ABSORPTION EDGE IN THE SEMICONDUCTING FERROELECTRICS SbSBr, BiSBr, AND SbSI

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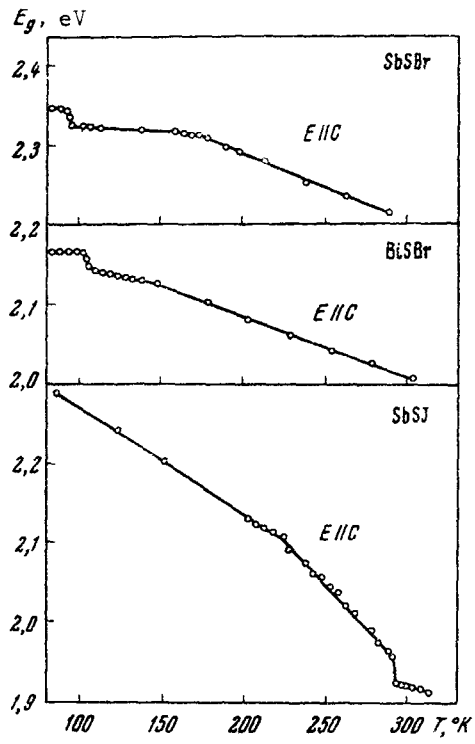
Nitsche and his co-workers [1] have recently synthesized several compounds of groups V, VI, and VII, and have shown that they are simultaneously ferroelectric and semiconducting. They have also investigated [2,3] the photoconductivity and the ferroelectric properties of these compounds. Harbeke [4] and Fridkin et al. [5] investigated the intrinsic absorption in SbSI. They have shown that the ferroelectric phase transition in SbSI is accompanied by a jump of the intrinsic absorption edge (or respectively the width of the forbidden band) of ~0.06 eV, and by a change in the coefficient of the temperature dependence of the width of the forbidden band (for SbSI $dE_g/dT \approx -22 \times 10^{-4}$ eV/deg in the ferroelectric region and $dE_g/dT \approx -9 \times 10^{-4}$ eV/deg in the paraelectric region [4,5]). One of us has shown [6] on the basis of a thermodynamic analysis that this anomaly is characteristic of first-order phase transitions. A jump in the position of the intrinsic-absorption edge was subsequently observed in barium titanate, which undergoes a ferroelectric first-order phase transition from the tetragonal to the cubic modification [7].

It seemed of interest to investigate the behavior of the intrinsic absorption edge for a series of ferroelectrics of groups V, VI, and VII, which undergo low-temperature phase transitions. To this end we undertook here an investigation of the optical absorption in SbSBr, BiSBr, and SbSI in the interval from room temperature to -190°C. According to the published data [3], SbSBr undergoes a phase transition at -180°C, and BiSBr at -170°C; the character of the transition has not been established.

We investigated SbSBr, BiSBr, and SbSI single crystals grown from the gas phase. The SbSBr and BiSBr crystals were in the form of thin needles (transverse dimension not larger than 0.1 mm, length 10 - 15 mm). The SbSI single crystals were larger (10 x 1 x 1 mm). All the investigated single crystals were rhombo-dipyramidal. The direction of the spontaneous polarization coincided with the twofold axis parallel to the needle axis. For all the foregoing crystals, we investigated the optical absorption in polarized light in the range from +40°C to -190°C. The measurements were made in a vacuum cryostat cooled with liquid nitrogen. The sample temperature was varied with the aid of an oven, and the temperature was maintained accurate to 0.2°C by an electronic stabilization circuit. The transmission spectra were investigated with a UM-2 monochromator and an FEU-19A photomultiplier. The temperature was measured with a copper-constantan thermocouple.

The figure shows the temperature dependence of the width of the forbidden band E_g of single-crystal SbSBr, BiSBr, and SbSI. The forbidden-band width was determined from the intrinsic-absorption edge, which was processed beforehand to determine the character of the transition. The relation $\alpha^{\frac{1}{2}} \sim h\nu$ (α - absorption coefficient, $h\nu$ - photon energy) was satisfied for all three crystals in the entire investigated temperature interval, thus pointing to the indirect character of the transitions. In addition, the $\alpha^{\frac{1}{2}}$ vs. $h\nu$ curve of SbSBr had two straight-line sections, connected apparently with the absorption and emission of a phonon. The phonon energy determined from the difference between the energies corresponding to the two sections turned out to be 0.03 eV and independent of the temperature.



