

*THE DE HAAS-VAN ALPHEN EFFECT IN BISMUTH ALLOYS CONTAINING SELENIUM,
TELLURIUM AND ZINC*

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The de Haas-van Alphen effect is investigated in Bi-Te, Bi-Se, and Bi-Zn alloys, the concentration of the second component being 0.04, 0.15 and 0.6 at. %, respectively. The measurements were made at temperatures from 1.6 to 4.2°K and in magnetic fields from 1.5 to 13 kOe. The dependence of the extremal cross sections of the electronic part of the Fermi surface on the impurity concentration is studied in detail. The structure of the energy spectrum of bismuth is discussed on the basis of the data obtained. A considerable increase in the cyclotron effective electron mass with increase in the Fermi energy is found in the Bi-Te and Bi-Se alloys.

INTRODUCTION

THE investigation of the effect of impurities on the de Haas-van Alphen effect in Bi is interesting from several points of view.

First, in view of the small number of carriers in Bi, the introduction of even a very small number of impurities from the elements close to bismuth in groups IV and VI of the periodic table allows us to vary the concentration of carriers over rather wide limits, which yields additional information on its dispersion law. In the study of the de Haas-van Alphen effect in Bi-Te alloys, a considerable departure from the dispersion law of the electrons from a square law was noted, which has been interpreted in terms of the ellipsoidal model of Cohen with a non-quadratic dispersion law.^[1]

Second, the possibility of a considerable change in the carrier concentration and the Fermi energy allows an investigation of the structure of the energy spectrum of Bi over a wide energy range. This question has acquired considerable urgency at the present time in connection with the appearance of theoretical papers in which various models of the structure of the energy spectrum in metals of the Bi type have been proposed.^[2,3] A number of researches^[2-4] show the existence in the Bi spectrum of energy minima located above the Fermi level, and the energy maxima located below it. Therefore, at definite impurity concentrations one can expect a disappearance of some and the appearance of other constant-energy surfaces in the Bi spectrum. To carry out these investiga-

tions, measurements are necessary over a wide range of concentrations.

Third, the problem of the mechanism of the effect of impurities on the energy spectrum of the electrons in bismuth has continued to remain unclear up to the present time. It is known that Pb and Sn impurities^[5,6] decrease and Te and Se^[1,5] increase the number of electrons in the conduction band, and to change the concentration by unity different numbers of impurity atoms are required for impurities of different types. The effectiveness of the impurities, which is characterized by the ratio of the amount of change of carrier concentration to the number of introduced atoms, is very different for different substances. Thus, the effectiveness of Pb^[5,6] is much less than unity, while that of Te is close to unity.^[1,7]

In this connection, it was of interest to study the effect of other impurities, for example, Se, of the same group as Te, and also impurities with a valence differing from the valence of Bi by more than unity, and to determine their effectiveness.

METHOD OF MEASUREMENT. SPECIMENS

The anisotropy of the magnetic susceptibility of the samples was measured in a null-type torsion magnetic balance^[8]. The measurements were carried out in a homogeneous magnetic field ranging from 1.5 to 13 kOe at temperatures 1.6-4.2 and 14-20.4°K.

The alloys were prepared by the method of successive dilution in order to avoid suspensions

Table I

Batch	No. of samples	Computed impurity concentration, at. %	Annealing		Batch	No. of samples	Computed impurity concentration, at. %	Annealing	
			°C	days				°C	days
Bi—Te									
I	1	0.0008	260	30	VII	19a,	0.007 (13)	without annealing	
	2a, 2b	0.0016				19b			
	3	0.0024				20,20a,	0.008 (12)		
II*	4	0.0037	21	0.013 (14)					
	5	0.005	22			0.0004 (1)			
III	6	0.0045	250	20			Bi—Se		
	7	0.006			I	23	0.013	250	45
IV	8	0.011	without annealing			24			
	9	0.016	»		25	0.053			
V	10	0.028	150—200	7	II	26	0.037	255	30
	11	0.016				without annealing			
	12	0.03			200	10	III	28	0.135
13	0.034	without annealing		29	0.038 (27)				
VI	14, 14a,	0.04	without annealing		30	0.085	»		
	14b, 14c	»	»		Bi—Zn				
	15a, 15b	0.018	»		30	0.01	without annealing		
VII**	16a, 16b	0.025	»		31	0.08	»		
	17	0.0017 (11)	»		32	0.6	»		
	18	0.0034 (15a)	»						

*Samples were annealed successively: 5 hr at 250°C, 24 hr at 250°C and 10 days at 250°C.

