THE INFLUENCE OF ANTIMONY IMPURITIES ON THE DE HAAS-VAN ALPHEN EFFECT IN BISMUTH

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The de Haas-van Alphen effect has been studied in Bi-Sb alloys with Sb concentration of 0—1 wt. % over a temperature range 1.6—4.2°K, for various orientations of the magnetic field relative to the crystallographic axes of the specimens. It was established that the shape of the Fermi surface and the electron effective-mass tensor do not change in first approximation with increasing Sb concentration, and the surface itself contracts toward its center, preserving its shape. At 1 wt. % Sb, the volume of every ellipsoid of the Fermi surface decreases to nearly one half. The limiting Fermi energy and the electron concentration decrease with increasing Sb concentration, changing by 24 and 38 %, respectively, for 0.8 wt. % Sb. The Sb impurity produces a nearly linear increase in the constant part of the magnetic susceptibility, amounting to 10—12 percent at one wt. % Sb. A comparison of the results with data on the influence of elastic deformations on the de Haas-van Alphen effect shows that changes in the energy spectrum of the Bi electrons can be fully explained by the change of the lattice parameters of Bi under the influences of the Sb impurities.

INTRODUCTION

In spite of the fact that a rather large number of researches[1-5] have been devoted to a study of the electrical and magnetic properties of Bi-Sb alloys, there have been no data to date which make possible a direct determination of the character of the change in the energy spectrum of Bi electrons with increasing Sb concentration.

The assumption has been made by Jones[6] that elements forming solid solutions with Bi should be regarded as donors or acceptors, depending on their position in the periodic system. This point of view has been emphasized in a number of researches.[7,8,2,3] In particular, it was shown in[8] that the Pb impurity, which is regarded as an acceptor, actually produces a decrease in concentration of conduction electrons in Bi, and that this process is not linear. The rate of change of the electron concentration increases with increase in Pb concentration and ~55 Pb atoms are required on average for a unit change in the electron concentration.

From Jones' viewpoint, impurities should not change the electron structure of the elements in the same group of the periodic system, as Bi. However, in the study of the effect of Sb impurities on the quantum oscillations of the magnetic susceptibility of Bi,[2] a decrease was observed in the lowest frequency of oscillations, to which the work mentioned was confined. Since the frequency of the oscillations is proportional to the area S_m of the extremal cross section of the Fermi surface in the plane perpendicular to the direction of the magnetic field **H**,[9] and the Fermi surface for Bi electrons consists of three strongly anisotropic ellipsoids, the result obtained shows a decrease in the area of the smallest of the three principal cross sections of the ellipsoids with increasing Sb concentration.* Moreover, in the study of the electrical properties of Bi-Sb alloys[6] a significant change has been discovered in the energy spectrum of the Bi electrons upon addition of Sb. Neither of these effects can be explained on the basis of the Jones model, since Bi and Sb are both located in the same (fifth) group of the periodic table.

X-ray studies of the structure of Bi-Sb alloys,[11,5] representing a series of solid solutions, demonstrate that the Sb produces a significant change in the parameters of the Bi lattice, even in the region of low Sb concentrations (Fig. 1).

*The ellipsoids are located in quasi-momentum space in such a way that the minor axes are parallel to the binary axes, while the major axes are inclined at an angle of $\zeta = 5.5°$ to a plane perpendicular to the trigonal axis. The ellipsoids transform into one another upon rotation through an angle of 120° about the trigonal axis.[10]

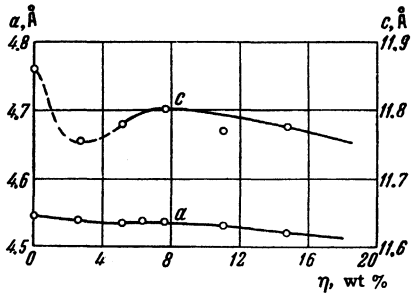

FIG. 1. Dependence of the lattice parameters of Bi, c (in the direction of the trigonal axis) and a (perpendicular to the trigonal axis), on the concentration of Sb.

Since hydrostatic compression also changes the band structure of Bi,[12-14] it can be assumed that the chief reason for the change in the energy spectrum of the Bi electrons upon addition of Sb is the decrease in the lattice parameters.

