Physics

K. GULYAMOV, V. A. LYAKHOVITSKAYA, N. A. TIKHOMIROVA, V. M. FRIDKIN

1965

SovietRxiv

Abstract

Full Text

Physics

K. GULYAMOV, V. A. LYAKHOVITSKAYA, N. A. TIKHOMIROVA, V. M. FRIDKIN

AN ANOMALOUSLY LARGE EFFECT OF PRESSURE ON THE OPTICAL AND FERROELECTRIC PROPERTIES OF SbSJ SINGLE CRYSTALS

(Presented by Academician A. V. Shubnikov on 27 I 1965)

In a number of compounds of the type AVBVICVII, Merz and Nitsche with collaborators discovered simultaneously photoelectric and ferroelectric properties ([1−3]). The single crystals of SbSJ, belonging in the paraelectric phase to the rhombic-pyramidal class (space group D_{2h}^{16} ([2])), have been studied in the greatest detail. According to optical data ([4]), these crystals have a forbidden-band width of ~ 2 eV, exhibit a photocurrent maximum at the absorption edge $\lambda \sim 600$ mμ, and also have a large coefficient of the temperature change of the forbidden-band width $dE_g/dt \sim -15 \cdot 10^{-4}$ eV/deg ([2]). In our work ([5]) it was shown that the photocurrent carriers are electrons and that their drift mobility at room temperature is ~ 50 cm^2/V·sec. According to ([2]), SbSJ crystals exhibit a phase transition from the ferroelectric to the paraelectric region at a temperature of 22°. In the same work the dependence of the spontaneous polarization (in the direction of the c axis of the crystal) and of the dielectric permittivity in the region of the phase transition was studied.

In studying the optical properties of SbSJ, Kern ([6]) discovered an effect consisting in a shift of the long-wavelength edge of intrinsic absorption toward shorter wavelengths under the action of a constant electric field. Thus the sign of this effect proved to be opposite to the sign of the Keldysh–Franz effect and, moreover, its magnitude proved to be an order of magnitude larger ([6]). Subsequently Harbeke ([4]) showed that the shift of the intrinsic-absorption edge has a maximum at the Curie point $t_c = 22°$ and depends linearly on the field strength in the ferroelectric region and quadratically in the paraelectric region. From this it was suggested in ([4]) that this effect is due to uniaxial deformation of the crystal (extension along the ferroelectric axis c) as a result of the inverse piezoelectric effect. On the other hand, it is not difficult to see that this suggestion leads to an anomalously large value of the coefficient describing the dependence of the forbidden-band width of the crystal on the magnitude of the mechanical stress, dE_g/dp (E_g is the forbidden-band width, $p \equiv p_{33}$ is a component of the mechanical-stress tensor). Indeed, if one uses the values of the piezoelectric modulus $d_{33} \sim 6 \cdot 10^{-5}$ CGSE and the elastic modulus $C_{33}^D \sim 4 \cdot 10^{11}$ dyn/cm^2, measured earlier for SbSJ ([7]), then at a field strength of 2 kV/cm, $p_{33} \sim 150$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

kG/cm^2. According to ([4]), at this same value of the field strength near the Curie point the shift of the absorption edge is $\Delta\lambda \approx 90$ Å ($\Delta u \sim 3 \cdot 10^{-2}$ eV), in accordance with which $dE_g/dp \sim +2 \cdot 10^{-4}$ eV/atm. Thus, the suggestion of the authors of ([4,6]) concerning the piezoelectric nature of the shift of the intrinsic-absorption edge in SbSJ under the action of an electric field leads, in turn, to anomalously high values of the coefficient dE_g/dp. (According to literature data ([8]), this coefficient does not exceed 10^{-6}-10^{-5} eV/atm.)

To test this suggestion, in the present work the task was posed of directly measuring the value of dE_g/dp from the shift

the edge of the intrinsic absorption of SbSJ under the action of hydrostatic pressure. In this case the absorption edge should shift into the long-wavelength region (which corresponds to compression of the crystal along the ferroelectric axis c). If the assumption made in ([4,6]) corresponds to reality, then the value of dE_g/dp measured in this way (here p is hydrostatic pressure) should prove to be close in magnitude to the value calculated above, since according to ([7]) the elastic compliance coefficients s_{13} and s_{23} are small in comparison with s_{33}, or are opposite in sign. As will be shown below, the results of these measurements led to the discovery

Fig. 1. Change in the forbidden-band width of SbSJ single crystals with pressure. The initial section is characterized by an anomalously large coefficient

$$\frac{dE_g}{dp} \sim -(1.0 \pm 0.3) \cdot 10^{-4}\ \frac{\text{eV}}{\text{atm}}$$

Fig. 2. Dependence of the Curie temperature on pressure for SbSJ single crystals, characterized by an anomalously large coefficient

$$\frac{dt_c}{dp} \sim -(1.5 \pm 0.2) \cdot 10^{-2}\ \text{deg/atm}$$

in SbSJ single crystals of an anomalously large shift of the edge of intrinsic absorption and of the Curie point with pressure.

SbSJ crystals grown from the gas phase and having the shape of needles of size $1.5 \times 1.5 \times 20$ mm were investigated. Aquadag electrodes were applied to the ends of the needles. At atmospheric pressure the crystals had an absorption edge near

600 mμ (at $\sim 18^{\circ}$) and a Curie point of $\sim 23.8^{\circ}$. The measurements were carried out in a high-pressure multiplier equipped with an electrical lead-in and a quartz window (for details of the method see ([9,10])). The pressure was transmitted by isopentane and measured with a manganin resistance manometer with an accuracy of up to 50 atm. At a specified pressure, the spectral distribution of the photocurrent was recorded using a UM-2 monochromator and an EMU-4 electrometer. The shift of the absorption edge with pressure was fixed from the shift of the photocurrent maximum ([11]).

