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The Crystaldiamagnetism of Bismuth Crystals

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A. Introduction. (A. Goetz and A. B. Focke)

The problem of crystaldiamagnetism (CDm) is a quality characteristic of the solid state. It depends on the coexistence of a *large* number of atoms in crystalline array (10^3 atoms in each direction), is "structure sensitive" and does not follow Curie's law. Previous work on polycrystalline material has shown large influences by metallic admixtures when within the solubility limits. Discrepancies were shown for polycrystalline material solidified *in vacuo*. The purpose of this investigation is to study these relations quantitatively on single crystals with special regard to the problem of solid solution.

B. Experimental Procedure and Results. (A. B. Focke)

The method of the magnetic measurement was the Gouy method, the field strengths used between 2500 and 22,500 gauss. The temperature control was cryostatic down to −185°C and thermostatic up to 271°C (melting point of Bi). For the *production of the crystals* spectroscopically analyzed material was used, for the growth the method of Goetz in a modified form. A special apparatus was built for growing the crystals *in vacuo* but no discrepancy with crystals grown in a neutral atmosphere was found. The results derived from several hundred crystals are partly given in tabulated form. The susceptibilities at 21°C for the purest Bi are $\chi_\perp = -(1.482 \pm 0.014) \times 10^{-6}$; $\chi_{||} = -1.053 \pm 0.010 \times 10^{-6}$. The values for alloyed crystals depend on the speed of growth for low speeds.

C. Description of Results and Discussion. (A. Goetz and A. B. Focke)

The effect of the type of insertion of admixtures upon CDm is found to be nonexisting in case of complete insolubility (Bi-Cu), to be random for macroscopic solubility (eutectic mixture) (Bi-Ag) and to be large and directional for atomic solubility, no matter whether the admixture enters the crystal as an atom (Sn, Pb and probably Ge) or as an intermetallic compound (BiSe, Bi_2Te_3). For atomic solubility the effect is smallest for an isomorphous admixture (Bi-Sb). The specific effect of the admixture is the larger the smaller the solubility limit. The effect of the nature of the dissolved atom upon the magnetic anisotropy is studied for the immediate neighbors of Bi in the periodic system; the electropositive admixtures Ge, Sn, Pb and the electronegative admixtures Se and Te. All of the former type increase the anisotropy $\chi_\perp/\chi_{||} = R$, all of the latter decrease it. The size of the influence among atoms of the same valency configuration is studied. The dependence of the anisotropy on the temperature is characterized by a decrease with increasing temperature irrespective of the sign and the magnitude of the effect of the admixture. The effect for high concentrations of electronegative admixtures can be so large for high concentrations that R becomes infinite: the crystal becomes paramagnetic in one and diamagnetic in the other direction. The relation $1/R = \rho = f(T)$ is linear for both types of admixtures. It is described by:

$$\chi_{||}/\chi_\perp = \rho = \rho_0 - (\gamma_0 + \gamma)(T_0 - T),$$

where ρ_0, T_0 are independent of the admixture. The discontinuity at the transformation point for Bi at 75°C changes only the value of ρ_0. The temperature coefficient γ is positive for electropositive and negative for electronegative admixtures, it increases with increasing concentrations (N). The dependence of the anisotropy on the concentration of the admixture is of exponential type at room temperature; at liquid air temperature a "critical" concentration is found at which the value of $d\rho/dN = \alpha'$ decreases suddenly. It lies for Pb at 0.08 percent, for Sn at 0.027 percent. It appears that the magnitude of the effect, admixtures of a certain valency configuration inflict upon χ for a certain low temperature, is definite; to produce this effect three times as many Pb (and probably Ge) atoms are necessary as Sn atoms. Electronegative admixtures show this effect much less distinctly. The dependence of $\chi_{||}$ and $\chi_\perp$ on the concentration and the type of admixture shows a critical concentration N_c for low temperatures normal to [111] for electropositive and parallel to [111] for electronegative admixtures. A number of other effects can be summarized: an electropositive admixture acts upon the CDm normal to [111] in the same way as an electronegative admixture parallel to it and *vice versa.* An isomorphous admixture has an electropositive effect normal to [111] and electronegative parallel to [111]. N_c has the following values: for Te $\leqq 0.01$ percent, for Sn 0.03 percent, for Pb and Se 0.09 percent. For high temperatures another critical concentration occurs around 0.01 percent, being the same for all admixtures studied. The temperature coefficient γ for pure Bi is: $\gamma_{||} = -1.1 \pm 0.05 \times 10^{-3}$ deg.$^{-1}$ and $\gamma_\perp = -1.5 \pm 0.08 \times 10^{-3}$ deg.$^{-1}$. The $\chi - T$ function does not show any fundamental difference between electropositive and electronegative admixtures. The transformation point at 75° is marked in the same way for all admixtures for small concentrations by a discontinuity which is positive for $\chi_{||}$ and negative for $\chi_\perp$. The discontinuity disappears for $N \gg N_c$. A hypothesis about the influence of the admixture upon the CDm encounters serious difficulties if one assumes a volume effect due to a superstructure in the usual sense.

Introducing a superstructure of planes according to previous suggestions of the authors with a parameter of 10^3-10^4A on which the admixture is adsorbed and accepting the Ehrenfest-Raman theory, the entire phenomenology can be accounted for satisfactorily in a qualitative way. The parameters for the plane structure thus obtained are in good agreement with the results of etch figures and the "critical" sizes of colloidal crystals. The interpretation of the pseudo-allotropic transformation at 75°C leads to the conclusion that this superstructure becomes instable at this point without however affecting the lattice.

A. Introduction. By A. Goetz and A. B. Focke

1. The problem of crystaldiamagnetism (CDm)

The following paper is to describe experiments covering CDm in Bi crystals as a function of the concentration and the type of admixtures of foreign atoms; it forms as such a part of a more general research program which was started a number of years ago and of which some results have been published already in a fragmentary manner.[1, 2, 3]

The problem under discussion divides itself naturally into two parts: to gain material for a better understanding of the nature of CDm as such, as well as a closer insight into the disturbing effect upon the electron configuration within the crystal lattice caused by the presence of small concentrations of admixed foreign atoms. The phenomenology of CDm so far known can be put as follows:

(1) The CDm is by definition a property of matter (chiefly of metals) in the crystalline state. Its magnitude and sign seem to be independent of the magnitude or sign of the susceptibility (scz) of the atoms or molecules in the gaseous or liquid state.

(2) The CDm is dependent on the crystallographic arrangements. Substances with different allotropic modifications show wide variations of scz. For example in α-Sn, $\chi=-0.35\times10^{-6}$, in β-Sn, $\chi=+0.025\times10^{-6}$. For C in diamond, $\chi=-0.46\times10^{-6}$, C in graphite $\chi=-3.5\times10^{-6}$.[4, 5]

(3) The scz in general increases very rapidly with decreasing temperature and does not follow Curie's law.

