Excitonic Insulator Phase in $TmSe_{0.45}Te_{0.55}$

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We measured the Hall constant, resistivity, and magnetoresistance of the narrow-band-gap semiconductor $TmSe_{0.45}Te_{0.55}$ at pressures up to 17 kbar and down to 4 K. As the band gap can be closed with pressure, a semiconductor-metal transition occurs. Above 5 kbar, when the gap is partially closed, a transition to a more insulating phase is detected. The Hall effect at low temperature and high pressure reveals that the resistivity increase is caused by a condensation of free carriers, which strongly supports this as the first observation of the excitonic insulator ground state of condensed matter.

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Thirty years ago, Mott [1] advanced the idea that an anomaly should exist around the semiconductor-semimetal transition (SST). Because of the small number of carriers, the long-range Coulomb interaction between hole and electron is only weakly screened, resulting in a bound state: the so-called excitons. As excitons are neutral quasiparticles, the material should become insulating. Knox [2] also speculated about an anomaly at the SST of an indirect-band-gap semiconductor: When the energy level of excitons (lying below the indirect conduction-band minimum) crosses the energy of the valence band by applying external pressure, i.e., closing the gap, the carriers of the valence band deliberately start to form excitons. Again, the ground state would be insulating. Subsequently, a lot of theoretical work was done on this new hypothetical ground state of condensed matter [3,4] and several phase diagrams were proposed.

However, the very existence of the excitonic insulator has never been proven [5]. Experimentally, the phase transition to the excitonic state should be monitored by the resistivity behavior as a function of closing the gap. Last year, Neuenschwander and Wachter [6] published data of resistivity measurements on the narrow-band-gap, magnetic semiconductor $TmSe_{1-x}Te_x$ ($x=0.55,0.68$). The gap could be continuously closed by external pressure. Their data have been tempting to interpret as a transition to an excitonic insulator [7]. The resistivity $\rho(T,p)$, with T the temperature and p the applied pressure, showed a huge peak as a function of pressure which they attributed to an excitonic phase transition [Fig. 1(a)]. However, it was not clear whether the resistivity peak was only due to either an anomalous scattering mechanism or an effective-mass effect, or whether the free carriers vanished owing to a condensation to bound excitons as is required by the concept of an excitonic insulator. In this Letter, we will present the first Hall-effect measurements at high pressure and low temperature of $TmSe_{0.45}Te_{0.55}$. The result gives strong evidence of an excitonic insulator ground state of $TmSe_{0.45}Te_{0.55}$ between 5 and 9 kbar as the free carriers are condensed indeed when the resistivity peak has developed.

In semiconducting $TmSe_{0.45}Te_{0.55}$, a direct energy gap (130 meV) is formed between the localized $4f^{13}$ levels and the $5d$ conduction-band states [8,9]. On the other hand, band-structure calculations [10] of intermediate-valent TmSe, as well as group-theoretical arguments, have revealed, as a function of the lattice constant, i.e., applied pressure, a maximum of the highest $4f$ level Γ_{15} at the Γ point due to p(Se,Te)-f(Tm) (covalent) hybridi-