The present research was undertaken to obtain similar data on the character of the energy spectrum of the electrons in Bi-Sb alloys, as well as a comparison of the results with the data of[12-14].

METHODS OF MEASUREMENT; SPECIMENS

The anisotropy $\Delta\chi$ of the magnetic susceptibility of the samples was measured on a magnetic torsion balance with an automatic recording system.[15] The measurements were carried out in a homogeneous magnetic field up to 13 koe for temperatures 1.6—4.2°K in two modes; with continuous application of the magnetic field and recording the signal on the chart of an ÉPP-09 electronic potentiometer, and (as a control) with sudden application of the magnetic field and recording the output signal with a pointer galvanometer of the M-101 type. The temperature was determined from the vapor pressure of liquid helium.

Samples of cylindrical shape, with diameter ~3.8 and length 6—7 centimeters, were prepared from "Hilger" Bi (purity 99.998 %), purified by twenty vacuum recrystallizations, and from "Hilger" Sb. The method of preparation of the samples was similar to the method described earlier.[8] After preparation, the specimens were annealed in an atmosphere of gaseous helium at 260°C over a period of 40 days.

The crystallographic orientation of the specimens was determined by a goniometer with accuracy to within 0.2—0.3°.

To eliminate possible systematic error in the determination of the Sb concentration, two groups of samples were prepared with overlapping concentration values: 0; 0.1; 0.4; 0.6 and 0.3; 0.8; 1.0 wt. % Sb.

The correctness of the relative distribution of the impurities among the specimens is also confirmed by the monotonic increase in the residual electron resistance of the samples with increasing Sb concentration.

RESULTS OF MEASUREMENT

To obtain the most complete data on the character of the change in the Fermi surface for Bi electrons, measurements were carried out for a so-called "non-symmetric" orientation of the samples in the magnetic field: the trigonal axis is perpendicular, and the twofold axis is parallel, to the axis of suspension of the balance. For each specimen we plotted the dependence of the moment of forces N on the direction of the magnetic field H for different values of the angle x between the direction of the trigonal axis and the field. Measurements were obtained for the angles x = 0, ± 1, ± 2, ± 3, ± 4, ± 5, ± 6, ± 10, ± 82, ± 84° at 1.67°K, and x = −25, −30, −35, ± 40° at 3.37 and 1.685°K. Measurements were not made at other angles, since the N(H) curves observed for them are superpositions of adjacent frequencies with comparable amplitudes, which complicates their interpretation.

The dependence of the anisotropy of the magnetic susceptibility $\Delta\chi = N/H^2 \sin\psi \cos\psi$ on 1/H is shown in Fig. 2 for specimens of the original Bi and for Bi with 0.4 and 0.6 wt. % Sb (for $\psi = -35°$), and 0.8 and 1.0 wt. % Sb (for $\psi = -30°$), at 3.37 and 1.685°K. As is seen from the drawing, the amplitude of the oscillations ω falls off with increase in the Sb concentration. It should be noted that although the oscillations in the magnetic susceptibility continue at concentrations exceeding 1 wt. % Sb, analysis of the temperature dependence of the amplitude of these oscillations is exceedingly difficult, which forces us to limit ourselves to the concentration region 0 to 1 % Sb.

Curves are plotted in Fig. 3 for the angular dependence of the frequency of oscillations $E_0/\beta_i(\psi) \sim S_m(\psi)$ (see the formulas of Landau in[10]) for samples of the original Bi and Bi-Sb alloys with 0.8 and 1.0 wt. % Sb. It is seen from the drawing that the Sb impurities cause a decrease in the oscillation frequency for all values of ψ, and that the angle of rotation of the Fermi-surface ellipsoids around the twofold axes does not change within the limits of accuracy of the experiment (± 0.3°).

