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Pressure-driven metal-insulator transition in La-doped SmS: Excitonic condensation

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The long-predicted excitonic condensed phase, the excitonic insulator, has been verified once more. After the discovery of two intermediate valent $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$ alloys a few years ago, for which the excitonic phase has been verified under pressure at low temperatures, another rare-earth chalcogenide alloy system, namely, $\mathrm{Sm}_{1-x}\mathrm{La}_x\mathrm{S}$, has now turned out to be also an excitonic insulator under pressure at low temperatures. The effect is caused by Coulomb interaction of electron and holes in an intermediate valent state when pressure is decreasing the interaction volume and low temperature is preventing the ionization of the condensed phase.

INTRODUCTION

In an extended medium such as a crystal, electrons in the conduction band and holes in the valence band attract each other by means of the Coulomb force and in general can form bound states—the excitons. In a semiconductor we expect an anomaly when the binding energy E_B of such excitons becomes larger than the energy gap ΔE between the conduction and valence bands. We may expect exciton condensation and thus a new ground state of matter—the excitonic insulator. The same phenomenon may occur in a semimetal if the number of free carriers is small, so that charge screening, reducing the Coulomb interaction, is not yet important.

The theory for the excitonic insulator was developed about 30 years ago, noticeably by Mott,[1] Knox,[2] Kohn,[3] Halperin and Rice,[4] and Keldysh and Kopaev,[5] but the experimental verification of the existence of an excitonic insulator had to wait until recent times. A proposal that some experiments on intermediate valent $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$ may be explained under the assumption of an excitonic insulator was given by Neuenschwander and Wachter[6] and an experimental proof by means of the Hall effect was given by Bucher, Steiner, and Wachter one year later.[7] The experiments were very demanding and one had to use low temperatures, high pressure, and high magnetic fields.

It is generally accepted that the application of pressure to a solid will eventually drive the solid into the metallic state, even when one starts from an insulator. In such a case the resistivity will decrease with increasing pressure due to a more intimate overlap of wave functions, also at low temperatures. It is thus a very important hint of something unusual going on, especially for a rare-earth compound, when one observes with increasing pressure an increase in resistivity (with no crystallographic change observable and no magnetic order) and this has been interpreted in Refs. 6 and 7 as the transition to an excitonic insulator state. Further pressure enhancement eventually drives the materials nevertheless into the metallic state. In this paper we discuss the observation of an excitonic condensation in another pseudobinary alloy system, namely, $\mathrm{Sm}_{1-x}\mathrm{La}_x\mathrm{S}$, by means of resistivity measurements in function of temperature and pressure. As in $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$, a precursor to the excitonic insulator is the state of intermediate valence.

A REMINDER OF THE RESULTS ON $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$

Neuenschwander and Wachter[6] found in the pressure and temperature variation of the intermediate valent semiconductors[8,9] $\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ and $\mathrm{TmSe}_{0.32}\mathrm{Te}_{0.68}$ an unexpected new feature, displayed in Fig. 1 for $\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ after Bucher, Steiner, and Wachter.[7] The pressure dependence of the resistivity at 300 and 4.2 K is shown in Fig. 1(a). At room temperature and ambient pressure the material is a semiconductor with a gap of about 100 meV.[8,9] After an initial decrease of resistivity with pressure at 300 K due to the closing of the $4f^{13}$-$5d$ gap, followed by a semimetallic intermediate valent state, we observe below 200 K, and more pronounced for lower temperatures, an increase of resistivity with increasing pressure, followed again by a decrease and a first-order semiconductor-metal transition. At 4.2 K the resistivity goes up by a factor of 370 with increasing pressure; to the best of our knowledge such behavior has never been seen before. A critical experiment has been performed by Bucher,

