SOVIET PHYSICS JETP VOLUME 20, NUMBER 2 FEBRUARY, 1965

OPTICAL PROPERTIES OF BISMUTH AND ANTIMONY IN THE INFRARED REGION OF THE SPECTRUM AT LOW TEMPERATURES

E. V. POTAPOV

Institute for Physico-technical and Radio Measurements

Submitted to JETP editor March 19, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 47, 464-472 (August, 1964)

Measurements were made of the optical constants n and κ - the refractive index and the absorption index - of bulk polycrystalline samples of Bi, Sb, Bi + 0.5% Te. The measurements were carried out by the absorption method in the wavelength range 1—14 μ at 2.5°K. The real and imaginary components of the permittivity ϵ were calculated and compared with Abrikosov's theory.[2] It is shown that in the case of Bi + 0.05% Te the behavior of Re ϵ and Im ϵ differs little from the behavior of the corresponding quantities for Sb; this similarity is due to the same carrier density in the Bi alloy and in Sb.

THE optical properties of metals are completely represented by the complex permittivity ϵ, which is related to the refractive index n and the absorption index κ by the following dependence [1]

$$\varepsilon(\omega) = [n(\omega) - i\kappa(\omega)]^2, \tag{1}$$

where ω is the angular frequency of the incident light. For metals of the Bi type, the optical properties in the infrared are determined not only by the free carriers in the conduction band but also by the carriers whose energy is considerably different from the Fermi energy.[1)]

Recently, Abrikosov [2] put forward a theory of the dependence of the permittivity of these metals on the frequency of incident light for a wide range of energies of light quanta. According to this theory, for frequencies

$$\omega \ll |\gamma| \tag{2}$$

(where $|\gamma| \approx 0.01$—0.1 eV is a parameter which represents the deviation of the Bi lattice from cubic; this quantity corresponds to the frequency of direct interband transitions) we can write the following expression for the real component of the permittivity:[2)]

$$\mathrm{Re}\,\varepsilon = \varepsilon_0 - \Omega^2 / \omega^2. \tag{3}$$

Here the first term, ϵ_0, represents virtual interband transitions and is constant ($\epsilon_0 = 100$) at the frequencies considered here; the second term represents transitions within bands; $\Omega \approx E_F$, where E_F is the Fermi energy. The imaginary component of the permittivity is small (≈ 1 at these frequencies).

When the incident frequency is increased to

$$\omega \sim |\gamma| \tag{4}$$

the expression (3) retains its previous form but Re ϵ changes its sign and becomes negative while Im ϵ increases. At these frequencies, real interband transitions begin to be important.

On further increase of ω when

$$\omega \gg |\gamma|, \tag{5}$$

we have

$$\mathrm{Re}\,\varepsilon \approx -(E_0 / \omega)^2, \tag{6}$$

where $E_0 \approx 0.1$—1 eV, and Im ϵ decreases rapidly in accordance with the law Im $\epsilon \propto E_0^2\gamma^2/\omega^4$.

Since, at present, we do not know the numerical values of all the parameters occurring in Abrikosov's theory, we shall make only a qualitative comparison of the experimental values of n and κ for Bi and Sb with the results of this theory. The experimental results were obtained for polycrystalline samples and, therefore, the comparison is carried out for the isotropic case.

MEASUREMENT METHOD

Measurements were made of the absorption of linearly polarized light in the wavelength range 1—14 μ incident on the samples at an angle $\psi = 70°$. This method was used previously by the present author.[3] However, in the present work,

---

[1)] The Fermi energy for Bi is $\sim 3 \times 10^{-14}$ erg, which corresponds to wavelengths of ~ 66 μ.

[2)] Formula (3) applies to polycrystals. In the case of single crystals, ϵ is a tensor, and then $\mathrm{Re}\,\epsilon_{ik} = \epsilon_{0ik} - \Omega_{ik}^2\omega^{-2}$.

in contrast to that just cited, the adiabatic conditions were replaced by isothermal. A similar method was used by Nanney[4] and Biondi.[5]

An electrically heated Silit rod was used as the source of light. The optical dispersion system consisted of a monochromator with a Wadsworth system and an NaCl prism. The polarizer comprised six free selenium films set at an angle of 70° to the light beam.[6]

