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FERROELECTRIC PHASE TRANSITIONS IN IV-VI SEMICONDUCTORS ASSOCIATED WITH OFF-CENTER IONS

ALEXANDER I.LEBEDEV and IRINA A.SLUCHINSKAYA
Department of Physics, Moscow State University
119899 Moscow, Russia

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Abstract New ferroelectric phase transitions were found in ternary and quaternary solid solutions of IV-VI semiconductors. Their analysis shows that off-center ions play important role in the appearance of ferroelectricity in these crystals.

Two different approaches have been proposed to explain the appearance of ferroelectricity in IV-VI semiconductors: the ferroelectric phase transition in GeTe, SnTe and $Pb_{1-x}Sn_xTe$ was explained by the softening of TO-phonon mode at Γ-point of Brillouin zone [1], while one in $Pb_{1-x}Ge_xTe$ was attributed to the ordering of dipoles of off-center ions [2-4]. Our studies of ternary and quaternary solid solutions of IV-VI semiconductors have recently found new phase transitions, whose analysis enabled to propose the unified description of ferroelectricity in IV-VI semiconductors.

We started our experiments with studying the temperature dependence of resistivity ρ in $Pb_{1-x}Ge_xSe$ solid solution [5], whose optical data [6] indicated the possibility of phase transition. Fig. 1 shows ρ(T) plots on which anomalous resistivity peaks are clearly observed. The ferroelectric type of phase transition was proved by dielectric measurements. Low-temperature X-ray measurements [5] revealed cubic-to-rhombohedral distortion below T_c so that $O_h^5 \rightarrow C_{3v}^5$ (not $O_h^5 \rightarrow D_{2h}^{16}$ as proposed in [6]) phase transformation takes place in this solid solution. The dependence of phase transition temperature T_c on x (see insert in Fig. 1) was very similar to that for $Pb_{1-x}Ge_xTe$. Thus, we had all reasons to suppose that Ge atoms are off-center in $Pb_{1-x}Ge_xSe$ like Ge in $Pb_{1-x}Ge_xTe$ [4]. This supposition was recently confirmed by EXAFS studies [7].