The values of the relative change of the oscillation frequency (and, consequently, of the quantity

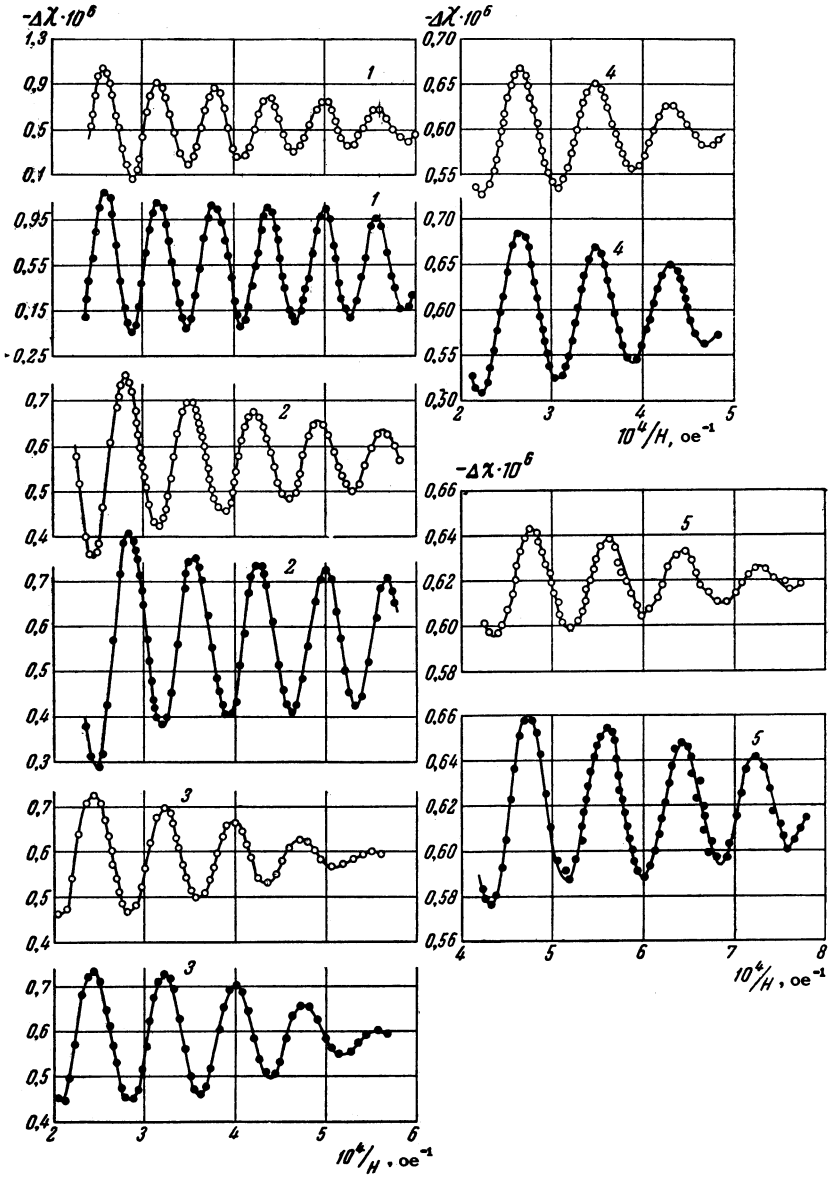

FIG. 2. Dependence of the anisotropy of the magnetic susceptibility for Bi-Sb alloys on the magnetic field intensity. Curves: 1 – original Bi, 2 – Bi with 0.4 % Sb and 3 – Bi with 0.6 % Sb (for $\psi = -35°$); 4 – Bi with 0.8 % Sb, and 5 – Bi with 1.0 % Sb (for $\psi = -30°$); white circles, T = 3.37°K, black circles, T = 1.685°K.

$\Delta S_m/S_m$) for different values of the angle ψ are shown in Fig. 4. The angle $\psi = 82—84°$ corresponds to a change in the smallest principal cross section S_1 of the Fermi surface ellipsoids (which Shoenberg observed[2]). The change in the average principal cross section S_2 can easily be obtained by extrapolation of the curves of Fig. 4 from the region of negative values of ψ through the value $\psi = 0$ to 5.5°. It is thus evident that the minimum, average, and all intermediate cross sections of the Fermi surface are decreased by the same percentage, in first approximation. The small increase in the ratio $\Delta S_m/S_m$ as $\psi \to 0°$ for the sample with 0.3 % Sb (which, to be sure, was observed earlier[13]), is obviously connected with secondary reasons, and is not characteristic of the change in the Fermi surface of Bi upon change in the lattice parameters. Evidently certain divergences in the data for minimum S_1 and average S_2 of the principal cross sections also have the random character associated with possible inaccuracy of orientation of the specimens (especially for the specimen with 1.0 % Sb).

