Change in the symmetry of the Fermi surface induced by structural phase transitions in IV–VI semiconductors with a noncentral ion

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Electrical and oscillation phenomena in IV–VI semiconductors with a noncentral ion suggest that there are two structural phase transitions which are caused by order-disorder transformations of the dipole system.

Interest in the study of the phase transition in IV–VI crystals with noncentral ions was stimulated by the discovery of a phase transition in the solid solution $PbTe_{1-x}S_x$, where the noncentral sulfurions play the role of the extrinsic dipoles. The study of the temperature dependence of the resistivity ρ and width of the band gap of $PbTe_{1-x}S_x$ single crystals has revealed the presence of special features in the temperature range T_1, which are attributable to the phase transition.[1]

In the present study the principal attention is focused on the analysis of ρ and the Shubnikov–de Haas effect at temperatures below T_1. The composition $x = 0.038$–0.045 is determined from the curve[1] $T_1(x)$ within $\pm 10^{-3}$. The oxygen content in

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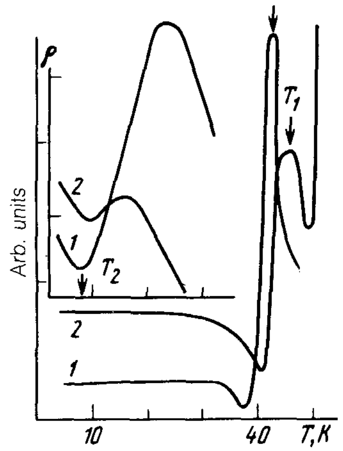

FIG. 1. Typical curve for the resistivity ρ of the $PbTe_{1-x}S_x$ samples. 1—$p = 6.3\times10^{17}$ cm^{-3}, $x = 0.039$; 2—$p = 9.6\times10^{17}$ cm^{-3}, $x = 0.042$. Inset—the initial part of the curves with an enlarged ρ scale.

crystals, determined by the method of electrochemical extraction by means of hard electrolytic cells,[2] is $\sim 10^{-4}$ wt.%. A study of the temperature dependence $\rho(T)$ of the n- and p-type $PbTe_{1-x}S_x$ samples with a carrier density of 2×10^{17}–2×10^{18} cm^{-3} in the temperature range 4.3–50 K (Fig. 1) showed that in addition to the features occurring at T_1, which are associated with the phase transition, these samples exhibit a similar change in $\rho(T)$ in the temperature range 4.3–25 K (the inset in Fig. 1), but with a considerably smaller (by a factor of 10^2 or 10^3) difference in the extremal values of ρ. Analysis of the Shubnikov–de Haas effect in the temperature range 4.3–10 K and magnetic fields up to 40 kOe (Fig. 2) with $\mathbf{H}\|\langle 100\rangle$ reveals the appearance of an additional oscillation frequency (F_a) as the temperature is raised. A clearly defined F_a coincides in temperature with the minimum on the $\rho(T)$ curve ($T_2 \cong 8 \pm 1$ K). A further increase in the temperature causes blurring of the oscillation peaks.

In the temperature range 4.3–10 K we can assume that the effective mass of the current carriers remains constant if there is no phase transition. In this case $\ln A$ (A is the oscillation amplitude) must be a linear function of temperature. In $PbTe_{1-x}S_x$, however, we see a slope change in this curve near $T_2 \cong 8$ K, where the additional frequency F_a appears. An important point here is that the Hall coefficient is, within the experimental error, independent of the temperature range 4.3–4.2 K. At $T = 4.3$ K $< T_2$ the crystal has a cubic symmetry, as indicated by the fact that the oscillation of the magnetoresistance has only a single frequency at this temperature. The constant-energy surface corresponds to the PbTe crystal.