As was expected, the sign of the effect proved to be opposite to the sign of the effect in the experiments of Kern and Harbeke ([4,6]), i.e., with pressure the absorption edge shifted into the long-wavelength region (the forbidden-band width decreased with pressure). Figure 1 presents the dependence of the change in the forbidden-band width ΔE_g on the pressure p in the range from 1 to 10^4 atm, taken at a temperature of 18°. In the region of low pressures (up to 250 atm) a considerable shift ($\Delta\lambda \sim 75$ Å) of the absorption edge with pressure was found (the section is indicated by a dashed line), after which saturation was observed over a broad pressure range. The initial section of this dependence corresponds to a coefficient

$$dE_g/dp \sim -(1.0 \pm 0.3)10^{-4} \text{ eV/atm},$$

and for the saturation section

$$dE_g/dp < 10^{-6} \text{ eV/atm},$$

i.e., the initial section corresponds to an anomalously large change in the forbidden-band width of SbSJ with pressure. The coefficient dE_g/dp measured by us for SbSJ in this section is almost two orders of magnitude larger than in other crystals for which analogous measurements had previously been carried out. The magnitude of the anomalously large coefficient dE_g/dp was found, in absolute value, to be close to that calculated above. To explain the presence on the curve of the dependence of the forbidden-band width of SbSJ on pressure of a saturation section, we assumed that in the process of increasing pressure there occurs a simultaneous shift of the Curie point toward

toward lower temperatures. In this case, saturation can be explained by the transition of the crystal from the ferroelectric region to the paraelectric region, where the value of the coefficient dE_g/dp is lower by at least 2 orders of magnitude. Since the transition to the saturation region occurs in the low-pressure range (up to 10^3 atm, see Fig. 1), this explanation, in turn, presupposed for SbSJ an anomalously large shift of the Curie point with pressure (according to the data of Fig. 1, not less than $0.6 \cdot 10^{-2}$ deg/atm).

To verify this supposition, we investigated for SbSJ the dependence of the Curie temperature t_C on pressure. The temperature of the phase transition was recorded by the usual method of taking the hysteresis loop (by the disappearance of the loop). The dependence presented in Fig. 2 in fact revealed for SbSJ an anomalously large shift of the Curie point with pressure, the shift occurring toward lower temperatures. According to these data, for SbSJ

$$dt_C/dp \sim -(1.5 \pm 0.2) \cdot 10^{-2} \text{ deg/atm},$$

and, consequently, it is an order of magnitude larger than in other ferroelectrics studied so far. It is also essential that, according to the data presented in Fig. 2, at a temperature of 18° the transition of the crystal to the paraelectric region should occur already at a pressure of 400 atm, which agrees with the data of Fig. 1. (Therefore the transition to saturation in Fig. 1 is marked precisely in this region.) Thus, it may be considered established that the presence on the curve of Fig. 1 of two regions (with an anomalously large and a normal coefficient dE_g/dp) is due to a phase transition in SbSJ. The results obtained also indicate that at lower temperatures (far from the phase-transition point) the transition to saturation on the curve of Fig. 1 should shift into the region of higher pressures, which may make it possible to obtain a large shift of the absorption band of SbSJ. These measurements are being continued by us.

Thus, there is no doubt that the shift of the absorption edge in SbSJ under the action of an electric field observed in ([4], [6]) is due to the anomalously strong dependence of the width of the forbidden band of the crystal on pressure. The latter dependence, as well as the anomalously large shift of the Curie temperature with pressure, are of independent interest.

Institute of Crystallography
Academy of Sciences of the USSR

Received
27 I 1965

REFERENCES

1. R. Nitsche, W. J. Merz, J. Phys. Chem. Solids, **13**, 154 (1960).
2. E. Fatuzzo, G. Harbeke, W. J. Merz, R. Nitsche, H. Roetschi, W. Ruppel, Phys. Rev., **127**, 6, 2036 (1962).
3. R. Nitsche, H. Roetschi, P. Wild, Appl. Phys. Letters, **4**, 12, 210 (1964).
4. G. Harbeke, J. Phys. Chem. Solids, **24**, 7, 957 (1963).
5. L. M. Belyaev, I. S. Zheludev, V. A. Lyakhovitskaya, V. N. Nosov, V. V. Pospelov, I. M. Silvestrova, V. M. Fridkin, Abstracts of Reports, IV All-Union Conference on Ferroelectrics in Rostov, 1964.

6. R. Kern, J. Phys. Chem. Solids, **23**, 249 (1962).

7. D. Berlincourt, H. Jaffe et al., Appl. Phys. Letters, **4**, 61 (1964).

8. R. Bube, Photoconductivity of Solids, IL, ch. VII, 1962.

9. G. P. Shakhovskoi, N. A. Tikhomirova, Instruments and Experimental Techniques, **6**, 194 (1963).

10. N. A. Tikhomirova, V. M. Fridkin, Fiz. Tverd. Tela, **5**, 2709, 1963.

11. V. M. Fridkin, N. A. Tikhomirova, Physica Status Solidi, **4**, No. 6 (1964).

Note: Figure translations are in progress. See original paper for figures.