**Batch VII was obtained by dilution of samples of different batches (the original numbers are shown in parentheses).

of small amounts of the material. As initial components, we used Bi of "Hilger" grade—purity 99.998%, purified by thirty recrystallizations in vacuum; Bi (GIREDMET) with less than 1×10^{-4} lead impurity, less than 1×10^{-5} As, and less than 3×10^{-4} % Ni; Te (Hilger) purified by 10 zone meltings; Se (Hilger); and spectrally pure Zn. Alloys were prepared initially with from 0.15 to 0.6 at. % impurity. Pieces from different parts of the ingot were then broken off to produce alloys of the necessary concentration. All the melts were carefully placed in sealed ampoules of pyrex glass, filled with gaseous helium and stored in the liquid state at a temperature of 300–400°C for from 6 hours up to several days, after which they were cooled quickly. Single crystal seeds were grown from the polycrystalline ingots and used (by the Kapitza method^[9]) to prepare single crystal specimens of cylindrical shape, of length 6–12 mm and diameter 2.5–4 mm, with the trigonal axis parallel to the longitudinal axis of the sample. The rate of growth varied from 5 mm/min to 1 mm/hour. To decrease the gradient in the impurity distribution along the specimen, the method of counter recrystallization was applied, which was repeated up to four times on single specimens. Part of the sample was annealed at temperatures of 200–265°C for times of 3–40 days. The direction of the binary axes was determined on a goniometer according to an etching spot, with accuracy up to $\pm 0.5^\circ$.

As a control on the reproducibility of the results, several parts of the samples were prepared

in each system of melts, with overlapping concentrations. For this purpose, specimens with a high impurity content were diluted after the measurements to much lower concentrations (batch VII). In many cases, the measurements were made on several specimens for a given calculated impurity concentration.

The characteristics of the studied samples are shown in Tables I and II.

RESULTS OF MEASUREMENT

The measurements were carried out principally at orientations where the trigonal axis of the specimen was perpendicular and the binary axis parallel to the axis of suspension, since the measurements at these orientations make it possible to obtain maximum information on the shape of the constant-energy surfaces. The orientation in which the trigonal and binary axes of the specimen are perpendicular to the suspension axis was studied only in special cases for control. For each sample, the dependence of the moment M on the magnetic field H was plotted for various field

Table II. Samples grown with small rate of growth

Alloy	No. of samples	Computed impurity concentration, in at. %	Rate of growth mm/hr
Bi—Se	33	0.015	2 mm/hr
Bi—Te	34	0.0024	1 »
Bi—Te	35	0.001	5 »

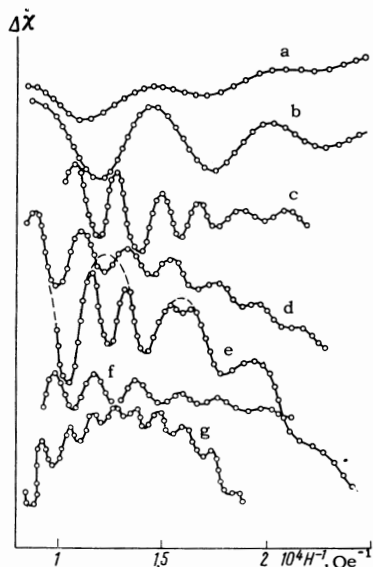


FIG. 1. Characteristic examples of the dependence of the anisotropy of the magnetic susceptibility $\Delta\chi$ on $1/H$ for Bi-Te and Bi-Se alloys: a—sample No. 18, $\psi = 83^\circ$; b—sample No. 27, $\psi = 78^\circ$; c—sample No. 28, $\psi = 64^\circ$; d—sample No. 19a, $\psi = 73^\circ$; e—sample No. 8, $\psi = 80^\circ$; f—sample No. 15b, $\psi = 117^\circ$; g—sample No. 13, $\psi = 110^\circ$ (for the composition of the samples, see Tables I and II; the scale on the ordinate is different for each curve).

directions relative to the trigonal axis (angle ψ). Typical examples of the dependence of $\Delta\chi \sim M/H^2$ on $1/H$ are shown in Fig. 1. The results obtained are conveniently systematized in the following fashion.

1. **Beats.** In a number of cases the studied samples of Bi-Te and Bi-Se alloys exhibit a sharply expressed periodic change in the amplitude of oscillations of the dependence of $\Delta\chi$ on $1/H$, recalling the picture of beats. The clearest beats are those of the Bi-Te alloys in the region of low concentration of Te (Figs. 2a, b). As a rule, the best frequency is proportional to the frequency of the observed oscillations, and amounts to about 15–20% of the fundamental frequency. As a result of this, on going to small cross sections of the electronic surface (the frequency of oscillation is connected with the extremal cross section S of the Fermi surface, perpendicular to the direction of the magnetic field \mathbf{H} , by the formula $\omega = [\Delta(1/H)]^{-1} = (c/eh)S^{[10]}$), the period of the beats increases and, at orientations of the magnetic field close to the bisector axis, includes practically the entire region of fields from 1.5 to 13 kOe (Fig. 2c).