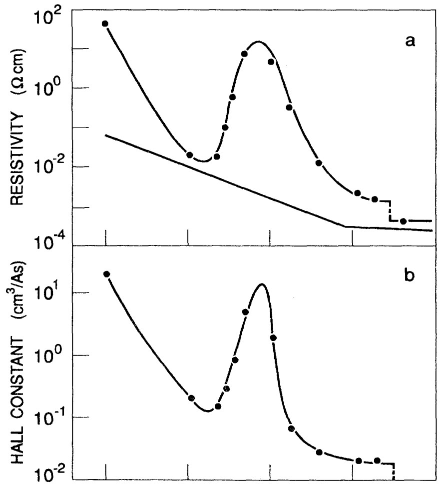

FIG. 1. (a) Pressure dependence of the resistivity of $\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ at 300 K (lower curve) and at 4.2 K (upper curve). At 300 K the semiconductor-metal transition is at 11.5 kbar, at 4.2 K near 14 kbar, and it is of first order. (b) The Hall constant at 4.2 K.

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Steiner, and Wachter[7] where the Hall effect at low temperatures and high pressures has been carried through [Fig. 1(b)]. This experiment combines extremely difficult experimental techniques because, in addition to high pressure and low temperature, a large magnetic field of about 5 T was necessary to separate the normal from the anomalous Hall effect. Whereas Neuenschwander and Wachter[6] still had to speculate whether the resistivity rise with pressure at 4.2 K was caused by a freezing out of carriers or a mobility effect, the Hall constant of Fig. 1(b), going parallel with the resistivity increase, gives clear evidence that we are dealing with a loss of free carriers, or a condensation into an insulation phase—the excitonic insulator. To explain these unusual results in more detail, Neuenschwander and Wachter,[6] Bucher, Steiner, and Wachter,[7] and Wachter and Jung[10] have described the concept of an excitonic insulator in more detail.

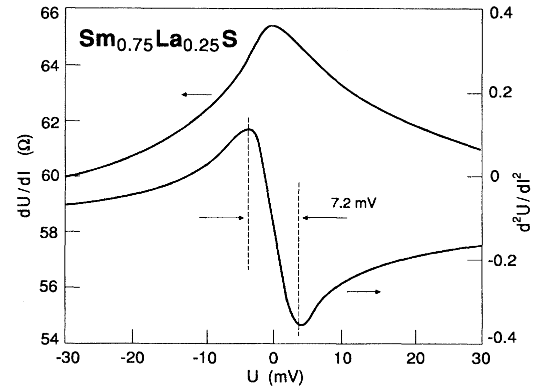

FIG. 2. Point contact spectroscopy (PCS) of intermediate valent $Sm_{0.75}La_{0.25}S$ at 4.2 K.

PSEUDOBINARY ALLOY SYSTEM $Sm_{1-x}La_xS$

It is well established that at room temperature SmS under pressure of only 6.5 kbar performs a transition from semiconductor to intermediate valent metal.[11] Substituting part of the divalent Sm with trivalent ions, noticeably Y or Gd, results spontaneously in the formation of the intermediate valent state,[12] where it is thought that the smaller trivalent ions exert a chemical (lattice) pressure on the divalent, larger Sm, thus avoiding the more difficult physical pressure experiments. However, this chemical substitution not only creates lattice pressure but also introduces per trivalent ion one free carrier in the conduction band, in addition to those due to the valence transition, resulting in hybridized *f* and *d* states. In the past, electronic and chemical pressure effects have not been separated and the chemical pressure effect alone was made responsible for the valence transition.[12]

It was not until a few years back that Elmiger and Wachter[13] showed that chemical pressure and real pressure showed different behavior on a SmSe system. The comparison has been made by comparing SmSe single crystals under real physical pressure with SmSe doped with Y (Ref. 14) and then with Ce.[13] Trivalent Ce has a larger ionic radius than divalent Sm so pressure effects rather go in the opposite direction, but all trivalent ions donate one electron into the conduction band. So SmSe doped with Ce in the absence of a lattice pressure nevertheless shows lattice softening and a tendency to become intermediate valent. It is thus the electrons that drive the transition towards intermediate valence and pressure is only an additional effect. This has been envisaged by the Falicov-Kimball model.[15]