The sample was placed in the vacuum part of a metal cryostat.[7] The detailed arrangement in the cryostat is shown in Fig. 1. The sample S was fixed in a special copper holder by means of screw 1. To improve the thermal contact of the holder with the sample, the back of the sample was soldered to the holder at two points. The same holder carried a helix H_1, which acted as a black body. The positions of the sample and the helix (the view from below) are shown in Fig. 1 on the right. A bronze resistance thermometer T_1 was soldered to the holder from below. The holder was attached to a copper plate 2 by means of a tube 3 made of stainless steel. A copper wire 4 was used to conduct heat. The plate 2 was connected to a liquid helium bath by means of a thick copper rod. Above the sample S and the helix H_1, a separate heat conductor carried another helix H_2 with a thermometer T_2. The light from the monochromator reached simultaneously the sample and the left-hand aperture in the helix H_2. The absorption coefficient was determined from the ratio of the temperatures to which the sample and the helix H_2 were heated by the incident radiation. Since the heat capacities of these two parts were not identical, it was necessary to determine a correction factor. For this purpose, light was directed simultaneously to the helix H_1 and the right-hand aperture in the helix H_2. The ratio of temperatures due to radiant heating in this case gave a correction factor for the determination of the absorption coefficient. The change in the thermometer resistance was measured with a dc potentiometer and a sensitive galvanometer. The deflection of the light spot of the galvanometer was recorded with an automatic recording potentiometer.[8] Instead of a galvanometer, a photomultiplier F16 with an automatic recorder was also used. The sensitivity of the circuit was 10^{-8} W.

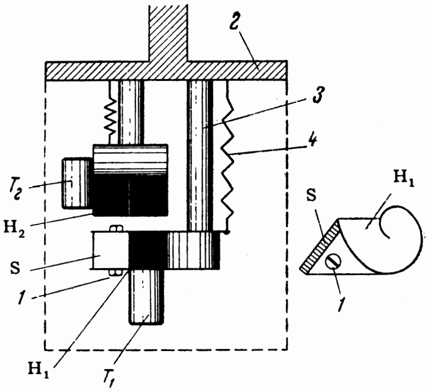

FIG. 1. Location of the sample (S) and helices (H) in a cryostat (view from the direction of the light beam; notation explained in text).

The low sensitivity of the system made it possible to carry out measurements only on metals which had a sufficiently high absorption coefficient. However, the simplicity of the measurements and the ability to determine the optical constants of bulk metals made this method fully acceptable for studies of Bi-type metals.

The reliability of the instrument was checked by measuring the absorption coefficient for light incident normally on electrolytically polished copper. In the wavelength region 2–5 μ, an absorption coefficient of ≈ 0.5% was obtained. This value agreed well with Biondi's data.[5]

Using light linearly polarized in the plane of incidence and then light polarized at right angles to the plane of incidence, we determined two absorption coefficients: A_p and A_s. From these two measurements, the values of n and κ were calculated using the formulas

$$1 - A_s = r_s = \frac{a^2 + b^2 - 2a\cos\varphi + \cos^2\varphi}{a^2 + b^2 + 2a\cos\varphi + \cos^2\varphi},$$

$$1 - A_p = r_p = \frac{a^2 + b^2 - 2a\sin\varphi\,\mathrm{tg}\,\varphi + \sin^2\varphi\,\mathrm{tg}^2\varphi}{a^2 + b^2 + 2a\sin\varphi\,\mathrm{tg}\,\varphi + \sin^2\varphi\,\mathrm{tg}^2\varphi}\, r_s, \tag{7*}$$

$$2a^2 = [(n^2 - \varkappa^2 - \sin^2\varphi)^2 + 4n^2\varkappa^2]^{1/2} + (n^2 - \varkappa^2 - \sin^2\varphi),$$

$$2b^2 = [(n^2 - \varkappa^2 - \sin^2\varphi)^2 + 4n^2\varkappa^2]^{1/2} - (n^2 - \varkappa^2 - \sin^2\varphi). \tag{7a}$$

In the present work, a graphical method was used to determine n and κ.

The accuracy of the determination of r_p and r_s was governed only by the scatter of the experimental points due to various disturbances. The average scatter of these points in measurements of r_p and r_s represented an experimental error of 1.5–2%. In the calculations of n and κ, the error rose markedly and amounted approximately to 10% for n and about 15% for κ.

SAMPLES

The sample of pure Bi was in the form of a

---

*tg = tan.