The observed beats cannot be the consequence of the superposition of oscillations from the neighboring cross sections of the constant-energy surfaces, since the changes were brought about in

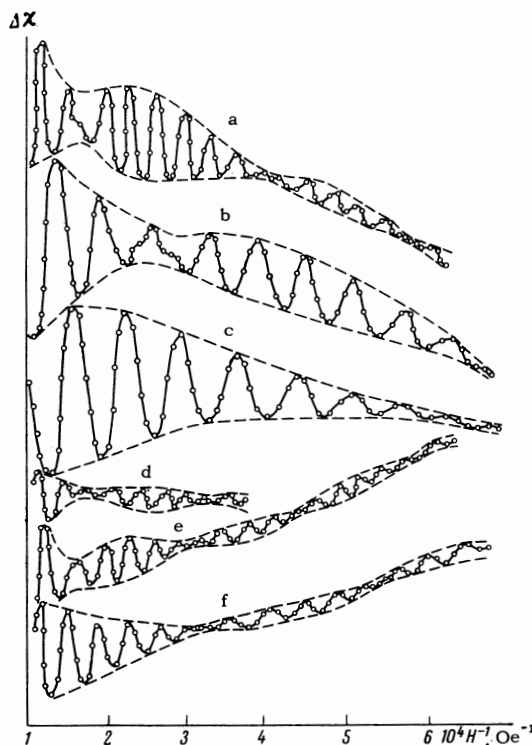


FIG. 2. Dependence of $\Delta\chi$ on $1/H$ for Bi-Te, and Bi-Se alloys; a—sample No. 1, $\psi = 165^\circ$; b—sample No. 1, $\psi = 140^\circ$; c—sample No. 1, $\psi = 79^\circ$; d—sample No. 25, $\psi = 160^\circ$; e—sample No. 34, $\psi = 160^\circ$; f—sample No. 2a, $\psi = 155^\circ$.

that range of angles ψ where the decisive contribution to the oscillation is made by only one constant-energy surface. The changes produced in parts of the sample obtained by cleavage perpendicular to its longitudinal axis show that the picture of beats is entirely preserved. This supports the idea that the beats are not the result of macroscopic inhomogeneity in the distribution of impurities along the specimen. Prolonged annealing of samples for 30 days at a temperature close to the melting temperature of bismuth (260–265°C) also does not change the picture of the beats to any appreciable extent. The character of the beats evidently does not depend on the growth rate of the crystals. Thus, for example, a decrease in the rate of growth from 5 mm/min to 1 mm/hour did not lead to any appreciable change in the dependence of $\Delta\chi$ on $1/H$ (Fig. 2e). The observation of beats in the region of high concentrations is made very difficult as the result of the narrowing of the interval of fields in which the oscillations are observed.

2. **Effectiveness of the impurities.** The curves of the dependence of $\Delta\chi$ on $1/H$, obtained in the study of Bi-Te and Bi-Se alloys (Figs. 1a, b, c, d), show that the same change in frequency of oscillations is produced by very different concen-

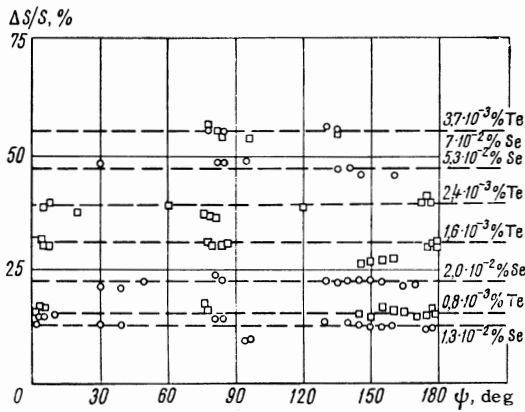


FIG. 3. Angular dependence of the relative changes of the areas $\Delta S/S$ of the extremal cross sections of the electron constant energy surfaces for alloys of Bi-Te (\square), Bi-Se (\circ) in the region of low impurity concentrations (at. %).

trations of impurities of Te and Se. A single atom of Te in the alloy has the same effect as about 20 atoms of Se, and this proportionality is preserved through the entire range of concentrations investigated.

3. Angular dependence of the oscillation frequency. Figure 3 shows the relative changes of the extremal cross sections of the electron constant-energy surfaces for different values of the angle ψ between the direction of the field H and the trigonal axis of the crystals for the Bi-Se and Bi-Te samples, in the region of low impurity concentrations.¹⁾ At high concentrations of Te and Se, the only oscillations observed were connected with cross sections close to the small extremal cross section of the electronic ellipsoid. The angular dependence of the frequencies of these oscillations is given in Fig. 4.

4. Dependence of the oscillation frequency on the impurity concentration. In the Bi-Te and Bi-Se alloys, the dependences of the percent change of the extremal cross sections, averaged over the different values of ψ in the region of low impurity concentrations, on the impurity content have a similar character and can be made identical by a corresponding change (by 20 times) in the scale on the concentration axis. This dependence is shown in Fig. 5. In the same drawing are shown data obtained earlier for the alloys Bi-Pb^[6] and Bi-Sb^[11] to the same effectiveness scale, and also data for the alloy Bi-Te, taken from [1,5].

