HE 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 he anomalous shift of the absorption edge of the ferro-lectric SbSI under the influence of an electric field ap-lied in the direction of the spontaneous polarization of he crystal. The shift was towards shorter waves and id not depend on the direction of the external electric ield applied to the crystal. The sign of this effect urned out to be opposite to that of the Franz–Keldysh ffect, and its magnitude turned out to be larger by an rder of magnitude. The temperature dependence of the Kern–Harbeke effect exhibited a maximum near the Cu-rie temperature. The magnitude of the shift ΔE_g de-ended on the field linearly in the ferroelectric and uadratically in the paraelectric region. The maximum f the spectral distribution of the photocurrent in SbSI[3] vas similarly shifted under the influence of an external ield. Subsequently the same effect was observed in a eries of independent papers[4-6] in single crystals of BaTiO$_3$, the sign of the effect as well as the nature of ts field and temperature dependence turning out to be he same.

Thermodynamically the Kern–Harbeke effect can be lescribed in a way similar to the electro-optic effect in erroelectrics. According to [7] the width of the forbid-len 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

$$E_g = E_{g0} + aP^2 + \dots \tag{1}$$

In the absence of an external field the quantity ΔE_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 ser-ies of papers.[8-10] For SbSI and BaTiO$_3$ 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 polari-zation:

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

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

$$\Delta E_g^E \approx \Delta E_g^0 + a\varepsilon EP / 2\pi. \tag{3}$$

Here ΔE_g^E is the magnitude of the Kern–Harbeke ef-fect, ΔE_g^0 is the magnitude of the spontaneous effect, E is the intensity of the external field, and ϵ is the di-electric 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 de-pendence 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 criti-cal 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 Ginz-burg,[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 ferroelec-tric SbSI indicated the existence of a triple point with the coordinates $T = -40°$ and $P = 1500$ atm, in the vi-cinity of which the line of first-order phase transitions goes over to the line of second-order phase transi-tions.[12-14] From this point of view it was of interest to investigate the Kern–Herbeke effect in SbSI in a suf-ficiently 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-