Possible appearance of the dipole-glass phase in solid solutions of the semiconductors of the group IV–VI

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Additional scattering of electrons characteristic for a dipole-glass phase has been observed in the study of the electrical conductivity of $Pb_{1-x}Ge_xTe_{1-y}Se_y$ and several other solid solutions. The appearance of a dipole-glass phase in solid solutions can be explained in terms of the disordering effect their statistical structure has on the dipole order.

The study of cooperative phenomena in disordered systems has recently stimulated considerable interest. The introduction of noncentral impurities into strongly polarized matrices gives rise to the appearance of a ferroelectric phase. The possible appearance of a dipole-glass phase in such systems has essentially not been studied. On the basis of an experimental study of the electrical conductivity of a semiconductor, the ferroelectric material $Pb_{1-x}Ge_xTe_{1-y}Se_y$, we assume that a dipole-glass phase forms and that it is stable over a rather wide temperature interval.

We recall that the dipole-glass state in a crystal is characterized by configurational expectation values, $\overline{\mathbf{P}}=0$ and $\overline{\mathbf{P}}^2\neq 0$. According to the molecular field theory, below the phase-transition temperature T_g the order parameter $\overline{\mathbf{P}}^2$ varies in proportion to $T_g - T$ (Ref. 1). In contrast with spin glass (in which the transition from the paramagnetic state to the spin-glass state has only a slight effect on the electrical conductivity), the appearance of the dipole-glass phase should be accompanied by a strong scattering. The appearance of polarization at $T<T_g$, which varies randomly in space, produces a stray electric field which affects the motion of free carriers.

Let us consider the characteristics of this scattering. Solving Poisson's equation in k space with allowance for screening, we find the potential for the interaction of an electron with a frozen polarization wave with a wave vector $\mathbf{q}$:

$$V_{\mathbf{q}} = -e\varphi_{\mathbf{q}} = \frac{4\pi i e(\mathbf{q}\cdot\mathbf{P}_{\mathbf{q}})}{\in(q^2+q_0^2)}, \qquad q_0^2 = \frac{4m^*e^2}{\in\hbar^2}\left(\frac{3n}{\pi}\right)^{1/3}.$$

The fluctuation strength $\overline{\mathbf{P}}_{\mathbf{q}}\overline{\mathbf{P}}_{-\mathbf{q}}$ is expressed in terms of the Fourier components of the correlation function, which we assume to be $\overline{\mathbf{P}(0)\mathbf{P}(r)}=\overline{\mathbf{P}}^2\exp(-q_Dr)$, where $q_D=1/r_D$ is determined by the length scale r_D of the "domain." The scattering by such a potential occurs elastically. Calculation of the contribution of this scattering mechanism to the resistivity $\rho(T)$ of a degenerate semiconductor based on the kinetic equation yields in the limiting cases $q_D \gg k_F$ and $q_D \ll q_0$ (k_F is the wave vector of an electron on the Fermi surface) the following behavior of $\Delta\rho$ as a function of the electron density n and temperature: $\Delta\rho \sim q_D^{-3}(T_g - T)n^{-4/3}$ and

$\Delta\rho \sim q_D (T_g - T) n^{-7/3}$. The same characteristics should be observed in the scattering of electrons by domain walls in a ferroelectric. In this case T_g should be equal to the temperature T_c of the ferroelectric phase transition. Such an additional scattering $[\Delta\rho \sim (T_c - T) n^{-2}]$ was observed by Abdullin *et al.*[2] in $PbTe_{1-x}S_x$ samples.

The study of quaternary solid solution $Pb_{1-x}Ge_xTe_{1-y}Se_y$ made it possible to identify several new unusual features which allowed us to assume the appearance of a dipole-glass phase in it. The composition of the samples corresponds to the formula $(Pb_{0.975}Ge_{0.025}Te)_{1-z}$ $(Pb_{0.96}Ge_{0.04}Se)_z$ (z is the parameter of the composition). This composition was chosen in such a way that the temperature of the ferroelectric phase transition, calculated in the molecular-field approximation, would remain constant. We studied annealed polycrystals of n-type conductivity.