Figure 5 shows that the monotonic increase in the oscillation frequency with increase in concen-

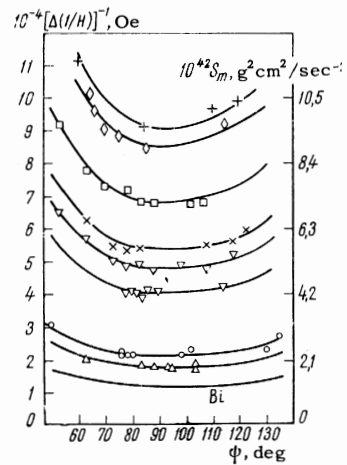


FIG. 4. Angular dependence of the oscillation frequencies and extremal cross sections of the electron Fermi surface for Bi-Te alloys. Points—experimental data; Δ —sample No. 18, \circ —sample No. 5, ∇ —samples No. 19a and 19b, \times —sample No. 11; \square —sample No. 16b; \diamond —sample No. 12, +—sample No. 13. The curves are drawn in correspondence with the angular dependence of the frequencies for pure Bi.

tration of Te, observed from zero to 0.005 at. %, becomes violated at concentrations $c > 0.005$ at. %, Close to this concentration, the appearance of a high-frequency component is observed with approximately double the frequency. The doubled frequency of the oscillations is observed in all samples with concentrations of Te from 0.005 to

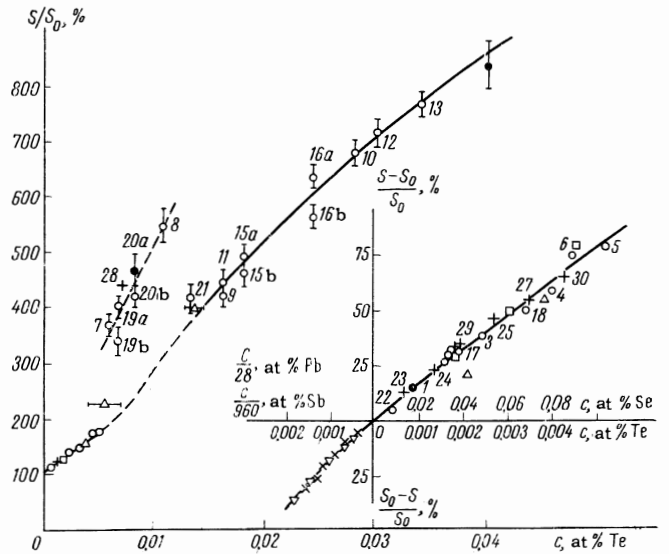


FIG. 5. Dependence of the relative change of the extremal cross sections S/S_0 on the impurity content c . The number at the experimental points represents the number of samples given in Tables I and II; \circ —data of the present research for Bi-Te alloys, +—the same for Bi-Se alloys, \bullet —values resulting from the averaging of experimental data for several samples with the given impurity concentration; Δ —data for Bi-Te alloys from [1], \times —for Bi-Pb alloys from [6], ∇ —for Bi-Sb alloys from [11], \square —for Bi-Te alloys from [5].

¹⁾A number of measurements on samples with low content of Se and Te were carried out by one of the authors together with S. N. Sidneva and N. A. Karnaukhova.

0.011 at. %. A similar effect is observed for Bi-Se alloys. It is of interest to note that, at the concentrations of Te corresponding to the limits of this region, a low-frequency component can be observed along with the doubled frequency on the curves of $\Delta\chi$ vs. $1/H$. This low-frequency component is most marked in the region of weak fields (Fig. 1e). In samples corresponding to the middle of this region (for example, with concentrations 0.007–0.008 at. % Te), definite single-period oscillations are observed with doubled frequency (Figs. 1c, d). At Te concentrations $c > 0.011$ at. %, the high-frequency component vanishes. Further increase in the frequency of oscillation with concentration bears a monotonic character.

The angular dependence of the doubled frequency duplicates the angular dependence of the fundamental frequency at concentrations outside of the region considered (Fig. 4).

5. Measurements at temperatures 14–20.4°K. For a number of samples of Bi-Se and Bi-Pb alloys, the oscillations of $\Delta\chi$ were measured in the range of temperatures of liquid hydrogen (20.4–14°K). The frequency of the oscillations, in the limits of accuracy of its determination (approximately $\pm 7\%$ for these temperatures), does not change in comparison with the temperatures of liquid He (4.2–1.6°K).

6. Bi-Zn alloys. Measurements were carried out on samples with Zn content up to 0.6 at. %. In spite of the large Zn content, oscillations were observed for the investigated samples of Bi-Zn alloys with amplitude and frequency practically unchanged from that of pure bismuth.

DISCUSSION OF RESULTS

1. Beats. The character of the beats shows that they are the super-position of adjacent frequencies with almost equal amplitudes. The most trivial reason for beats can be microinhomogeneities in the impurity distribution in the specimen. One can show that the periodic, monotonic change of the concentration of impurities in the specimen should lead to a picture resembling beats with a period corresponding to frequencies for the regions with maximum and minimum impurity concentrations. Figure 6 shows the dependence of the relative change of the frequencies $[\Delta(1/H)]: [\Delta(1/H)]^{-1}$ producing the beats (averaged over the angles φ) on the calculated impurity concentration in the specimen.

