlated electron systems and many new concepts on solid state physics have been constructed. However, there are still many problems to be solved and the understanding of these systems is not complete.

The Tm monochalcogenide series, which crystallize in the NaCl structure, is one of these mysterious strongly correlated electron systems. TmSe has been studied from the standpoint of the valence fluctuation between  $4f^{12}$  and  $4f^{13}$ , Kondo effect, antiferromagnetic order, and metal-insulator transition. This compound has the peculiarity that two magnetic valence states  $Tm^{2+}$  and  $Tm^{3+}$  are concerned in the valence fluctuation. However, the situation is so complicated that there is no clear explanation of the physical properties of this compound.

TmTe is a divalent semiconductor with thirteen *4f* electrons (with one *4f* hole). The lattice constant and the Curie constant show that the Tm ions in TmTe are divalent at ambient pressure [1]. The localized  $4f^{13}$  level is situated within the energy gap between a filled Te-5*p* valence band and an empty Tm-5*d* conduction band [2,3]. The gap  $\Delta$  for the electronic excitation of one *4f* electron from the localized *4f* level to the 5*d* conduction band is estimated to be 350 meV [4].

In TmSe, due to the smaller ion radius of Se than that of Te, the closer distance between Tm ions leads to an increase in the strength of the crystalline field

that splits the 5*d* band into  $5d-e_g$  and  $5d-t_{2g}$  bands [2]. Consequently the energy gap  $\Delta$  between the *4f* level and the bottom of the conduction band is narrowed. Then the valence fluctuating state appears due to the strong mixing between the *4f* electrons and the 5*d* conduction electrons. In TmSe, both the lattice constant and the Curie constant are intermediate between those of divalent and trivalent values [1]. The resistivity of TmSe shows a Kondo-like logarithmic temperature dependence at high temperatures followed by a sharp increase at  $T_N = 3.5$  K, which is thought to be a transition into an insulating state [5–7]. This anomaly in the vicinity of  $T_N$  shows a very complicated response to external magnetic fields or pressures [8,9]. The most important behavior in relation with the present experimental result on TmTe is that the sharp resistivity increase at  $T_N$  is initially enhanced by the pressure up to 1.35 GPa.

TmS has a lattice constant and a Curie constant of almost trivalent values [1]. The behavior of the electrical resistivity, however, is not that of normal metals. It also shows a Kondo latticelike behavior [10–12].

The physical mechanisms of these valence fluctuation related phenomena in TmSe and in TmS have not been understood well. One of the missing, important, and effective experimental approaches to the understanding of TmSe and TmS is to study the change in magnetic and transport properties with pressure from TmTe to TmS through TmSe. The application of high pressure to TmTe should lead to a similar electronic structure as in TmSe or TmS through the shrinking of the lattice constant [13,14]. Therefore, the high pressure measurements on TmTe would give important information to the understanding of valence fluctuations in TmSe and in TmS. In this Letter, we report the electrical resistivity of TmTe under high pressure and compare the results to the previous data on TmTe and  $TmSe_{1-x}Te_x$ .

We have prepared the sample by synthesizing the starting materials (commercial 99.9% thulium metal and

99.9999% tellurium) directly in a vacuum sealed tungsten crucible with a high frequency induction furnace. A large single crystal was obtained with a lattice constant of 6.357 Å. The ingot has been named as No. 2(9309). The temperature dependence of the resistivity and the magnetic susceptibility of the sample used in the present high pressure measurements are shown in Fig. 1, which shows that the sample is insulating and almost divalent at ambient pressure.

In order to measure the temperature dependence of the resistivity under high pressures, we have used a cubic anvil press that consisted of six anvils made of tungsten carbide. The six cubic anvils press a pyrophyllite gasket in which the sample is immersed in a fluid pressure transmitting medium of Fluorinert in a Teflon cell. In order to keep the pressure constant during the heat cycle, the load was maintained constant by controlling the oil press equipment. The electrical resistivity was measured with the usual four probe dc method.

In Fig. 2 the pressure dependence of the electrical resistivity at room temperature is shown. The resistivity initially decreases exponentially with increasing pressure up to 2 GPa. Above 2 GPa the resistivity becomes almost pressure independent, indicating that the sample has gotten into the metallic regime. The resistivity abruptly decreased at 5.7 GPa. This corresponds to the structural transition into a tetragonal structure as has been observed in the x-ray diffraction [15,16].