The dependence of the percentage change in S_m on the concentration of Sb impurity is given in Fig. 5. This dependence differs markedly from the linear in the region of small concentrations. The values of $\Delta S_1/S_1$ obtained by Shoenberg[2] for Bi-Sb alloys (0.67 and 0.9 % Sb) are in good agreement with the data given here.

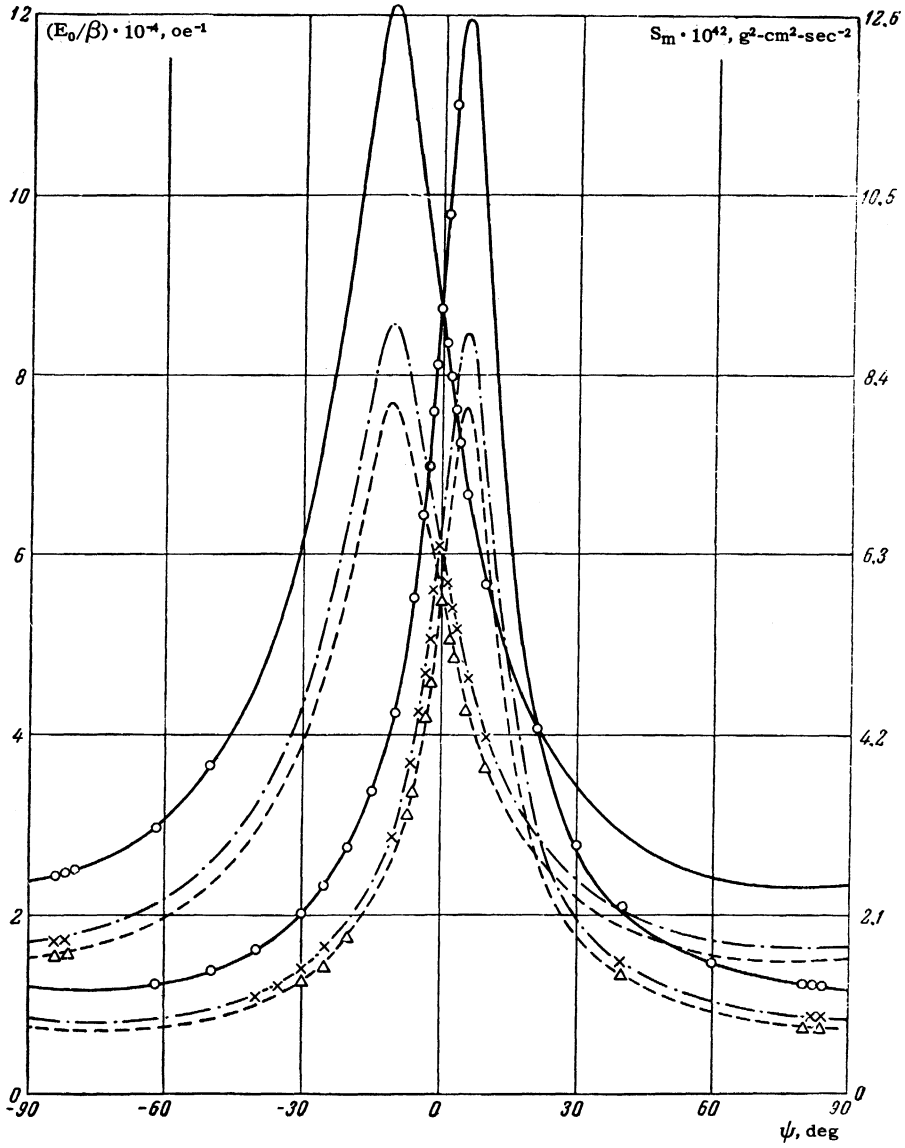

FIG. 3. Dependence of the oscillation frequency $E_0/\beta_i \sim S_m$ on the angle between the direction of the trigonal axis of the sample and the magnetic field (the two-fold axis is parallel to the suspension of the sample). o – original Bi (solid lines) × – Bi with 0.8 % Sb (dot-dash curve), Δ – Bi with 1 % Sb (dashed curve).