We note that the formation of regions with different impurity concentrations during the growth of the crystal from the melt is evidently not con-

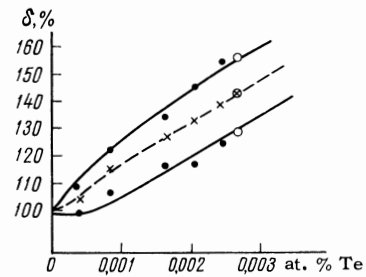


FIG. 6. Dependence of the relative change of frequencies $\delta \equiv [\Delta(1/H)]^{-1}: [\Delta(1/H)]_{\text{Bi}}^{-1}$ on the computed impurity concentration in the specimen. The upper points correspond to the greater, and the lower to the lesser of two frequencies which give the beats; the intermediate points \times correspond to the average value of the oscillation frequency. The open circles give the data for Bi-Se alloy.

nected with the formation, which appears at large rates of growth, of a cellular substructure under conditions of normal supercooling.^[12] The volume of the regions with increased content of impurities on the boundaries of the cells is usually much less than the volume of the sample. Moreover, the insensitivity of the character of the beats to the technology of preparation of the specimens and the absence of notable substructure in the measured sample, as given by metallographic-investigation data, evidently eliminates this possibility completely.

However, the possibility that the appearance of beats in Bi alloys with impurities of the donor type may be connected with the mechanism considered in^[13,14] has not been eliminated. The positive excess potential of the impurity ion can lead to the formation of a bound electron state. Upon ordering of spins of the bound electrons in the magnetic field, which at low temperatures can take place in rather weak fields (≈ 10 kOe), the Fermi electrons with parallel and antiparallel spins (relative to the field) move in different effective potential fields, which should lead to different periods of the van Alphen oscillations. In this connection, it should be noted that no beats were observed in the Bi-Pb alloys,^[6] where Pb is an acceptor.

Regardless of the nature of the beats, it is convenient to take the mean value of the frequency as the frequency of oscillation which characterizes the cross section of the constant-energy surface (the dotted line in Fig. 6). Here, however, it must be kept in mind that in the region of high concentrations, where only limited sections of the dependence of $\Delta\chi$ on $1/H$ are observed, the largest amplitude may be possessed by the low-frequency component of the oscillations. Therefore, regard-

less of the nature of the beats, the experimental values of the frequency of oscillations for alloys in the region of large impurity concentrations can only be undervalued compared with the mean value of the frequency.

2. Dependence of the extremal cross sections on the Te and Se impurity concentrations. On the basis of the assumption that impurities of the donor type increase the concentration of electrons, it can be expected that after filling the constant energy-surface for holes, the rate of filling of the electron ellipsoids should increase. For an analysis of the dependence of S/S_0 on c (Fig. 5) it is convenient to transform to the quantity $(S/S_0)^{3/2} - 1$, since it is proportional to the relative change of volume of the electron ellipsoids in this case if the shape of the electron ellipsoids does not change with increase in concentration. The dependence of $(S/S_0)^{3/2} - 1$ on the impurity concentration c is shown in Fig. 7.

In the regions of small and large concentrations, this dependence can be approximated by two straight lines (a and b) with different slopes. The line a characterizes the increase in volume of the electron surface for simultaneous filling of the hole constant energy surface. The line b denotes the changes in the volume of the electron surface after the hole surface has been completely filled. In both cases the dependence of $(S/S_0)^{3/2} - 1$ on c is linear within the limits of accuracy of the measurements. This indicates that when the volume of the electron surface is increased by about 25 times, the possible change in the anisotropy of the electron ellipsoids does not exceed 15–20%. In the determination of the frequency of oscillation (as shown above), the measured minimal cross sections can be only undervalued. Therefore, one can assume that, only a decrease is possible in the anisotropy of the electron ellipsoids upon increase in the concentration.

3. The effect of frequency "doubling." The appearance of a higher frequency in the region of concentrations of Te (at. %) of $0.005 < c < 0.012$, which is not in agreement with the monotonic character of the dependence of S/S_0 and $(S/S_0)^{3/2} - 1$ on c , can, generally speaking, be due to two reasons: the change in the value of the spin splitting of the Landau levels upon increase in the concentration of impurity atoms of the donor type and the effect of deformation of the lattice upon filling of the valence band with electrons. A small deformation of the lattice upon filling of one of the Brillouin zones was observed in the study of alloys of In with Sn, Cd, and Pb^[15]. However, in carrying out the dilatometric measurements, we did not

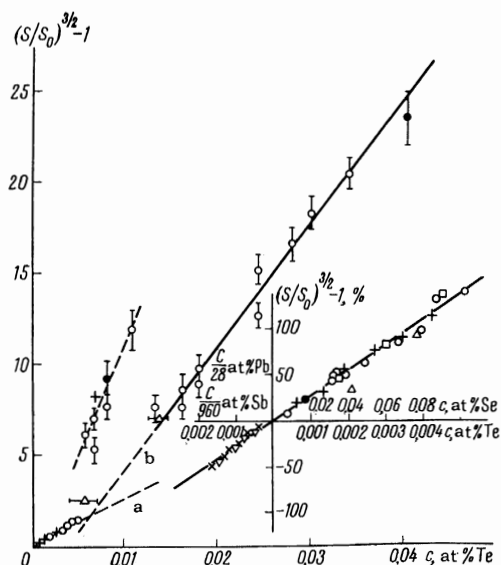


FIG. 7. Dependence of the quantity $(S/S_0)^{3/2} - 1$ on the impurity concentration c . The notation corresponds with that of Fig. 5.

