

# The optical transmittance of semiconducting $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions

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The experimental technique is described and the results presented of investigations of the optical transmittance of thin single-crystal plates of  $\text{Bi}_{1-x}\text{Sb}_x$  with  $10.3 \leq x \leq 18$  at.% in the range of wavelengths from 50 to 130  $\mu\text{m}$  at 4.2 K. Lattice-absorption bands were observed. The dependence of the refractive index  $n$  and of the optical width  $E_{G,\text{opt}}$  of the forbidden band on the antimony content was determined from the interference component of the transmission spectra and the fundamental absorption edge. For the indicated values of  $x$   $n$  varies from 11.8 to 13.7, and  $E_{G,\text{opt}}$  from 10.5 to 20 meV.

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## 1. INTRODUCTION

Among the narrow-gap semiconductor materials, the properties of the  $\text{Bi}_{1-x}\text{Sb}_x$  solid solutions attract special attention. This is a binary system which can now be made relatively reproducibly in the form of monocrystals of high purity with an electron concentration of  $n_{4,2\text{K}} \sim 10^{13} - 10^{14} \text{ cm}^{-3}$  and an electron mobility of  $\mu_{4,2\text{K}} \sim 10^6 - 10^7 \text{ cm}^2/\text{V} \cdot \text{s}$ .<sup>[1]</sup> The interest in this material is particularly linked with the fact that, as measurements of the galvanomagnetic characteristics have shown, the thermal width of the forbidden band is strongly dependent on the antimony content and can assume values in the range 0–25 meV (see, for example, the review<sup>[2]</sup>). To determine the parameters of the electronic band structure of BiSb it is essential to know the composition dependence of the energy gap between the extrema of the electron-hole branches of the spectrum at the characteristic points of the Brillouin zone. Optical investigations are one of the most direct routes to this end, since measurements of the optical width of the forbidden band should provide information on the energy gap at the point  $L$  in the Brillouin zone of  $\text{Bi}_{1-x}\text{Sb}_x$  over the whole range in which the semiconductor state exists.

The optical properties of BiSb have as yet been little studied.<sup>[3–7]</sup> Tichovolsky and Mavroides<sup>[3]</sup> investigated the magnetoreflexion of solid solutions of  $\text{Bi}_{1-x}\text{Sb}_x$  with  $n_{4,2\text{K}} \geq 10^{15} \text{ cm}^{-3}$  and  $x \leq 0.15$ . Determination of the gap at the point  $L$  from these measurements requires extrapolation of the obtained values to zero magnetic field and, as a result of the high concentration of free carriers, the results must be affected by the Burstein shift. The reflection spectra of  $\text{Bi}_{1-x}\text{Sb}_x$  ( $0.04 \leq x \leq 0.12$ ) were measured in the plasma-frequency range by Egorov and Kulakovskii<sup>[4]</sup> in the wavelength band 20–200  $\mu\text{m}$  at a temperature of 82 K. They obtained an estimate for the permittivity of BiSb at this temperature. In the literature<sup>[5]</sup> measurement of the dependence of the transmittance of  $\text{Bi}_{0.85}\text{Sb}_{0.15}$  on the magnetic field has been reported for the two wavelengths  $\lambda = 85.56$  and 118.6  $\mu\text{m}$ , and data have been given<sup>[6]</sup> for the temperature dependence of light absorption in BiSb near the edge of the fundamental band.

In the present work the results are presented of the

determination of the optical width of the forbidden band and of the refractive index of the BiSb solid solution from measurements of the optical transmission spectra. The  $\text{Bi}_{1-x}\text{Sb}_x$  samples with an antimony content of  $0.103 \leq x \leq 0.18$  were investigated in the wavelength range from the fundamental absorption edge up to  $\lambda = 130 \mu\text{m}$  at a temperature of 4.2 K. All the samples had an electron density  $n_{4,2\text{K}} \lesssim 10^{14} \text{ cm}^{-3}$ , except samples 2, 4, and 5,<sup>1)</sup> in which  $n_{4,2\text{K}} \gtrsim 10^{15} \text{ cm}^{-3}$ . Special features of the material under investigation, which impose specific requirements on the experimental procedure, are discussed.

