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UNUSUAL PHASE TRANSITIONS IN $Pb_{1-x}Sn_xTe_{1-y}Se_y$ AND $Pb_{1-x}Sn_xTe_{1-y}S_y$ CRYSTALS INDUCED BY Sn OFF-CENTER IONS

A. I. LEBEDEV and I. A. SLUCHINSKAYA
Physics Dept., Moscow State University, Moscow, 119899, Russia

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Electrical studies of quaternary solid solutions $Pb_{1-x}Sn_xTe_{1-y}Se_y$ in a wide composition range revealed the phase transition, occurred at unexpectedly low x ($x > 0.08$). It is shown that this phase transition may be associated with Sn off-center ions. The unusual enhancement of T_c, induced by substitutional disorder, was explained by strong reduction of tunneling of Sn off-center ions resulting from the increase of displacement of Sn atoms when substituting the large atoms in anion sublattice by smaller ones. This hypothesis was confirmed by the observation of similar effects in $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solutions and of low-temperature enhancement of resistivity in $Pb_{1-x}Sn_xSe_{1-y}S_y$.

Keywords: phase transition, off-center ions, substitutional disorder, random fields, tunneling effects

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I. INTRODUCTION

The simple crystal structure and unique electronic properties of IV–VI narrow-gap semiconductors make them ideal objects for studying of "impurity ferroelectricity," induced in crystals by off-center ions. At present two types of off-center ions (Ge, S) are known, which induce the ferroelectric phase transition in PbTe.[1,2] In the present work we shall show that similar properties are characteristic for Sn atoms in IV–VI compounds as well.

II. EXPERIMENTAL

The measurements were performed mainly on polycrystalline samples of quaternary solid solutions $Pb_{1-x}Sn_xTe_{1-y}Se_y$ and $Pb_{1-x}Sn_xTe_{1-y}S_y$, annealed at 600–650°C for 70–160 hours. Monocrystals prepared by sublimation method were also investigated. The composition of the samples was chosen within whole single-phase regions with cubic structure of Pb-Sn-Te-Se and Pb-Sn-Te-S phase diagrams. The homogeneity of samples was checked by X-ray method. The main method of investigation was the study of anomalous resistivity resulting from the scattering of free carriers by ferroelectric fluctuation near the phase transition temperature T_c, which is a powerful method of studying phase transitions in IV–VI semiconductors.[3]

III. RESULTS

Studies of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ samples with constant tin concentration ($x = 0.2$) found that the substitution of a small amount of Te by Se resulted in the appearance

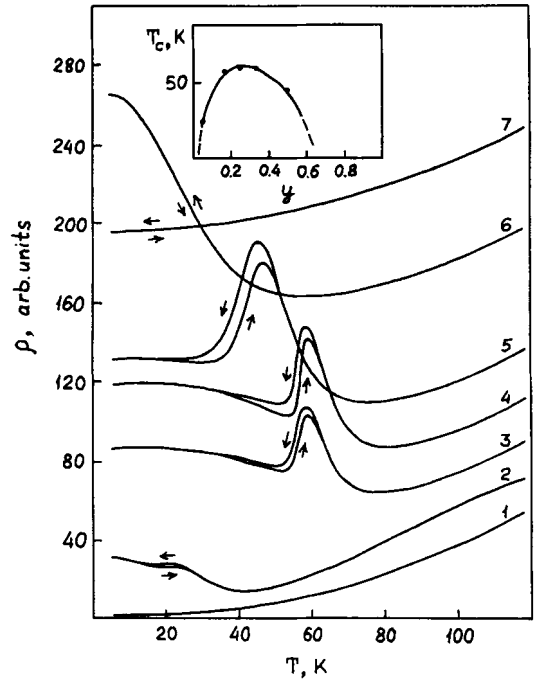

FIGURE 1 Temperature dependence of resistivity $\rho(T)$ for $Pb_{0.8}Sn_{0.2}Te_{1-y}Se_y$ samples. 1, $y = 0$; 2, $y = 0.05$; 3, $y = 0.25$; 4, $y = 0.33$; 5, $y = 0.5$; 6, $y = 0.67$; 7, $y = 0.83$. Curves 3–7 are shifted up by 35, 55, 75, 130, and 165 units, respectively. All samples are of n-type. Arrows indicate the direction of temperature change during recording the curves. The insert shows the dependence of T_c on y.