Within a simple semiconductor statistics, we calculated the number of charge carriers excited from  $4f^{13}$  donor

levels into a parabolic conduction band with effective mass  $m$  and orbital degeneracy  $d$ . The donor level is located below the bottom of the conduction band with energy gap  $\Delta$  and density  $N_d = 1.555 \times 10^{22} \text{ cm}^{-3}$ , which is the density of Tm ions. Each donor can supply one conduction electron and become  $4f^{12}$ . The degree of freedom of the donor was taken to be 8 for  $4f^{13}(J = 7/2)$  and 13 for  $4f^{12}(J = 6)$ . The band degeneracy  $d$  was taken to be 3 because the conduction band may be considered to arise from the Tm  $5d - t_{2g}$  orbitals. The calculation was performed exactly by considering the Fermi distribution function at  $T = 300 \text{ K}$ , and the calculation is valid even after the gap has closed. The resistivity was assumed to be inversely proportional to the number of excited electrons. The best fit parameters were  $\Delta = 396 \text{ meV}$ ,  $d\Delta/dP = -207 \text{ meV/GPa}$ , and  $m = 30m_0$ . The initial gap of 396 meV is consistent with the estimation from the optical measurements [4]. The gap closing rate is twice as large as the previously reported value of 100 meV/GPa. This is because the resistivity can be approximated to be  $\rho = \rho_0 \exp(\Delta/2k_B T)$  in the gap closing process in this calculation, while the previous papers analyzed the data without the factor 2.

The recent precise measurement of the magnetic susceptibility and the volume change under high pressure by Tang *et al.* shows that the valence of Tm ions are divalent from 0 to 2 GPa and that the intermediate valence regime starts from 2 GPa [16]. The above calculation, however, without the contribution from the lattice energy, is too simple to explain the pressure dependences of the volume and of the magnetic susceptibility.

Figure 3 shows the temperature dependence of the resistivity in the metallic regime above 2 GPa. From 2 to 5.3 GPa the resistivity shows  $\ln T$  dependences at high temperatures though the lattice contributions are not

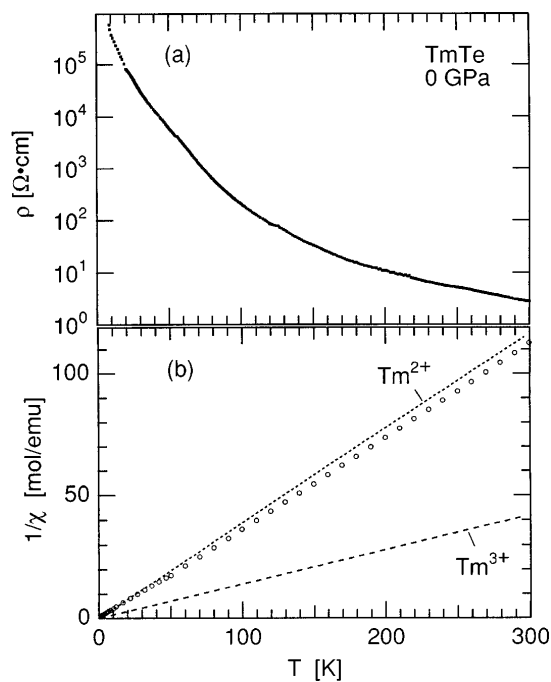


FIG. 1. (a) Temperature dependence of the electrical resistivity and (b) the inverse magnetic susceptibility of TmTe at ambient pressure.

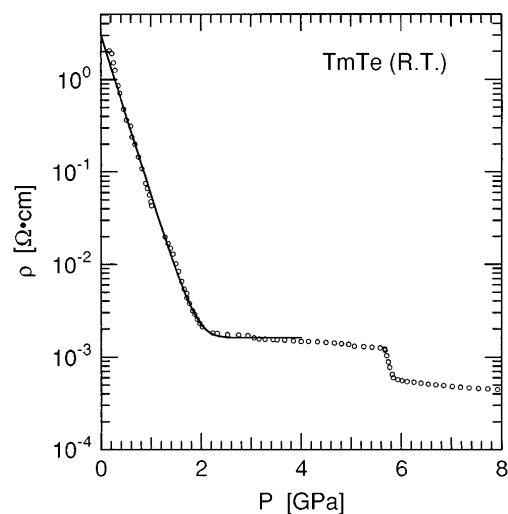


FIG. 2. Pressure dependence of the resistivity of TmTe at room temperature. Solid line is a fit with a model described in the text.

