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A SUPERFLUID PHASE IN A BOSE CONDENSED EXCITONIC STATE*

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A condensed excitonic phase has been realized in intermediate valent $\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ at low temperatures and high pressures. In this paper we report about some thermodynamic properties such as the heat conductivity and the thermal diffusivity which have been obtained between 300 K and 1 K and between ambient pressure and 17 kbar (1.7 GPa). Pressure and temperature are used to navigate in the intermediate valent semiconducting phase, in the condensed excitonic phase and in the intermediate valent metallic phase of the complete phase diagram. In the condensed excitonic phase the heat conductivity λ of the excitonic phase increases exponentially below about 20 K suggesting a superthermal current for $T \to 0$. In a solid this has never been seen before. Also the thermal diffusivity a strongly increases below 20 K, giving evidence for second sound.

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1. Introduction

TmSe and TmTe are some well known rare earth chalcogenide compounds [1] which crystallize in the fcc rocksalt structure and, with the exception of a narrow miscibility gap between $0.2 < x < 0.4$, can be alloyed in the whole concentration range [2,3] of $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$. It has been found [4–6] that for a certain region $0.5 < x < 0.68$ these compounds exhibit under pressure and at low temperature the phenomenon of exciton condensation in the sense of an excitonic insulator, as predicted by Mott [7]. The Tm chalcogenides are not the only system in which this phenomenon has been observed, also in the $\mathrm{Sm}_{1-x}\mathrm{La}_x\mathrm{S}$ [8–10], $\mathrm{Sm}_{1-x}\mathrm{Tm}_x\mathrm{S}$ [10,11], YbO and YbS [8,12]. They all crystallize in the fcc structure.

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The prerequisites for exciton condensation are an intermediate valent condition [4–6] (usually realized in a rare earth compound) and a certain range of carrier concentration prior to exciton condensation, which is not too high and thus avoids screening the Coulomb interaction between electrons and holes, and not too low to enable the formation of enough excitons which then can condense. This is usually achieved by alloying an intermediate valent metal with a semiconductor, such as TmSe and TmTe to form $\mathrm{TmSe}_{1-x}\mathrm{Te}_x$. Within the range $0.5 < x < 0.68$ $\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ has shown the largest effects, so we concentrate in the following on this composition.

Intermediate valence provides us due to f–d hybridization with a narrow f band and as consequence with a large effective hole mass ($50\,m_e$–$100\,m_e$) reducing the diffusive mobility of excitons and thus increasing their stability [6]. Also an indirect band gap between $4f$ band and $5d$ band is of advantage so the exciton condensation can be of the Bose type with the help of phonon interaction [13], *i.e.* we have a positive and a negative charge coupled via Coulomb interaction and a strongly bound phonon.

$\mathrm{TmSe}_{0.45}\mathrm{Te}_{0.55}$ is at ambient conditions an indirect semiconductor with weak f–d hybridization, with a gap of $\Delta E = 130$ meV between the top of the $4f$ valence band at Γ and the bottom of the $5d$ conduction band at X of the Brillouin zone. With pressure and at 300 K this gap can be linearly closed and an intermediate valent semimetal results [4,6]. At low temperatures, pressure leads to an intercepting condensed excitonic insulating phase as proposed by Mott [7] and Kohn [14], which has been experimentally verified with many publications [4–6, 8–11]. The excitonic phase is obtained for a certain pressure and temperature region and it exists without any external excitation (*e.g.* light) also for $T \to 0$. It is thus a new ground state of matter.

In Fig. 1 we show the temperature–pressure phase diagram of the condensed excitonic phase. At temperatures above about 250 K, *e.g.* 300 K, one crosses with increasing pressure (upper scale going towards the left) between 10 and 11 kbar the dashed line, separating the semiconductor–semimetallic phases. At lower temperatures instead, one enters with increasing pressure the condensed excitonic state (above 5 kbar) and leaves the excitonic state between 11 and 15 kbar. In the lower abscissa the energy gap ΔE is plotted, negative values refer to the metallic state [6]. Either the pressure scale (top) or the energy gap scale (bottom) is non-linear. Of interest and experimentally simply accessible are the isobars, where in a clamped pressure cell at a chosen pressure the temperature is decreased and thus one navigates in the pressure–temperature phase diagram.