(4) The fundamental mechanism which produces CDm must involve a large number of atoms or molecules in an undisturbed crystalline array. This conclusion is to be drawn from the following two types of observations:

(4.1) The CDm is "structure-sensitive" since it can be changed considerably even for polycrystalline material by plastic deformation.[6, 7] In addition it has been proved recently that it is very sensitive to different states in superstructural (*Ueberstruktur*) configurations as, for instance, in Cu-Au alloys.[8]

(4.2) Observations on the magnitude of the scz in dependence on the size of the crystal have proved that below a certain magnitude of the latter the CDm becomes size-dependent.[9, 10, 11, 12]

The theoretical treatment of the problem of CDm is not very satisfactory. The theories of Langevin and Pauli do not apply. Any theory which describes it as an atomic property cannot succeed. Such theories do not explain the increase of negative scz at the transition into the solid state. The critical size below which the scz becomes dependent upon the dimensions of the crystal is of the order of 10^4A which suggests that cooperation of many thousand atoms is necessary to produce the diamagnetism typical of the crystal. The analogy to ferromagnetism is obvious.

Theories of the scz of a free electron gas are unsatisfactory since it appears that even for the alkali metals the assumption of completely free valency electrons is inconsistent so far as the calculation of the scz is concerned.[13]

To account for the behavior of metals having large CDm, P. Ehrenfest[14, 15] first proposed that electron orbits surrounding two or more nuclei are responsible for CDm.*

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* The idea seems to be especially suggestive since the atoms in the Bi lattice are grouped along the axis [111] definitely in pairs which would mean that the probability of the electronic sharing among two close neighbors in the direction of the shortest distance is much larger than in any other direction. Thus the area of the electron orbits must be characterized by a larger projection into a plane perpendicular to the principal axis of the lattice than parallel to it. The result would be accordingly a maximum diamagnetic scz parallel to [111]. This, however, is just the opposite to the facts since the maximum diamagnetism occurs in a plane normal to this axis.

Raman[16] extended this hypothesis even farther by assuming electron orbits over large regions of the crystal, suggesting herewith the mentioned experiments on the size-dependence of the susceptibility due to artificial limitation of these orbits.

Because of the fundamental importance of CDm for an understanding of the electronic structure of solids, it seemed to us interesting to attack the problem by a method other than by measuring critical sizes of crystals. The production of very fine crystalline powders involves methods which do not exclude possible disturbances of the lattice, and also the lattice structure of small particles is not well known, especially with regard to the question whether or not and to what extent the surface forces affect the lattice structure of the crystal.

The following method was developed for determining the "effective cross section" of a foreign atom inserted into the lattice of a pure metal. If the type and size of the disturbance caused by foreign atoms be known as a function of their concentration, one is able to determine either the volume which is disturbed by one foreigner (effective cross section) or the volume within the lattice which has to remain undisturbed in order to have an intact mechanism of the CDm typical for the crystal lattice under investigation. If a crystal lattice of anisotropic character is used one should thus expect that the anisotropy as such should be changed by an insertion; and by this one expects to throw more light on the causes of the general inconsistency between the crystallographic anisotropies and the anisotropy of different physical properties in metallic crystals.

2. Discussion of previous work

Previous work by Johansson and Linde,[17] Endo,[18] Spencer and John,[19] on polycrystalline metals has shown the importance of admixtures. We find that their results on binary metallic systems may be summarized as follows:

(1) For a binary mixture of metals in the *liquid* state the scz follows the additive law

$$\chi_N = \chi_A + N(\chi_B - \chi_A)/100 \qquad (1)$$

and $\alpha^* = d\chi_N/dN = \text{constant}$, in which χ_N, χ_A and χ_B are the scz's of the mixture (N) and the components A and B, respectively, and N the percentage atomic concentration of B in A.

(2) The above law is fulfilled approximately* for binary systems with continuous solubilities in the solid state if χ_A and χ_B are taken for the solid metal. Such a case is shown in Fig. 1 for Bi-Sb. The equilibrium curves refer to the right ordinate, the left ordinate indicates the scz. The upper straight line (1) gives the scz for the liquid mixtures, the dashed curve (s) gives the values for the solid state obtained by Shimizu[20] and the full-drawn curve those by Endo. Both refer to the polycrystalline solid state (cf. below).

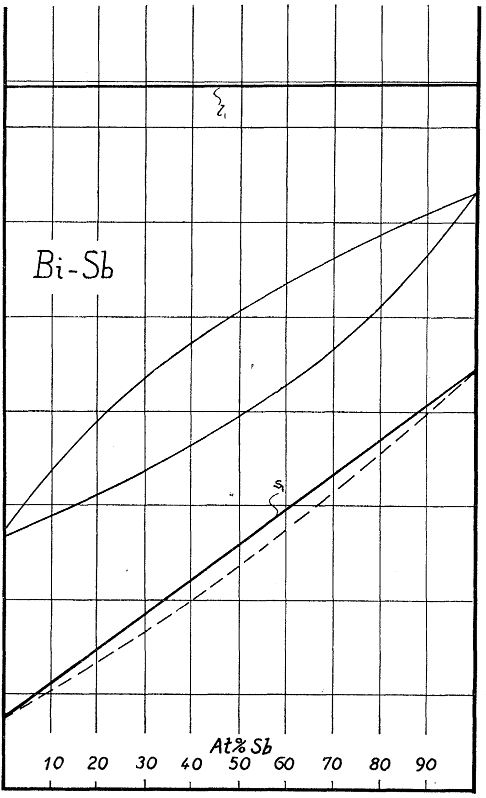

FIG. 1. Equilibrium diagram Bi-Sb (Otani).[21] Left ordinate indicates the scz's for the system in a liquid state (600°) (l) and the solid state (22°) (s). The dashed scz-curve gives the values of Shimizu, the full drawn lines those of Endo.[18, 20]

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* Since there are many ways in which the components of a binary solid solution can arrange themselves (*Ueberstrukturen*), the function α^* (N) can be influenced largely by heat treatment (*Vergütung*, etc.)[8, 17], hence the constancy of α^* is a correct statement only in view of the distinctly different behavior in the following cases.

