THE EFFECT OF HYDROSTATIC PRESSURE ON THE KERN–HARBEKE EFFECT IN FERROELECTRIC SbSI

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The effect of hydrostatic pressures up to 2000 atm on the anomalous shift of the absorption edge in ferroelectric SbSI with the field near the transition phase (the Kern–Harbeke effect) is investigated. Thermodynamic relations are obtained for the temperature dependence of the effect in the case of first and second-order phase transitions. A qualitative confirmation of these relations is obtained. Additional indications of the existence in SbSI of a critical Curie point at P = 1500 atm and T = −40°C are found.

KERN[1] and Harbeke[2] have previously observed the anomalous shift of the absorption edge of the ferro-electric SbSI under the influence of an electric field applied in the direction of the spontaneous polarization of the crystal. The shift was towards shorter waves and did not depend on the direction of the external electric field applied to the crystal. The sign of this effect turned out to be opposite to that of the Franz–Keldysh effect, and its magnitude turned out to be larger by an order of magnitude. The temperature dependence of the Kern–Harbeke effect exhibited a maximum near the Curie temperature. The magnitude of the shift ΔE_g depended on the field linearly in the ferroelectric and quadratically in the paraelectric region. The maximum of the spectral distribution of the photocurrent in SbSI[3] was similarly shifted under the influence of an external field. Subsequently the same effect was observed in a series of independent papers[4-6] in single crystals of BaTiO₃, the sign of the effect as well as the nature of its field and temperature dependence turning out to be the same.

Thermodynamically the Kern–Harbeke effect can be described in a way similar to the electro-optic effect in ferroelectrics. According to [7] the width of the forbidden band of a ferroelectric semiconductor E_g near a phase transition can be expanded in a series in powers of the polarization P. Restricting ourselves, as in [7], to the quadratic term, we have

$$E_g = E_{g0} + aP^2 + \dots \qquad (1)$$

In the absence of an external field the quantity $\Delta E_g^0 = E_g - E_{g0}$ represents a spontaneous effect of a change in the width of the forbidden band in the phase transition in a ferroelectric which has been investigated in a series of papers.[8-10] For SbSI and BaTiO₃ the parameter $a > 0$. In order to describe the Kern–Herbeke effect, one should according to Gähwiller[6] understand P in (1) to be the sum of the spontaneous and induced polarization:

$$E_g \approx E_{g0} + a(P + \varepsilon E / 4\pi)^2. \qquad (2)$$

In the ferroelectric region, restricting ourselves to the linear term, we have

$$\Delta E_g^E \approx \Delta E_g^0 + a\varepsilon E P / 2\pi. \qquad (3)$$

Here ΔE_g^E is the magnitude of the Kern–Harbeke effect, ΔE_g^0 is the magnitude of the spontaneous effect, E is the intensity of the external field, and ϵ is the dielectric constant. In the paraelectric region there is in accordance with (2) a quadratic dependence of ΔE_g^E on the field E. It is seen from (3) that the temperature dependence of ΔE_g^E turns out to be essentially different for first- and second-order phase transitions. In fact, for a first-order phase transition substituting in (3) $\epsilon \sim (T - T_0)^{-1}$ and $P = P_0$, we have $\Delta E_g^E \sim (T - T_0)^{-1}$. In the case of a second-order transition, substituting in (3) $\epsilon \sim (T - T_0)^{-1}$ and $P \sim (T - T_0)^{1/2}$,[11] we find $\Delta E_g^E \sim (T - T_0)^{-1/2}$. Thus, although in both instances ΔE_g^E has a maximum at the Curie point $T = T_0$, this maximum should be less steep for a second-order phase transition.

The temperature dependence of ΔE_g^E near the critical Curie point should change analogously. According to V. Ginzburg[11] for first-order phase transitions far from the critical point $\Delta E_g^E \sim (T - T_0)^{-1}$, and for first-order phase transitions close to the critical point $\Delta E_g^E \sim [\alpha_{T_0} + \alpha'_{T_0}(T - T_0)]^{-1/2}$. Using the results of Ginzburg,[11] it is readily shown that for second-order phase transitions close to the critical point $\Delta E_g^E \sim (T - T_0)^{-1/2}$.

