Carrier mobility and photoluminescence in lead magnesium-niobate in the region of the ferroelectric phase transition

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A decrease of the drift mobility (μ) of the carriers and an increase in the intensity of the photoluminescence (PL) was observed in the course of a phase transition in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN). The minimum of the temperature dependence of μ shifts towards higher temperatures with increasing electric field. The results are interpreted by resorting to a model of autolocalized "phason" states of the carriers in the region of the ferroelectric phase transition.

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The nature of the electron-phonon interaction in ferroelectrics, especially in the region of the phase transition, has not yet been explained. Different opinions, sometimes contradictory, have been expressed with respect to the mechanism of the carrier scattering in these compounds: carrier splitting by LO phonons[1-3], the small-radius polaron model,[4] etc. It was concluded in[5] that in ferroelectric perovskites the value of μ is determined by the scattering of the soft TO mode by phonons. In this case the carriers are scattered by critical fluctuations of the lattice polarization, which cause disordered changes in the energy level at the bottom of the conduction band (CB). A minimum of μ, corresponding to the maximum of the dielectric constant ϵ_0, should be observed in the region of the phase transition, as follows from the relation $\mu \sim 1/\epsilon_0 + \text{const}$ derived in[5]. However, no direct investigations of the temperature dependence of μ in the region of the phase transition have been made, because of experimental difficulties which are apparently connected with the narrowness of the temperature interval of the phase transition. Investigations of this type in the region of the ferroelectric phase transition can yield valuable information on the nature of the electron-phonon interaction, as well as the possibility of verifying the theoretical premises that predict, in particular, the existence in the phase-transition of autolocalized phason states of the carriers, which have not yet been observed experimentally in ferroelectric crystals.[6]

We have investigated the temperature dependence of μ in the most thoroughly investigated ferroelectric with smeared phase transition, namely PMN, in which the temperature region of the fluctuations in broadened.[7] The value of μ was measured by the time-of-flight procedure[8] in samples made in the form of polished plates oriented in the [100] direction, of thickness ~ 50–300 μm, with gold electrodes sputtered on the opposite faces. The carriers were photo-injected by a molecular-nitrogen laser LGI-21 ($\lambda \approx 337$ nm, pulse duration ≈ 8 nsec). The light was effectively absorbed at a depth ~ 1 μm, inasmuch as for PMN the energy of the incident-radiation quanta was $h\nu > E_g$. Experiments performed on samples with different thicknesses and in different electric fields have shown that the observed charge pulse is of the "time-of-flight" type, and to determine μ one can use the expression $\mu \approx 0.8L^2/tV$, where L is the sample thickness, t is the time that the carrier takes to traverse the distance between the electrodes, and V is the applied voltage. When an electric field E was applied, a homogeneous bleaching was observed in the sample through crossed polarizers, thus indicating a relatively homogeneous distribution of the field in the range $E = 3$–20

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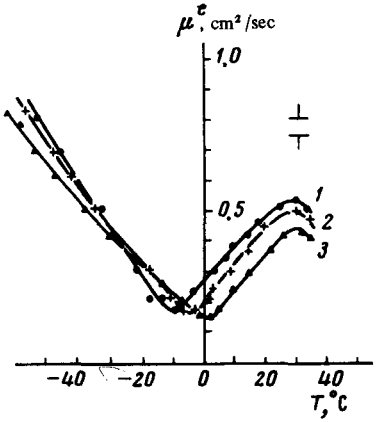

FIG. 1. Temperature dependence of the electron drift mobility μ^e in $PbMg_{1/3}Nb_{2/3}O_3$ at electric field intensities 1—3.6 kV/cm, 2—5.7 kV/cm, and 3—8.3 kV/cm.

kV/cm. The values of μ of the carriers at 20 °C were $\mu^e \approx 0.5$ and $\mu^P \approx 0.35$ cm²/V-sec for electrons and holes, respectively.

Figure 1 shows the temperature dependence of the drift mobility μ^e in PMN at different values of E. μ^e decreases in the intermediate Curie-temperature region. With increasing E, the temperature corresponding to the minimum of μ^e increases, as does the temperature corresponding to the maximum of ϵ_0.[5,7] The behavior of μ^p is similar. The result agrees with the conclusions of[5]. According to[6], phason states of carriers can be produced in the phase-transition region and are capable of assuming the role of sticking levels, which also leads to a decrease of μ.