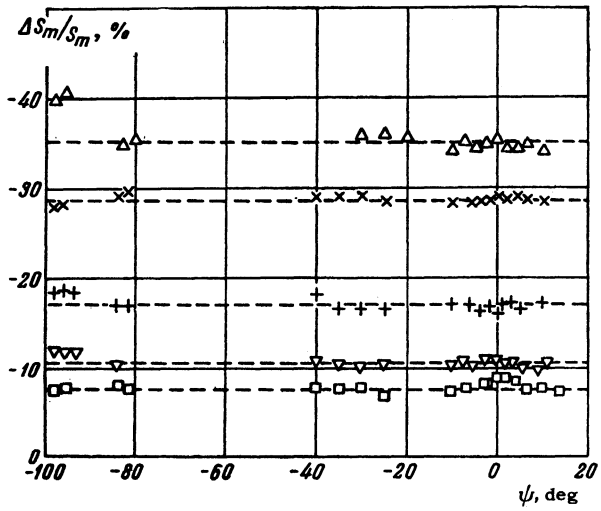

FIG. 4. Angular (ψ) dependence of the relative change in the area $\Delta S_m/S_m$ of the extremal cross sections of the Fermi surface; □ – Bi with 0.3 % Sb, ▽ – Bi with 0.4 % Sb, + – Bi with 0.6 % Sb, × – Bi with 0.8 % Sb, Δ – Bi with 1 % Sb.

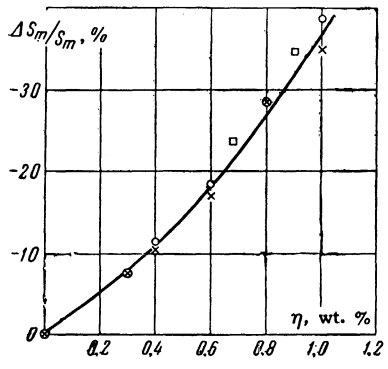

FIG. 5. Change in the area of the extremal cross sections of the Fermi surface with increase in the Sb concentration: o – for cross sections close to S_1, × – for cross sections close to S_2; □ – data of [2] for orientation of H perpendicular to the trigonal axis of the sample.

DISCUSSION OF RESULTS

1. Change in the shape of the Fermi surface for electrons. The anisotropy of the Fermi surface for electrons is determined on the basis of the anisotropies of the cross sections S_1 and S_2, which differ in area by a factor of about 10 (Fig. 3). The cross section S_3, according to Shoenberg's data,[10] exceeds S_2 by a factor of 3.2, while, from cyclotron resonance data,[10] the cross sections S_2 and S_3 are close to one another. It should be noted that the Shoenberg data on the cross section area S_3 are inaccurate, since the quantum oscillations of the magnetic susceptibility, which correspond to the cross section S_3 and cross sections close to it, have not been observed to date, because of their small amplitude, and the quantity S_3 was determined by an overextended extrapolation.

Taking it into account that the anisotropy of the cross sections S_2 and S_3 is not large in any case, while the cross sections S_1 and S_2 change under the action of the Sb impurity in the same percentage ratio, it is natural to assume that the cross section S_3 also changes in similar fashion. Thus, one can conclude that upon increase in the Sb concentration, the shape of the Fermi surface for the Bi electrons does not change, while the surface itself is drawn toward the central point, remaining similar to itself. At a concentration $\eta = 1$ wt. % Sb, the volume of each ellipsoid is reduced approximately by a factor of two. We note that the possibility of extrapolation of the dependence of $\Delta S_m/S_m$ on η (Fig. 5) in the region of large values of the Sb concentration depends on the mechanism of the effect of Sb on the energy spectrum of the Bi electrons. If this mechanism results in the change of the lattice parameters (Fig. 1), then, because of the lack of accurate data for the lattice parameters in the region of concentrations of less than ~3 % Sb, it is difficult to say in what manner the change of the volume of the ellipsoids will take place upon further increase in the Sb concentration, and whether the ellipsoids manage to reduce to points before the lattice parameter c reaches a minimum.

