Ferroelectrics, 1995, Vol. 169, pp. 293–301
Reprints available directly from the publisher
Photocopying permitted by license only

INFLUENCE OF RANDOM FIELDS ON THE FERROELECTRIC PHASE TRANSITION IN IV–VI SEMICONDUCTORS

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

(Received August 22, 1994)

The results of experimental studies of the influence of substitutional disorder, doping impurities and of mutual influence of different off-center atoms on the ferroelectric phase transitions induced in IV–VI semiconductors by off-center atoms are reviewed.

Keywords: Phase transition, off-center ions, substitutional disorder, random fields, impurities.

1. INTRODUCTION

Investigation of the influence of disorder produced by defects and impurities on phase transitions has been a subject of intensive studies since the middle of 1970s. The most detailed studies have been performed on magnetic systems. They showed that the disorder decreases the phase transition temperature, changes critical behavior and dynamics of response, and sometimes can destroy the long-range order. In the dipolar systems there exists one more interesting class of defects—so called soft defects, which enhance the phase transition temperature when adding to the crystal. The example of such defects is off-center ions.

The cooperative phenomena in a system of off-center ions placed in highly polarizable crystal have attracted much interest in recent years. Off-center ions, which interact each with other via indirect dipole-dipole interaction, can induce the ferroelectric state in nonpolar media.[1] In our laboratory we have studied the physical properties of narrow gap IV–VI semiconductors in which there are three types of impurity atoms (Ge_{Pb},[2–5] S_{Te}[6,7] and Sn_{Pb}[8]) manifesting the off-center behavior. Owing to the simplicity of the crystal structure of IV–VI semiconductors (cubic NaCl structure with two atoms in a primitive cell), they can be considered as model object for studying the cooperative phenomena of off-center ions.

The aim of this work is to review the experimental investigations of the influence of substitutional disorder in solid solutions, mutual influences of different off-center ions and the influence of doping impurities on the ferroelectric phase transitions induced by off-center ions in IV–VI semiconductors.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

Both single crystals and polycrystalline samples of quaternary solid solutions of IV–VI semiconductors containing at least one off-center ion were studied. The

disorder was created by isoelectronic substitution of atoms in anion or cation sublattices, or by doping the crystals with nonisoelectronic (Cd, Ga, In, Tl, Sb, Bi and Mn) impurities.

A set of experimental techniques including electrical, dielectric, optical and X-ray methods was used. The data of only electrical measurements will be presented in this work. As the narrow gap IV–VI semiconductors are usually degenerate and have high electrical conductivity, traditional dielectric techniques are useless for their studies. However the information on the temperature dependence of dielectric permittivity can be obtained from the electrical data. In the vicinity of Curie temperature the scattering of charge carriers by thermal fluctuations of polarization results in the increase of resistivity (anomalous resistivity peak[9,10]) that is ultimately proportional to the permittivity $\varepsilon(q)$ averaged over some range of wave vectors $\mathbf{q}$. This method has been widely used to study phase transitions in IV–VI semiconductors since the earliest works.[9,11]

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Isoelectronic Substitution in Crystals with Ge and S Off-Center Ions

To investigate the influence of substitutional disorder on the ferroelectric phase transition, several quaternary solid solutions were studied. The main features found in our experiments will be demonstrated using $Pb_{1-x}Ge_xTe_{1-y}Se_y$ solid solution as an example. As established previously,[2–5] ternary solid solutions $Pb_{1-x}Ge_xTe$ and $Pb_{1-x}Ge_xSe$ undergo similar ferroelectric phase transitions induced by off-center Ge atoms. When substituting a part of Te atoms by Se, we can create the substitutional disorder in anion sublattice and observe for its influence on the phase transition.

Figure 1 shows the temperature dependence of specific resistivity $\rho(T)$ for $(Pb_{1-x}Ge_xTe)_{1-z}(Pb_{1-y}Ge_ySe)_z$ samples.[12] The concentration of off-center atoms in crystals was nearly constant ($x \approx y$), and the degree of substitutional disorder was determined by parameter z. For most of the samples the curves consisted of anomalous resistivity peak with a maximum at Curie temperature T_c, and the background associated with carrier scattering by acoustic and LO-phonons. As follows from Figure 1, the substitutional disorder in quaternary solid solutions manifests in: 1) broad minimum on the dependence T_c (z) (see also Figure 2); 2) noticeable hysteresis on the curves recorded during cooling and heating; 3) strong increase of low-temperature scattering which accompanies the decrease of T_c.