discover any noteworthy anomaly in the temperature dependence of the expansion coefficient of the Bi-Te alloy ($c = 0.008$ at. % Te) at temperatures 80–200°K. Furthermore, x-ray data on the samples in the indicated region of concentration testify to the negligible deformation of their lattice. Therefore the second assumption appears improbable to us. Here one must bear in mind that the mechanism of deformation of the lattice upon filling of the hole band, while not explaining the observed strong change in the oscillation frequency in the Te concentration range (at. %) $0.005 < c < 0.012$, can lead to an explanation of the transition from a four-ellipsoid to a three-ellipsoid model in the region of somewhat higher impurity concentrations.

On the other hand, the character of the appearance of the high frequency (Fig. 1d) and also the fact that its value is approximately twice the frequency expected in this region of concentration show the possible connection between the effect of frequency doubling and the change in the value of the spin splitting of the Landau levels. It was found in^[16] that, for small cross sections of the electron ellipsoids, the ratio of the orbital effective mass to the spin mass is $m^*/m_s = 1.06$, which means that the spin splitting somewhat exceeds the orbital. For a doubling of the frequency it is necessary that the ratio m^*/m_s be equal to 0.5 or 1.5. In the former case the value of the spin splitting should decrease, and in the latter, increase with increase in the concentration. Unfortunately, it is impossible to show which case

actually takes place on the basis of the data of the present research.

To determine the direction of the change of the ratio m^*/m_S , it is necessary to study the combined resonance in alloys in this region of concentration. According to the data of [16] the ratio m^*/m_S for the electrons in Bi remains constant when the Fermi energy (and, consequently, m^*) is varied by means of a strong magnetic field. If this assumption is correct, then the change in the ratio m^*/m_S should take place not as the result of a change in m^* due to a change in the Fermi energy, but as the result of the presence of impurity atoms in the Bi lattice.

The data on the change of the phase of the oscillations in one half cycle, obtained in this region with the help of extrapolation of the dependence of the location of the maxima on the curves of $\Delta\chi$ vs. $1/H$ to the region of fields $1/H \rightarrow 0$, also support foregoing explanation of the frequency doubling. It should be noted that the physical reason for the change in the ratio m^*/m_S with increase in the concentration of Te and Se impurities remains unclear.

4. Effectiveness of the Te and Se impurities in Bi. In a number of works in which the oscillating and galvanomagnetic effects in alloys of Bi with Pb, Sn, Te, and Se were investigated, [5,6,17,18] attention was called to the fact that the introduction of a single impurity atom changes the concentration of carriers by much less than unity, although the reason for this phenomenon continues to remain unexplained. Therefore, each impurity in Bi can be characterized phenomenologically by some coefficient of effectiveness $\xi = \Delta N/\Delta c$, where Δc is the number of impurity atoms per cm^3 , and ΔN the change in the number of carriers under the action of the impurity. Assuming a similar (in first approximation) change in the form of the Fermi surface, one can determine the effectiveness of Te in Bi from the slope of line b in Fig. 7 in the region where there remain only the electron ellipsoids. By recognizing that a change of the concentration of Te by 0.01 at. % in 1 cm^3 of the alloy introduces about 2.8×10^{18} impurity atoms, we obtain for ξ the value 0.7 ± 0.1 (the concentration of the electrons in pure Bi is assumed to be $N_0 = 2.8 \times 10^{17} \text{ cm}^{-3}$ [19]). Correspondingly, for Se we get the value $\xi = 0.035$, which is in satisfactory agreement with the value $\xi = 0.03 \pm 0.003$ determined from the value of the Hall coefficient in the Bi-Se alloys in strong magnetic fields. [20]

We consider first the possibility that the low effectiveness of Se and Pb is connected with the

fact that not all the impurity atoms go to form a substitution solid solution. This may be caused also by such mechanisms as the settling of impurities on the dislocations, the entry of impurity atoms in the interstices, cellular-substructure formations, and formation of structure complexes and chemical compounds of the impurity with Bi and with other impurities in Bi. [21] In the study of Bi-Se and Bi-Te alloys, we have established the absence of any significant influence on the effectiveness of the impurities of annealing at different durations and temperatures, quenching of the samples, rate of growth of crystals and the values of the temperature gradient, the independence of the effectiveness of the impurity concentration, and also the absence of appreciable cellular substructure in the entire region of concentrations studied (according to the data of metallographic analysis). Therefore, there is no sufficient basis for assuming any of the mechanisms enumerated above to be responsible for the lowered (in comparison with Te) effectiveness of the Se.