2. Change in the concentration of the electrons. On the basis of data on the change in the principal cross sections of the Fermi-surface ellipsoids brought about by changes in the Sb concentration, one can easily compute the change in the electron concentration (see[9]). The percent change in the electron concentration is shown in Fig. 6 (curve A).

3. Change in the limiting Fermi energy E_0 for electrons. The curves of the dependence of $\Delta\chi$ on H, taken at various temperatures, were used for the calculation of E_0 (Fig. 2). The value of $\beta(\psi)$ was determined from the increase in the ratio of the oscillation amplitudes, and E_0 was determined from the value of $E_0/\beta(\psi)$ known for each angle ψ. For each ψ, the oscillation amplitudes at different magnetic field intensities were compared and an average value was obtained from the data. The scheme of calculation, which is similar to that described earlier,[8] is illustrated in Table I, which applies to a Bi sample with 0.3 % Sb at $\psi = -30°$.

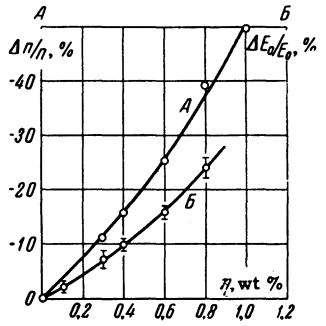

FIG. 6. Per cent change in the electron concentration n (curve A) and the limiting Fermi energy E_0 for Bi electrons (curve B) with increasing Sb concentration.

The values of E_0 computed for the specimens of Bi and Bi-Sb studied are shown in Table II for different values of the angle ψ. Data for a specimen with a 1% Sb content are not given, since the analysis of the temperature change of the amplitude becomes very difficult for such a concentra-

Table I

$(1/H)\cdot 10^4$	ω, arbitrary units			$\beta\cdot 10^{16}$, ergs/oe
	3,37°K	1,685° K	ω (1,685° K) / ω (3,37° K)	
3,1	198	282	1,42	1,60
3,4	128	196	1,53	1,57
3,7	90	147	1,63	1,58
4,0	64	112	1,75	1,58
4,3	47	86	1,83	1,63
4,6	36	70	1,93	1,65
4,9	28	57	2,04	1,68
5,2	22	48	2,20	1,65
5,5	18	42	2,33	1,69
5,8	14,8	37	2,50	1,69
6,1	11	31	2,82	1,65
			β_{av}=1,63±0,04	

Table II

η, %	$E_0\cdot 10^{14}$, ergs				$E_0\cdot 10^{14}$, ergs
	ψ=−25°	−30°	−35°	−40°	
0,00	2,77	2,73	2,73	2,74	2,74±0,02
0,11	2,64	2,67	2,74		2,68±0,03
0,30	2,54	2,60	2,62	2,42	2,54±0,06
0,40	2,45	2,46	2,55	2,44	2,47±0,03
0,60	2,32		2,34	2,25	2,30±0,03
0,80	2,08	2,01	2,15	2 10	2 08±0,05

tion. The dependence on the Sb concentration of the percent change in the limiting Fermi energy is pictured in Fig. 6 (Curve B).

4. Change in the effective masses. As has been noted, all three principal cross sections of the ellipsoids S_1, S_2 and S_3 change in the same ratio upon increase in the concentration. It is easy to show that[8] in this case the change in the effective masses m_1, m_2 and m_3, in a system of coordinates connected with the principal axes of the Fermi-surface ellipsoids, is determined by the relation

$$\frac{\Delta m_1}{m_1} = \frac{\Delta m_2}{m_2} = \frac{\Delta m_3}{m_3} = \frac{\Delta S_m}{S_m} - \frac{\Delta E_0}{E_0}. \quad (1)$$

As is seen from Figs. 5 and 6, the curves for the dependence of $\Delta S_m/S_m$ and $\Delta E_0/E_0$ on η coincide with one another within the limits of accuracy. Therefore, it can be assumed that the effective masses for Bi do not change in the increase of Sb concentration from 0 to 1 per cent.