## 2. SAMPLES AND MEASUREMENT TECHNIQUE

We used single crystals of BiSb obtained by the zone-leveiling method.<sup>[1,7,8]</sup> To measure the transmittance it was essential to have plates of 0.5 mm thickness or less. Attempts to obtain thin plates which were transparent in the infrared region of the spectrum by mechanical polishing or chemical etching did not give satisfactory results. We therefore prepared the samples by cleaving them from single crystals perpendicular to the trigonal axis. The thinnest plates (50  $\mu\text{m}$ ) were cleaved in liquid nitrogen. Because of the brittleness of the crystals it was very difficult to avoid the occurrence of cleavage steps, as a result of which individual regions of the plates may have different thicknesses. To take account of this in analyzing the transmission spectra, the distribution of thickness over the area of the plates was measured.

The composition of the samples was investigated by means of an electron-probe  $x$ -ray microanalyzer type JXA-5A. The conditions of analysis and the methods of introducing corrections are indicated in<sup>[9]</sup>. The composition of the plates intended for optical measurements was determined at separate points distributed over the whole cleavage surface ( $\sim 3 \times 5 \text{ mm}$ ) at distances of 1–2 mm from each other. Thick samples were analyzed on both sides. The relative accuracy in determining the atomic concentration of antimony (the root mean square error) on going from point to point over the surface of the sample amounted to  $\pm(1-2)\%$  of the measured value, and the accuracy of the absolute determinations of the antimony concentration in the samples was

$\pm 5\%$  of the measured value, i. e.,  $\Delta x = \pm 0.007$  for  $x = 0.15$ .

Plates intended for detailed transmission studies were initially selected for transparency in the 50–130  $\mu\text{m}$  wavelength region. We present here only results for samples in which the root-mean-square scatter in the antimony concentration over the surface lies within the limits 0.1–0.9 at. %.

The equipment used in the measurements included a long-wave grating monochromator type FIS-21, a cryostat, a narrow-band amplifier, and an automated system for gathering and processing data based on a WANG-2200 minicomputer.

The radiation was directed into the cryostat by a light-guide. The construction of the cryostat allowed the cold filters and the samples to be changed during the experiment. A photoresistor made of germanium doped with gallium was used to detect the radiation. The detector, the plates under investigation, and the filters were in liquid helium.

The sensitivity and differential resistance of the detector are strongly dependent on the intensity and spectral composition of the background radiation. It was found that this dependence was maintained for any of the filters which could be used to cut off the background. Moreover, the sensitivity of the detector varies markedly with change in the thickness of the plate under investigation. As a consequence of this, in determining the transmittance of BiSb plates it was necessary to measure the total and differential resistance of the detector every time and to calculate its actual sensitivity. This was relatively easy to do, provided the detector was protected from the part of the background radiation which causes intrinsic transitions in it.

We were faced with the problem of determining the basic optical characteristics of the material—the refractive index  $n$  and the absorption coefficient  $K$ —from the transmission spectrum  $T(\omega)$ . As is well known, to do this it is necessary for the measured transmission spectrum to have a region of weak absorption with marked interference. The standard formula for transmittance<sup>[10]</sup> can be written in the form<sup>[11]</sup>

$$T(\omega) = \frac{b}{1 + a^2 - 2a \cos(2nd\omega/c + \psi)} \quad (1)$$

$$= \frac{b(\omega)}{1 - a^2(\omega)} \left\{ 1 + 2 \sum_{j=1}^{\infty} a^j(\omega) \cos \left[ j \frac{2nd\omega}{c} + j\psi \right] \right\},$$

where  $a = Re^{-Kd}$ ,  $b = (1 - R)^2 e^{-Kd}$ ,  $R$  is the reflection coefficient,  $d$  is the thickness of the plate, and  $\psi$  is the phase shift. In the long-wave region, where  $R$  and  $K$  change little in the interference period, the addend in formula (1) describes the spectral behavior of the transmittance averaged over the interference period. Usually, after  $n$  has been determined experimentally from the interference frequency, the dependence of  $K$  on  $\omega$  is found from the average transmittance  $\langle T(\omega) \rangle$ . But this method cannot be used in determining the behavior of the absorption coefficient in a region in which it changes markedly over the interference period.