Optical constants of bismuth and antimony

λ, μ	Bi		Bi + 0,05% Te		Bi + 0,5% Te		Sb	
	n	κ	n	κ	n	κ	n	κ
1	1.7	3.3	1.5	2.6	1.6	2,6	2,8	4,5
2	2,0	3,2	1.8	2.8	2,0	2,8	3,4	4,4
3	2.1	3.3	2,0	2,9	2,4	2,9	4,0	4,3
4	2.2	3,4	2.2	3,0	2.7	3,0	4,4	4,1
5	2.3	3,4	2,3	3,0	2,8	2,9	4,8	4,0
6	2,4	3,5	2.4	3,1	2,9	2,6	5,0	4,0
7	2,4	3,6	2.5	3,1	2,9	2,2	5,1	3,9
8	2,5	3,7	2.8	3,1	2,7	1,9	4,9	3,9
9	2.5	3,9	3.2	3,1	2,0	1,8	4,4	3,8
10	2,6	4,0	3.7	3,0	1.2	2,0	2,0	3,9
11	2,9	4.1	3.5	2,8	0.8	2,4	2,0	5,0
12	3,8	4,3	2.4	2.4	0,6	3,0	6,0	9,0
13	5,6	4,4	1.7	2,0				
14			1.5	2,1				

polycrystal measuring 5 × 16 mm and 2 mm thick. It was prepared in vacuum by pouring out spectroscopically pure "Hilger" Bi, subjected to zone purification on a glass plate; this was followed by electrolytic polishing. The ratio of the resistance of the sample at room temperature and at liquid helium temperature was ρ (300°K) $/\rho$ (4.2°K) = 130.

The Sb sample had the following composition: 99.7 Sb + 0.02% Ca + 0.01% Mg. In its dimensions and method of preparation it was identical with the Bi sample, except for electrolytic polishing. The cast Sb sample was polished only mechanically.

RESULTS OF MEASUREMENTS AND DISCUSSION

Bismuth. The measured values of r_p and r_s for the pure sample of Bi are shown in Fig. 2 as a function of the incident light wavelength.[3)] The calculated values of n and κ are shown in Fig. 3 (curves 1) and in the table. Figure 4 gives the values of Re ϵ and Im ϵ (curves 1).

Figure 5 gives the values of Re ϵ obtained by various authors. Curve 1 represents the data reported in the present work, curve 2 the data of Boyle and Brailsford, [9] obtained for a bulk single-crystal sample at T = 2°K. Boyle and Brailsford measured the transparency of Bi sample up to 40 μ thick in the wavelength range 70—20 μ. Curves 1 and 2 are, in the present author's opinion, two branches of the same curve (if we neglect the difference due to anisotropy), which join somewhere in the 15—20 μ region. This composite curve is similar to curves 3a and 3b obtained by Markov and Khaĭkin [10] for bulk polycrystalline samples at room temperature (curves

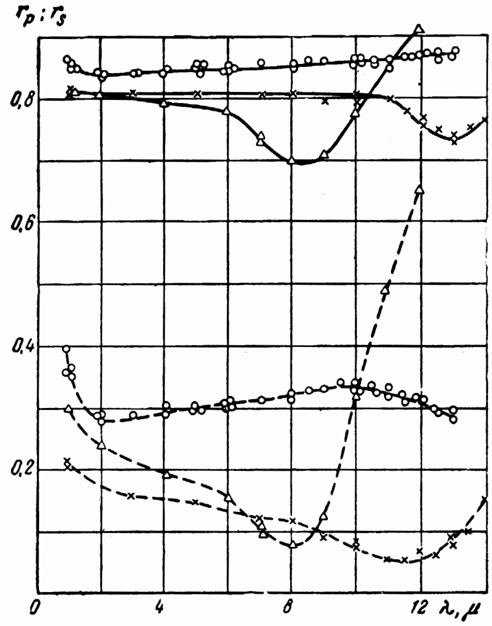

FIG. 2. Values of r_p (dashed curves) and r_s (continuous curves) as functions of the wavelength: o – pure Bi; × – Bi + 0.05% Te; △ – Bi + 0.5% Te.

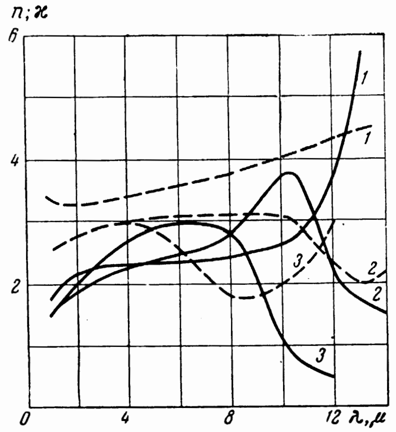

FIG. 3. Refractive index n (dashed curves) and absorption index κ (continuous curves) as functions of the wavelength: 1) Bi; 2) Bi + 0.05% Te; 3) Bi + 0.5% Te.