Stimulated by these results we prepared La-substituted SmS because trivalent La has also a larger ionic radius than divalent Sm; thus the argument with the chemical pressure is invalid. However, again the doping results in one free electron per La ion. Thus in $Sm_{0.75}La_{0.25}S$ one expects 25% additional electrons to those due to intermediate valence. This is not the first time that $Sm_{1-x}La_xS$ has been prepared but to our knowledge the above questions have not been addressed.[16] In spite of the missing lattice pressure the compound is intermediate valent at ambient pressure and from the lattice constant of 5.8660 Å one derives a valency of about 2.3, in contrast to, e.g., $Sm_{0.75}Y_{0.25}S$, which has a valency of 2.7. So the effect of the additional lattice pressure in the latter compound is evident. It is thus clear that the valence transition is basically driven electronically, but valence mixing can be enhanced with additional physical pressure or chemical pressure.

It is generally accepted that intermediate valence is caused by the hybridization of initially localized $4f^n$ states with extended, bandlike $5d$ states, resulting in hybridization gaps in the meV range. The Fermi level lies in this gap when the only electrons in the conduction band are those originally coming from the $4f^n$ state and the Luttinger theorem of an even $4f$ and $5d$ electron count is fulfilled.[17–19] Thus only Sm, Yb, and antiferromagnetic Tm compounds fulfill this condition. Thus in undoped SmB_6, SmS, SmSe and SmTe under pressure, YbB_{12}, and antiferromagnetic TmSe these hybridization gaps have been observed experimentally by tunneling, point contact spectroscopy (PCS), optical absorption, reflectivity, resistivity, Hall effect, NMR, and other effects (for a review see Wachter[20]). However, in intermediate valent SmS doped with trivalent ions there are more electrons in the conduction band than only those originating from the $4f^6$ state of Sm and as a consequence the Fermi level will not be in a gap and the resistivity exhibits metallic behavior.[16] In addition, the fcc SmS compounds seem to have in the intermediate valent state a hybridization gap which is not open over the whole Brillouin zone due to symmetry conditions.[17] This is confirmed by the existence of a γ term of the specific heat due to free electrons.[21,22] It is thus no surprise that in trivalently doped SmS a metallic temperature dependence of the resistivity prevails.

It is nevertheless a question whether in trivalently doped SmS a hybridization gap, at least in part of the Brillouin zone, exists, in spite of the fact that due to the doping the Fermi level will not be in the gap. Thus a point contact experiment has been carried out at 4.2 K on $Sm_{0.75}La_{0.25}S$ and it is shown in Fig. 2. The dU/dI versus U characteristics, being inversely proportional to the density of states, are practically the same as for other intermediate valent compounds,[20] especially the high-pressure "gold" phase of SmS.[23–25] In the second derivative d^2U/dI^2 the separation of the two extremes yields the half-width of dU/dI, which is taken as the gap width, and it is with 7.2 meV nearly the same size as gold SmS, where it was 6.4 meV.[25]

With Brillouin scattering[26] first experiments have shown a negative c_{12}, an infallible evidence of lattice softening con-

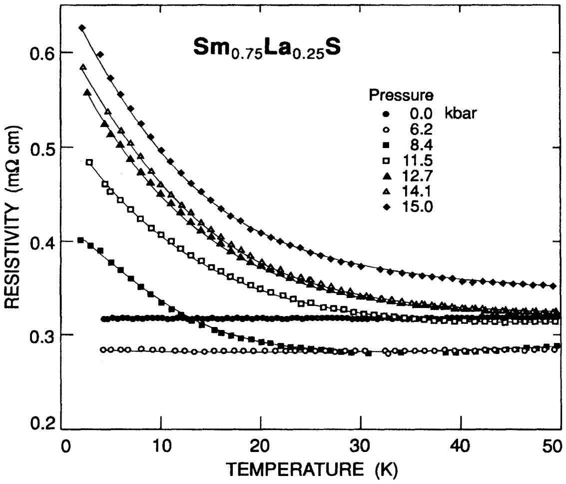

FIG. 3. Temperature dependence of the resistivity below 50 K for selected pressures (measured *in situ*).

nected with intermediate valence.[27,28] The electronic structure of $Sm_{0.75}La_{0.25}S$ has to be visualized like Fig. 6 of Ref. 22, consisting of two sharp density-of-states peaks with a hybridization gap in between, not extending over the whole Brillouin zone, superimposed on a broad *d* band, where the alloying with La has increased the electron concentration so much as to shift the Fermi level somewhat into the bottom of the upper density-of-states peak.

