

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 $T = -40^\circ\text{C}$ are found.

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KERN^[1] and Harbeke^[2] have previously observed the anomalous shift of the absorption edge of the ferroelectric 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

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

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-Harbeke effect, one should according to Gähwiler^[6] understand P in (1) to be the sum of the spontaneous and induced polarization:

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

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

$$\Delta E_g^E \approx \Delta E_g^0 + a\epsilon EP / 2\pi. \quad (3)$$

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 $T = -40^\circ$ 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-Harbeke 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-