The use of the full formula (1), which includes all the harmonics of the interference, instead of  $\langle T(\omega) \rangle$  to calculate  $K(\omega)$  can also lead to errors at large values of  $R$ , since in this case high-frequency harmonics of the interference make a substantial contribution to the calculated value of  $T(\omega)$ , while a real measuring system (because of the finite resolving power of the spectrometer and other factors) only registers a limited number of interference harmonics. To avoid the necessity of explicitly taking account of factors which blur the interference, only that number of harmonics should be left in formula (1) which is present in the measured spectrum without appreciable distortions.<sup>2)</sup>

Account is taken of the nonuniformity of the plates in terms of thickness resulting from the presence of steps by introducing a relative weight  $p_i$  for each thickness such that

$$T(\omega) = \sum_{i=1}^N p_i T(\omega, d_i), \quad \sum_{i=1}^N p_i = 1. \quad (2)$$

### 3. RESULTS AND DISCUSSION

Figure 1 shows the detector spectral response curves, plotted point-by-point with an automatic measuring system, for the radiation passing through the plate under investigation (a) and for the incident radiation (b). Each curve contains about 1300 points. Besides the filters in the spectrometer, we used teflon (1.5 mm thick) at room temperature and a cold filter made of InSb. The ratio of curves (a) and (b) is the transmittance of the BiSb sample (curve (c) in Fig. 1). To find the absolute value of the transmittance, the method described above had to be used to take account of the detector-sensitivity variation caused by the difference in background radiation when recording curves (a) and (b). From the 1300 points of curve (c) we calculate the first 238 coefficients of the discrete Fourier cosine transform (the remaining Fourier coefficients were not computed as they only contained noise). The dependence of these coefficients on the number gives a sufficiently good representation of the Fourier transmission spectrum.<sup>[12]</sup> Convolution of the Fourier spectrum over different frequency intervals yields both the transmittance  $\langle T(\omega) \rangle$  averaged over the interference period and a transmittance curve  $T(\omega)$  contain-

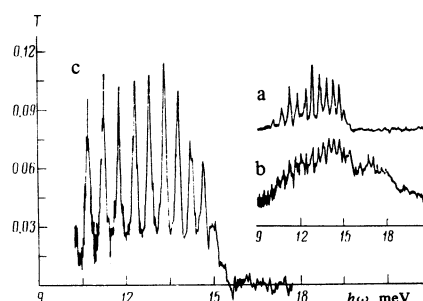


FIG. 1. Spectral photoresponse curves for the detector: a) to radiation passing through the plate under investigation; b) to incident radiation; c) BiSb transmittance. Curves (a) and (b) relate to sample No. 7 (average thickness 85  $\mu\text{m}$ ). Interference in the InSb filter is evident in curve (b).

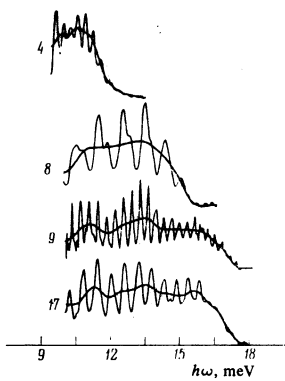


FIG. 2. Transmission spectra  $\langle T(\omega) \rangle$  and  $T(\omega)$  for  $\text{Bi}_{1-x}\text{Sb}_x$  samples. In this and the subsequent figures the numbers beside the curves are the sample numbers. The average thicknesses of the samples in  $\mu\text{m}$  are: 4–120, 8–50, 9–130, 17–89.

ing a fixed number of interference harmonics. Figure 2 shows the corresponding results for several samples. The reduction in noise in the curves of Fig. 2 compared with the original curves (see Fig. 1) was achieved by discarding the high-frequency part of the Fourier spectrum.<sup>[13]</sup>

In the region of the  $\langle T(\omega) \rangle$  curves of Fig. 2 in which the samples are transparent, a decrease can be seen in the transmittance around 10 and 12 meV and at  $\hbar\omega > 13.5$  meV. Evidence that this peculiarity is due to bulk absorption is provided by the decrease in the interference amplitude in these portions of the spectrum. Moreover, as is evident from Fig. 3, the depths of the dips in the transmittance of different samples is greater, the greater their thickness, and their position does not appreciably depend on the antimony content  $x$ . This leads us to conclude that the observed peculiarity is due to participation of the lattice in optical absorption. The lack of dependence of the position of the transmittance minima on  $x$  allows one to be guided by the known spectra of the lattice vibrations of pure bismuth<sup>[14,15]</sup> in analyzing our spectra. As is well known, single-phonon absorption of light is not possible in bismuth. Nor is single-phonon absorption observed in our BiSb samples. However, it turns out that phonon combinations that are close in energy to each of the dips observed by us can be chosen at the extremal points of the Brillouin zone (see Table I).