As the temperature is raised, at $T = T_2$ the energy spectrum of the carriers may change. Such a change manifests itself in the rotation of one of the ellipsoids through an angle φ in the $\{110\}$ plane in the direction in which the angle between the ellipsoid axis and the $\langle 100\rangle$ direction increases. This change accounts for the appearance of additional oscillation frequencies F_a. On the basis of the ratio of the effective masses the angle φ is estimated to be in the range of 15°–20°. The crystal thus acquires a rhombohedral symmetry. A rotation of the ellipsoid through an angle $\varphi \cong 14°$ as a result of a phase transition was observed in $Pb_{0.71}Sn_{0.29}Te$ in the analysis of the Shub-

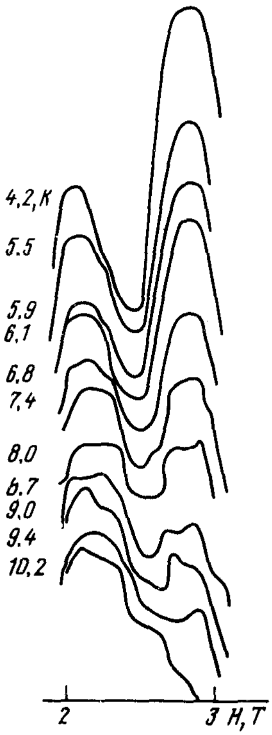

FIG. 2. Temperature dependence of the oscillation curves. One sample.

nikov–de Haas effect.[3] Note that the $\rho(T)$ curve for $Pb_{1-x}Sn_xTe$ has small spikes ($<3\%$) near the phase transition,[4] as in the case of $PbTe_{1-x}S_x$ at $T \cong T_2$.

Thus, at $T = T_2$ the phase transition which we observed here is probably accompanied, as in the case of $Pb_{1-x}Sn_xTe$, not only by a shift of the Pb and Te sublattices along the body diagonal but also by a rotation of the ellipsoid through an angle φ,

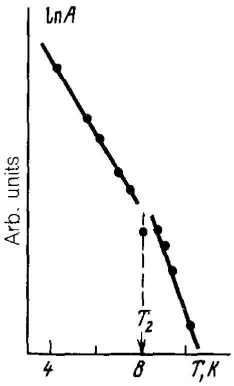

FIG. 3. The amplitude of the oscillation peaks versus the temperature. One sample.

since the shift alone cannot account for the doubling of the oscillation frequency ($F_{100} = 76.6$ kOe, $F_a = 135$ kOe).

A comparison of the $\rho(T)$ curve and the data on the Shubnikov–de Haas effect in our case suggests that the symmetry of the Fermi surface changes when the temperature of the characteristic feature reaches a minimum on the $\rho(T)$ curve at $T = T_2$.

It can be assumed that the phase transition of $PbTe_{1-x}S_x$ occurs as a result of the ordering of dipoles which are associated with the noncentral sulfur ions. The interaction of dipoles in a slightly polarized matrix, which PbTe is acknowledged to be, was evaluated in Ref. 5. This interaction is a sum of the isotropic and anisotropic terms. These competing contributions are conducive for the formation of the ferroelectric phase and dipole glass, respectively. In a magnetic material, a similar process is usually modulated by a shifted Gaussian distribution of a random interaction and the phase diagram contains cross sections with two transitions: at $T_2 < T < T_1$—ferroelectric material and at $T < T_2$—spin glass.[6,7] The phase diagram with two phase transitions was observed in EuSrS in Ref. 8, where at $T < T_2$ the nature of the phase is not clear and may possibly be a paramagnetic phase.[9] The similarity to magnetism suggests that $PbTe_{1-x}S_x$ undergoes two phase transitions. At $T < T_1$ it undergoes a transition to the ferroelectric state, i.e., we see a preferred parallel orientation of the dipoles, a preferred parallel orientation of the dipoles, a preferred $\langle 111 \rangle$ axis resulting from this orientation, and a distortion of the lattice along this axis. At $T < T_2$ we observe a transition to a phase which is not characterized by a preferred polar axis, and the electron spectrum has parameters which are characteristic of a cubic crystal. Whether the low-temperature state is a dipole-glass phase or a paraelectric phase cannot be answered on the basis of the available experimental data and requires further study.

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