The plots of T_c vs. z for three quaternary solid solutions with general formulae $(Pb_{1-x}Ge_xTe)_{1-z}(Pb_{1-y}Ge_ySe)_z$ and different values of x and y are shown in Figure 2. One can see that the disorder was able to suppress the phase transition completely in the samples with the lowest concentration of off-center ions.

The manifestations of disorder found in PbGeTeSe were not specific for this solid solution only, but they were observed in other solid solutions (PbGeTeS,[13] PbSnTeS,[14–16] PbSSeTe,[16] PbGeSnTe) with off-center Ge and S atoms. It is interesting that in solid solutions containing two off-center atoms in different sublattices (Ge and S, for instance) the influence of one off-center atom on the phase transition induced by the other off-center atom was the same as for normal (on-

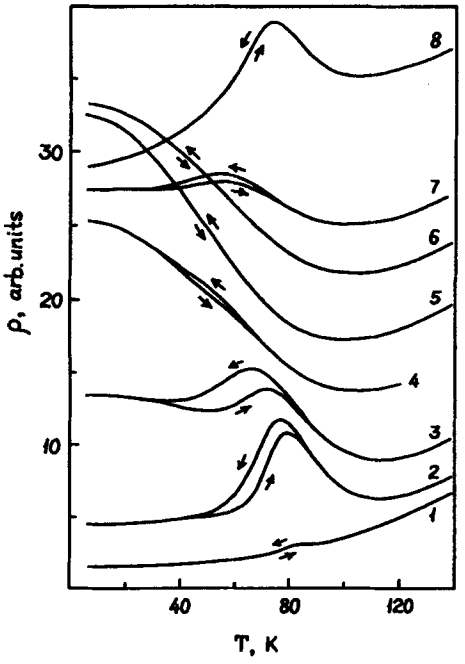

FIGURE 1 Temperature dependence of resistivity for $(Pb_{0.975}Ge_{0.025}Te)_{1-z}(Pb_{0.96}Ge_{0.04}Se)_z$ samples. 1, $z = 0$; 2, $z = 0.42$; 3, $z = 0.57$; 4, $z = 0.67$; 5, $z = 0.77$; 6, $z = 0.86$; 7, $z = 0.94$; 8, $z = 1$.[12] The curves were arbitrary shifted along vertical axis. The arrows show the direction of temperature change during recording the curves.

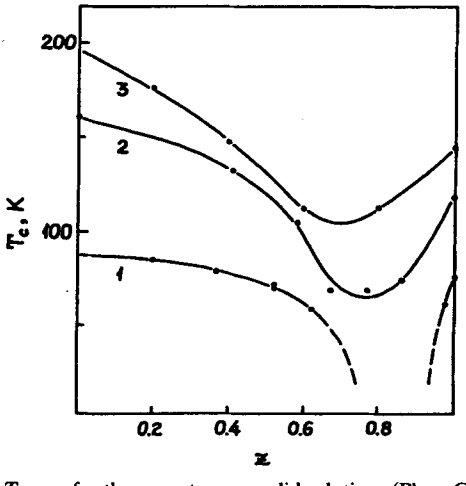

FIGURE 2 Dependence of T_c on z for three quaternary solid solutions $(Pb_{1-x}Ge_xTe)_{1-z}(Pb_{1-y}Ge_ySe)_z$: 1, $x = 0.025$, $y = 0.04$; 2, $x = y = 0.06$; 3, $x = y = 0.08$.

center) substituting atoms. So, in spite of similar displacement of Ge and S off-center atoms in ⟨111⟩ direction from the site, one type of off-center atoms prevents the establishing of long-range order produced by the other type of off-center ions.

Figure 3 shows the hysteresis behavior of resistivity in the region of anomalous resistivity peak for typical sample of $Pb_{1-x}Ge_xTe_{1-y}S_y$.[13] The curves were recorded

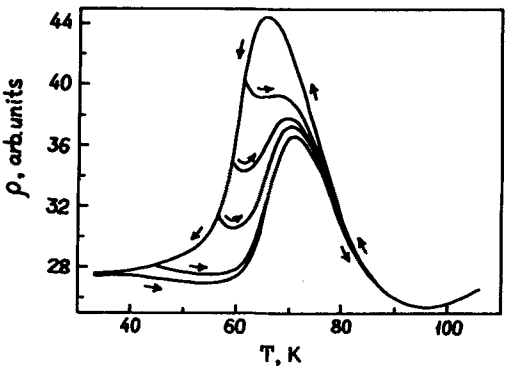

FIGURE 3 Hysteresis behavior of resistivity near T_c for typical sample of $Pb_{1-x}Ge_xTe_{1-y}S_y$ with $x = 0.009$, $y = 0.068$.[13]