[3)] If the Bi sample is mechanically polished, the values of r_p remain the same as before but the values of r_s are reduced by 3%.

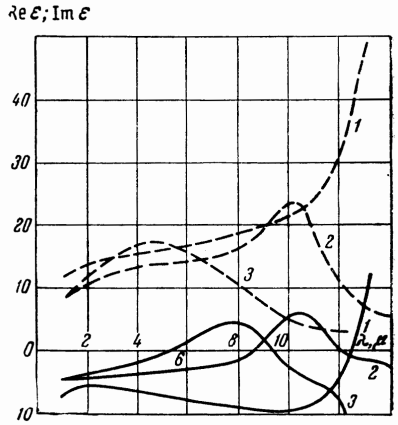

FIG. 4. Dependence of the values of Re $\epsilon = n^2 - \varkappa^2$ (continuous curves) and Im $\epsilon = 2n\varkappa$ (dashed curves) on the wavelength: 1) Bi; 2) Bi + 0.05% Te; 3) Bi + 0.5% Te.

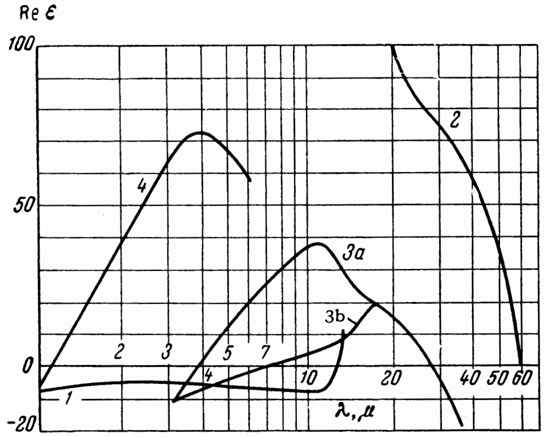

FIG. 5. Dependence of Re ε of Bi on the wavelength according to different authors: 1) present work; 2) according to[9]; 3) according to[10]; 4) according to[11].

3a and 3b represent two different samples). In the same Fig. 5, curve 4 represents Hodgson's results [11] for a bulk polycrystalline sample at room temperature.

As mentioned in Abrikosov's work [2], the variation of Re ε with the incident light wavelength reported in [9] is in qualitatively good agreement with the theory. According to the theory, the Re ε = f(λ) curve should have a maximum at $\lambda < 20\ \mu$ and then it should change sign at some value of λ. Indeed curve 1 and Fig. 5 shows that Re ε = 0 at λ = 13 μ and that Re $\epsilon < 0$ at $\lambda < 13\ \mu$.

As far as Im ε is concerned, the beginning of the absorption corresponding to the beginning of interband transitions was observed by Boyle and Brailsford [9] in the region $\lambda \approx 20\ \mu$. According to the theory, at shorter wavelengths Im ε should have a maximum and then it should decrease in accordance with the law Im $\epsilon \propto \lambda^4$. Curve 1 in Fig. 4 shows that the value of Im ε does indeed decrease rapidly at $\lambda < 13\ \mu$. However, it is not possible to determine the decay law of Im ε over such a narrow range of wavelengths. This range of wavelengths obviously corresponds to interband transitions in Bi.

We shall now return to the region where Bi is transparent and Eq. (3) is valid ($\lambda \approx 60\ \mu$). Since we may assume that the condition for plasma oscillations is independent of the directions of crystallographic axes, we can write this condition in the form

$$\mathrm{Re}\,\varepsilon = \varepsilon_0 - \Omega^2 / \omega_{pl}^2 = 0. \qquad (8)$$

This condition allows us to estimate the change in the frequency of plasma oscillations (ω_{pl}) on increase of the carrier density. Since the spectrum is in this case complex, this estimate can be obtained only for two limiting cases. At low carrier densities (for example in pure Bi), $\Omega^2 \propto N$ where N is the carrier density. At high values of N the variation is $\Omega \propto p_0 v$, where $p_0 \propto N^{1/3}$ and v = const. Consequently, at high values of N we have $\Omega^2 \propto N^{2/3}$. In [9] the condition (8) for pure Bi was satisfied at $\lambda_{\mathrm{pl}} = 63\ \mu$, which corresponds to the normal carrier density in Bi ($N = 5 \times 10^{17}\ \mathrm{cm}^{-3}$). The carrier density in Bi may be increased by adding a small amount of Te. In [12–14] it was shown that the addition of Te and Se to Bi increases the electron density approximately in the following proportion: one atom of Te gives one electron.[4)] Thus 0.05% Te (by weight) should increase the electron density of Bi by a factor of 40 and this, in turn, should increase the plasma oscillation frequency by a factor of $40^{1/2}$—$40^{1/3}$, and the condition (8) should now be satisfied at $\lambda \approx 10$—$18\ \mu$.