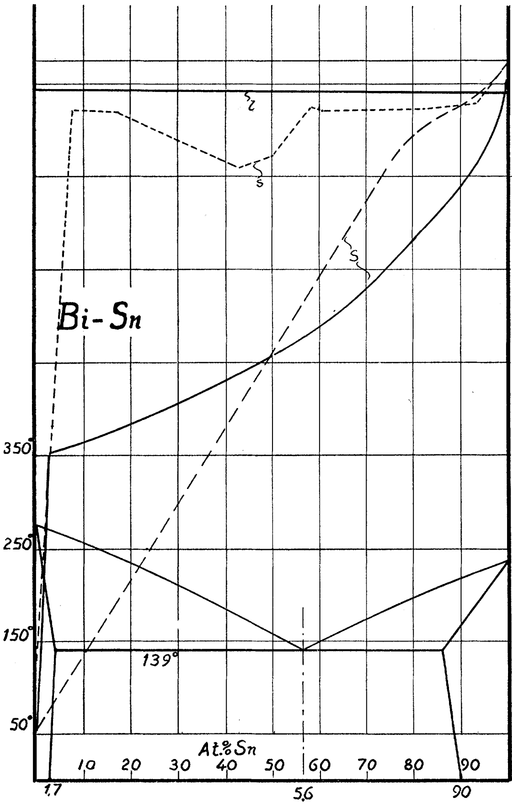

FIG. 2. Equilibrium diagram Bi-Sn (Endo).[18] The central ordinates indicate the scz's for the liquid (*l*) and the solid (*s*) states. The full drawn curve represents the results of Endo, the dashed curve those of Shimizu,[20] the dotted curve those of Spencer and John.[10]

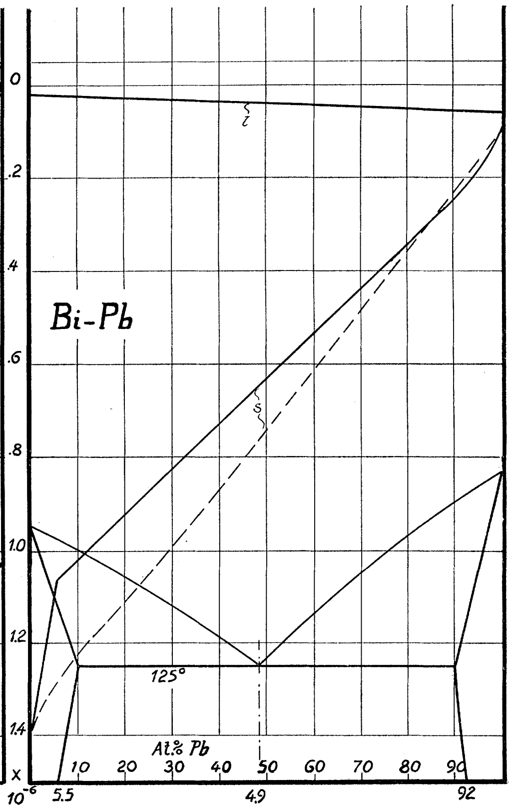

FIG. 3. Equilibrium diagram Bi-Pb (Barlow).[22] The central ordinate indicates the scz's for the liquid (*l*) and the solid (*s*) states. The full drawn curve represents the results of Endo, the dashed curve those of Shimizu.[20]

(3) If the system has a limited solubility the above additive law does not hold, since the region of solubility is characterized in such cases by a large dependence of the CDm on the concentration of the admixture (large α^*); as soon, however, as the solubility limit is transgressed α^* decreases considerably. Such cases are the systems Bi-Sn (Fig. 2) and Bi-Pb (Fig. 3).† It is interesting to note that in contradistinction to the solubility region the eutectic point in both systems is not at all reflected in α^*.

(4) If the system is, in addition to (3), characterized by the existence of one or more intermetallic compounds, α^* is greatly affected, as should be expected since one has to deal in this case with interatomic valency shifts suggesting influential changes in the electron configuration. The diagram of the system Bi-Te (Fig. 4) shows this clearly.†

The observations described by Endo[18] have been made questionable by recent investigations of Shimizu[20] who repeated the measurements of previous authors, preparing however his alloys *in vacuo*. The results thus obtained are at great variance with the previous ones since his values of α^* (though the values of χ_A and χ_B, i.e., for the pure substances, are in precise agreement with the values for metals crystallized in the open) do not indicate at all in what form B is admixed to A. His obvious conclusion is that the effects previously observed are due only to

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† The solubility region at the Bi side of the Bi-Sn system has not yet been confirmed metallographically but is thought to be correct in our opinion. As will be discussed later, it seems to be that very small solubilities can escape the usual metallographic analysis since, for instance, Bucher's results[23] do not show such a solubility. The same is true apparently for the systems Bi-Se and Bi-Te (cf. below).

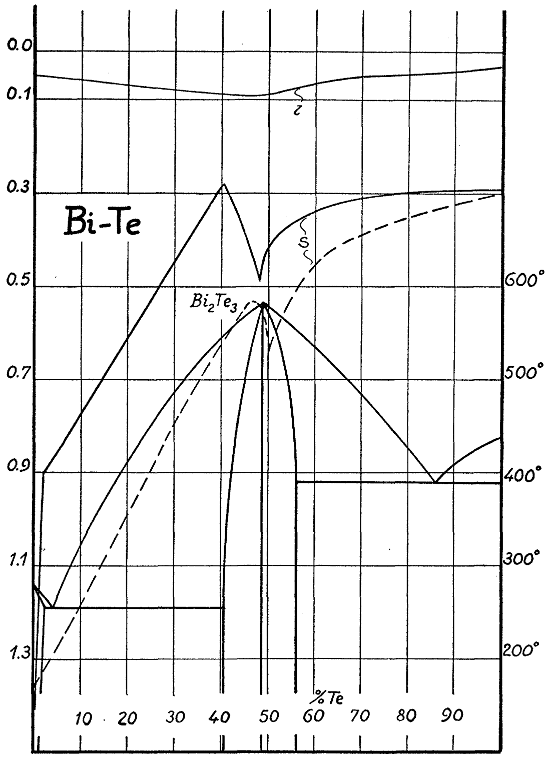

FIG. 4. Equilibrium diagram Bi-Te (Mönkemeyer[24] and K. Honda and T. Soné).[25] The left ordinate shows the scz for the liquid (*l*) and the solid (*s*) states. The full drawn curve represents the results of Endo,[18] the dashed curve those of Shimizu.[20]

absorbed gases. If this should be the case it seems very unexpected that the admixtures in a metal reflect the equilibrium-diagram in detail and perfectly only in the presence of uncontrolled amounts of gases and do not show the slightest effect in that respect in their absence. It may be anticipated at this point that our results for alloyed single crystals prepared *in vacuo* show that Shimizu's results cannot be transferred from the polycrystalline state for single crystals.