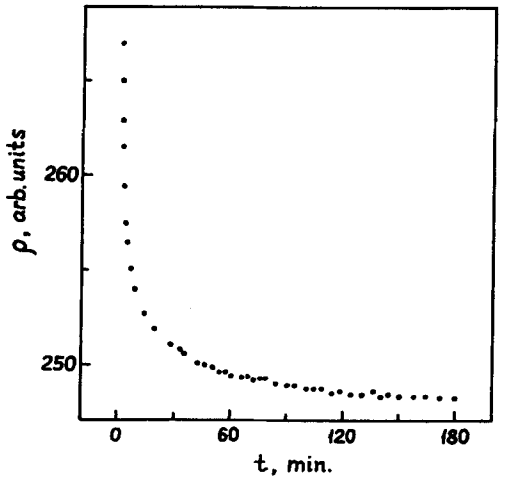

FIGURE 4 Relaxation curve observed after quick cooling the sample $Pb_{1-x}Ge_xTe_{1-y}S_y$ with $x = 0.009$, $y = 0.068$ from 83 to 55 K.

in the cycles of slow cooling down to different minimal temperatures followed by slow heating. The directions of change the temperature are shown by arrows. It is seen that the shape of anomalous resistivity peak (and thus of the permittivity) depends on the history of cooling.

At any fixed temperature inside the hysteresis loop a slow relaxation of ρ was observed, the direction of relaxation (down or up) being dependent on the cooling history. This observation indicates that the dipole system is in nonequilibrium state near T_c even at slow changing the temperature (about 1 K/min). Figure 4 shows typical relaxation curve after quick cooling the sample presented in Figure 3 from 83 to 55 K. The relaxation curve could be approximated by power-low dependence $\Delta\rho \propto t^{-\alpha}$. The value of α changed from 0.1 to 0.6 with increase of the temperature at which the relaxations were studied. The analysis of these results brought us to the conclusion that the hysteresis and relaxations are associated with extreme slowing down of all processes of establishing of both thermal fluctuations and long-range order.

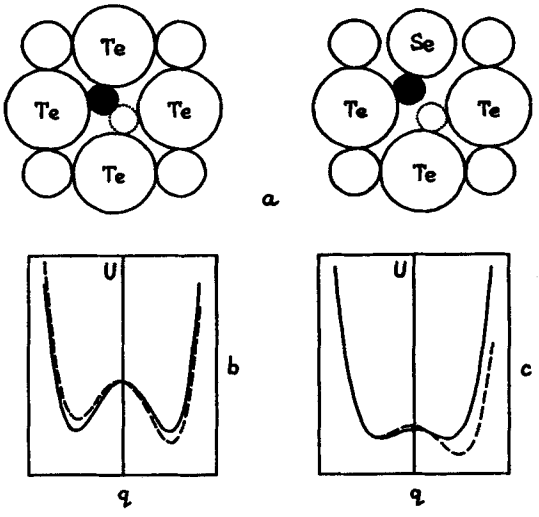

FIGURE 5 a—Local environment of off-center atom in ternary and quaternary solid solutions. Full and dotted circles show different positions of off-center atom. Figure b and c show the potential wells of off-center atom for ternary (solid line) and quaternary (dashed line) solid solutions for the case of high and low barrier height, respectively.

The low-temperature scattering was observed for the first time in ternary solid solutions with low off-center concentration and was attributed to Kondo-like effect.[17] Our studies have established that this scattering was especially strong in quaternary solid solutions (in some crystals the resistivity increased more than 10 times) and grew with increasing the disorder in a system (Figure 1). The low-temperature scattering had the following properties: 1) it was nearly linear function of temperature below some temperature T_g; 2) its dependence on the carrier concentration was $n^{-1/3}$; 3) its temperature derivative didn't change significantly at T_c. All these features evidently contradict the Kondo model. On the other hand, it was noticed experimentally that the changes in mobility induced by low-temperature scattering in different solid solutions can be regarded as a measure of the disorder in crystals. Unfortunately, at present we cannot indicate any particular mechanism of this scattering.