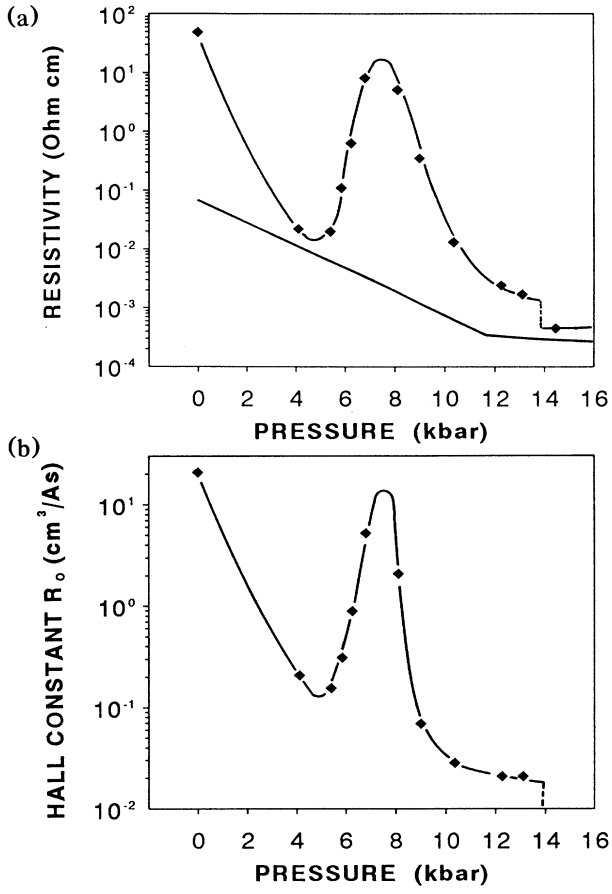

FIG. 1. (a) Resistivity of $TmSe_{0.45}Te_{0.55}$ as a function of pressure at 300 K (lower curve) and at 4.2 K (upper curve). At 300 K, a linear closing of the semiconductor gap is visible with a semiconductor-metal transition at 11.5 kbar. The onset of the resistivity peak depends on the temperature as displayed in the phase diagram (Fig. 5). (b) Ordinary Hall constant R_0 of $TmSe_{0.45}Te_{0.55}$ at 4.2 K. The peak structure of the resistivity is obviously caused by a condensation of the free carriers.

zation and a minimum at the X point of the Brillouin zone for the lowest $5d$ states $\Delta_{2'}$ in addition to the $4f$-$5d$ cation-cation hybridization (intermediate valence). Hence, when the gap of $TmSe_{0.45}Te_{0.55}$ is closing with external pressure, and f-d hybridization is increasing, a band structure similar to that in intermediate-valent TmSe is to be expected; i.e., an indirect band gap develops between the broadened Tm $4f^{13}$ states at the Γ point and the $\Delta_{2'}$ $5d$-band states at the X point, providing the presupposition of Knox. The $4f$ states now show a small dispersion because of hybridization. At the pressure at which the excitonic energy level reaches the $4f$ states, the excitonic instability should take place. An even higher pressure results in a metallic state. Then, because of the cation-cation hybridization of the $4f$ and $5d$ states, an intermediate-valent (IV) state is achieved with a ferromagnetic long-range order below 6 K [6].

The experimental results are shown in Fig. 1. At 300 K, the resistivity decreases exponentially as a function of hydrostatic pressure [Fig. 1(a)]; the gap closes linearly with applied pressure, reaching the metallic state at 11.5 kbar. The absolute value in the metallic state of about 400 $\mu\Omega$ cm is universal for the IV Tm compounds. The gap at zero pressure can be calculated from the gap closing rate to be 130 meV, taking the Fermi-level energy pinned at the $4f$ level. At 4 K, a huge peak starts to develop around 5 kbar, reaching the highest value at 7.5 kbar. There is only a weak temperature dependence at 5 kbar, in contrast to the expectation of a semiconducting behavior as the gap is still open. Above 7.5 kbar, the resistivity falls again, showing a first-order transition around 13.5 kbar to the metallic, ferromagnetic, IV ground state. For lucidity, we have not shown the isothermal curves for temperatures other than 300 and 4.2 K but in the deduced phase diagram (Fig. 5) one can see that the peak structure starts to develop below 250 K. Our results are in excellent agreement with the data published by Neuenschwander and Wachter [6].

As mentioned above, a critical experiment to decide whether the peak is due to the excitonic phase transition is to measure the Hall constant at low temperature and high pressure. In Fig. 2, we represent the experimental data of the Hall resistivity ρ_H for different pressures at 4.2 K. A problem arises with the interpretation of the data, since in substances with local magnetic moments (ordered or paramagnetic) and especially in IV compounds, an anomalous Hall constant is a common feature. To separate the normal Hall constant R_0 from the anomalous Hall constant R_S, one makes the ansatz

$$\rho_H = R_0 B + 4\pi M R_S ,$$

with M the magnetization of the sample. In the paramagnetic region ($p < 13.5$ kbar), the normal R_0 is seen as the slope of $\rho_H(B)$ when the induced magnetization has saturated. R_S can be determined from the axis intersection of the extrapolated linear ρ_H. Under pressure, the Tm ions undergo a valence transition ($Tm^{2+}, {}^2F_{7/2}$