3. The purpose of this investigation

The purpose of the present investigation was chiefly to study the effect on single crystalline materials of atoms dissolved in the metallic crystal lattice. Concentrations from the smallest measurable up to the limit of solubility were used to determine the functional dependence of α on the concentration. Single crystals were used to avoid the deposition of unknown amounts of foreign materials within the boundaries of crystallites.

Because of its large CDm and anisotropic qualities Bi was used. It also possesses limited solubilities with a number of other metals and has been studied from various points of view in this laboratory.[3, 26, 27, 28, 29, 30, 31]

The effect of admixtures upon the CDm in different directions of the crystal, the influence of elements with respect to their relative position to A in the periodic system, and the dependence of the scz on the temperature were studied. Such studies should yield information concerning which of the differences between A and B (atomic volume, valency configuration, etc.) is effective. They should also give more definite conclusions about the equilibrium conditions of dissolved admixtures.

Finally one could expect more information about the causes of the discrepancies between the results obtained from crystals grown in a gas atmosphere (Endo) and those grown in vacuo (Shimizu). It has to be realized at the same time that the results to be expected even from an extended investigation of this kind will give only very limited information, since the problem of the limited solubility, especially between heteromorphous components in a microscopic single crystal is very complex and very little knowledge about such processes in general has so far been obtained.

B. EXPERIMENTAL PROCEDURE AND RESULTS.

BY A. B. FOCKE[32]

1. Method and apparatus

(1.1) *Method of magnetic measurements.* Because of its distinct advantages for large single crystals the Gouy method was used. The twinning lamellae which always occur when a Bi crystal is cut or cleaved were located in the uniform region of the field and the perfect regions of the crystal extended over the inhomogeneous part of the field. Measurements showed that the scz did not change for field strengths varying from 2500 to 22,500 gauss so that the variable field used in the Gouy method introduced no errors and there were no ferromagnetic impurities.

The principal factors limiting the accuracy of the measurements were: (1) the determination of the area of the cross section of the crystals, (2) the sensitivity of the balance and (3) the measurement of the strength of the magnetic field. The cross section was not measured directly but was calculated from the weight, length and density of each crystal for the part over which the field gradient occurred. All forces were measured with an accuracy of one-tenth of a milligram, which was in general less than one-half of one percent of the total forces produced by the magnetic field. The field strength was measured with a Grassot fluxmeter, with an accuracy of one percent. The theory and mechanical arrangement are described elsewhere.[1]

(1.2) *The temperature control.* The furnace is sketched in Fig. 5. It is wound non-inductively so that no correction to the field had to be made. The spacings of the winding, thickness of insulation and sheet aluminum lining were arranged to give a uniform temperature over the length of the crystal.

For measurements at liquid air temperature, a small flask (Fig. 6) was designed so that the crystal could be brought to this temperature without coming in actual contact with the liquid air. The crystal hangs in the inner tube which is open at the top only and is completely surrounded by liquid air. The liquid air chamber is further surrounded by an evacuated compartment. The upper part of the flask is provided with storage space for liquid air to insure the complete surrounding of the crystal chamber. This flask is found to be satisfactory, the only trouble encountered being the formation of liquid oxygen in the crystal tube when the liquid air was fresh.

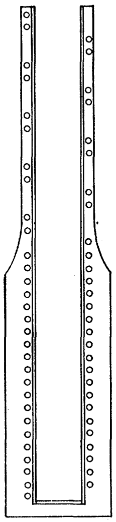

Fig. 5

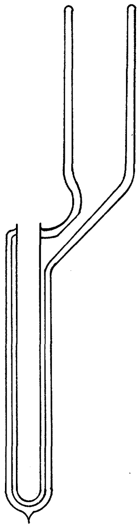

Fig. 6

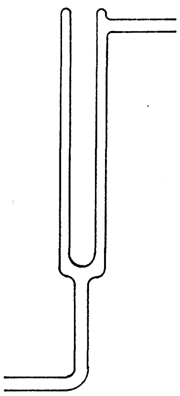

Fig. 7

FIG. 5. Furnace for heating the crystal during the determination of scz.

FIG. 6. Dewar flask for keeping the crystal at liquid air temperature during the determination of scz.

FIG. 7. Cryostatic arrangement for cooling the crystal during the determination of scz.

For some measurements at temperatures between -185°C and 22°C a cooling jacket similar to that used by Kapitza[34] was employed (Fig. 7). Cold gas from boiling liquid air passed through the jacket. The temperature was controlled by varying the rate of boiling of the liquid air. This control was very good but the cooler was very inefficient with this apparatus and was not used to any great extent.

2.1. The material

The Bi was the commercial grade sold by the Merck Chemical Company. Spectroscopic analysis performed by Mr. Hasler proved this grade to be freer from impurities than the so-called CP grades from various sources. Table I gives the atomic percentages of the impurities found and also the ratio of the principal scz's, (R).

TABLE I. *Atomic percentages of impurities in various bismuth samples. A,* Baker Corporation CP; *B,* Hartmann & Braun CP; *C,* Hartmann & Braun electrolytic; *D,* Kahlbaum-Berlin CP; *E, F, G, H,* Merck commercial.

Impurity	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Copper	0.002	0.011	0.006	0.003	0.007	0.001		
Silver	.017	.028	.012	.046	.013	.006		
Tellurium	.000	.001	.000	.004	.000	.000		
Thallium	.000	.002	.000	.005	.000	.000		
Lead	.025	.061	.019	.020	.014	.002		
Total	.044	.103	.037	.075	.034	.009		
$R=$	1.499	1.597	1.440	1.460	1.430	1.410	1.430	1.435
				(Distilled)	1.423			

Lots *G* and *H* from Merck were not analyzed but their magnetic properties agree with bismuth *E*. The other metals used in making up the alloy samples were of commercial reagent quality. No special precautions were taken to insure their great purity, as all the alloys were limited to small percentages of the added metal.

The alloys were compounded by direct weighing. An attempt to use a base solution containing ten percent of the impurity (Pb and Ag) and to dilute further this solution was abandoned as some Pb was lost at each melting.

2.2. Production of crystals in an atmosphere

The procedure used in growing the crystals followed closely that developed by Goetz.[27] There were several variations which will be described. The desired amount of Bi was melted in a Pyrex crucible in an atmosphere of purified hydrogen and raised to about 500°C to reduce any oxide present. Then the Bi was cooled to 350°C and the impurity added. This procedure reduced the amount of chemical combination of the impurity with either the hydrogen or the glass. For alloys containing Pb and Sn it was necessary to use quartz crucibles as the metals reacted with the Pyrex.