The peculiarities of ferroelectric phase transitions found in quaternary solid solutions were explained by the influence of random fields.[13] The physical origin of this influence is evident from Figure 5a. Owing to the difference in the interaction between off-center atom and chemically different surrounding atoms, different displacements of off-center atom become unequivalent. According to the symmetry classification, the perturbation induced by substitutional disorder has a vector symmetry. Such vector random fields are known to exert the strongest influence on the ferroelectric systems, and always lower T_c.[18] In a solid solution where each off-center atom is polarized by its local environment, a competition occurs between indirect dipole-dipole interaction that orders dipoles, and random fields that act in the opposite way. If random fields are strong, they can destroy the ferroelectric long-range order completely, and the quenched dipolar disorder state appears. The splitting of energy of different minima resulting from random fields (Figure 5b) was estimated to be about 5 meV in PbGeTeSe. The extreme slowing down in

quaternary solid solutions is explained by the frustrations and slow reorientation of polar clusters in the presence of random fields (such clusters arise in a crystal already above T_c due to statistical fluctuations of local concentration of off-center atoms).

3.2 *Isoelectronic Substitution in Crystals with Sn Off-Center Ions*

Studies of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ and $Pb_{1-x}Sn_xTe_{1-y}S_y$ solid solutions have found a qualitatively different influence of substitutional disorder on T_c in comparison with that observed in crystals with Ge and S off-center atoms.

Figure 6 shows $\rho(T)$ dependence for $Pb_{1-x}Sn_xTe_{1-y}Se_y$ crystals with fixed Sn concentration ($x = 0.2$) and variable parameter y.[8,15] It is seen that the phase transition appears only in quaternary solid solutions and is absent in ternary ones. The unexpected growth of T_c with increasing substitutional disorder (see insert in Figure 6) is opposite to the effect found in systems with off-center Ge and S atoms, where the disorder always suppressed the phase transition. All other features of the phase transition in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ were similar to those observed in quaternary solid solutions with Ge and S off-center atoms.

To explain the growth of T_c with increasing substitutional disorder we have supposed that Sn in PbTe is off-center atom moving in the multi-well potential with low height of barrier separating different minima (Figure 5c).[8] High tunneling rate characteristic for such off-center atom can explain the absence of the phase

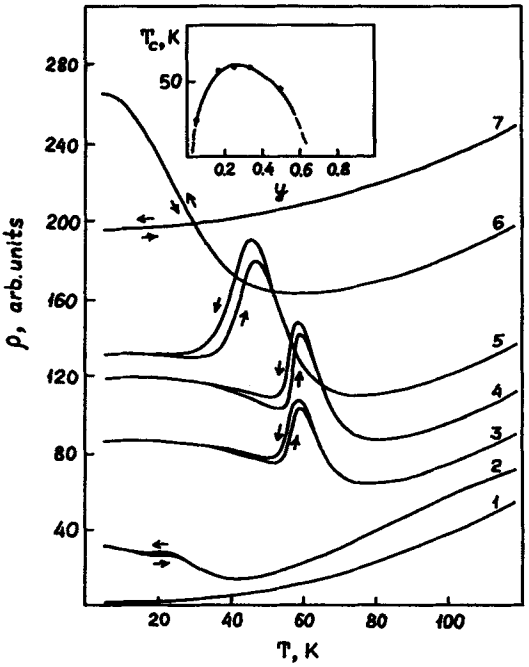

FIGURE 6 Temperature dependence of resistivity for $Pb_{1-x}Sn_xTe_{1-y}Se_y$ crystals with fixed Sn concentration ($x = 0.2$) and variable y.[15] 1, $y = 0$; 2, $y = 0.05$; 3, $y = 0.25$; 4, $y = 0.33$; 5, $y = 0.5$; 6, $y = 0.67$; 7, $y = 0.83$. The insert shows the dependence of T_c on y.

transition at low concentration of off-center atoms. In quaternary solid solution the substitution of large neighboring atoms with smaller ones increases both the distance between different positions of off-center atom and the height of the barrier, thus decreasing the tunneling rate. As a result, T_c can be increased despite of the splitting of the energies of different off-center minima due to random fields.

In crystals with $x > 0.35$ the features that give evidence for the order-disorder character of the phase transition (hysteresis loops, relaxations) disappeared, and the phase transition behaved like the displacive one. These changes were in qualitative agreement with the theoretical predictions for cooperative motion of a system of particles residing in multi-well potential with low energy barrier.[19] The barrier height estimated for $Pb_{1-x}Sn_xTe_{1-y}Se_y$ was about 4 meV.