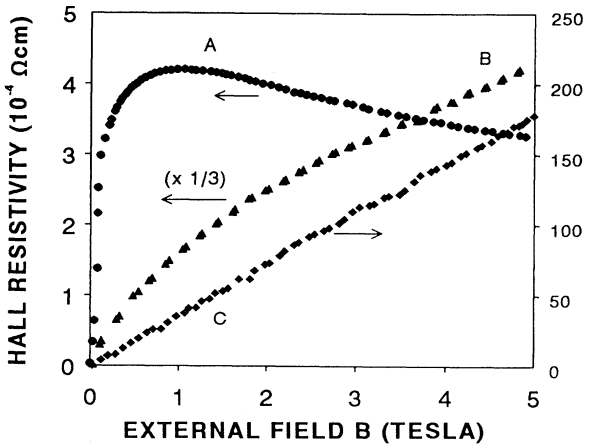

FIG. 2. Hall resistivity ρ_H at 4.2 K for pressures of, curve A, 14.5 kbar; curve B, 12.2 kbar; and curve C, 6.25 kbar. The $p = 12.2$ kbar data reveal an anomalous Hall constant with a saturation of the magnetization at 2.5 T. In the IV state at 14.5 kbar, the normal Hall constant has changed sign and the anomalous R_S has increased.

$\rightarrow Tm^{3+}, {}^3H_6$) concomitant with an enhanced magnetic moment on the Tm ions. Thus, the magnetization increases at higher pressures, making the anomalous part of ρ_H more dominant. In our experiments, an anomalous R_S is clearly visible for pressures above 10 kbar. In the paramagnetic region, the values were always positive and quite independent of pressure. But, for the magnetic saturation, a higher field has to be applied as the pressure is enhanced. In the metallic state (13.5 kbar $< p$) the sign of the normal Hall constant has changed to hole conduction. But, as a saturation of the magnetization is not yet reached with 5 T, the normal R_0 of the metallic state ($p = 14.5$ kbar) could not be extracted. The external magnetic field seems to influence strongly the magnetic structure of the metallic state. The extracted R_0's are depicted in Fig. 1(b). One recognizes an astonishing correlation of resistivity ρ and carrier density n (in the one-band model, $R_H \propto 1/n$), proving that the interesting resistivity behavior is caused by a localization (condensation) of the free carriers and not by a giant scattering or an effective-mass enhancement. However, the resistivity peak has a height of about 3 orders of magnitude. The Hall effect reveals a peak of about 2 orders of magnitude. So, exploiting the formula $\rho = (ne\mu_H)^{-1}$, the Hall mobility μ_H also has to change. The calculated mobility μ_H is shown in Fig. 3. The shape of the curve resembles the behavior of the carrier density. But there are marked differences. The size changes by only 1 order of magnitude. Further, the minimum at 9 kbar does not coincide with the top of $\rho(p)$ at 7.5 kbar as the enhanced admixture at high pressure of localized $4f$ states to the $5d$ conduction band depresses the mobility and increases the effective mass. The absolute values of less than 10 cm^2/Vs are appropriate for magnetic semiconductors

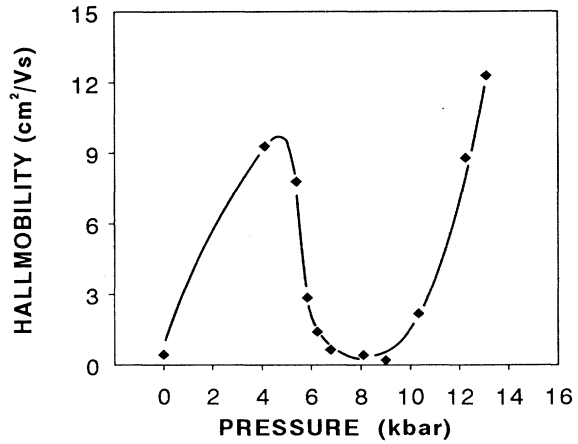

FIG. 3. Hall mobility μ_H as calculated from $\rho=(ne\mu_H)^{-1}$. The phase transition to the high-resistivity peak is also accompanied by a reduced mobility.