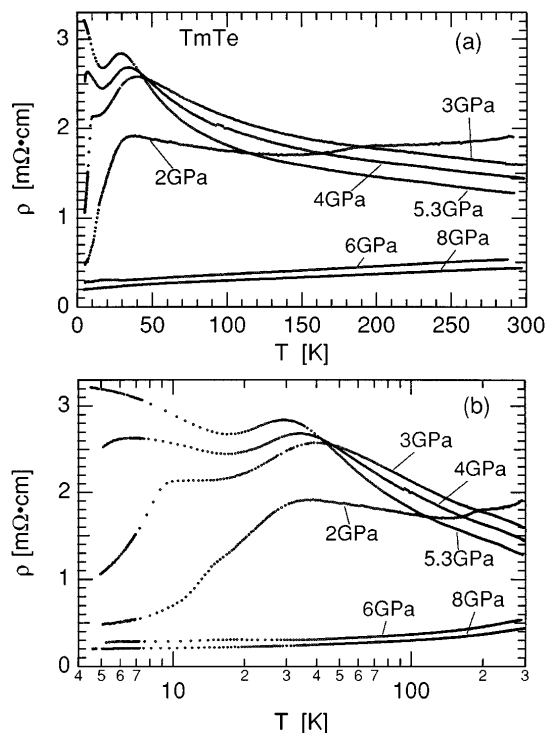


FIG. 3. Temperature dependence of the resistivity of TmTe in the metallic regime under high pressures.

subtracted. This may be attributed to the Kondo effect as in TmSe or in TmS. The slope  $|d\rho/d \ln T|$ , shown in Fig. 4, increases with pressure as in TmSe.  $|d\rho/d \ln T|$  is related to the degree of hybridization between  $4f$  electrons and conduction electrons in the Kondo impurity problem. The increase in  $|d\rho/d \ln T|$  suggests an increase in hybridization with pressure. Therefore, we suppose that TmTe under high pressure of about 2 GPa is at the beginning of the valence fluctuation regime where the overlap between the  $4f$  level and the conduction band is still small. Application of the higher pressure enhances

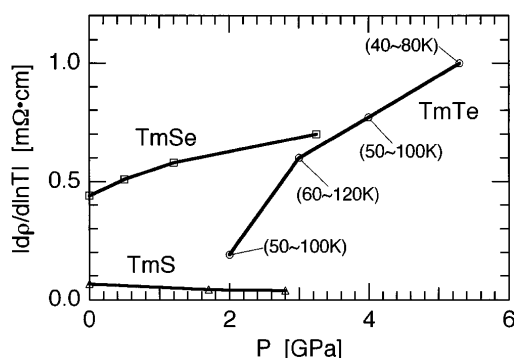


FIG. 4. The slope of the resistivity with respect to  $\ln T$  for three Tm monochalcogenides. The slope for TmTe was determined within the temperature range written in the figure. For TmSe and TmS, data were taken from Refs. [9,12], respectively.

the overlap and the valence begins to have the intermediate values and then  $|d\rho/d \ln T|$  increases.

The resistivity peak around  $T_{\max} \sim 30$  K may be assigned to a transition from a Kondo impurity scattering regime to a coherent Kondo lattice regime.  $T_{\max}$  increases from 2 to 3 GPa but decreases above 3 GPa. In TmSe,  $T_{\max}$  shows little dependence to pressure, and in TmS,  $T_{\max}$  shows a slight increase with pressure [9,12]. If we consider  $T_{\max}$  as the value that is relevant to the Kondo temperature  $T_K$ , the increase in  $T_{\max}$  in TmTe from 2 to 3 GPa can be interpreted as the increase in  $T_K$  accompanied by the increase in the hybridization. The experimental results above 3 GPa, however, cannot be understood in this way.  $|d\rho/d \ln T|$  increases with pressure while  $T_{\max}$  decreases above 3 GPa. On the other hand, in TmS, which is almost trivalent and is thought to be at the end of the valence fluctuation,  $|d\rho/d \ln T|$  decreases with pressure while  $T_{\max}$  slightly increases. What the experimental  $T_{\max}$  correspond to is an open problem.

