Structural phase transition in the solid solution $PbTe_{1-x}S_x$

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(Submitted 18 July 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 6, 229–231 (25 September 1984)

The electrical and photoelectrical properties indicate that there is a second-order phase transition in $PbTe_{1-x}S_x$. A change in the behavior of the curves $\rho(T)$ near T_c at $x \geqslant 0.2$ is associated with the appearance of a critical-scattering region.

Structural phase transitions (PT) in A^4B^6 semiconductors are now being studied extensively. These studies[1,2] involve primarily the cation-substituted solid solutions in which one or both components are ferroelectrics. In this letter we report the observation of a phase transition resulting from anionic substitution in the solid solution PbTe–PbS, both components of which are isostructural and nonpolar.

The single crystals $PbTe_{1-x}S_x$ ($x = 0.02$–0.35) with n-type conductivity [$n = (1{,}6 - 7) \times 10^{18}$ cm^{-3}] were grown by the method of sublimation. Upon completion of growth, the crystals were annealed in order to avoid decomposition in the solid phase.[3] At $T = 300$ K the crystals have an NaCl-type structure.

The electrical properties of the samples were studied by using the procedure described in Ref. 4. For all samples with $x \geqslant 0.02$ the temperature dependence of the resistivity $\rho(T)$ exhibits a sharp peak (Fig. 1a), which is missing both in PbTe and in PbS. The position of the peak (T_c) varies systematically as a function of x (Fig. 2) and does not depend on whether the $\rho(T)$ curves are recorded with increasing or decreasing temperature. Since the carrier density in the crystals does not change with the temperature, the appearance of a peak is associated with the anomalous decrease in the mobility. This anomalous scattering seems to be caused by phase transitions occurring in the crystals.

The existence of a phase transition in $PbTe_{1-x}S_x$ has also been confirmed by other measurements. The temperature dependence of the width of the forbidden band was determined from the photo-emf spectra of p-n junctions, which were fabricated by diffusing chalcogen into the crystals. At $T = T_c$, the slope on the $E_g(T)$ curve (Fig. 3a) changes sharply, which is typical of a second-order phase transition. The temperature dependence of the capacitance of these p-n junctions, whose square (for sharp p-n junctions) is proportional to the dielectric constant $\epsilon(T)$, was measured. In contrast to other A^4B^6 compounds in which a phase transition occurs (for example, $Pb_{1-x}Ge_xTe$), at T_c there was no evidence of a divergence in $\epsilon(T)$ characteristic of ferroelectric phase transitions ($\mathbf{q} = 0$) (Fig. 3b): In samples with $x = 0.04$–0.1 the peak in $\epsilon(T)$ occurred in a narrow range (60–80 K) and did not coincide with T_c.

The fact that a phase transition occurs in $PbTe_{1-x}S_x$ is not a trivial matter. Indeed, both binary compounds PbTe and PbS are nonpolar and have the same type of crystal lattice, so that it would appear that there is no justification for the appearance

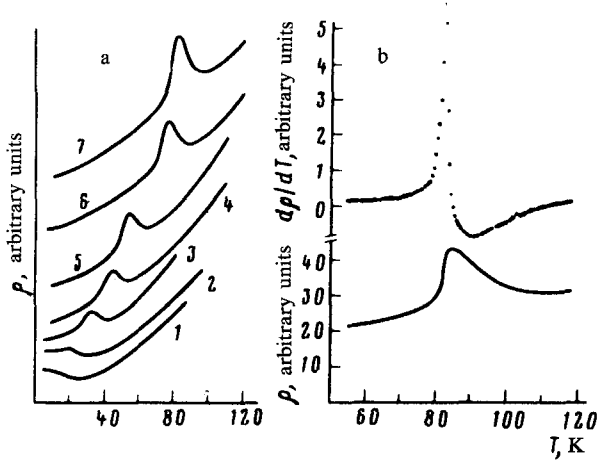

FIG. 1. (a) Temperature dependences of the resistivity of $PbTe_{1-x}S_x$ samples. $x = 0.02$ (1), 0.025 (2), 0.03 (3), 0.04 (4), 0.05 (5), 0.08 (6), and 0.10 (7). The curves are arbitrarily displaced vertically. (b) Temperature dependences of the resistivity and its derivative with respect to temperature for the $PbTe_{0.75}S_{0.25}$ sample.

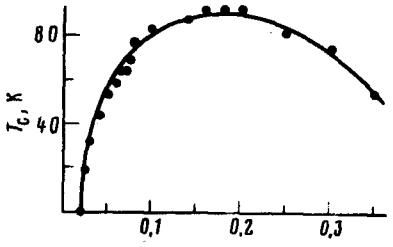

FIG. 2. Dependence of the phase-transition temperature on the composition of the solid solution $PbTe_{1-x}S_x$. The solid curve shows the calculation based on the Ising model (see text) for the following parameters: $\Delta_0 = 109$ K, $A = 1506$ K, and $c = 1.3$.

of a phase transition. However, the large difference in ionic radii of Te and S can cause the symmetrical position of the S atom at a site to be unstable (by analogy with Ge impurity in PbTe[2]), and the dipoles—randomly distributed noncentral sulfur atoms—become ordered at low temperatures.