The temperature dependences $\rho(T)$ for several samples are shown in Fig. 1. Above 120–140 K the $\rho(T)$ curves, typical for IV–VI semiconductors, are determined by the interaction of electrons with phonons. Below these temperatures, there is an additional scattering consisting of two terms: a "resonance" peak, which is attributable to the scattering by polarization fluctuations near T_c, and an approximately linear increase in ρ with decreasing T, which we attribute to the scattering mechanism considered above. The values of T_g which are determined from the point at which the extrapolated low-temperature and high-temperature linear parts of the curves cross (the dashed curve in Fig. 1) differ markedly (by 20–40 K) from T_c. This allows us to assume that at $T_c < T < T_g$ a dipole-glass phase is formed in the crystals and below T_c a ferroelectric phase coexists in them with the dipole-glass phase. The $\rho(T)$ curves plotted during heating are at variance with those recorded during cooling. The relaxation of ρ observed after cooling the sample through T_c suggests that below T_c the dipole-glass phase is metastable and that the noncentral impurities tend toward ferroelectric order.

In the region $z = 0.75$–0.95 the structural feature observed at T_c is not detected

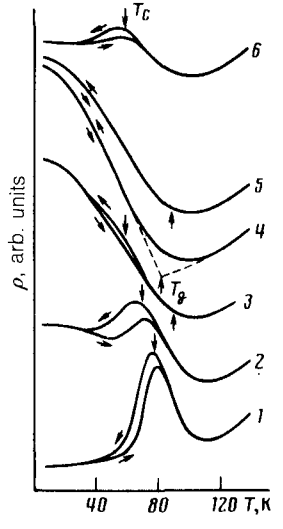

FIG. 1. Temperature dependences of the resistivity of PbGeTeSe samples. z:1—0.36; 2—0.52; 3—0.62; 4—0.76; 5—0.85; 6—0.975. The curves are arbitrarily shifted along the vertical axis. The arrows at the curves indicate the direction in which the temperature changes during the recording. The vertical arrows denote the values of the temperatures T_c and T_g.

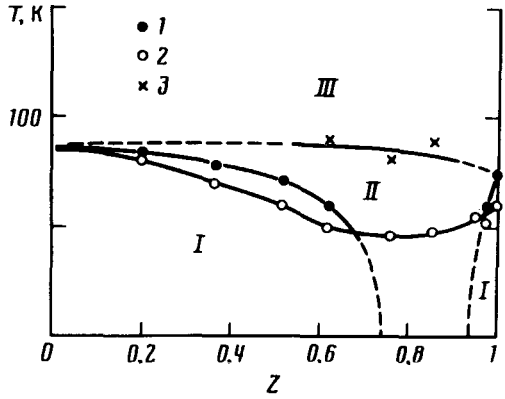

FIG. 2. Phase diagram of the PbGeTeSe system. I—Ferroelectric phase; II—dipole-glass phase; III—paraelectric phase. The points give the values of T_c (1), of the temperature corresponding to the maximum hysteresis on the curves (2), and of T_g (3).

(see also Fig. 2). This result is surprising, since the two initial solid solutions ($z = 0$ and $z = 1$) undergo identical ferroelectric phase transitions[3] and the system should have no competing interactions. Analysis of the capacitance of the *p-n* junction fabricated from one of these samples ($z = 0.78$) revealed a strong variance of the dielectric constant ϵ and a temperature shift of its maximum ϵ' as a function of the frequency, indicating that the onset of the ferroelectric phase in the samples is greatly retarded kinetically.

The particular features of the electrical conductivity, which are similar to those described above, were also observed in other quaternary solid solutions ($Pb_{1-x}Sn_xTe_{1-y}S_y$, $Pb_{1-x}Ge_xTe_{1-y}S_y$, and $PbTe_{1-x-y}Se_xS_y$) and in $Pb_{1-x}Ge_xSe$ (Ref. 3), in which a strong additional scattering appeared when $x \lesssim 0.04$ (when $T_c < T_g$) and disappeared at larger values of x.

The appearance of a dipole-glass phase as a result of ordering of the dipole moments of the noncentral impurities in solid solutions is not a random process. A statistical disorder in the arrangement of atoms in the solid solution disrupts the equivalence of various displacements of the noncentral impurities and leads to the appearance in the crystal of a frozen random (stray) field which is the conjugate of the order parameter.[4] At $T \approx T_g$ this random field gives rise to the formation of a disordered dipole structure: the dipole glass. Stable polar-phase domains can appear in the crystal only when the molecular field is higher than the random field. Clearly, as the difference between these fields increases (i.e., as the statistical disorder increases), the ferroelectric phase transition will occur at lower temperatures. At low T_c the probability for the formation of a critical nucleus of the ferroelectric phase in the dipole-glass phase may turn out to be so small as to preclude the appearance of the polar phase.

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