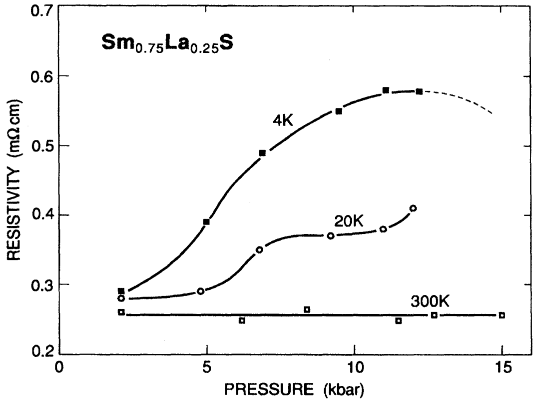

FIG. 4. Pressure dependence of the resistivity for three selected isotherms (4, 20, and 295 K) (pressure measured *in situ*).

Additional real pressure (at least at room temperature) will now in any case enhance the degree of valence mixing in $Sm_{0.75}La_{0.25}S$ and create even more conduction electrons. The experience with the $TmSe_{1-x}Te_x$ systems stimulated us to do the pressure experiment also at low temperatures in search for excitonic condensation. Pressure has been applied in a self-clamping piston cylinder Berylco cryo cell, loaded by a Teflon capsule, containing sample, *n*-pentane-isoamyl alcohol as pressure medium, and a manganin gauge for *in situ* pressure measurements. The resistivity has been measured with a four-probe technique and the experimental method is described in more detail in Ref. 6. In Fig. 3 we show the electrical resistivity as function of temperature at ambient pressure, with a clear-cut metallic behavior down to the lowest temperatures, and up to 15 kbar (applied at room temperature), where we observe below about 50 K an increase of resistivity. This is the anomalous signal which we expected for an exotic phase, namely, an increase of resistivity with increasing pressure. The excitonic phase transition commences near 8 kbar, where we assume that for pressures up to 8 kbar the hybridization gap has been closed, which, however, cannot be observed experimentally, because the compound is in any case a semimetal. In Fig. 4 we show three isotherms at temperatures of 4, 20, and 295 K. The 4-K curve of Fig. 4 should be compared with the $TmSe_{0.45}Te_{0.55}$ curve in Fig. 1(a) at the lowest temperature. In the Sm compound the initial decrease of the resistivity with pressure of the Tm compound is missing, because we do not start from a semiconductor and at first have to close the $4f^n$-$5d$ gap. Thus we start already from the intermediate valent semimetallic state. This corresponds to about 5 kbar in the Tm compound. From then on the two compounds are comparable in their resistivity behavior. In the Sm compound we would have to apply more than 15 kbar to get the resistivity down again, but indications of a saturation near 13 kbar are evident and we have extrapolated an expected behavior at higher pressures. Figure 3 can be plotted in the form of Arrhenius plots [$\rho \propto \exp(\Delta E/2kT)$] from which energy gaps (symbol ▲) can be obtained. This is shown in Fig. 5 with only minute energy gaps not exceeding 1 meV.