The refractive index was calculated from the interference frequency;

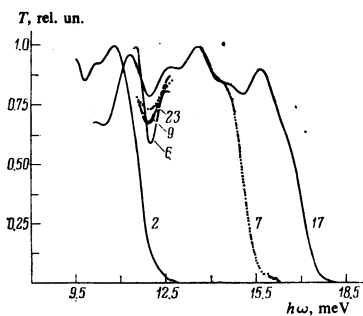


FIG. 3. Transmission spectra  $T(\omega)$  for samples with various thicknesses and compositions. The average thicknesses of the samples in  $\mu\text{m}$  are: 2–220, 6–210, 7–85, 9–130, 17–89, 22–110.

TABLE I. The minima in the transmittance of  $\text{Bi}_{1-x}\text{Sb}_x$  samples and the expected position of the two-phonon absorption bands in Bi.

Ascribed combinations of phonons	Expected positions of two-phonon absorption bands, meV	Observed positions of minima in transmittance of BiSb, meV
$\sigma_A^1(\Lambda') + \sigma_A^1(\Lambda')$ *	10.1	10.3
$\sigma_A^2(\Lambda') + \sigma_A^1(\Lambda')$	11.3	11.2
$\sigma_A^1(\Lambda') + \sigma_A^1(\Lambda')$	11.9	12.0
$\sigma_A^2(L) + \sigma_A^1(L)$	12.9	13.0
$\Lambda_A^1(T) + \Lambda_A^1(T)$	15.0	15.0
$\Sigma_A^2(X) + \Sigma_B^2(X)$	16.5	16.5
$\Lambda_A^2(T) + \Lambda_B^2(T)$	47.2	47.3
$\Lambda_A^3(T) + \Lambda_B^1(T)$	18.5	18.6
$\sigma_A^1(\Lambda') + \sigma_B^1(\Lambda')$	18.5	
$\sigma_A^1(\Lambda') + \sigma_B^2(\Lambda')$	18.5	

\*The primes denote the higher energy branches of the phonon dispersion curves in Fig. 2 of<sup>[14]</sup>.

$$nd = \tau \hbar c Q_1 = 619.9 Q_1. \quad (3)$$

Here  $d$  is the thickness of the plate in  $\mu\text{m}$  and  $Q_1$  is the frequency of the first interference harmonic. The values of  $n$  obtained in this way are shown in Fig. 4. It is evident that for the samples investigated by us the value of  $n$  lies in the range 11.8–13.7,<sup>3)</sup> which is higher than the refractive index of bismuth ( $10^{[16]} - 10.5^{[4]}$ ). It is interesting that the minimum in the  $n(x)$  curve corresponds approximately to that concentration of antimony at which the maximum in the thermal width of the forbidden band  $E_{G, \text{therm}}^{[9] 4), [17]}$  is observed.

From Fig. 3 it is evident that the edge of the optical transmission of BiSb is displaced into the region of higher photon energies with increasing antimony concentration. Currently established data on the band structure of  $\text{Bi}_{1-x}\text{Sb}_x$  (see, for example,<sup>[18–23]</sup>) allow one to suppose that the sharp increase in absorption in the photon energy region under consideration, for solid solutions of the composition used by us, is due to inclusion of allowed direct transitions at the  $L$  point in the Brillouin zone.<sup>[3]</sup> In that case the position of the absorption edge must be linked to the width of forbidden band at the  $L$  point and can be used to determine the composition dependence of this width.

Figure 5 shows curves of the spectral behavior of the absorption coefficient  $K(\omega)$  for a number of  $\text{Bi}_{1-x}\text{Sb}_x$  samples with different values of  $x$ . Generally speaking, one can attempt to use the dependence of the absorption coefficient on photon energy in the region of the intrinsic absorption edge to identify the type of the optical transitions and to determine unambiguously the width of the forbidden band from the spectral dependence of the

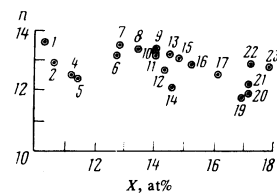


FIG. 4. Dependence of the refractive index of  $\text{Bi}_{1-x}\text{Sb}_x$  on the antimony concentration. The numbers beside the points are the numbers of the samples.