None of the three crystals exhibited a change in the shape of the absorption edge during the phase transition. These measurements were made in polarized light. The figure shows the results for $E \parallel C$. The width of the forbidden band for $E \parallel C$ was smaller than for $E \perp C$ for all the investigated crystals (Harbeke [4] obtained a similar result for SbSI).

As seen from the figure, a jump in the width of the forbidden band takes place in the region of the phase transition of all the ferroelectrics. For SbSBr, this jump is observed at -180°C and amounts to 0.02 eV when $E \parallel C$ and 0.03 eV when $E \perp C$. A striking fact is the jump in the temperature coefficient of the forbidden-band width observed in the case of SbSBr in the paraelectric region at a temperature -103°C, amounting to $\Delta(dE_g/dT) \simeq 8 \times 10^{-4}$ eV/deg, and apparently due to a second-order phase transition.

As seen from the figure, the temperature dependence of E_g of BiSBr also exhibits a jump. The jump is equal to ~0.02 eV (for $E \parallel C$) and occurs at a temperature (-170°C) corresponding to the previously observed ferroelectric phase transition in BiSBr [3]. Besides, in BiSBr, as in SbSBr, a kink appears in the temperature dependence of E_g in the paraelectric region near -140°C (the magnitude of the jump is $\Delta(dE_g/dT) \simeq 4 \times 10^{-4}$ eV/deg), apparently demonstrating the existence of a second-order phase transition. In addition, at -170 and -140°C, both phase transitions become manifest in the dependence of ln i on the reciprocal of the temperature (i = dark current), which we investigated and which exhibits in the case of BiSBr a kink near -170 and -136°C. No measurements were made of the temperature dependence of the electric conductivity of SbSBr.

As to the analogous results obtained for SbSI (see the figure), they confirm qualitatively the previously published data [4,5]. At the temperature t ≃ 22°C at which the crystal goes over from the ferroelectric into the paraelectric region, the width of the forbidden band de-

creases jumpwise by ~0.03 eV.

In addition, for SbSI in the ferroelectric region (just as for SbSBr and BiSBr in the paraelectric region), an appreciable kink in the temperature dependence of the width of the forbidden band E_g is observed at -43°C. Above t = -43°C, $dE_g/dT \simeq -30 \times 10^{-4}$ eV/deg (which agrees with the data of [4,5]), and below this temperature $dE_g/dT \simeq -12 \times 10^{-4}$ eV/deg. It is possible that a second-order phase transition takes place in this case.

The results shown in the figure not only confirm the existence of ferroelectric phase transitions in SbSBr, BiSBr, and SbSI at -180, -170, and +22°C respectively, but indicate unambiguously their character (first-order transitions). In addition to these transitions singularities in the temperature dependence of the width of the forbidden band are observed in the paraelectric region for SbSBr and BiSBr and in the ferroelectric region for SbSI. These are apparently evidence of the existence of second-order phase transitions in these crystals.

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SPIN MAGNETOPHONON AND MAGNETOPHONON OSCILLATIONS OF MAGNETORESISTANCE IN n-InAs

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We have shown earlier [1,2] theoretically and experimentally (for n-InSb) that inelastic resonant scattering of electrons by optical phonons with spin flip (spin-magnetophonon resonance - SMR) causes the appearance of oscillations of transverse and longitudinal magnetoresistance (ρ_{xx} and ρ_{zz}). The resonance condition is

$$\epsilon_{N,S} - \epsilon_{k,S'} = \hbar\omega_0, \quad S \neq S', \tag{1}$$

where $\epsilon_{N,S}$ is the energy of the N-th Landau level with the given value of spin, ω_0 is the limiting frequency of the optical phonon, and S, S' = 1/2. When S = S' Eq. (1) describes the conditions for magnetophonon resonance (MPR) [3].

The minimum of ρ_{zz} observed in n-InAs at ~160 kG [4,5] is connected either with SMR