Again we propose that near 8 kbar we are entering the excitonic phase and with pressures of more than 16 kbar we will eventually reach the metallic state again. This then would be the second example of the realization of an excitonic insulator. But it is the first time, to the best of our knowledge, that one goes from a metallic, or more precise semimetallic intermediate valent state into an insulating state with increasing pressure. The reason why this compound makes this observation possible is the reduced carrier concentration compared with, e.g., $Sm_{0.75}Y_{0.25}S$, which does not show a resistivity increase with pressure at low temperatures. A reduced screening of the Coulomb interaction between electron and holes is a prerequisite of an exciton formation, as has been discussed also by Keldish and Kopaev.[5] The long-range Coulomb potential U_C will exponentially de-

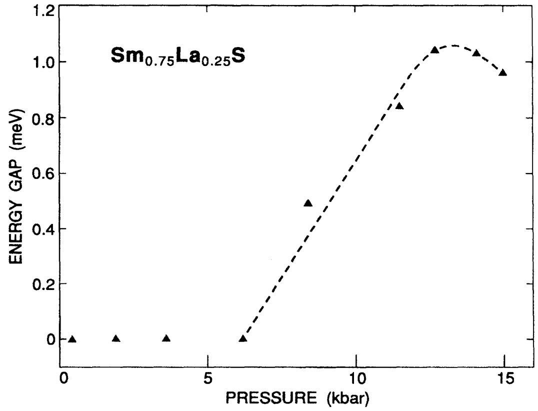

FIG. 5. Relation between pressure and energy gaps. The symbols are the gaps taken from Arrhenius plots of the isobars of Fig. 3: at 8 kbar a gap opens, indicating the onset of the excitonic phase (pressure applied at 295 K). The dotted line serves as a guide to the eye.

crease with the Thomas-Fermi constant λ according to $U_C \propto (1/r)\exp(-\lambda r)$, with λ being proportional to the excess electron concentration.

CONCLUSION

Although the Hall effect under pressure and at low temperatures has not yet been performed for $Sm_{0.75}La_{0.25}S$, we conclude alone from the resistivity behavior under pressure and at low temperatures an excitonic condensation, in analogy with the more completely investigated $TmSe_{0.45}Te_{0.55}$.[6,7] $Sm_{0.75}La_{0.25}S$ would then be the second material system in which such an exciton condensation has been observed. We expect that also different La concentrations will exhibit the same phenomenon, and experiments in this direction are underway.

It is interesting that in the Tm compounds as well as in the Sm compounds the phase to start the excitonic condensation is the intermediate valence state. For the Tm compounds this is achieved by applying a pressure of about 5 kbar [see Fig. 1(a)] and for the Sm compounds by alloying with La. By applying pressure at low temperatures we increase the electron-hole Coulomb interaction, but only when there are not too many excess free electrons, because they would screen the Coulomb interaction. Thus in $TmSe_{1-x}Te_x$ the alloying of TmSe with TmTe serves to reduce the free-carrier concentration in TmSe from about 10^{22} to about 10^{20} cm^{-3} at 300 K.[6,9] On the other hand, $Sm_{0.75}La_{0.25}S$ is an intermediate valent semimetal to start with, but, compared to the high-pressure phase of SmS or to $Sm_{0.75}Y_{0.25}S$, with a much reduced carrier concentration and thus less screening of the Coulomb interaction than in the other compounds. Nevertheless, there are more excess electrons in the Sm compound than in the Tm compound. It is thus only at the lowest temperatures that Coulomb interaction wins and the minute binding energy of the excitonic phase or the gap of an excitonic insulator with only 1 meV is an indication that we just are able to make the phase transition.

So why has it taken so long after the proposal of excitonic condensation by Mott[1] for an experimental realization?[6,7] The search for an excitonic insulator has been performed in the past always on classical semiconductors with narrow gaps, such as $Hg_{1-x}Cd_xTe$. Electrons and holes in these compounds have small effective masses and are highly mobile. When bound states form the drift velocity of the excitons will be large and imperfections of the crystal and ambient temperature will destroy the bound state again. The intermediate valent state is characterized by hybridized f and d states with the consequence of narrow (meV-wide) f-like bands with large effective masses (between 10^2 and 10^3 m). We assume that this nearly localization of at least the holes in the "f bands" is the main reason that the intermediate valence state is a primary requisite to form an excitonic insulator.

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