An isobar should be a vertical line in the diagram of Fig. 1. However, the pressure transmitting medium contracts upon cooling and the pressure relaxes somewhat. The pressure is monitored in the cell and thus an isobar at 12 kbar starting at 300 K looks like the full line in Fig. 1. It will be of

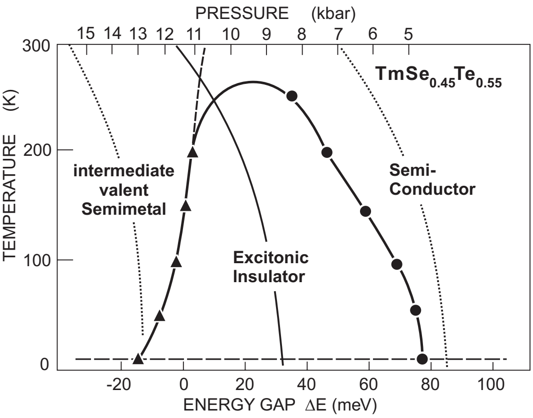

Fig. 1. The excitonic phase diagram of $\mathrm{TmSe_{0.45}Te_{0.55}}$. Experimental points designated by symbols. "Isobars" in the semiconducting and semimetallic phase are shown as dotted lines, whereas an "isobar" entering the excitonic phase is shown by a full line.

relevance in the whole paper that *e.g.* an isobar, starting at about 7 kbar or below at 300 K, will not enter the excitonic phase, but remain in the semiconducting phase and an isobar, starting at about 14 kbar and above at 300 K, will remain in the metallic phase. This is indicated by 2 dotted lines in the phase diagram.

2. Experimental arrangement

To measure the heat conductivity λ and the thermal diffusivity a bar shaped single crystals of $\mathrm{TmSe_{0.45}Te_{0.55}}$ were placed in a Cu–Be pressure cell withstanding pressures up to 20 kbar. Small Au–Chromel and Au–Ni thermocouples were used at both ends of the crystals and a Mäander like thin film heater was placed at one end. The pressure inside the cell was monitored with a calibrated manganin coil. Details of the arrangement are described in Ref. [15]. The pressure cell could be cooled in a bath cryostat down to about 1 K. Pressure was applied at room temperature in a power press and the cell was clamped at the desired pressure. To our knowledge it is the first time that heat conductivity and thermal diffusivity have been measured under pressure and down to low temperatures.

The heat conductivity λ is obtained in a static measurement in which the temperature difference between both ends of the crystal with length L and cross section A is monitored for a certain rate of heat input: $Q/t = \lambda A \Delta T/L$, with $\Delta T > 0$, (steady state equation of heat flow). The thermal diffusivity a is measured essentially with the same arrangement, but it is a dynamical method. The sample is heated periodically and the temperature along the sample varies with the same period but with diminished amplitude. Moreover, as the temperature wave travels along the sample with finite velocity there is a varying phase relationship. Measurement of the amplitude decrement and the phase difference with a lock — in technique enables the diffusivity a to be determined. As the temperature distribution throughout the sample varies with time, the complete differential equation of heat flow is involved: $\partial T/\partial t = a\nabla^2 T$ (non-stationary equation of heat flow), with $a = \lambda/\rho c_v$. The heat conductivity as a static measurement had good precision and a good reproducibility. The absolute value of λ may be influenced by non-negligible heat losses into the pressure transmitting liquid. The thermal diffusivity was less precise which we recognize with an error bar in the figure. Both type of measurements were taken point by point.

3. Results and discussion

The motivation to measure heat conductivity and thermal diffusivity in the phase of excitonic condensation is due to a long-standing controversy amongst theorists. Keldysh and Kopaev [16] and Kozlov and Maximov [17] proposed that in a condensed excitonic phase at low temperatures a superthermal current could exist. They used an analogy to superconductivity where, as in our case, two charged particles strongly couple to a phonon. This was opposed by Zittartz [18], who claimed that the heat conductivity in a condensed excitonic state would be quite normal. Since only in recent years the phenomenon of exciton condensation was realized [4–10] the time has come to settle the dispute.