The present author measured the optical constants of pure Bi to which 0.05 or 0.5% Te had been added. The results of these measurements are shown in Fig. 2, which gives the dependence of r_p and r_s on the wavelength. The calculated values of n and κ are shown as a function of the wavelength in Fig. 3 (curves 2 and 3) and in the table. The values of Re ε and Im ε are given as a function of the wavelength in Fig. 4 (curves 2 and 3). From curve 2 (continuous) in Fig. 4, it is evident that the condition Re ε = 0 for Bi + 0.05%

[4)] 0.003% of Te by weight doubles the number of electrons in Bi and compensates holes. Further increase of the electron density is proportional to the amount of Te impurity. Pb impurity in Bi increases the number of holes but the effectiveness of Pb is about 33 times less than that of Te.[14]

Te is satisfied at $\lambda_{pl} = 12.5\ \mu$, which is in good agreement with the simple estimates carried out above. When the wavelength is reduced, Re ϵ exhibits a maximum and finally at $\lambda \approx 9\ \mu$ it changes its sign. Im ϵ (dashed curve 2 in Fig. 4) has a maximum in the region of $\lambda \approx 12\ \mu$, and, as in the case of pure Bi, it has a minimum at $\lambda \approx 60\ \mu$ although the latter is not as small as for Bi. Therefore, the Bi + 0.05% Te sample is not transparent in this region of wavelengths. We see that high electron densities (positive carriers - holes - are absent [14]) narrow the transparent region so much that in the case of Bi + 0.05% Te it disappears completely. At wavelengths $\lambda > 14\ \mu$, a region of purely "metallic" reflection begins immediately (as observed in Sb). The Fermi energy for Bi + 0.05% Te should also increase and should become of the same order as the Fermi energy of Sb.

For 0.5% Te in Bi (curves 3 in Fig. 4) these estimates are not valid since a high concentration of Te in Bi the solution may be inhomogeneous.5) These curves are given only for comparison.

Antimony. The experimental values of r_p and r_s for Sb are given as a function of the wavelength in Fig. 6. The calculated values of n and κ are given in Fig. 7 and in the table. To check the correct operation of the instrument, the same sample of Sb was used to make measurements employing normal incidence of light. The experimental points are shown in Fig. 6. The continuous curve drawn through these points represents the values calculated from n and κ using the formula

$$r_\perp = [(n-1)^2 + \varkappa^2] / [(n+1)^2 + \varkappa^2].$$

It is evident from the figure that the results of direct measurements are in good agreement with the calculations.

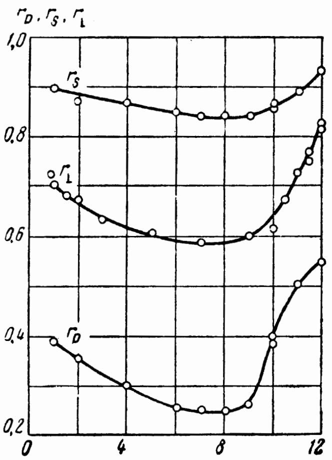

FIG. 6

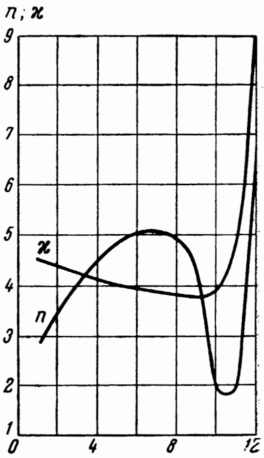

FIG. 7

FIG. 6. r_p, r_s, and $r_\perp$ for Sb as functions of the wavelength.

FIG. 7. Refractive index n and absorption index $\varkappa$ for Sb as functions of the wavelength.