A similar conclusion can be obtained on the basis of Fig. 6. The dependences of $\Delta n/n$ and $\Delta E_0/E_0$ on the concentration η shown in Fig. 6 satisfy the relation $\Delta n/n = 3\Delta E_0/2E_0$, which is valid in the region of small changes of $\Delta E_0/E_0$ under the assumption that the effective mass of the electrons does not change upon increase in the Sb concentration.

5. Comparison of the results with experiments on the influence of elastic deformation on the de Haas-van Alphen effect in Bi. According to the data of Bridgman, the change in the lattice parameters in Bi, for unilateral compression (at room temperature), is given by the formula

$$-\Delta l/l_0 = \alpha \cdot 10^{-7} p, \quad (2)$$

where α are the coefficients of compressibility, equal, respectively, to 15.9 and 6.6 in directions parallel and perpendicular to the trigonal axis, and p is the pressure in kg/cm^2.

The maximum changes in the lattice parameters of Bi, brought about by Sb impurities in the region of small concentrations (for η = 2.5 % Sb) (Fig. 1) are: $-\Delta c/c$ = 0.9 %; $-\Delta a/a$ = 0.18 %. Since different pressures p (5700 and 2700 kg/cm^2) correspond to such changes in the parameters c and a [according to Eq. (2)], their change does not correspond to the conditions of hydrostatic compression. The effect of the change in the Bi lattice under the action of Sb can be represented as the result of hydrostatic (p) and a unilateral (σ) compression (along the c axis) of the specimen. Unfortunately, since the compressibility coefficients of Bi are not known at low temperatures, nor is there an accurate form of the dependence of the lattice parameter c for small Sb concentrations, we must limit ourselves to a rough comparison only, making use of the data at hand.

The changes in the parameters of the lattice under the action of impurities are associated with the values of p and σ by the relations

$$-(\Delta c/c) = 15.9 \cdot 10^{-7}(p + \sigma),$$
$$-(\Delta a/a) = 6.6 \cdot 10^{-7} p + 15.9 \cdot 10^{-7} j\sigma, \quad (3)$$

where j is Poisson's ratio, equal to −0.33 for Bi. For a concentration of 1 wt. % we have $-\Delta c/c \approx 0.6$ % and $-\Delta a/a \approx 0.12$ %. On the basis of Eq. (3), this change corresponds to a hydrostatic compression p ≈ 2400 kg/cm^2 and a unilateral compression with stress $\sigma \approx 1300$ kg/cm^2.

It is well known that a hydrostatic compression of ~1200 kg/cm^2 changes the relative area $\Delta S_m/S_m$ of the extremal cross sections of the Fermi surface for Bi by about −7 per cent,[12,13] while a unilateral compression with a stress σ = 350 kg/cm^2 causes a change of −6.5 %.[14] Extrapolation of these values to the region of high pressures gives (for p = 2400 kg/cm^2 and σ = 1300 kg/cm^2) changes in $\Delta S_m/S_m$ of ~14 and ~24 %, respectively. The general change of $\Delta S_m/S_m$ under the action of elastic deformations of the lattice, which is equivalent in magnitude to the deformations produced by an impurity of 1 wt. % Sb, amounts to about 38 % which is in excellent agreement with the experimental data given in Fig. 5.

It should be noted also that the data on the change of the constant part of the anisotropy of the magnetic susceptibility $\Delta\chi_0$ in Bi for hydrostatic compression, and for an increase in the Sb concentration, agree with one another within the limits of accuracy of the experiment. The Sb impurity produces an approximately linear increase in $\Delta\chi_0$ (see Fig. 2), amounting to 10—12 % for 1 wt % Sb. By considering this effect as the result of a change in the lattice parameters for Bi, one can expect hydrostatic compression to produce a small increase in $\Delta\chi_0$, not exceeding 2—3 % for a pressure of 1200 kg/cm^2. An effect of just this order was observed in a previous research.[13] Thus, one can assume that the change in the energy spectrum of the Bi electrons under the effect of the Sb impurities, in the region of small concentrations, is evidently connected in a fundamental way with changes that take place in this case in the parameters of the crystalline lattice of Bi.

In conclusion, we take this opportunity to thank A. I. Shal'nikov for his interest in the work and Yu. A. Bychkov for discussion of the results.

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