Figure 2 shows the temperature dependence of the photoluminescence in PMN with a maximum emission at $\lambda \approx 590$ nm when excited with an LGI-21 laser. The photoluminescence intensity is maximal in the region of -16 °C. The low photoluminescence intensity did not make it possible to reveal the structure of the spectrum and to draw any conclusion concerning the temperature dependence of the contour of the observed broad (~ 60 nm) band. Sihvonen[9] has previously observed an increse of the photoluminescence intensity in the ferroelectric (~ 35 K) and the structural (~ 100 K) phase transitions in the insulator $SrTiO_3$, but the nature of this phenomenon remains unexplained. In perovskite ferroelectrics doped with rare earths, the photoluminescence reveals no singularities in the region of the phase transition.

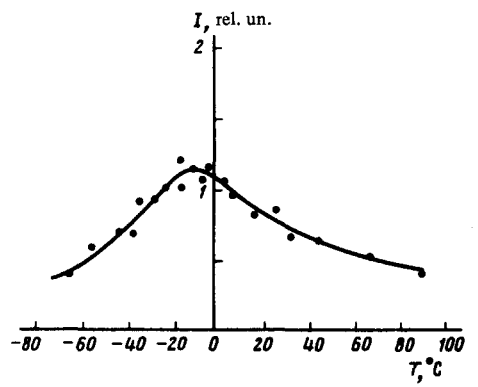

FIG. 2. Temperature dependence of the photoluminescence intensity I in $PbMg_{1/3}Nb_{2/3}O_3$ in the region 590 ± 20 nm (wavelength of exciting light $\lambda \approx 337$ nm).

The maximum of the photoluminescence intensity in the phase-transition region can be explained in the following manner: assume that in the course of the photoexcitation the elecrons are ejected into the conduction band, and then some of them, after becoming localized on a heterophase fluctuation and after the phason is attached to the impurity, relaxes with emission to a deep level of the impurity. We note that the radiative relaxation is most probable from phason states. The intensity I of the photoluminescence is determined by the number N_1 of the phasons secured to the impurity centers:

$$I = N_1 I_0 \tag{1}$$

where I_0 is the contribution from one luminescence center. If the impurity concentration is low enough, then $N_1 \ll N_p$, where N_p is the total number of phasons. Assuming that even when the phason states are taken into account the time of the intraband relaxation is much shorter than that of the interband relaxation, we can obtain, using,[6]

$$N_p = N\frac{a\zeta}{2}\exp\left(-\frac{\Delta\Phi}{kT}\right)\left[1+\frac{a\zeta}{2}\exp\left(-\frac{\Delta\Phi}{kT}\right)\right]^{-1} \tag{2}$$

The number $a \sim 1$ takes into account the smearing of the energy of the phason states, $\zeta \sim 10^3$, N is the total number of electrons ejected into the conduction band, and $\Delta\Phi$ is the change of the thermodynamic potential (TP) upon production of a phason—an electron localized on a nucleus of the paraphase (in ferroelectrics of the perovskite type, the volume of the conduction band in the paraphase lies lower than in the ferroelectric phase). It can be shown that if $N_1 \ll N_i$, where N_i is the number of impurity atoms, then N_1 is determined from the expression

$$N_1 = \frac{N_i N_p}{N_c}\exp\frac{\Delta\Phi - \Delta\Phi_1}{kT} = \frac{N_i N a\zeta}{2N_c}\exp\left(-\frac{\Delta\Phi_1}{kT}\right)\left[1+\frac{a\zeta}{2}\exp\left(-\frac{\Delta\Phi}{kT}\right)\right]^{-L}, \tag{3}$$

where N_c is the number of unit cells in a crystal, and $\Delta\Phi_1$ is the change of the TP for a phason secured to an impurity. When the region of the phase transition from the ferroelectric phase is approached, the formation of nuclei of the para phase is facilitated, therefore $\Delta\Phi$ and $\Delta\Phi_2$ decrease.[6] Since $\zeta \gg 1$, practically all the electrons are in phason states already at a certain value $\Delta\Phi_1 > 0$ [metastable phason—see formula (2)]. In the case of an abrupt phase transition, the phasons vanish at $T > T_0$, where T_0 is the transition temperature, and consequently N_1, meaning also I, is maximal at a certain $T^* \leqslant T_0$. It follows from the foregoing that the PL reaches a maximum in the phase transition region when the photoelectron is excited into the band. The existence in PMN of a level with an activation energy ~ 2.0 eV was demonstrated in[10]. Phasons can also lead to the observed[11] abrupt increase of the contribution of the slow component of the photoconductivity in the region of the phase transition in $Ba_{0.25}Sr_{0.75}Nb_2O_6$.

Thus, the foregoing estimates show that the existence of phason states of carriers, accompanied by the appearance of the minimum of the drift mobility of the carriers, leads to an increase of the intensity of the photoluminescence in the phase-transition region.

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