After thoroughly stirring the melted alloy, it was drawn into Pyrex tubes (2–3 mm diam.) and quickly cooled. The rapid cooling prevented loss of impurities even of Pb and Sn. The alloys sometimes stuck to the glass tube. To prevent this, Bridgman's method[47] of heating the tube with a trace of oil in it until a light deposit of carbon was formed, was found to be satisfactory except for Te and Se. For these a clean tube was used and broken while wet with water. The capillary action of the water in the cracks formed in breaking the glass seemed to admit a film of water between glass and metal, so that the glass came off with ease.

The "second generation" of crystals as described by Goetz[27] was omitted. The lighter impurity metals tended to separate from Bi at each melting and Te, Se and Sb seemed to form gaseous hydrides, hence the single crystals were grown with as few operations as possible.

The "third generation" was carried out in the usual manner, the crystals being grown as rapidly as possible to obtain uniform distribution of the impurity.

2.3. Production of crystals *in vacuo*

Shimizu's paper[20] intimating that previous work on polycrystalline material was largely influenced by absorbed gases appeared when most of the measurements had been taken. To test the influence of gases on single crystals, some were grown *in vacuo.*

A "first generation" of rod was melted in an evacuated glass tube (a, Fig. 8) and degassed. The molten metal then was passed into a tube (c, Fig. 8) having the same size as those used in the ordinary "first generation" and the tube sealed. When the final single crystal was made, the glass was cracked off and the rod placed in a soapstone trough T and enclosed in an evacuated tube. Soapstone was used in preference to graphite because of its lower heat conductivity. A short light furnace F was then moved without mechanical vibration along the glass tube. The seed crystal was attached to the rod by melting a part of it with a tiny hydrogen flame.

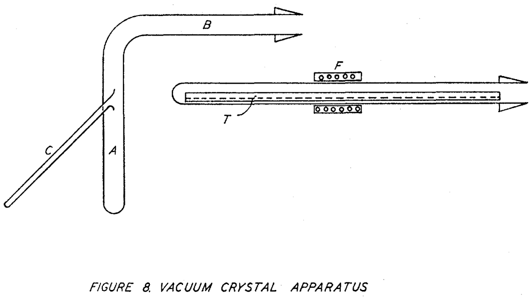

FIG. 8. Arrangement for growing single crystals in vacuo.

Crystals grown in vacuo were found to have magnetic properties identical with those grown in the presence of hydrogen or carbon dioxide, showing that for *single* crystals dissolved gases play little if any rôle. Those grown *in vacuo* did, however, show much brighter reflections after being etched than did any other crystals.

3. Results

(3.1) *The magnetic properties of pure bismuth.* It was first shown that the scz of Bi is independent of the field strength within wide limits and that the scz is invariant within any direction normal to the principal axis [111].

The measurement of the scz of five crystals at room temperature from $\theta^* = 0°$ to $\theta = 90°$ proved an excellent validity of the Voigt-Thomson law ($\cos^2$) and gave the following values:[1]

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* All angles θ in this paper are taken with reference to the principal axis [111].

$$\chi_\perp = -(1.482 \pm 0.014) \times 10^{-6},$$

$$\chi_{\parallel} = -(1.035 \pm 0.010) \times 10^{-6},\ R = \chi_\perp / \chi_{\parallel} = (1.408).$$

From these the value of the susceptibility to be expected of a polycrystalline aggregate is given by

$$(2\chi_\perp + \chi_{\parallel})/3 = -(1.340 \pm 0.013) \times 10^{-6},$$

which is in very good agreement with the values found by previous authors.[35]

The ratio of the principal scz's of the various kinds of Bi are given in Table I. These values do not involve errors of measurements of field strength or cross section.*

(3.2) *Dependence of the distribution of impurity on the speed of growth of crystals.* Materials are usually purified by crystallization. This effect is always amplified by slow crystallization and has been used to obtain pure Bi.[36] To determine the separation of Bi from the alloys and the effect on the magnetic properties, several samples of Bi containing Pb were made into similar rods and grown into crystals. One was grown at the rate of 6 mm/min. and the other at the rate of 1 mm/min. The magnetic anisotropy R was then measured at each end. Those grown at the fast or normal rate n showed uniform magnetic properties, and those grown at the slow rate s show large variations. Table II gives data on such crystals. The first two columns show the type of crystal and source of supply. The last two columns present the anisotropy at the beginning (R_1) and at the end (R_2) of the crystal.

Table II. *Ratio of principal susceptibilities for various kinds of Bi.*

		Pb content	R_1	R_2
188/11*n*	*G*	3.00%	2.619	2.625
188/21*s*	*G*	3.00%	2.130	2.764
166/12*n*	*G*	0.15%	1.630	1.627
166/22*s*	*G*	0.15%	1.605	1.751
192/11*n*	*G*		1.430	1.428
192/21*s*	*G*		1.438	1.429

The choice of the proper speed of growth is important for if the speed is too great no uniform single crystals were obtained, and if too slow the properties vary along the crystal length. For example: A rod originally containing 2 percent of lead when grown at one-sixth the normal speed (1 mm/min.) was found to have magnetic properties of a normal one percent crystal at the end which crystallized first and of a normal three percent crystal at the other.

(3.3) *Tabulation of results.* An abbreviated account of the numerical results is given in Tables III and IV. The data in Table IV are so arranged that the first column gives the number of the individual crystal; the second column ("kind") indicates the chemical composition of the crystal; i.e., *G* 0.025 percent Cu shows that the sample is composed of *G* bismuth (see Table I) to which 0.025 atomic percent of copper has been added; this is followed by the force exerted by the field upon the crystal, in tenths of milligrams, the orientation of the crystal being indicated by the subscript of the letter χ; column R gives the magnetic anisotropy; and the other columns of data are self-explanatory. In all cases the scz used is the specific or mass scz (χ), i.e., the ratio of the magnetic moment per unit mass, to the magnetizing field.

Table III. *Data for crystals of uniformity sufficient to make determination of χ possible.*

Temp. °C	H	$F_\perp$	$F_{\parallel}$	R	$1/R$	$-\chi_\perp \times 10^6$	$-\chi_{\parallel} \times 10^6$
Crystal 123/41*F*							
−185	7 920	566	362	1.565	0.639	1.944	1.226
− 84	9 900	770	502	1.534	0.652	1.691	1.104
22	9 900	675	482	1.406	0.711	1.482	1.063
126	9 900	561	419	1.340	0.746	1.237	0.921
268	9 900	419	346	1.210	0.826	0.922	0.760
Crystal 224/21*G* 5.00% Sn							
−185	7 650	119	−76	− 1.56	−0.639	0.433	−0.283
−135	9 900	162	−81	− 3.18	−0.314	0.698	−0.219
−115	— —	144	−36	− 4.08	−0.250	—	—
− 84	9 900	F=385		− 4.48	−0.224	0.850	−0.190
− 56	— —	162	−18	−10.1	−0.099	—	—
+ 32	— —	213	14	15.2	0.066	—	—
62	— —	224	27	8.30	0.121	—	—
72	— —	225	33	6.82	0.147	—	—
75	10 560	F=567		6.78	0.148	1.102	0.161
126	10 560	219	50	4.38	0.228	1.129	0.257
185	10 360	195	66	2.85	0.351	1.054	0.369
232	10 560	155	62	2.50	0.400	0.895	0.358

Since the determination of the absolute value of the scz requires crystals of very uniform

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* These variations support the view of Goetz and Hasler[28] concerning the great differences observed in their work on crystals in a magnetic field. From the Table I it would be expected that bismuth *B* would be most affected by growth in a magnetic field, because of the larger torque acting on it. This is exactly the result found.