The other anomaly that appears at  $T_{\text{anomaly}} = 15$  K and 2 GPa becomes more clear at 9 K and 3 GPa and is more and more enhanced with increasing pressure. Compared with TmSe and the TmSe $_{1-x}$ Te $_x$  system, this anomaly is likely to be of a magnetic order. For TmSe $_{0.6}$ Te $_{0.4}$  and TmSe $_{0.45}$ Te $_{0.55}$ , ferromagnetic order has been observed just after the transition into the metallic regime [17–21]. Their ordering temperatures are as high as 5 K while it is below 1 K in the semiconducting regime. The ordering temperature decreases with increasing pressure [19,20]. The present results on TmTe are in good correspondence with these results. Therefore, we speculate that this anomaly corresponds to a magnetic order.

The resistivity decreases below  $T_{\text{anomaly}}$  for 2, 3, and 4 GPa, indicating TmTe is metallic. For 5.3 GPa, however, there is no sign of decrease in resistivity down to 4.5 K and it appears that TmTe is approaching TmSe. This behavior may be associated with the type of the magnetic order. Initially for 2 and 3 GPa, just after the semiconductor to metal transition, the ordering may be ferromagnetic as in TmSe $_{1-x}$ Te $_x$ . The resistivity, therefore, shows a sharp decrease below the ordering temperature. On increasing pressure, the sample would get into the intermediate valence regime and the type of order might change into the antiferromagnetic one as in TmSe. Then the resistivity would behave like TmSe. This may be the case for TmTe at 5.3 GPa. If we were able to apply higher pressures, the increase in resistivity below  $T_{\min} = 18$  K would be more enhanced and would finally reach a situation as in TmSe. In TmSe, the sharp increase in resistivity below  $T_N$  initially increases with pressure up to 1.36 GPa [9]. We suppose that this behavior in TmSe corresponds to the enhancement of the resistivity anomaly from 4 to 5.3 GPa in TmTe. In TmTe, however, the crystal structure has changed from a NaCl type to a tetragonal type and it was impossible

to investigate the sample at higher pressures [15,16]. It should be noticed that these resistivity curves in Fig. 3 are those in the metallic regime and they correspond to curve f in Fig. 1 in Ref. [18] for  $\text{TmSe}_{0.45}\text{Te}_{0.55}$ . An anomalous insulating state, which is called an excitonic insulator, is said to appear in the semiconducting regime in  $\text{TmSe}_{1-x}\text{Te}_x$  [18]. To check the possibility of such a state in  $\text{TmTe}$ , more detailed measurements in the semiconducting regime are necessary.

According to a theory of valence fluctuation of Tm impurities, the ground state is a Kondo singlet [22]. The Kondo temperature  $T_K$  would approach zero when the Tm valence is almost trivalent or divalent [22]. In the intermediate valence regime  $T_K$  would have a finite value and a  $\ln T$  behavior in resistivity would be observed. The valence of a Tm ion in  $\text{TmTe}$  at 2 GPa is very close to divalent. Therefore the application of higher pressures would lead to an increase in  $T_K$  and  $|d\rho/d \ln T|$  through the increase in hybridization. On the other limit in TmS in which the Tm ions are almost trivalent, the application of high pressure would lead to a decrease in  $T_K$  and  $|d\rho/d \ln T|$ . Furthermore, in an intermediate state between these two limits, not only the Kondo-like behavior but also an anomalous magnetic state in the vicinity of the magnetic ordering temperature as in  $\text{TmSe}$  would be possible to occur. All of these processes must result from the variation of the hybridization between the  $4f$  electrons and the conduction electrons.

In summary, our experimental results on  $\text{TmTe}$  show that  $\text{TmTe}$  under high pressure also exhibits Kondo-like behavior as in  $\text{TmSe}$  and  $\text{TmS}$ . This indicates that pressure can be an external parameter that connects these three Tm monochalcogenides through the variation of the hybridization. In order to make clear the state of  $\text{TmTe}$  under high pressure and connect it to  $\text{TmSe}$ , the resistivity data at still lower temperatures below 4.2 K and other various measurements under high pressures are needed.

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