Another confirmation of the multi-well potential for Sn atom has been obtained from the study of the phase transition in another solid solution—$Pb_{1-x}Sn_xTe_{1-y}S_y$,[14,15] in which off-center behavior of Sn atoms was expected. These crystals containing two off-center atoms (Sn, S) were especially interesting because both effects of the disorder were observed in them—the decrease of T_c in the composition region where the phase transition was induced by S off-center atoms, and the increase of T_c in the region where it was induced by Sn off-center atoms.

3.3. *Influence of Doping Impurities*

The random-field model proposed to explain the influence of substitutional disorder on the ferroelectric phase transitions supposes that doping (nonisoelectronic) impurities can affect the phase transition in a similar way. To check this supposition, we have studied the phase transitions in $PbTe_{1-x}S_x$ and $Pb_{1-x}Ge_xTe$ crystals doped with various impurities.[20]

Figure 7 compares $\rho(T)$ dependence for $PbTe_{1-x}S_x$ doped with different amounts of In (doping impurity) and Se (isoelectronic impurity). It is seen that the changes observed for both impurities (the lowering of T_c, the appearance of hysteresis loops and low-temperature scattering) are very similar. The only difference is the rate of decrease of T_c, which was 60 times higher for In than for Se.

The dependence of T_c on the concentration N_i of various impurities for $PbTe_{0.92}S_{0.08}$ is presented in Figure 8. It is seen that the adding of impurities always decreases T_c, but for each impurity the dependence $T_c(N_i)$ is individual. Nevertheless the doping impurities always influenced T_c much stronger than isoelectronic ones. The rate of decrease of T_c for some doping impurities reached the value of 50 K/at.%.

The further analysis of these data shows that there is a correlation between the rate of decrease of T_c and electrical activity of impurity. The charged impurities (In, Sb, Bi) exert a more pronounced influence on T_c in comparison with neutral impurities (Cd, Mn). This indicates a noticeable role of (random) Coulomb fields that polarize off-center ions and decrease T_c.

As follows from Figure 8, the influence of electrically neutral Cd and Mn atoms on T_c is also stronger than that of isoelectronic impurities. We attribute this effect to the interaction of elastic quadrupole moments of off-center atoms with random local deformations created by impurities. The origin of these deformations is the distinction in chemical bonds in CdTe, MnTe and PbTe. Our EXAFS studies indeed

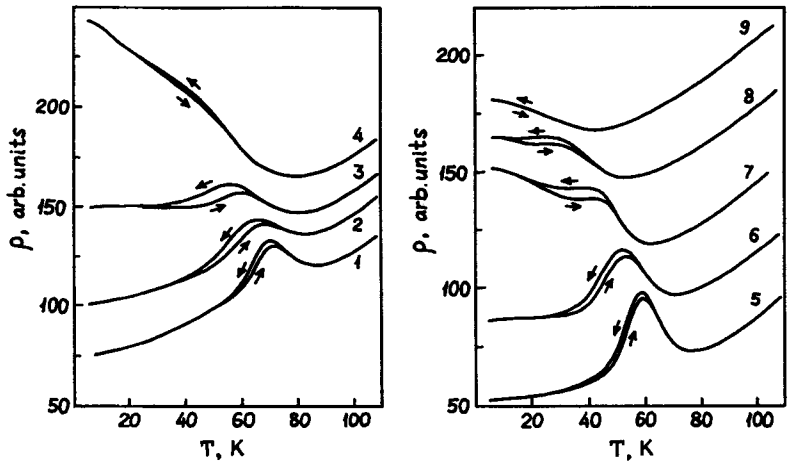

FIGURE 7 Temperature dependence of resistivity for $PbTe_{0.92}S_{0.08}$ crystals doped with different amounts of In (on the left) and Se (on the right). The concentration of indium (in at.%): 1, 0.15; 2, 0.31; 3, 0.49; 4, 0.71. The concentration of Se in the samples of $Pb(Te_{1-y}Se_y)_{0.92}S_{0.08}$ (in mol.%): 5, 21; 6, 27; 7, 34; 8, 40; 9, 46.[20]