The equation of heat conductivity is $\partial Q/\partial t = -\lambda\,\mathrm{grad}\,T$ with $\lambda = 1/3Cv\ell$; C is the heat capacity per volume $C = \rho c_v$ with ρ the density and c_v being the specific heat for constant volume. v is the velocity of sound and ℓ the mean free path. Thus $\lambda = 1/3\rho c_v v\ell$ or $\lambda = 1/3\rho c_v v^2\tau$. The thermal diffusivity $a = \lambda/\rho c_v$ so that $a = 1/3v\ell$. The independent measurement of λ and a thus permits the evaluation of $c_v = \lambda/a\rho$. Since both entities λ and a are measured with pressure and as a function of temperature, we obtain also for the first time the specific heat under pressure in the whole temperature range from 1 K towards 300 K. This will be discussed in a forthcoming paper.

Generally speaking the various contributions to the heat conductivity λ are additive: $\lambda_{\mathrm{tot}} = \lambda_{\mathrm{el}} + \lambda_{\mathrm{ph}} + \lambda_{\mathrm{ex}}$. λ_{el} is the metallic part given by the Wiedemann–Franz ratio, λ_{ph} is the phonon part and λ_{ex} the excitonic contribution. The sound velocity v and the density ρ will not have an excessive temperature dependence outside the excitonic region, thus the temperature dependence of the heat conductivity due to phonons, λ_{ph} is mainly depending on the specific heat c_v and on the mean free path for phonon scattering ℓ_{ph}. With the same argumentation the thermal diffusivity a will be mainly proportional to the mean free path ℓ_{ph}, which will be a steadily rising function with decreasing temperature. If we assume in an insulator only phonon–phonon scattering, ℓ_{ph} will be zero for $T \to \infty$ and then increase, at first proportional to $1/T$ because the density of phonons decreases proportional to T. At lower temperatures we have Umklapp processes involving 3 phonons, so ℓ_{ph} will rise proportional to $\exp(\Theta/gT)$, with Θ being the Debye temperature and $g \approx 2$ for the 2 phonons with wave vector outside the first Brillouin zone [19]. For still lower temperatures the mean free path ℓ_{ph} becomes so large as the geometrical dimensions of the sample and thus depends only on surface scattering and defects. The mean free path ℓ_{ph} then becomes temperature independent.

In Fig. 2 we show the thermal diffusivity a as a function of temperature. At 7 kbar (dash-dotted curve) we remain in the semiconducting phase outside the excitonic region (see dotted curve in Fig. 1). The curve follows the description above and is mainly proportional to the mean free path ℓ_{ph} for phonon scattering, reaching for temperatures below about 20 K the linear dimensions of the crystal. At 15 kbar we stay in the metallic (semimetallic) phase (dashed curve), again outside the excitonic region. The thermal diffusivity follows also the temperature dependence of the mean free path, this time for electron–phonon scattering, but since the concentration of electrons in a metal is largely temperature independent, it is again the phonon scattering which determines a. The weak maximum near 30 K in the thermal diffusivity curves has no explanation at present.

Before discussing the excitonic region of a in Fig. 2, we look at Fig. 3 for the heat conductivity λ. We have derived above that the heat conductivity follows mainly the temperature dependence of c_v and ℓ_{ph}. Since c_v definitely will go towards zero for $T \to 0$, the heat conductivity outside the excitonic region generally displays a maximum near 50 K, as well for the insulating case at 7 kbar as also for the metallic case at 15 kbar. The difference of the heat conductivity near 300 K for both cases is due to the electronic part of the heat conductivity in the metallic state and it corresponds roughly to the Wiedemann–Franz relation. Thus the heat conductivity and the thermal diffusivity behave very “normal” under pressure, as well in the insulating as in the metallic phase, which gives confidence in the experimental method. (We show only a selection of curves in order not to overload the pictures and the reader).

We continue the discussion of the heat conductivity in Fig. 3, but now in the excitonic region at 13 kbar and 14 kbar. The first thing which is unexpected are the downward jumps in a first order transition when entering the excitonic phase. Consulting Fig. 1 it is obvious that at different pressures