On the other hand, the change in the amplitude of oscillations in Bi-Te, Bi-Se, Bi-Pb alloys has the same character when compared on an equal effectiveness scale. This is attested by data on the value of the Dingle factor κ [22] in Bi-Te, Bi-Se, Bi-Pb, Bi-Sb alloys, given in Fig. 8. The relatively weak effect of Sb on the amplitude of the oscillations shows that the basic effect on the broadening of the energy levels of the electrons in a periodic field of the lattice is made by the ionized impurity scattering centers. Therefore, the given data on the value of κ in alloys show that in impurities with a small effectiveness (Se, Pb) not all the atoms are in the ionized state.

5. The group of "heavy" holes in Bi. As has already been shown, the study of Bi alloys allows us to obtain additional information on the charac-

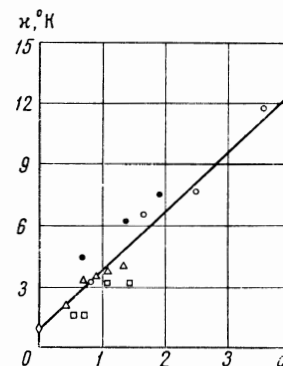


FIG. 8. Dependence of the Dingle factor κ for Bi on the impurity concentration in the scale of their same effectiveness ($\psi = 165^\circ$); —Bi; O—c, 10^{-3} at. % Te; ●—c/20, 10^{-3} at. % Se; Δ —c/28, 10^{-3} at. % Pb; \square —c/960, 10^{-3} at. % Sb.

ter of the energy spectrum of Bi, since in the region of low impurity concentrations any change in the spectrum as the result of a change in the parameters of the lattice Bi can be neglected on the basis of^[23]. The character of the dependence of $(S/S_0)^{3/2} - 1$ on c (Fig. 7) for Bi-Se and Bi-Te alloys shows that in Bi there is no group of so-called "heavy holes" with a high density of states, the existences of which has been assumed in a number of researches^[1,24] to explain the large value of the coefficient γ in the electronic specific heat of Bi, since the presence of such a group of "heavy" holes should have led to the formation of an area at the beginning of the curve of $(S/S_0)^{3/2} - 1$ from the intense filling of this group by the donor electrons.

6. Number of electron ellipsoids. Data given in Fig. 7 for the high concentrations, when the hole ellipsoid is already filled, allow us to draw a conclusion on the number of electron ellipsoids in Bi, which was discussed in a number of papers.^[1,18,25] The number of atoms of the impurity, $2.8 \cdot 10^{18} \text{ cm}^{-3}$, changes the volume of the electron ellipsoid by a factor of about seven, i.e., the electron concentration here is increased by $7n_0x$, where $n_0 = 0.93 \times 10^{17} \text{ cm}^{-3}$ ^[19] is the electron concentration in a single ellipsoid and x is the number of electron ellipsoids. Since $7n_0x = 6.5 \times 10^{17}x \leq 28 \times 10^{17} \text{ cm}^{-3}$, we get $x \leq 4.3$, i.e., the number of electron ellipsoids cannot be equal to seven, even if the effectiveness is $\xi = 1$. Thus it is natural to assume that, in correspondence with^[25,18], the Fermi surface in Bi consists of three electron and one hole ellipsoid with carrier densities $N_e = N_h = (2.8 \pm 0.05) \times 10^{17} \text{ cm}^{-3}$.

7. Densities of states for electrons and holes in Bi. Data on the change in the rate of filling of the electron ellipsoids (Fig. 7) after filling of the hole surface allow us to determine the ratio of the mean values (averaged over the range of energies corresponding to the depth of the conduction band and the Fermi energy) of the densities of states for electrons and holes. We denote the ratio of the filling probabilities W of the electron band and the hole band by η . Then

$$\begin{aligned} \overline{W}_h / \overline{W}_e &= \eta, \quad \overline{W}_h + \overline{W}_e = 1, \\ \overline{W}_e &= 1 / (1 + \eta), \quad \overline{W}_h = \eta / (1 + \eta). \end{aligned}$$

In the region of high impurity concentrations $\overline{W}_e = 1$, and the ratio of the slopes of the lines a and b (Fig. 7) is equal to

$$\left[\frac{\partial(\Delta V_e/V_0)}{\partial c} \right]_a : \left[\frac{\partial(\Delta V_e/V_0)}{\partial c} \right]_b = \frac{1}{1 + \eta},$$

where $V = (S/S_0)^{3/2} - 1$ is the volume of the electron ellipsoid. It follows from Fig. 7 that this ratio is equal to 0.4 and

$$\eta = \overline{W}_h / \overline{W}_e = \left(\frac{\partial N}{\partial E} \right)_h \left/ \left(\frac{\partial N}{\partial E} \right)_e \right. \approx 1.5 \pm 0.2.$$

We note that this value should exceed the ratio of the densities of states of holes and electrons on the Fermi surface, as a consequence of the nonquadratic nature of the dispersion law for electrons.