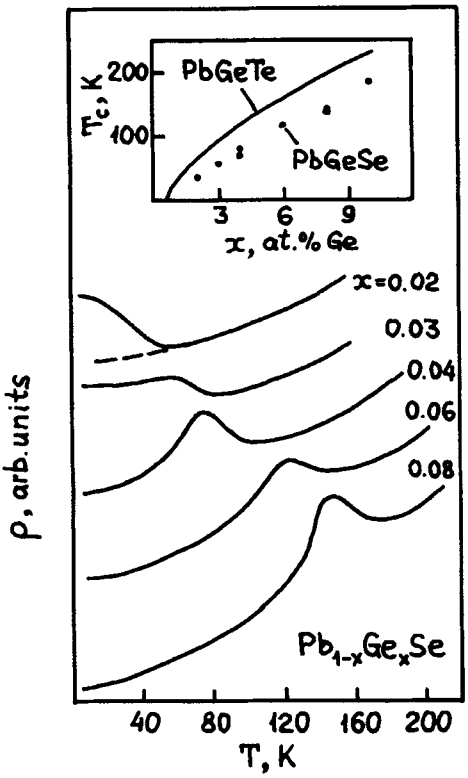

FIGURE 1

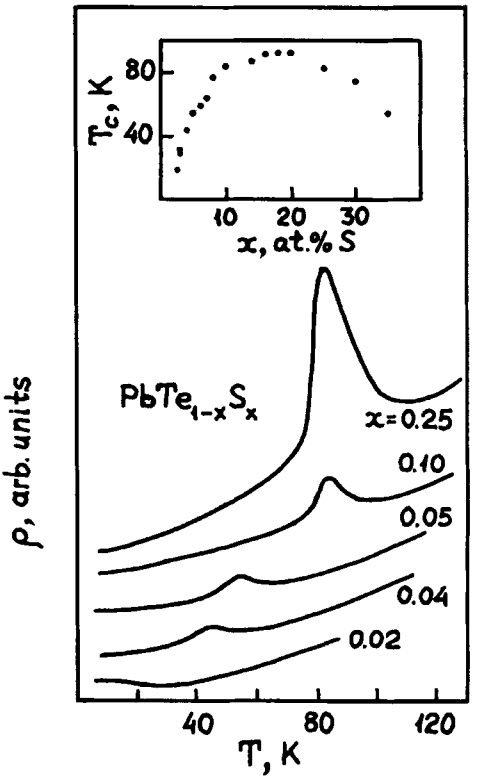

FIGURE 2

Investigations of $PbTe_{1-x}S_x$ unexpectedly revealed the appearance of anomalous resistivity peaks (see Fig. 2) indicating the phase transition in this solid solution [8]. Phase transition in $PbTe_{1-x}S_x$ was confirmed by optical data [8]; the ferroelectric nature of it was proved by dielectric measurements. The dependence $T_c(x)$ was not monotonous (see insert in Fig. 2) in contrast to $Pb_{1-x}Ge_xTe$ and $Pb_{1-x}Ge_xSe$; the maximum of T_c was reached at about x=0.18. When approaching binary compounds, the phase transition disappeared. As both PbTe and PbS are isostructural and nonpolar, the unique reason for ferroelectricity in $PbTe_{1-x}S_x$ may be off-centering of S atoms. This statement was confirmed recently by EXAFS experiments [9].

The investigation of quaternary solid solutions was undertaken to study the influence of substitutional disorder, which is characteristic for solid solutions, on

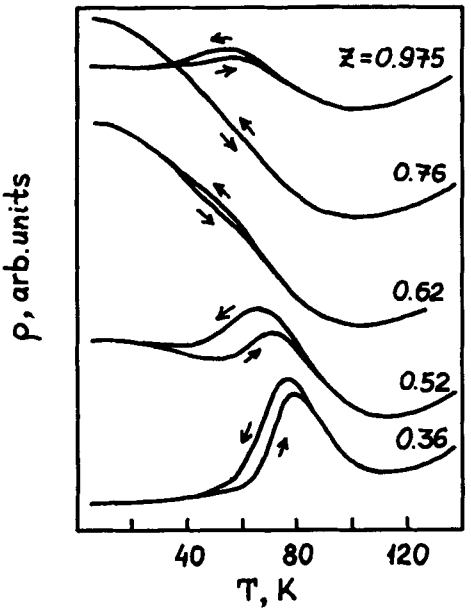

FIGURE 3

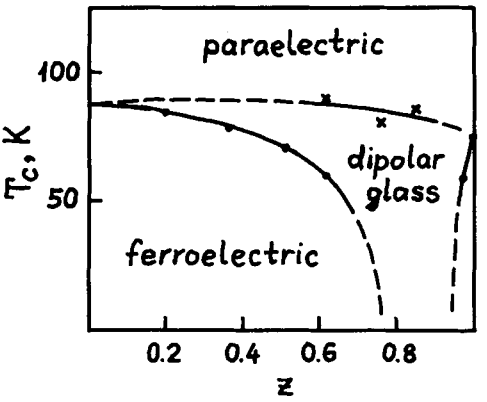

FIGURE 4

the ordering of off-center ions. First we investigated solid solutions in which there was at least one off-center ion ($Pb_{1-x}Ge_xTe_{1-y}Se_y$, $Pb_{1-x-y}Ge_xSn_yTe$, $Pb_{1-x}Sn_xTe_{1-y}S_y$, $PbS_xSe_yTe_{1-x-y}$). In $Pb_{1-x}Ge_xTe_{1-y}S_y$ there are two off-center ions - Ge and S. The studies of these solid solutions revealed new phenomena that we had never seen before in ternary solid solutions with off-center ions [10]. These effects are clearly seen in Fig. 3 and 4.

Fig. 3 shows typical ρ(T) curves for quaternary solid solution $(Pb_{0.975}Ge_{0.025}Te)_{1-z}(Pb_{0.96}Ge_{0.04}Se)_z$ [11]. Hysteresis loops on anomalous resistivity peaks and slow relaxations of ρ in hysteresis region appeared in quaternary solid solutions. When increasing the substitutional disorder (by increasing z) the width of hysteresis loops increased, strong low- temperature scattering appeared on ρ(T) curves, and the temperature T_c decreased strongly (see phase diagram in Fig. 4). For some compositions the phase transition could be depressed completely [11]. These phenomena were observed on all quaternary solid solutions mentioned above.

The appearance of these effects was attributed to the influence of quenched random fields. Due to random

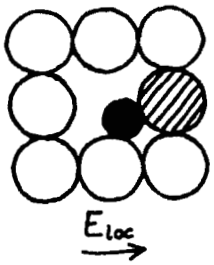

FIGURE 5

distribution of substitutional atoms in solid solution, off-center ions are randomly surrounded by different atoms and by this way are polarized in random directions [10] (Fig. 5). The competition between molecular field and local random fields results in decreasing T_c (up to depressing of phase transition) and in appearance of extreme slowing-down of dynamical processes in vicinity of T_c.