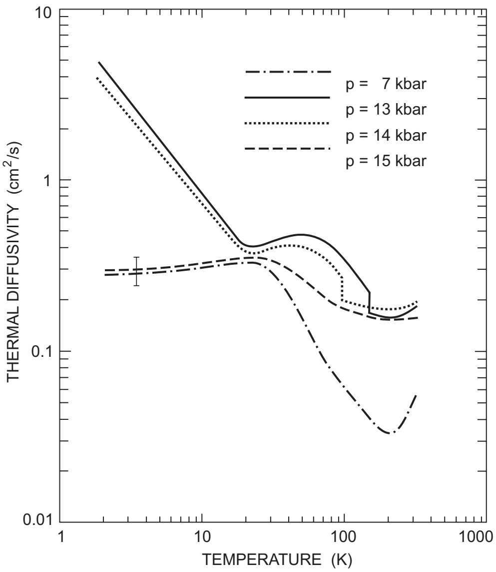

Fig. 2. The thermal diffusivity a of $TmSe_{0.45}Te_{0.55}$ for various pressures as a function of temperature. Dotted and full line in the excitonic region, dashed in the metallic region and dash-dotted line in the semiconducting phase.

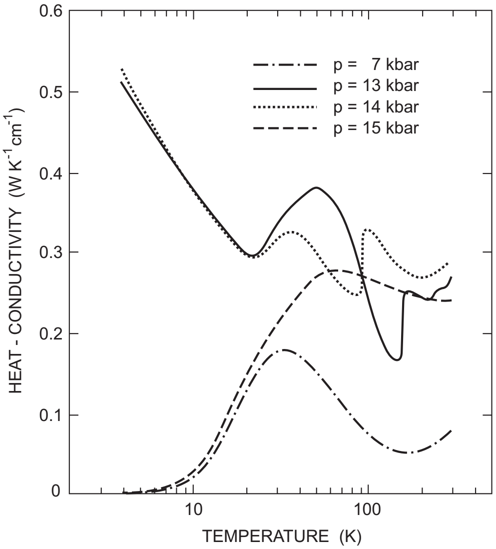

Fig. 3. Heat conductivity λ of $TmSe_{0.45}Te_{0.55}$ at various pressures as a function of temperature. Dotted and full line in the excitonic region, dashed in the metallic region and dash-dotted line in the semiconducting phase.

one enters the excitonic phase at different temperatures. At these temperatures and pressures one enters the insulating excitonic phase mainly from the semimetallic phase, thus with a metal–insulator transition. It is conceivable that the downward jumps in λ reflect the loss of the electronic part of the heat conductivity. But measuring an isobar at 11 kbar one enters the excitonic region from the semiconductor phase (see Fig. 1), but the downward jump in λ exists just as well and is of the same size as the other jumps in the excitonic region. Here we have to realize that many phenomena occur simultaneously at the excitonic phase transition. We have stated above that λ_{tot} is a sum of many contributions, all of which can and will change at the phase transition, such as λ_{ex}, when excitons suddenly appear and simultaneously condense with a density of about [6] 4×10^{21} cm^{-3}. Also λ_{ph} may change due to a renormalization of the phonon spectrum when certain phonons strongly couple to the excitons. On the other hand, the thermal diffusivity a in Fig. 2 displays at the same temperatures an upward jump. Since $a = 1/3\ell_{\mathrm{ph}}\, v$, we may wonder which of the two entities jumps upwards. In fact it is the sound velocity v which increases sharply when entering the excitonic phase, as a separate measurement reveals (not shown). So in the above formula $\lambda = \rho c_v a$, when entering the excitonic phase λ jumps downward, a jumps upwards, thus c_v must jump downward and not because of the metal–insulator transition but because many phonons suddenly couple to the condensed excitons and no longer act as oscillators or running waves.

Observing further the heat conductivity λ in the excitonic phase now at lower temperatures than the phase boundary , λ displays in Fig. 3 the typical maximum due to the competition of an increasing ℓ_{ph} and a decreasing c_v. But then it rises again below about 20 K and continues to do so even until the lowest measured temperatures. This is certainly very new and unexpected. There is only one case prior to these results where the heat conductivity becomes infinite and this is in the case of superfluidity in ^{4}He (and in ^{3}He) [20], but there in a first order transition, accompanied by the famous λ-anomaly in the specific heat at 2.3 K. We propose that in our case we also have a superthermal current in the two-fluid model, where the superfluid part increases gradually towards zero temperature. However, a λ-anomaly in the specific heat as in the first order transition in ^{4}He is here not to be expected and also not found.