8. Dispersion law for electrons in Bi. At the present time it is accepted that the dispersion law for electrons in Bi is satisfactorily described by the ellipsoidal model of Cohen with the nonquadratic dispersion law,^[26] according to which the area of the smallest principal cross section and its corresponding cyclotron mass are expressed by the formula

$$S_1(E) = 2\pi m^*(0)E [1 + \alpha(E)], \quad m^*(E) = m^*(0) [1 + 2\alpha(E)],$$

$$\alpha = \lambda E / E_g,$$

where $m^*(0) = (m_1 m_3)^{1/2}$ is the cyclotron mass at the bottom of the band, λ is some constant, E the Fermi energy, and E_g the width of the gap between the conduction band and the valence band.

To determine the effective mass in the alloys, we use the formula

$$\frac{\omega_{T_2} T_1}{\omega_{T_1} T_2} = \frac{\text{sh}(2\pi^2 k T_1 / \beta_i H)}{\text{sh}(2\pi^2 k T_2 / \beta_i H)} \quad \beta_i = \frac{e\hbar}{m^* c},$$

which is valid under the assumption that the Dingle factor κ is temperature independent at liquid helium temperatures. Here ω_{T_2} and ω_{T_1} are the amplitudes of oscillation in the field H at the temperatures T_2 and T_1 , k is the Boltzmann constant, and β_i is double the effective Bohr magneton. The values of the mass m^* computed from this formula (averaged over the data for different values of the magnetic field and cross sections close to S_1) are shown in Fig. 9. In this same drawing is shown the dependence of the effective mass on the corresponding cross section of the Fermi surface S which, in the Cohen theory, is given by the formula

$$m^*(S_1) = m^*(0) [1 + 2\lambda S_1 / \pi m^*(0) E_g]^{1/2}.$$

It is seen that the value of m^* increases with increase in the concentration of impurities Te and Se, more than doubling at concentrations of 0.02 at. %. It must be noted that the accuracy of determination of m^* decreases upon increase in the concentration of impurities because of the increase in the Dingle factor. However, the change

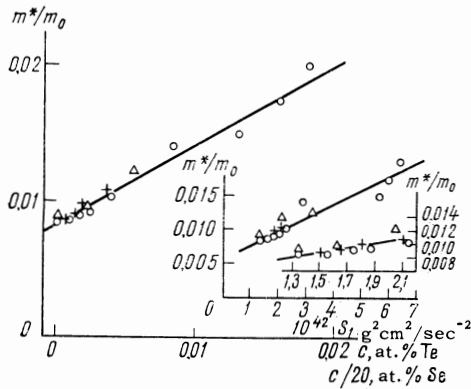


FIG. 9. Dependence of the ratio of the cyclotron effective mass to the mass of free electrons on the impurity concentration c and on the value of the extremal cross section of the Fermi surface S_1 ($\psi = 78^\circ$); \circ —for Bi-Te alloys; $+$ —for Bi-Se alloys; \triangle —data [1] for Bi-Te. The possible error in the determination of m^* amounts to 7-10% in the range of low impurity and 20-30% in the region of high concentrations.

of m^* greatly exceeds the possible error in its determination.

9. The existence of unfilled energy minimize in the Bi spectrum. According to the data of [2] the structure of the energy spectrum in Bi has the form shown in Fig. 10. According to these data, there should be an unfilled minimum of energy above the Fermi energy over the holes, distinct from the energy corresponding to the maximum of the valence band, with the energy gap $E_{g_2} = 0.732$ eV. In the conduction band one can expect a strong increase in the anisotropy of the electron constant energy surfaces for an increase in the Fermi energy by 0.017 eV. In [4], the value $E_{g_2} = 0.015$ eV was obtained, which is much less than in [2].

A rough estimate of the change in the Fermi energy for a nonquadratic dispersion law shows that the Fermi energy in alloys with a high impurity concentration is increased more than threefold. With such a significant change in the energy, the curve $(S/S_0)^{3/2} - 1 = f(c)$ (Fig. 7) show no significant kink connected with the initial filling by the electrons of the new electronic constant-energy surfaces if the density of states in them is not anomalously small. Therefore, one can draw the conclusion that the energy gap E_{g_2} should exceed 0.05 eV, which is in accord with the picture of the spectrum considered in [2]. On the other hand, the fact that the dependence of $(S/S_0)^{3/2} - 1$ on the concentration, for a minimal cross section of the electron ellipsoid, does not reveal any tendency toward saturation evidently shows the absence the appreciable increase, which was expected in [2], in the anisotropy of the electron surface in this range of energies.

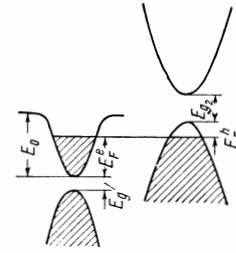


FIG. 10. Scheme for the band structure of Bi. According to [2]; $E_F^h = 0.013$ eV, $E_F^e = 0.031$ eV, $E_0 = 0.048$ eV, $E_{g_1} = 0.013$ eV and $E_{g_2} = 0.732$ eV; according to [4]: $E_{g_1} = 0.02$ eV and $E_{g_2} = 0.015$ eV.

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