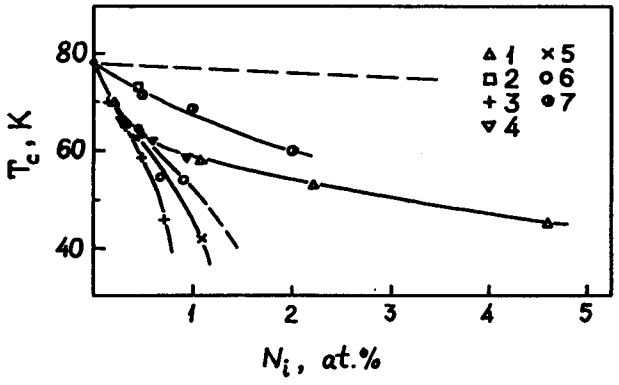

FIGURE 8 Dependence of T_c upon the concentration N_i of different impurities for $PbTe_{0.92}S_{0.08}$. 1, Cd; 2, Ga; 3, In; 4, Tl; 5, Sb; 6, Bi; 7, Mn.[20] Dashed line corresponds to the isoelectronic impurity Se.

have found strong contraction of bond lengths by 0.18 Å for Cd and 0.24 Å for Mn impurities in PbTe. Moreover, even stronger local deformations can be created by impurities entering interstitial positions in a lattice.

4. CONCLUSION

Isoelectronic substitution in solid solution and doping impurities are shown to affect the static and dynamical properties of the ferroelectric phase transitions in IV–VI semiconductors in a similar way. In both cases the observed phenomena can be considered as a result of the influence of random fields of different nature (quazi-electric, deformation, Coulomb) on the ordering of dipoles of off-center atoms. For off-center atoms moving in multi-well potential with low barrier height, the

disorder can depress the tunneling of off-center atoms and result in the increase of T_c.

It should be noted that the influence of substitutional disorder on the ferroelectric properties of IV–VI semiconductors is unexpectedly strong in comparison with that observed in most of ferroelectrics. It is as strong as in magnetic crystals. We think that the similarity between our and magnetic systems is due to small interaction radius inherent to both interactions. The radius of indirect dipole-dipole interaction in our crystals is 6–10 Å according to the data on inelastic neutron scattering.

ACKNOWLEDGEMENT

The present work was partially supported by Russian Foundation on Fundamental Science under contract 93-02-14712.

REFERENCES

1. B. E. Vugmeister and M. D. Glinchuk, *JETP*, **52,** 482 (1980).
2. Yu. A. Logachev and B. Ya. Moizhes, *Sov. Phys.-Solid State*, **19,** 1635 (1977).
3. S. Katayama and K. Murase, *Solid State Commun.*, **36,** 707 (1980).
4. Q. T. Islam and B. A. Bunker, *Phys. Rev. Lett.*, **59,** 2701 (1987).
5. V. F. Kozlovskii, A. I. Lebedev and Yu. E. Petrov, *Sov. Phys.-Solid State*, **28,** 2035 (1986).
6. Kh. A. Abdullin, A. I. Lebedev, A. M. Gas'kov, V. N. Demin and V. P. Zlomanov, *JETP Lett.*, **40,** 998 (1984).
7. Z. Wang and B. A. Bunker, *Phys. Rev. B*, **46,** 11277 (1992).
8. A. I. Lebedev and I. A. Sluchinskaya, *Sov. Phys.-Solid State*, **32,** 1036 (1990).
9. K. L. I. Kobayashi, Y. Kato, Y. Katayama and K. F. Komatsubara, *Solid State Commun.*, **17,** 875 (1975).
10. Yu. N. Epifanov, A. P. Levanyuk and G. M. Levanyuk, *Sov. Phys.-Solid State*, **23,** 392 (1981).
11. S. Takaoka and K. Murase, *Phys. Rev. B*, **20,** 2823 (1979).
12. A. I. Lebedev and I. A. Sluchinskaya, *JETP Lett.*, **46,** 536 (1987).
13. A. I. Lebedev and I. A. Sluchinskaya, *Bull. Acad. Sci. USSR Phys. Ser.*, **51,** 17 (1987).
14. A. I. Lebedev and I. A. Sluchinskaya, *Sov. Phys.-Solid State*, **34,** 793 (1992).
15. A. I. Lebedev and I. A. Sluchinskaya, *Ferroelectrics*, **143,** 91 (1993).
16. A. I. Lebedev and I. A. Sluchinskaya, *J. Alloys and Compounds*, **203,** 51 (1994).
17. H. Yaraneri, A. D. C. Grassie, He Yusheng and J. W. Loram, *J. Phys. C*, **14,** L441 (1981).
18. A. P. Levanyuk and A. S. Sigov, "Defects and Structural Phase Transitions," Gordon and Breach, 1988.
19. Y. Onodera, *Progr. Theor. Phys.*, **44,** 1477 (1970).
20. A. I. Lebedev and I. A. Sluchinskaya, *Physics of the Solid State*, **35,** 321 (1993).