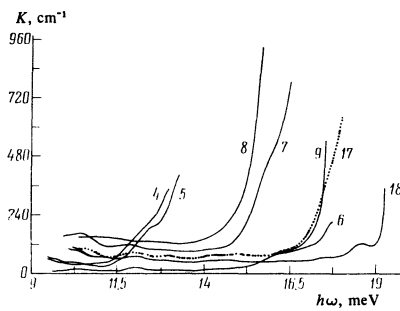


FIG. 5. The spectral behavior of the absorption coefficient of  $\text{Bi}_{1-x}\text{Sb}_x$  samples. The average thicknesses of the samples in  $\mu\text{m}$  are: 4-120, 5-100, 7-85, 6-210, 8-50, 9-130, 17-85, 18-140. In the range  $10.25 \leq \hbar\omega \leq 16.5$  meV curve (9) practically coincides with curve (17).

transmittance of the samples. To this end we made use of regression analysis to determine the parameters  $A$ ,  $N$ , and  $E_{G, \text{opt}}$  in the formula

$$K(\omega) = A(\hbar\omega - E_{G, \text{opt}})^N / \hbar\omega, \quad (4)$$

which describes the shape of the absorption edge in semiconductors that have been well studied. However, it was found that these parameters are strongly dependent on the choice of energy interval in which the regression analysis is carried out. In the interval of energies of the order of 0.5-1 meV the description of the absorption edge by formula (4) with  $N = \frac{3}{2}$  is good (see also<sup>[6]</sup>). In a wider photon energy interval the shape of the absorption edge cannot be described by a single law for all samples. Some of the  $K(\omega)$  curves shown in Figure 5 contain an exponential segment

$$K \sim K_0 \exp \frac{\hbar\omega - E_{G, \text{opt}}}{E_0},$$

which extends to a marked singularity at large  $K$ , while for other curves the dependence of  $K$  on  $\omega$  is steeper than exponential. For all the samples in which the absorption edge is described by an exponential dependence, the value of  $E_0$  is  $\sim 0.6$  meV.

Analysis of the difficulty which arose in describing the experimental dependence of  $K$  on  $\omega$  showed that the observed shape of the absorption edge may be made considerably more complicated by the uneven distribution of the antimony in the investigated plate and by the associated variation in the width of the forbidden band in different regions of the plate. A calculation for the case of smooth fluctuations in the composition of the plate<sup>[24]</sup> showed that when the variations in composition over the thickness are appreciable,  $N$  in formula (4) may be close to  $\frac{3}{2}$  or 1, depending on the nature of these variations. A theoretical analysis of the  $K(\omega)$  curve for the case where the variations in composition over the area of the plate are appreciable is made complicated by the large dimensions of the plate compared with the characteristic length of the variation of  $x$ . At the present time it would apparently be difficult to decrease the nonuniformity in the distribution of antimony in samples of the size needed to carry out the measurements. Moreover, other factors (e.g., nonuniformity in the distribution

of impurities) may also affect the shape of the absorption edge in samples similar to ours. We have therefore decided to reject any as yet unjustified complications in analyzing the dependence of  $K$  on  $\omega$  in the region of the intrinsic absorption edge, and for the purpose of determining the dependence of the optical width of the forbidden band  $E_{G, \text{opt}}$  on the composition we adopted the simple approximate method of determining  $E_{G, \text{opt}}$  from the intercept of the tangent to the  $K(\omega)$  curve at its point of greater curvature on the abscissa axis. A definition of  $E_{G, \text{opt}}$  in this way is of course arbitrary, but the values of  $E_{G, \text{opt}}$  so found give a satisfactory first approximation for ordinary semiconductors,<sup>[25]</sup> and in our case they allow one to characterize the variation in the position of the region of strong absorption from sample to sample.