of anomalous resistivity peak on $\rho(T)$ curves (Figure 1), which indicates the onset of phase transition.[4] With increasing y, the temperature of anomalous resistivity peak at first increased, reached a maximum at $y \approx 0.25$, and then decreased until the phase transition disappeared at about $y \approx 0.65$. One can see that the phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ at low x was characteristic just for quaternary solid solution and was absent in ternary solid solutions $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$ with the same x.

The $\rho(T)$ curves, recorded during heating and cooling the sample, showed appreciable hysteresis near T_c. The difference between anomalous peak positions was 1–2 K. Such hysteresis near T_c is a common feature of ferroelectric phase transition in IV–VI quaternary solid solutions containing off-center ions.[5–8] The anomalous resistivity peaks were observed on both p- and n-type crystals. However in n-type samples the resistivity anomaly was usually much stronger than in p-type samples with the same composition. Besides the resistivity anomaly, a strong increase of resistivity with lowering the temperature was observed in $\rho(T)$ curves.

Studies of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ samples with constant $y = 0.25$ and variable x (Figure 2) showed that the phase transition temperature depends strongly on x and follows $T_c(x) \propto (x - x_c)^\beta$ law with $\beta \approx 0.65$.

Figure 3 shows the dependence of T_c on the composition (x, y) of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution.[9] Points on this figure correspond to compositions of investigated samples. Solid curves represent computer approximation of experimental data. The

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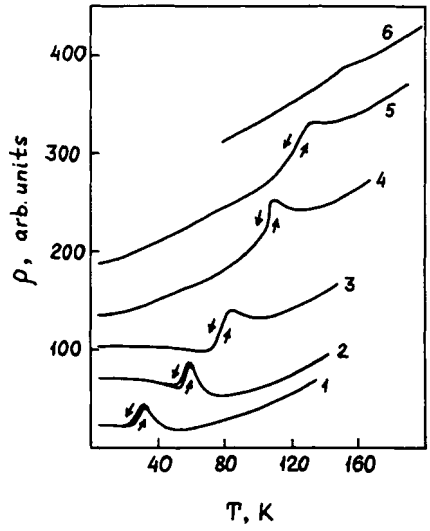

FIGURE 2 $\rho(T)$ curves for $Pb_{1-x}Sn_xTe_{0.75}Se_{0.25}$ samples. 1, $x = 0.075$; 2, $x = 0.2$; 3, $x = 0.3$; 4, $x = 0.5$; 5, $x = 0.625$; 6, $x = 0.85$. Curves 2, 3, 6 are shifted up by 30, 50, and 80 units, respectively, curve 4 is shifted down by 30 units. Samples 1, 2 are of n-type, 3–6—of p-type. Arrows indicate the direction of temperature change during recording the curves.

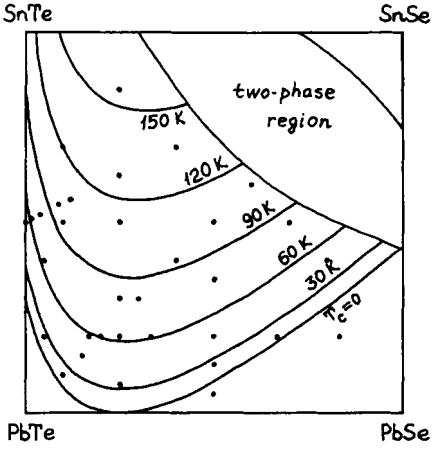

FIGURE 3 Compositional dependence of T_c in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution.

maximum value of $T_c = 151$ K was obtained on $Pb_{1-x}Sn_xTe_{1-y}Se_y$ sample with $x = 0.85$, $y = 0.25$; this value was 1.5 times higher than that for the best SnTe monocrystals.[10] It is seen that the phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ can be observed starting from very small Sn concentration, $x = 0.08$–0.1, in contrast to $x \approx 0.35$ for $Pb_{1-x}Sn_xTe$.

The phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ was observed directly in low-temperature X-ray studies, performed on the crystal with $x = 0.7$, $y = 0.4$. The strong splitting of the diffraction peaks of high-temperature fcc-structure below T_c corresponded to rhombohedral distortion. At $T = 93$ K (at about 50 K below T_c) the rhombohedral angle was reduced from 90 to 89.8 degrees.

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IV. DISCUSSION

The evolution of T_c, hysteresis loops, and low-temperature scattering on $\rho(T)$ curves with changing the composition of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ crystals was very similar to that observed in other IV–VI quaternary solid solutions containing known (Ge, S) off-center ions.[5–8] This fact enables us to suppose that the phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ can be also associated with some off-center ions.

This supposition is confirmed by high value of $\beta \approx 0.65$ in the dependence of T_c upon Sn concentration, which was close to $\beta \approx 0.68$ observed in $Pb_{1-x}Ge_xTe$[11] (in which the ferroelectric phase transition is associated with off-center Ge atoms[1]) and to the value $\frac{2}{3}$, predicted theoretically for the percolation model of phase transition induced by off-center ions.[12]

The experiments, which can supply additional arguments for our supposition, are the "quenching" experiments.[13] Figure 4 shows three curves for a characteristic sample of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ illustrating this effect. Curve (1) was recorded during slow heating of the sample (at a rate of about 0.02 K/sec) after its quenching from 77 K (above T_c) to 4.2 K at a rate of 5 K/sec. Curves (2) and (3) were obtained during subsequent slow cooling and slow heating. One can see that besides the above mentioned hysteresis effect, the curves, obtained after quick and slow cooling, differ appreciably below T_c. After quenching ρ(4.2 K) was usually 5% higher than after slow cooling. This effect was fully reproducible and was observed on different samples with low x.

We think that the "quenching" effect can be observed only for phase transitions of order-disorder type for which the critical slowing down is characteristic and in which neither the equilibrium thermodynamic fluctuation nor the equilibrium long-range order cannot be reached near T_c at high quenching rates. For the displacive phase transitions the appearance of "quenching" effect is impossible because the quenching rates used in our experiments are negligible in comparison with characteristic equilibration rates in such systems.

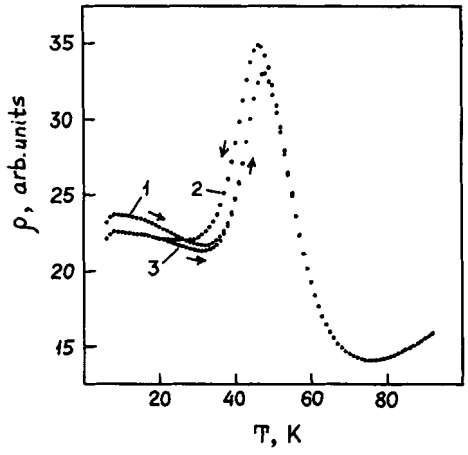

FIGURE 4 $\rho(T)$ curves of $Pb_{0.8}Sn_{0.2}Te_{0.5}Se_{0.5}$ sample, illustrating "quenching" effect. Curves were obtained during slow heating after quenching from 77 to 4.2 K (1) and during subsequent slow cooling (2) and slow heating (3).

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We suppose that after quenching a micro-domain state instead of true long-range order appears in our samples. The arising domain walls act as scattering centers which increase the resistivity in "quenched" samples. The slow relaxation of ρ to the equilibrium value, observed below T_c in "quenched" samples, can be associated with domain growth process.

Thus, the properties of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ crystals enable us to consider the phase transition in them (at least at low x) as the order-disorder type phase transition, associated with off-center ions.