TABLE IV. *Summary of data.*

Crystal	Kind	R	$1/R$	$-\chi_{\perp}\times 10^6$	$-\chi_{\parallel}\times 10^6$
Temperature: −185°C; H = 6850 gauss.					
249/11	*H* 0.01% Ag	1.564	0.639	1.920	1.228
251/11	*H* 0.09% Ag	1.595	0.626	1.920	1.200
253/11	*H* 0.81% Ag	1.618	0.618	1.950	1.203
254/11	*H* 2.43% Ag	1.575	0.634	1.900	1.203
256/11	*H* 0.01% Sn	1.850	0.541	2.232	1.207
257/12	*H* 0.03% Sn	2.325	0.429	2.568	1.104
258/11	*H* 0.09% Sn	2.460	0.406	2.275	0.925
260/11	*H* 0.81% Sn	3.740	0.267	1.070	0.286
261/11	*H* 2.43% Sn	−10.850	−0.092	0.704	−0.065
263/11	*H* 0.01% Pb	1.698	0.589	2.017	1.189
264/11	*H* 0.03% Pb	1.878	0.533	2.197	1.169
265/11	*H* 0.09% Pb	2.283	0.438	2.530	1.108
266/11	*H* 0.27% Pb	2.620	0.382	2.431	0.927
267/11	*H* 0.81% Pb	2.425	0.412	1.827	0.752
268/11	*H* 2.43% Pb	2.740	0.365	1.365	0.498
270/11	*H* 0.01% Te	1.080	0.925	1.682	1.478
271/12	*H* 0.03% Te	0.974	1.028	1.427	1.465
272/11	*H* 0.09% Te	0.830	1.205	1.224	1.474
273/11	*H* 0.27% Te	0.617	1.620	0.919	1.490
275/11	*H* 0.01% Se	1.306	0.765	1.800	1.376
276/11	*H* 0.03% Se	1.091	0.915	1.663	1.511
277/11	*H* 0.09% Se	0.995	1.005	1.530	1.535
278/11	*H* 0.27% Se	0.856	1.168	1.269	1.483
279/11	*H* 0.81% Se	0.772	1.295	1.004	1.333
280/11	*H* 0.01% Sb	1.552	0.644	2.025	1.303
281/11	*H* 0.03% Sb	1.514	0.660	1.920	1.270
282/11	*H* 0.09% Sb	1.462	0.684	1.875	1.330*
283/11	*H* 0.27% Sb	1.545	0.647	1.978	1.279
Temperature: 22°C; H = 20,800 gauss.					
249/11	*H* 0.01% Ag	1.430	0.699	1.489	1.041
251/11	*H* 0.09% Ag	1.428	0.700	1.488	1.043
253/11	*H* 0.81% Ag	1.430	0.699	1.492	1.043
254/11	*H* 2.43% Ag	1.420	0.705	1.490	1.051
256/11	*H* 0.01% Sn	1.470	0.680	1.539	1.046
257/11	*H* 0.03% Sn	1.570	0.637	1.562	0.994
258/11	*H* 0.09% Sn	1.803	0.555	1.658	0.916
260/11	*H* 0.81% Sn	2.965	0.337	1.573	0.531
261/11	*H* 2.43% Sn	4.655	0.213	1.289	0.265
263/11	*H* 0.01% Pb	1.443	0.692	1.478	1.023
264/11	*H* 0.03% Pb	1.478	0.677	1.533	1.040
265/11	*H* 0.09% Pb	1.542	0.648	1.520	0.990
266/11	*H* 0.27% Pb	1.737	0.576	1.636	0.941
267/11	*H* 0.81% Pb	2.021	0.494	1.655	0.816
268/11	*H* 2.43% Pb	2.459	0.407	1.604	0.652
270/11	*H* 0.01% Te	1.329	0.753	1.442	1.073
271/11	*H* 0.03% Te	1.197	0.836	1.325	1.108
272/11	*H* 0.09% Te	0.903	1.108	1.122	1.244
273/11	*H* 0.27% Te	0.697	1.435	0.897	1.288
275/11	*H* 0.01% Se	1.381	0.724	1.483	1.073
276/11	*H* 0.03% Se	1.280	0.781	1.424	1.111
277/11	*H* 0.09% Se	1.203	0.830	1.396	1.161
278/11	*H* 0.27% Se	1.020	0.980	1.244	1.220
279/11	*H* 0.81% Se	0.966	1.034	1.176	1.216
280/11	*H* 0.01% Sb	1.423	0.702	1.490	1.046
281/11	*H* 0.03% Sb	1.421	0.703	1.480	1.040
282/11	*H* 0.09% Sb	1.420	0.704	1.468	1.032
283/11	*H* 0.27% Sb	1.427	0.700	1.468	1.023
Temperature: 65°C; H = 8500 gauss.					
249/11	*H* 0.01% Ag	1.387	0.729	1.387	0.998
251/11	*H* 0.09% Ag	1.360	0.733	1.394	1.027
253/11	*H* 0.81% Ag	1.352	0.735	1.370	1.012
254/11	*H* 2.43% Ag	1.360	0.730	1.381	1.016
256/11	*H* 0.01% Sn	1.385	0.730	1.436	1.038
257/12	*H* 0.03% Sn	1.436	0.695	1.465	1.022
258/11	*H* 0.09% Sn	1.683	0.590	1.563	0.915
260/11	*H* 0.81% Sn	2.650	0.370	1.540	0.581
261/11	*H* 2.43% Sn	3.722	0.260	1.406	0.376
263/11	*H* 0.01% Pb	1.370	0.727	1.380	1.007
264/11	*H* 0.03% Pb	1.419	0.702	1.444	1.018
266/11	*H* 0.27% Pb	1.603	0.590	1.502	0.936
267/11	*H* 0.81% Pb	1.800	0.549	1.508	0.835
268/11	*H* 2.43% Pb	2.216	0.446	1.573	0.713
270/11	*H* 0.01% Te	1.287	0.775	1.330	1.050
271/12	*H* 0.03% Te	1.220	0.820	1.332	1.084
272/11	*H* 0.09% Te	0.958	1.041	1.132	1.182
273/11	*H* 0.27% Te	0.733	1.372	0.917	1.252
275/11	*H* 0.01% Se	1.340	0.743	1.418	1.058
276/11	*H* 0.03% Se	1.315	0.760	1.405	1.067
277/11	*H* 0.09% Se	1.197	0.833	1.358	1.133
278/11	*H* 0.27% Se	1.040	0.961	1.236	1.189
279/11	*H* 0.81% Se	1.022	0.979	1.194	1.167
280/11	*H* 0.01% Sb	1.351	0.736	1.384	1.023
281/11	*H* 0.03% Sb	1.340	0.742	1.328	0.990
282/11	*H* 0.09% Sb	1.351	0.736	1.440	1.064
283/11	*H* 0.27% Sb	1.351	0.736	1.400	1.040
Temperature: 75°C; H = 8500 gauss.					
249/11	*H* 0.01% Ag	1.379	0.725	1.381	1.001
251/11	*H* 0.09% Ag	1.342	0.745	1.381	1.030
253/11	*H* 0.81% Ag	1.378	0.726	1.375	0.995
254/11	*H* 2.43% Ag	1.364	0.733	1.358	0.995
256/11	*H* 0.01% Sn	1.394	0.717	1.441	1.034
257/12	*H* 0.03% Sn	1.398	0.715	1.438	1.029
258/11	*H* 0.09% Sn	1.670	0.598	1.488	0.890
260/11	*H* 0.81% Sn	2.245	0.445	1.437	0.639
261/11	*H* 2.43% Sn	3.534	0.283	1.402	0.397
263/11	*H* 0.01% Pb	1.372	0.728	1.383	1.007
264/11	*H* 0.03% Pb	1.339	0.747	1.412	1.053
266/11	*H* 0.27% Pb	1.581	0.629	1.484	0.940
267/11	*H* 0.81% Pb	1.813	0.551	1.500	0.826
268/11	*H* 2.43% Pb	2.120	0.466	1.520	0.717
270/11	*H* 0.01% Te	1.205	0.829	1.330	1.103
271/12	*H* 0.03% Te	1.149	0.870	1.268	1.102
272/11	*H* 0.09% Te	0.974	1.026	1.184	1.233
273/11	*H* 0.27% Te	0.778	1.290	0.954	1.225
275/11	*H* 0.01% Se	1.242	0.801	1.372	1.102
276/11	*H* 0.03% Se	1.230	0.810	1.371	1.112
277/11	*H* 0.09% Se	1.163	0.258	1.298	1.114
278/11	*H* 0.27% Se	1.048	0.953	1.214	1.160
279/11	*H* 0.81% Se	1.040	0.960	1.219	1.170
280/11	*H* 0.01% Sb	1.572	0.725	1.392	1.013
281/11	*H* 0.03% Sb	1.319	0.755	1.332	1.011
282/11	*H* 0.09% Sb	1.336	0.746	1.404	1.050
283/11	*H* 0.27% Sb	1.332	0.748	1.356	1.020