Figure 6 shows the dependence of  $E_{G, \text{opt}}$  obtained in this way on the composition of the samples. It is evident that  $E_{G, \text{opt}}$  increases with the antimony concentration. The values of  $E_{G, \text{opt}}$  belonging to the different samples in the region  $0.13 < x < 0.17$  are distributed in Fig. 6 along two parallel straight lines displaced along the ordinate axis by  $\sim 1.3$  meV. The regularity of the arrangement of the points on the two straight lines prevents us from ascribing this effect to possible measurement errors. For values of  $x$  in the range  $12.8 \leq x \leq 18.0$  at.% we have  $\Delta E_{G, \text{opt}} / \Delta x \sim 0.6$  meV/at.%. This increase in  $E_{G, \text{opt}}$  with  $x$  is appreciably less than the value which follows from<sup>[3, 20, 21]</sup>, but it is very close to the result obtained in<sup>[22]</sup>. To assume that this dependence of  $E_{G, \text{opt}}$  on  $x$  is maintained at low values of  $x$  would mean that inversions of the symmetrical and antisymmetrical  $L$ -terms do not occur on going to pure bismuth. However, the data for samples with  $x$  lying in the range 10.5-11.5 at.% indicate a sharper dependence of  $E_{G, \text{opt}}$  on  $x$  at  $x \leq 12$  at.%.

We had at our disposal a batch of samples in which the concentration of antimony amounted to 11.5-12.5 at.%. All these samples proved to be opaque. Since they were cleaved from the same ingots as the transparent samples with different values of  $x$ , it is difficult to ascribe their opaqueness to technological factors. At the same time it should be noted that  $E_{G, \text{opt}}$  at  $x = 11.5$  at.%, is less than the optical phonon energy at the  $\Gamma$  point of the Brillouin zone in bismuth ( $\hbar\omega_{\text{LO}} = 12.4$  meV). Consequently,  $E_{G, \text{opt}}$  passes in the region  $11.5 \leq x \leq 12.8$  at.% through a value equal to  $\hbar\omega_{\text{LO}}$ . For samples with  $E_{G, \text{opt}} < \hbar\omega_{\text{LO}}$ , a step is observed in the dependence of  $K$  on  $\omega$  at a photon energy of  $\sim 12.4$  meV (Fig. 5).

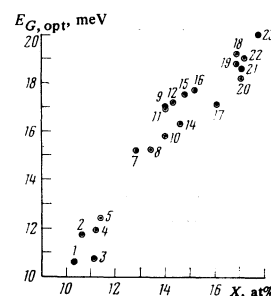


FIG. 6. Dependence of the optical width of the forbidden band of  $\text{Bi}_{1-x}\text{Sb}_x$  on antimony content. The numbers beside the points are the sample numbers.

It is well known that when the optical phonon energies are near the width of the forbidden band, phase transitions of the sublattice displacement type can arise. In analyzing such an electron-phonon interaction mechanism in ferroelectrics, it is usually assumed that only the phonon spectrum is modified in the phase transition, while the electron spectrum remains unaltered. However, according to the deformation theory of Abrikosov and Fal'kovskii,<sup>[27,28]</sup> in the case of bismuth and bismuth-antimony solid solutions, the parameters of the electron spectrum depend appreciably on the deformation that converts the unit cell of the cubic lattice into the bismuth or the bismuth-antimony cell. If, therefore, following Abrikosov, one assumes that on adding antimony to bismuth the energy spectrum of the electrons changes as a result of variation in the deformation of the unit cell, then it may be expected that either the value of the deformation at which the width of the forbidden band at the point  $L$  is equal to the optical phonon energy is unstable and is not realized, or that the electron spectrum undergoes appreciable modification at such values of  $x$ . The necessity of taking account of electron-phonon interaction in analyzing the electron spectrum of bismuth-antimony alloys has been pointed out by Gordyulin and Gor'kov.<sup>[29]</sup> The question as to what the final state will be in these conditions remains open.

The trend of the  $K(\omega)$  curve in the transparency region (for  $\hbar\omega < E_{G, opt}$ ) is identical for all the samples, but the value of the absorption coefficient measured by the method described above varies considerably from sample to sample, decreasing as a rule with increase in the thickness of the samples to  $K \sim 20 \text{ cm}^{-1}$  for a sample with  $d = 200 \text{ }\mu\text{m}$ . This fact alone indicates that in the region of photon energies under consideration the measured values of  $K(\omega)$  cannot be wholly attributed to bulk absorption. For samples in which the absorption edge is described by an exponential  $K(\omega)$  curve, the value of the absorption on extrapolating the exponent to  $\hbar\omega = E_{G, opt}$  proves to be of the order of  $K_0 \lesssim 1 \text{ cm}^{-1}$ . Apparently, the relatively large magnitudes of the measured values of  $K$  in the transparency region reflect both the influence of the scattering of light in the interior of samples on their transparency, and the state of their surface.