Among different atoms in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution only two of them, Sn and Se, can be regarded as candidates for off-center ions. Taking into account the absence of phase transition in $PbTe_{1-x}Se_x$ crystals and the lack of similar enhancement of T_c when substituting of Te by Se in $Pb_{1-x}Ge_xTe_{1-y}Se_y$,[6] we conclude that the phase transition in our crystals can be associated with Sn off-center atoms. This hypothesis is supported by a quadrupole splitting of ^{119}Sn line, observed in Mössbauer studies of $Pb_{1-x}Sn_xTe$,[14] which can indicate the lowering of symmetry of Sn atoms in the lattice sites.

The unusual feature of the phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ is the enhancement of T_c with increasing the substitutional disorder in crystal. This effect is qualitatively different from the influence of disorder observed in other IV–VI quaternary solid solutions containing off-center ions,[5,6,8] in which the isoelectronic substitution usually reduced T_c. This reduction of T_c was attributed to the influence of quenched random fields arising from unequivalence of bonds between off-center ions and surrounding atoms of different chemical nature. The origin of unusual influence of disorder on T_c in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ we explain as follows.[9]

It is known that off-center ions may be displaced from a lattice site to several energetically equivalent positions, between which thermal and tunnel jumps occur. If the overlap of wave functions of different off-center positions is large, the tunneling may depress the phase transition completely. In the theory of phase transitions this situation is described qualitatively by Ising model with tunneling. The phase transition temperature in it is expressed in terms of the interaction integral J and the tunneling energy Δ as

$$(J/\Delta)\tanh(\Delta/kT_c) = 1$$

It is seen that the ordering of off-center ion dipoles is impossible at $\Delta \geqslant J$.

We presume that the absence of phase transition in $Pb_{1-x}Sn_xTe$ crystals at $x < 0.35$ is due to strong tunneling of Sn off-center ions, which hinders the ordering of their dipoles at low temperatures. Small difference between ionic radii of Sn and Pb (0.24 Å) compared with that for other off-center ions in PbTe is favorable for strong tunneling.

The substitutional disorder existing in quaternary solid solution can change not only the energies of different potential wells of off-center ion,[5,6] but the distance and potential barrier height between different off-center positions also. When substituting the large atoms by the smaller ones, the larger displacements of off-center ion may lead to strong decrease of Δ (which depends exponentially on the distance between off-center positions) and so may increase T_c. Which of two concurrent effects—the increase of T_c resulting from the decrease of tunneling or the reduction of T_c due to random fields—will prodominate, is dependent on type of

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off-center ion, the difference between substituting atoms, and their positions in the lattice. We believe that the former effect is the origin of unusual composition dependence of T_c in $Pb_{1-x}Sn_xTe_{1-y}Se_y$.

An interesting feature of phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ is the decrease of hysteresis loops' width at $x > 0.3$ (see Figure 2). This effect has never been observed in other IV–VI quaternary systems studied before.[5-8] We think that this difference is due to the peculiarity of Sn off-center ion as well.

Onodera[15] has shown (see also Reference 16) that the properties of a system of interacting particles residing in a double-well potential depend on dimensionless parameter s, which is equal to the ratio of well energy to kT_c. In the limit $s \gg 1$ the system undergoes an order-disorder phase transition, and in the limit $s < 1$— a displacive one. Our supposition of strong tunneling of Sn off-center atom means that the well energy is not large. Consequently, as Sn concentration (x) increases, T_c increases as well, so that at high x we can observe a crossover from order-disorder limit to displacive one. In quaternary solid solutions with Ge and S off-center ions the well energy is high, and the system remains in order-disorder limit at all x.

If our hypothesis of suppression of tunneling of Sn off-center ions by substitutional disorder is valid, we have to observe similar effects in other IV–VI solid solutions with substitution Pb → Sn, i.e., in $Pb_{1-x}Sn_xTe_{1-y}S_y$ and $Pb_{1-x}Sn_xSe_{1-y}S_y$.