The behavior of such a system can be qualitatively described by using the Ising model with tunneling in a random molecular-field approximation.[5] In this model the dependence of T_c on the effective-interaction parameter I and on the tunneling parameter Δ has the form $\tanh(\Delta/2k_B T_c) = 2\Delta/I$. Assuming that the dipole moment **p** is proportional to the difference between the ionic radius of the S atom and the size of the cavity in which it is located [$p = p_0(1-x)$, $I \cong A\sqrt{x} \times p^2$] and that Δ varies slightly

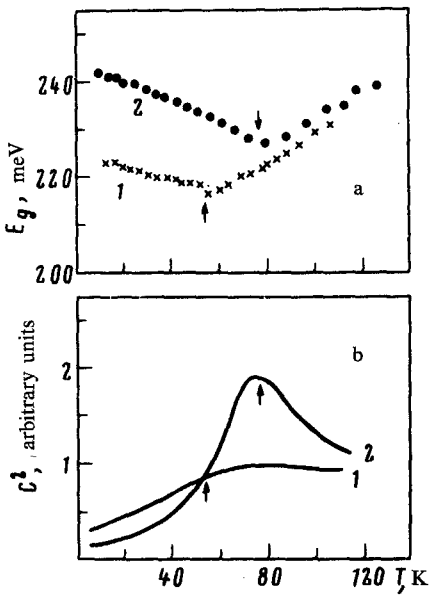

FIG. 3. Temperature dependences of the widths of the forbidden band (a) and of the square of the capacitance (b) in *p-n* junctions consisting of $PbTe_{1-x}S_x$ with $x = 0.05$ (1) and 0.08 (2). The arrows mark the phase-transition temperature.

with x as $\Delta = \Delta_0 \exp(cx)$, a good agreement between calculations and experiment can be established by adjusting the constants c and A (Fig. 2). The value $c > 0$ implies that the probability of tunneling of a sulfur atom increases with increasing value of x because of the convergence of the minima in a two-well potential.

The anomalous part of the scattering, which is associated with the phase transition, is singled out in the curves $\rho(T)$. The amplitude of anomalous scattering depends almost linearly on the concentration S. The temperature dependence of the anomalous part varies as $\Delta\rho \sim (|T - T_c|^{2\gamma} + B)^{-1/2}$, where γ, which lies in the range 1.07–1.27, exceeds the value $\gamma = 1$ predicted by Landau's theory. In samples with $x > 0.1$, the ratio of the rates at which the curves $\Delta\rho(T)$ fall off above and below T_c also exceeds the classical value, $C_+/C_- = 2$. For $x \simeq 0.25$ the quantity $C_+/C_- \approx 5$ corresponds to the three-dimensional Ising model, while the curves $\rho(T)$ and $d\rho/dT$ (Fig. 1b) resemble the analogous curves for critical scattering in magnetic materials.[6] The data presented above seem to suggest that there is a rather broad critical region in $PbTe_{1-x}S_x$, which can be expected to appear in systems devoid of long-range forces. This result, as well as the breakdown of the proportionality $\Delta\rho(T) \sim \epsilon(T, q \cong k_F)$, just as the absence of a sharp anomaly in $\epsilon(T)$ near T_c, indicates that below T_c, when the condition $N_s r_c^3 > 1$ is satisfied (r_c is the correlation radius), there is no macroscopic polarization of $PbTe_{1-x}S_x$ ($\mathbf{q} = 0$), even for large values of x. It is possible that the nature of the interaction of the dipoles favors their antiparallel orientation ($I < 0$), whereas a dipolar-glass phase appears in a system of randomly distributed S atoms.

[1]H. Kawamura, in: Proc. 3rd Int. Conf. Phys. of Narrow-Gap Semicond., Warszawa, 1977, p. 7.
[2]K. Murase, J. Phys. Soc. Jpn. **49** (Suppl. A), 725 (1980).
[3]M. Darrow, W. White, and R. Roy, Trans. AIME **236**, 654 (1966).
[4]Kh. A. Abdullin and A. I. Lebedev, Fiz. Tverd. Tela **25**, 3571 (1983) [Sov. Phys. Solid State **25**, 2055 (1983)].
[5]B. Fischer and M. W. Klein, Phys. Rev. Lett. **37**, 756 (1976).
[6]M. E. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).

Translated by M. E. Alferieff
Edited by S. J. Amoretty