The evidence of superfluidity within the condensed excitonic state necessitates a certain excitation spectrum of quasiparticles [20], namely rotons. Assuming in the low temperature excitonic region that $\lambda_{\mathrm{tot}} = \lambda_{\mathrm{ph}} + \lambda_{\mathrm{ex}}$, where λ_{ph} represents the heat conductivity due to phonons and being assumed proportional to T^3 when $T \ll \Theta$, we obtain for λ_{ex}, the excitonic part of the heat conductivity, an Arrhenius law for the increase of the heat conductivity towards zero temperature. This is shown in Fig. 4, where we find an activation energy or gap Δ of 0.5 meV or about 5 K, which is the right order of magnitude, because in ^{4}He, where λ increases only at 2.3 K, the roton gap is 8.65 K [21].

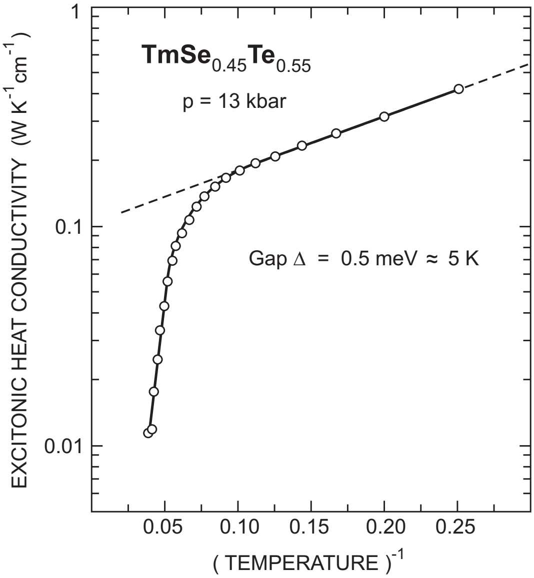

Fig. 4. Excitonic part of the heat conductivity λ_{ex} at 13 kbar shown in an Arrhenius plot.

Now we discuss the thermal diffusivity a in the excitonic region at low temperatures. At the same temperature where λ increases below about 20 K, also a increases, even faster than λ. We have argued before that the reason for a largely temperature independent thermal diffusivity below about 20 K in the **non** excitonic region is that the mean free path for phonon scattering ℓ_{ph} has reached the geometrical dimensions of the sample [19]. Why then, in the excitonic region at 13 kbar and 14 kbar, the dimensions of the crystal do not seem to be important now? The reason seems to be that heat is transferred now not via phonon–phonon scattering in a diffusive manner, but via a highly directional quantum mechanical wave, the second sound, aimed in the direction of the temperature gradient. This seems to be the reason that also a can increase strongly in the excitonic state at low temperatures. And in fact it has to increase strongly because c_v, which is proportional to λ (see above) still has to go to zero for $T \to 0$ even in the excitonic phase. Since $c_v = \lambda/\rho a$, so a must rise faster with decreasing temperature than λ.

Thus we have 3 independent pieces of evidence for the appearance of a superfluid phase in the condensed excitonic phase: The heat conductivity seems to become quite large with decreasing temperature, even infinite for $T \to 0$. A roton spectrum with a gap of about 0.5 meV seems to exist, and the second sound may be responsible for the sharp increase of the mean free path below about 20 K.

4. Conclusion

A condensed excitonic phase at low temperatures and high pressure has been realized in intermediate valent $\mathrm{TmSe_{0.45}Te_{0.55}}$, where excitons with a heavy effective mass strongly bind to phonons. In this paper new thermodynamic properties have been investigated, such as the heat conductivity λ and the thermal diffusivity a. These entities have been measured for the first time at high pressure and in function of temperature. The transition into the excitonic phase is of first order and connected with jumps in λ and a. Whereas heat conductivity and thermal diffusivity behave quite normal outside the excitonic phase they strongly increase below about 20 K in the excitonic phase, but not in a first order transition. It appears that a superfluid phase gradually augments with decreasing temperature. We find indications of a roton or vortex spectrum with a gap of about 5 K. The transition of the heat transport from a diffusive phonon scattering towards a quantum mechanical wave, the second sound, may be the explanation of the increase in the thermal diffusivity above the surface scattering mean free path. All these phenomena are unprecedented in a solid. In a forthcoming paper the specific heat, the Debye temperature and the sound velocity as a function of pressure and temperature will be discussed. What is needed in the future is the extension of these measurements under pressure to still lower temperatures.

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