Studies of $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solutions with $x = 0.5 + 0.5y$ did really find the enhancement of T_c with increasing y, whose rate was 2.5 times greater than that for $Pb_{1-x}Sn_xTe_{1-y}Se_y$. The more pronounced effect of Te → S substitution in comparison with Te → Se one was attributed to higher perturbation induced by the former substitution. However the interpretation of this effect is complicated by the existence, besides Sn off-center ions, of S off-center ions in $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solution.[2]

In order to distinguish the influence of two off-center ions on T_c, we examined $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solutions with constant S concentration ($y = 0.05$). As is shown in Figure 5, the temperature T_c first decreased quickly with increasing x so that the phase transition associated with S off-center ions was suppressed by random fields at $x = 0.1$ already. The phase transition, which appeared again with subsequent increase of x (at about $x \approx 0.2$), cannot be associated with S off-center ions because the random fields, acting on them, are very strong at this x. Therefore, the phase transition in this concentration range can be associated only with Sn off-center ions. Similarity between manifestation of phase transitions in $Pb_{1-x}Sn_xTe_{1-y}S_y$ at $x > 0.2$ and in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ ("quenching" effect, hysteresis loops near T_c, low-temperature scattering) indicates that in both quaternary solid solutions the phase transitions are associated with the common origin—off-center Sn atoms.

In our measurements performed on another solid solution, $Pb_{1-x}Sn_xSe_{1-y}S_y$, we failed to observe the anomalous resistivity peak in $\rho(T)$ curves because another phase transition (into orthorhombic phase) underwent in crystals with high x before the ferroelectric one. However in several crystals with $x = 0.2$–0.28 and $y = 0.1$–0.2 the low-temperature scattering was found, which usually precedes the ferroelectric phase transition in crystals with off-center ions.[7,8] We believe that the low-temperature scattering can be regarded as the evidence of possible off-center behavior of Sn in this solid solution.

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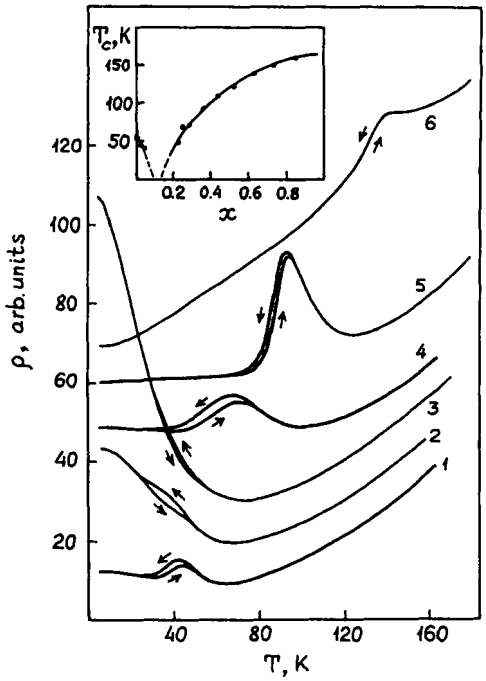

FIGURE 5 $\rho(T)$ curves for $Pb_{1-x}Sn_xTe_{0.95}S_{0.05}$ samples. 1, $x = 0.023$; 2, $x = 0.046$; 3, $x = 0.118$; 4, $x = 0.248$; 5, $x = 0.358$, 6, $x = 0.629$. Curves 2, 3, 4, 5 are shifted up by 10, 20, 25 and 20 units, respectively. Samples 1–3 are of n-type, 4–6—of p-type. Arrows indicate the direction of temperature change during recording the curves. The insert shows the dependence of T_c on tin concentration.

V. CONCLUSIONS

Electrical and X-ray studies of quaternary solid solutions $Pb_{1-x}Sn_xTe_{1-y}Se_y$ have revealed the phase transition, occurred at unexpectedly low x ($x > 0.08$). The unusual enhancement of T_c with increasing substitutional disorder was observed. The "quenching" effect, hysteresis loop on $\rho(T)$ curves and $T_c(x)$ dependence give evidence for order-disorder type of phase transition. The hypothesis, which supposes the existence of Sn off-center ions, was proposed. It explains the enhancement of T_c with increasing substitutional disorder by reduction of tunneling rate of off-center Sn ion. The decrease of hysteresis loops' width at $x > 0.3$, indicating a crossover from order-disorder phase transition to displacive one, do not contradict this idea. Similar effects observed in $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solutions at $x > 0.2$ confirm our hypothesis of off-centering of Sn atoms.

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