An investigation of the phase diagram of ferroelectric SbSI indicated the existence of a triple point with the coordinates $T = -40°$ and $P = 1500$ atm, in the vicinity of which the line of first-order phase transitions goes over to the line of second-order phase transitions.[12-14] From this point of view it was of interest to investigate the Kern–Herbeke effect in SbSI in a sufficiently broad range of hydrostatic pressures for the purpose of comparing the temperature dependences of the effect corresponding to phase transitions far from and close to the critical point.

The measurements were carried out with the aid of a high-pressure installation equipped with a thermo-

stated high-pressure chamber with two parallel flat windows whose construction is described in [13]. The absorption edge was measured in monochromatic light transmitted through the SbSI crystal. The spectra were recorded with the aid of an FÉU-38 electron photomultiplier. A UM-2 was used as the source of monochromatic light. At atmospheric pressure and room temperature the absorption edge of the investigated crystals was close to 630 mμ.

Figure 1 presents six curves of the temperature dependence of the absorption edge of SbSI in a field of 2 kV/cm which correspond to six different pressures in the range of 1 to 2000 atm and to Curie temperatures from 25 to −57°C. As is seen from Fig. 1, the maximum shift of the absorption edge is observed at atmospheric pressure at the Curie point (T_C = 25°C). The magnitude of this shift $\Delta E_g^E \approx 0.013 \pm 0.001$ eV is in good agreement with data in the literature. With increasing pressure one observes a decrease of this effect and for P = 1400 atm its value at the maximum amounts to 0.003 eV. At the same time, a washing out of the temperature maximum of the effect takes place with increasing pressure. In the region of pressures greater than 1400 atm the magnitude and nature of the temperature dependence of the effect do not change. Separate measurements have shown that everywhere in the ferroelectric region the dependence of ΔE_g^E on the field E is linear, whereas in the paraelectric region it is quadratic. The character of the field dependences of the effect is also the same in the range of pressures P > 1400 atm.

With the aid of data presented in Fig. 1 we plotted the dependence of $\ln(1/\Delta E_g^E)$ on $\ln(T - T_0)$ for the para- and ferroelectric regions of the crystal. As follows from Fig. 2, where these dependences are presented for the paraelectric region, they turned out to be straight lines; as was to be expected, at atmospheric pressure the straight line is inclined at 45° to the abscissa. On approaching the triple point this angle decreases and close to it amounts to ~20°. Further increase of the pressure does not change it noticeably. An analogous result is also obtained in the ferroelectric region. Let us add that at temperatures sufficiently different from the Curie point we observed an inversion of the sign of the effect which was due to the fact that
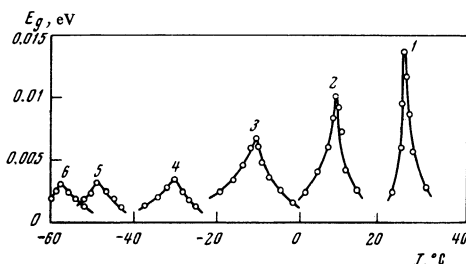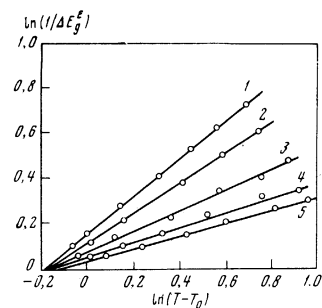

FIG. 2. The dependence of $\ln(1/\Delta E_g^E)$ on $\ln(T - T_0)$ for single crystals of SbSI in the paraelectric region for various values of the hydrostatic pressure (atm): 1 − 1, 2 − 400, 3 − 900, 4 − 1400, 5 − 1800, 6 − 2000.

then the magnitude of the Kern−Harbeke effect turned out to be comparable with the magnitude of the Franz−Keldysh effect.

Thus, an investigation of the Kern−Harbeke effect in SbSI in the pressure range of 1−2000 atm confirms, on the one hand, qualitatively the assumption made above about the temperature dependence of the effect, and is, on the other hand, an additional indication of the existence in SbSI of a critical point with the coordinates T = −40°C and P = 1500 atm.

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FIG. 1. The shift of the absorption edge of single-crystal SbSI in a field of 2 kV/cm as a function of the temperature for various hydrostatic pressures P in atm: 1 − 1, 2 − 400, 3 − 900, 4 − 1400, 5 − 1800, 6 − 2000.

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