[11].

Further, we have determined the magnetoresistance for different pressures at 4.2 K. In Fig. 4, we have plotted the relative change of the magnetoresistance $\Delta\rho/\rho_0$ for an applied field of 5 T. First of all, the overall value is negative, pointing to an improved mobility with an applied field. Between 5.5 and 6.5 kbar, a giant negative magnetoresistance has developed. The steep increase of the magnetoresistance coincides with the onset of the resistivity anomaly and stops at half of the resistivity rise. At 7.5 kbar, when the top of the resistivity peak is reached, the magnetoresistance has already fallen back to a moderate value. This eliminates the possibility that the peak itself is produced by, e.g., a strong fluctuation of spin-spin scattering which would be suppressed by the external magnetic field.

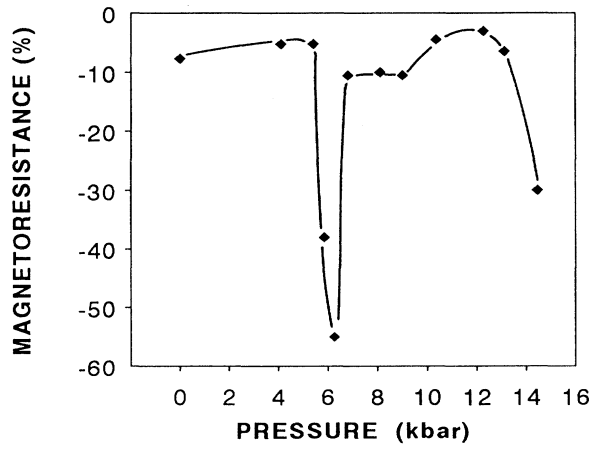

FIG. 4. Relative change of the magnetoresistance $\Delta\rho/\rho_0$ with an applied magnetic field of 5 T at 4.2 K. A giant change sets in at the onset of the resistivity peak [Fig. 1(a)]. At half of the resistivity rise, the relative change of the magnetoresistance has already fallen back to a moderate value.

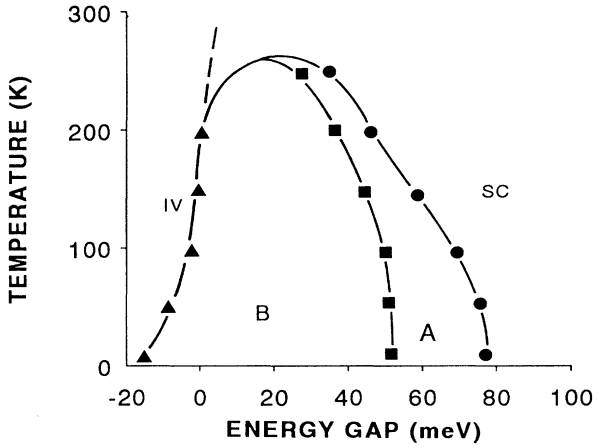

FIG. 5. Phase diagram of $TmSe_{0.45}Te_{0.55}$ as deduced from our resistivity data. The circles represent the onset of the resistivity rise [see Fig. 1(a)]. The squares indicate the summit of the resistivity peak. The triangles are the first-order transitions to the metallic state. The different phases are semiconducting (SC), excitonic phases A and B (see text), and intermediate-valent (IV) metallic.

Henceforth, we are going to discuss the phase diagram (Fig. 5) extracted from our data and compare it to theoretical predictions for the excitonic phase. The abscissa denotes the band-gap value which was calculated from the applied pressure using the linear closing rate of the gap of $dE_g/dp=-0.11$ meV/kbar. The circles indicate the onset of the resistivity anomaly [Fig. 1(a)]. The squares correspond to the top of the resistivity peak. Hence, in region A, the resistivity is rising, and in region B, it is decreasing with increasing pressure. The triangles represent the first-order transition to the IV metallic phase.