* Large stranger may cause this deviation.

cross section, it was possible to use only the best crystals for this purpose. This cross-section requirement was not of importance for anisotropy measurements, so the less uniform crystals were used for this purpose only, and are included in Table IV; the series in Table III are taken from crystals which were uniform enough to permit the evaluation of χ.

C. DESCRIPTION OF RESULTS AND DISCUSSION.

BY A. GOETZ AND A. B. FOCKE

1. The effect of the type of insertion of foreign atoms into the crystal

First of all it is important to state which of the different manners in which a foreign atom can be held within a macroscopic single crystal

TABLE IV. (*Continued.*)

Crystal	Kind	R	$1/R$	$-\chi_\perp\times10^6$	$-\chi_\parallel\times10^6$	Crystal	Kind	R	$1/R$	$-\chi_\perp\times10^6$	$-\chi_\parallel\times10^6$
Temperature: 101°C; H =8500 gauss.						*Temperature: 201°C; H =8500 gauss.*					
249/11	*H* 0.01% Ag	1.301	0.790	1.300	0.997	249/11	*H* 0.01% Ag	1.238	0.808	1.084	0.876
251/11	*H* 0.09% Ag	1.285	0.778	1.299	1.010	251/11	*H* 0.09% Ag	1.251	0.798	1.145	0.930
253/11	*H* 0.81% Ag	1.320	0.757	1.288	0.974	253/11	*H* 0.81% Ag	1.235	0.810	1.119	0.905
254/11	*H* 2.43% Ag	1.343	0.744	1.305	0.970	254/11	*H* 2.43% Ag	1.214	0.823	1,050	0.865
256/11	*H* 0.01% Sn	1.332	0.750	1.351	1.015	256/11	*H* 0.01% Sn	1.220	0.820	1.164	0.954
257/12	*H* 0.03% Sn	1.354	0.736	1.341	0.990	257/12	*H* 0.03% Sn	1.178	0.848	1.116	0.930
258/11	*H* 0.09% Sn	1.536	0.651	1.392	0.905	258/11	*H* 0.09% Sn	1.364	0.733	1.210	0.887
260/11	*H* 0.81% Sn	1.890	0.532	1.348	0.716	260/11	*H* 0.81% Sn	1.566	0.638	1.160	0.740
261/11	*H* 2.43% Sn	3.195	0.313	1.364	0.426	261/11	*H* 2.43% Sn	2.290	0.436	1.201	0.523
263/11	*H* 0.01% Pb	1.310	0.764	1.293	0.986	263/11	*H* 0.01% Pb	1.273	0.785	1.143	0.896
264/11	*H* 0.03% Pb	1.294	0.773	1.397	1.079	264/11	*H* 0.03% Pb	1.225	0.816	1.186	0.968
266/11	*H* 0.27% Pb	1.440	0.690	1.435	0.996	266/11	*H* 0.27% Pb	1.288	0.774	1.163	0.905
267/11	*H* 0.81% Pb	1.656	0.604	1.413	0.845	267/11	*H* 0.81% Pb	1.360	0.735	1.128	0.829
268/11	*H* 2.43% Pb	1.920	0.515	1.445	0.758	268/11	*H* 2.43% Pb	1.508	0.658	1.103	0.732
270/11	*H* 0.01% Te	1.196	0.835	1.259	1.052	270/11	*H* 0.01% Te	1.172	0.853	1.107	0.945
271/12	*H* 0.03% Te	1.109	0.902	1.221	1.102	271/11	*H* 0.03% Te	1.131	0.854	1.098	0.970
272/11	*H* 0.09% Te	1.000	1.000	1.168	1.169	272/11	*H* 0.09% Te	1.088	0.919	1.098	1.008
273/11	*H* 0.27% Te	0.776	1.285	0.958	1.225	273/11	*H* 0.27% Te	0.895	1.120	0.957	1.070
275/11	*H* 0.01% Se	1.228	0.813	1.304	1.063	275/11	*H* 0.01% Se	1.200	0.830	1.177	0.979
276/11	*H* 0.03% Se	1.197	0.833	1.273	1.063	276/11	*H* 0.03% Se	1.153	0.865	1.107	0.958
277/11	*H* 0.09% Se	1.171	0.852	1.264	1.080	277/11	*H* 0.09% Se	1.171	0.852	1.137	0.970
278/11	*H* 0.27% Se	1.050	0.952	1.178	1.123	278/11	*H* 0.27% Se	1.075	0.930	1.097	1.020
279/11	*H* 0.81% Se	1.060	0.941	1.210	1.142	279/11	*H* 0.81% Se	1.084	0.919	1.115	1.028
280/11	*H* 0.01% Sb	1.311	0.760	1.304	0.993	280/11	*H* 0.01% Sb	1.223	0.815	1.089	0.889
281/11	*H* 0.03% Sb	1.287	0.774	1.269	0.986	281/11	*H* 0.03% Sb	1.223	0.814	1.109	0.906
282/11	*H* 0.09% Sb	1.280	0.777	1.332	1.040	282/11	*H* 0.09% Sb	1.240	0.805	1.148	0.925