Figure 8 shows the values of Re ϵ and Im ϵ for Sb as a function of the wavelength. These curves are very similar to the corresponding curves for Bi + 0.05% Te. This is explained by the fact that the free carrier densities in Sb and Bi + 0.05% Te are approximately equal.6)

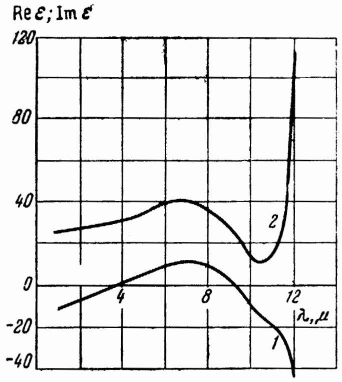

FIG. 8. Re ϵ (curve 1) and Im ϵ (curve 2) for Sb as functions of the wavelength.

If we determine the condition for plasma oscillations in Sb using the number of free carriers, as was done for Bi + 0.05% Te, we obtain $\lambda_{pl} \approx 7.5$–$15\ \mu$. Experiment gives $\lambda_{pl} = 9.3\ \mu$. Such an agreement can be regarded as fully satisfactory.

Near this region of wavelengths, Im ϵ has a minimum value, as in the case of Bi + 0.05% Te, and on reduction of the wavelength Im ϵ increases. This increase obviously corresponds to the beginning of interband transitions. Therefore, Sb is not transparent at these wavelengths. At $\lambda > 10.5\ \mu$, the value of Im ϵ increases sharply, which may be ascribed to the presence of two closely spaced absorption thresholds in Sb. However, the data of Nanney [4] indicate that in Sb at $\lambda > 12\ \mu$ the purely "metallic" absorption begins. Therefore, the sharp rise of Im ϵ is due to the scattering on impurities. (Similar behavior is found for Bi + 0.05% Te.)

---

5)The solid-solution region for Te in Bi extends up to ~0.2% Te (by weight).[15]

6)For Sb, this value is $N = 3.6 \times 10^{19}$ cm^{-3}; for Bi + 0.05% Te, the density is $N \sim 2 \times 10^{19}$ cm^{-3}.

Re ϵ for $\lambda > 10.5\ \mu$ becomes negative but its absolute value increases with increase of λ. This is due to the beginning of the "metallic" reflection, which is confirmed by Nanney's measurements.[4] At shorter wavelengths Re ϵ of Sb varies like Re ϵ of Bi + 0.05% Te and is in qualitative agreement with Abrikosov's theory.

In conclusion, the author expresses his gratitude to N. E. Alekseevskiĭ for his constant help in this work and for his valuable advice, to A. A. Abrikosov for consultation on and discussion of the present paper, and to A. Golovashkin and V. Starunov for their help in this work.

---

[1] V. L. Ginzburg and G. P. Motulevich, UFN **55**, 469 (1955).

[2] A. A. Abrikosov, JETP **44**, 2039 (1963), Soviet Phys. JETP **17**, 1372 (1963).

[3] N. E. Alekseevskiĭ and E. V. Potapov, JETP **33**, 283 (1957), Soviet Phys. JETP **6**, 183 (1958).

[4] C. Nanney, Phys. Rev. **129**, 109 (1963).

[5] M. A. Biondi, Phys. Rev. **102**, 964 (1956).

[6] Elliott, Ambrose, and Temple, J. Opt. Soc. Am. **38**, 212 (1948).

[7] E. V. Potapov, PTÉ No. 1, 192 (1962).

[8] G. I. Kosourov, PTÉ No. 3, 90 (1956).

[9] W. S. Boyle and A. D. Brailsford, Phys. Rev. **120**, 1943 (1960).

[10] M. N. Markov and A. S. Khaĭkin, Optika i spektroskopiya **9**, 487 (1960).

[11] J. N. Hodgson, Proc. Phys. Soc. (London) **B67**, 269 (1954).

[12] Alekseevskiĭ, Brandt, and Kostina, DAN SSSR **105**, 46 (1955).

[13] N. E. Alekseevskiĭ and T. I. Kostina, JETP 41, 1722 (1961), Soviet Phys. JETP **14**, 1225 (1962).

[14] N. B. Brandt, Tezisy Vsesoyuznogo soveshchaniya po fizike nizkikh temperatur (Abstracts of the All-Union Conference on Low-Temperature Physics), Moscow, 1963.

[15] Hansen and K. Anderko, Structure of Binary Alloys (Russ. Translation) Metallurgizdat, 1962, p. 365.

Translated by A. Tybulewicz
68