Thus, the account given above leads to the following conclusions:

1. Bismuth-antimony solid solutions are transparent in the infrared region of the spectrum for photon energies less than the energy gap between the  $L_a$  and  $L_s$  terms.

2. The refractive index of solid solutions with  $10.3 \leq x < 18 \text{ at.}\%$  depends on the composition  $x$ . This dependence is nonmonotonic. The maximum of  $n(x)$  corresponds to the value of  $x$  at which a maximum is observed in the  $E_{G, therm}(x)$  curve.<sup>[9]</sup>

3. The optical width of the forbidden band  $E_{G, opt}$  increases with  $x$  at a rate of  $\sim 0.6 \text{ meV/at.}\%$ .

4. Peculiarities (dips) in the transmission spectra can be seen, and their positions on the photon energy scale do not depend on the antimony content of the sam-

ples and correspond to the expected positions of the two-phonon absorption bands.

5. Samples containing antimony in quantities from 11.5 to 12.5 at.% are opaque in the entire region of the spectrum investigated ( $9 \leq \hbar\omega \leq 20 \text{ meV}$ ). The anticipated value of the optical width of the forbidden band for these samples is close to the longitudinal optical phonon energy in bismuth. It may be expected that in these circumstances the corresponding configuration of the unit cell of the bismuth-antimony solid solution is unstable, this being due to the opaqueness of such samples.

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<sup>1)</sup> These samples were obtained from Professor R. Herrmann's laboratory (Berlin University, German Democratic Republic).

<sup>2)</sup> From formula (1) it follows that a suitable criterion is the relationship  $A_1 A_j \approx 2 A_0 A_{j+1}$ , where  $A_0$  is a constant component in the Fourier transmission spectrum, and  $A_j$  is the amplitude of the  $j$ -th interference harmonic ( $j \geq 1$ ).

<sup>3)</sup> The values of  $n$  given in<sup>[6]</sup> are too high because the uneven plate thickness was not taken into account in their calculation.

<sup>4)</sup> We are grateful to the authors of<sup>[9]</sup> for giving us an opportunity to familiarize ourselves with the results of their work before its publication.

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## Investigation of phase transition in $\text{Qn}(\text{TCNQ})_2$ by the nuclear magnetic resonance method

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The temperature dependences of the paramagnetic shifts and of the line widths of proton resonance in  $\text{Qn}(\text{TCNQ})_2$  are investigated in the temperature interval 1.6-78 K in a magnetic field 47.4 kOe. The observed nonmonotonic dependence of the paramagnetic shift on the temperature indicates that a restructuring due to a phase transition takes place in the electron system of the complex near 10 K.

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### 1. INTRODUCTION

By now there is practically no doubt that at temperatures above 20-30 K the quasi-one-dimensional electron system of the complex<sup>[1]</sup>  $\text{Qn}(\text{TCNQ})_2$  is in a metallic state that becomes possibly stabilized because of the presence of an internal structural disorder due to the random packing of the asymmetrical cations. In particular, the temperature dependence of the conductivity and of the dielectric constant of this complex can be described quite satisfactorily within the framework of the single-electron theory that takes into account the joint influence of the disorder and of the phonons on the kinetics of a one-dimensional metal.<sup>[1]</sup>

At the same time, an analysis of the unusual low-temperature magnetic properties of the complex<sup>[2,3]</sup> has led to the conclusion that it can undergo a phase transition, in the region 10-20 K, from the state of a one-dimensional disordered metal into the state of a one-dimensional disordered dielectric of the Mott type. The subsequent study of the temperature dependence of the heat

capacity of the complex<sup>[4]</sup> has revealed at 14 K a heat-capacity jump whose existence and magnitude favor the foregoing conclusion.

To obtain more detailed information on the character of the low-temperature phase transition in  $\text{Qn}(\text{TCNQ})_2$ , we have investigated the behavior of the proton magnetic resonance lines in this compound in the temperature interval 1.6-78 K. In view of the smallness of the electron-proton hyperfine interaction constant in the TCNQ molecule and the smallness of the paramagnetic susceptibility of the complex, the measurements were made in fields of the order of 50 kOe to obtain measurable paramagnetic line shifts.

### 2. MEASUREMENT PROCEDURE

We used the simplest NMR spectrometer variant. The main magnetic field, 47376.75 Oe, was produced with a superconducting solenoid operating in the short-circuit regime. The sample was a pellet of 5 mm diameter and 5 mm length. The inhomogeneity of the field