The qualitatively different effect of random fields was observed in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution, where the increase of T_c was found when increasing substitutional disorder [12]. This influence can be easily seen on the phase diagram of Pb-Sn-Te-Se system (see Fig. 6). In quaternary solid solution the phase transition was observed at Sn

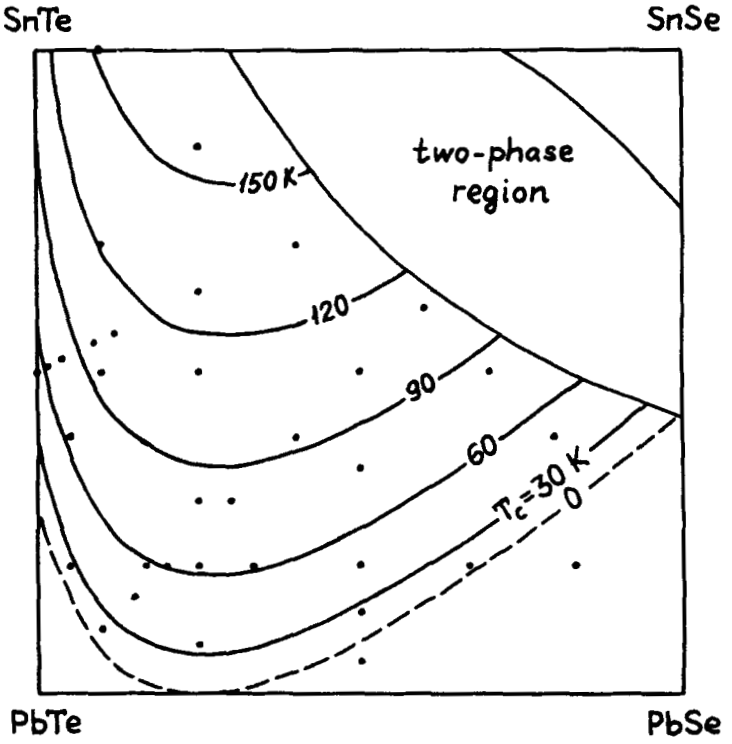

FIGURE 6

concentration as low as x=0.08 while in $Pb_{1-x}Sn_xTe$ it can be observed at x>0.35 only.

This increase of T_c was explained by the influence of substitutional disorder on the tunneling of off-center ion [12,13]. We supposed that, like in other investigated solid solutions, Sn atoms are off-center in $Pb_{1-x}Sn_xTe$ and related solid solutions but the strong tunneling of Sn (due to small displacement from the site) prevents the ordering of dipoles at low Sn concentrations and temperatures. The substitution of Te atoms by Se (which have smaller atomic sizes) results in the increase of off-center displacement in some directions (see Fig. 7). This may strongly decrease the tunneling rate of off-center ion and therefore increase T_c. This effect is very important for Sn off-center ions whose potential wells are not deep, but is less important for Ge and S, which have deeper potential wells.

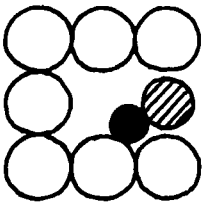

FIGURE 7

It should be noted that our supposition about off-centering of Sn does not contradict the observation of soft mode and other manifestations of displacive phase transition in $Pb_{1-x}Sn_xTe$. As was shown by Onodera [14], the dynamics of a system of particles residing in double-well potential depends on dimensionless parameter $s=W/kT_c$, where W is potential barrier height. When $s\leq 1$, the soft mode can be observed despite of the existence of double-well potential. The crossover from order-disorder to displacive phase transition was observed in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ with increasing x [12], that enabled to estimate the barrier height W=5-10 meV for Sn off-center ion.

The analysis of our experimental data brings us to the conclusion that the off-centering of Ge, S and Sn in IV-VI solid solutions is a primary cause of ferroelectricity in them. Our analysis enables to predict the existence of ferroelectric phase transition in PbGeSeS, PbGeSnSe, PbGeSnS, GeTeSeS, SnTeSeS, SnGeTeS, SnGeTeSe, PbSnSeS

quaternary solid solutions, which were not investigated yet. In last of them, PbSnSeS, we have observed the low-temperature scattering that usually precedes the appearance of phase transition [13].

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