In Fig. 6, we have drawn the phase diagram as predicted by theoretical considerations [4] of the excitonic insu-

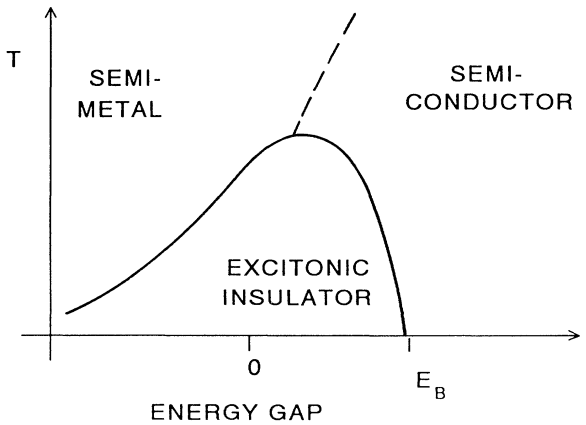

FIG. 6. Phase diagram as proposed by Kohn (Ref. [4]) for the excitonic ground state of condensed matter. E_B is the binding energy of an exciton.

lator phase. This phase diagram is based on a Hartree-Fock approximation neglecting correlations between excitons and on assumptions such as wide bands, $m_{\text{hole}} = m_{\text{electron}}$, and a small anisotropy. The critical gap E_B at 0 K is just given by the binding energy of the exciton. As regards our more subtle substance, one has to admit an acceptable agreement of the experimental and theoretical results.

Halperin and Rice [3] have tried to go beyond the Hartree-Fock theory and treat the more elaborate case of a heavy-hole mass as we would expect for our $4f$ holes. They concluded that for E_g close to E_B, the excitons do not form a Bose fluid of single excitons but build up exciton molecules which condense in a periodic array. This state would be insulating and we associate it with our region A (Fig. 5). Then, if the density of exciton molecules happens to increase further, the long-range Coulomb interaction becomes screened and the electrons begin to delocalize, whereas the heavy holes suffer a Wigner crystallization. In this phase, the resistivity decreases and, hence, is to be identified with region B of our experimental phase diagram. As the density is enhanced still further, the Wigner array of holes is expected to melt and the crystal becomes a normal metal in a first-order transition. $TmSe_{0.45}Te_{0.55}$ is intermediate valent in the metallic state because of d-f hybridization.

Our phase diagram reveals a quite small region A, i.e., a high density of excitons is easily reached under pressure. This is understandable with the narrow-band dispersion of the $4f$ states and the considerable gap closing rate dE_g/dp. The exciton level effectively crosses the $4f$ states at applied pressure, whereby the $4f^{13}$ electrons decay to excitons. The localization to excitons should be manifest by a decreasing carrier density as actually seen in Fig. 1(b) between 5 and 7.5 kbar. As regards the giant magnetoresistance, one could imagine that the excitons are in the singlet state and, consequently, an applied magnetic field breaks the excitons. In our model, we do not assume a crossing of an indirect conduction-band minimum with the valence band resulting in a semimetal, but, following Knox [2], the lowering of an indirect, deep exciton level below the valence-band maximum at the Γ point. Thus, the delocalization in region B above 7.5 kbar does not end in a metallic state because there is still a narrow gap to the $5d$ band.

There are other investigations which support the excitonic model. Near-normal reflectivity at normal pressure [6] has shown an optical excitation E_{ex} at 60 meV which corresponds to an exciton with the binding energy of $E_B = E_g - E_{\text{ex}} = 70$ meV, in agreement with the phase diagram (Fig. 5). Further, neutron diffraction [12] at high pressure has not pointed out a *structural* phase transition which could be responsible for the disappearance of the free carriers. More likely, they disappeared because of a correlation (excitons).

To conclude, we have shown that the resistivity anomaly of $TmSe_{0.45}Te_{0.55}$ as a function of the energy gap (pressure) is caused mainly by a localization of free carriers and by a more modest change of the mobility. The results are consistent with the assumption of a phase transition to an excitonic ground state of condensed matter.

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