283/11	*H* 0.27% Sb	1.309	0.760	1.279	0.978	283/11	*H* 0.27% Sb	1.189	0.839	1.062	0.894
Temperature: 150°C; H =8500 gauss.						*Temperature: 245°C; H =8500 gauss.*					
249/11	*H* 0.01% Ag	1.267	0.790	1.228	0.968	249/11	*H* 0.01% Ag	1.169	0.855	0.958	0.820
251/11	*H* 0.09% Ag	1.212	0.825	1.211	1.000	251/11	*H* 0.09% Ag	1.213	0.824	1.058	0.872
253/11	*H* 0.81% Ag	1.256	0.796	1.198	0.953	253/11	*H* 0.81% Ag	1.153	0.866	0.981	0.850
254/11	*H* 2.43% Ag	1.241	0.805	1.156	0.930	254/11	*H* 2.43% Ag	1.142	0.875	0.968	0.845
256/11	*H* 0.01% Sn	1.300	0.769	1.268	0.975	256/11	*H* 0.01% Sn	1.170	0.855	1.044	0.892
257/12	*H* 0.03% Sn	1.281	0.780	1.230	0.958	257/12	*H* 0.03% Sn	1.135	0.880	0.979	0.863
258/11	*H* 0.09% Sn	1.416	0.706	1.338	0.944	258/11	*H* 0.09% Sn	1.304	0.766	1.105	0.847
260/11	*H* 0.81% Sn	1.650	0.606	1.251	0.757	260/11	*H* 0.81% Sn	1.473	0.679	1.030	0.700
261/11	*H* 2.43% Sn	2.619	0.382	1.270	0.484	261/11	*H* 2.43% Sn	1.893	0.528	0.985	0.520
263/11	*H* 0.01% Pb	1.296	1.296	1.229	0.947	263/11	*H* 0.01% Pb	1.215	0.823	1.044	0.859
264/11	*H* 0.03% Pb	1.268	0.789	1.254	0.989	264/11	*H* 0.03% Pb	1.188	0.841	1.022.	0.860
266/11	*H* 0.27% Pb	1.287	0.774	1.248	0.972	266/11	*H* 0.27% Pb	1.223	0.813	1.057	0.863
267/11	*H* 0.81% Pb	1.442	0.693	1.217	0.842	267/11	*H* 0.81% Pb	1.310	0.763	1.005	0.766
268/11	*H* 2.43% Pb	1.629	0.608	1.239	0.760	268/11	*H* 2.43% Pb	1.397	0.710	0.906	0.650
270/11	*H* 0.01% Te	1.151	0.868	1.160	1.008	270/11	*H* 0.01% Te	1.145	0.873	1.014	0.836
271/12	*H* 0.03% Te	1.133	0.882	1.161	1.048	271/12	*H* 0.03% Te	1.220	0.819	0.992	0.814
272/11	*H* 0.09% Te	1.020	0.980	1.139	1.116	272/11	*H* 0.09% Te	1.104	0.903	1.038	0.940
273/11	*H* 0.27% Te	0.843	1.190	0.961	1.141	273/11	*H* 0.27% Te	1.003	0.995	0.929	0.925
275/11	*H* 0.01% Se	1.211	0.823	1.234	1.019	275/11	*H* 0.01% Se	1.153	0.865	1.087	0.940
276/11	*H* 0.03% Se	1.170	0.852	1.188	1.014	276/11	*H* 0.03% Se	1.148	0.870	1.018	0.886
277/11	*H* 0.09% Se	1.182	0.843	1.201	1.015	277/11	*H* 0.09% Se	1.096	0.910	0.992	0.905
278/11	*H* 0.27% Se	1.093	0.913	1.163	1.064	278/11	*H* 0.27% Se	1.041	0.961	0.940	0.902
279/11	*H* 0.81% Se	1.078	0.928	1.222	1.134	279/11	*H* 0.81% Se	1.106	0.900	0.987	0.892
280/11	*H* 0.01% Sb	1.228	0.810	1.179	0.958	280/11	*H* 0.01% Sb	1.208	0.825	0.998	0.828
281/11	*H* 0.03% Sb	1.242	0.801	1.197	0.964	281/11	*H* 0.03% Sb	1.277	0.279	0.972	0.761
282/11	*H* 0.09% Sb	1.252	0.796	1.240	0.990	282/11	*H* 0.09% Sb	1.180	0.845	1.076	0.911
283/11	*H* 0.27% Sb	1.242	0.801	1.201	0.965	283/11	*H* 0.27% Sb	1.159	0.861	0.951	0.820

affects the CDm. The types of insertion can be enumerated as follows:

(a) *Complete separation of both components*, i.e., neither atomic nor microscopic solubility. Example, the system: Bi-Cu.[37] It has been found that the anisotropy of Bi crystals grown from a melt to which Cu was admixed in different proportions (from 0.025 to 1.00 percent in 20 different crystals) is *not* affected within the limits of experimental error.

(b) *Existence of a eutectic mixture*, i.e., microscopic but no atomic solubility. Example, the system: Bi-Ag.[38] The phase-diagram (Fig. 9) shows no atomic solubility on the Bi-side, however a eutectic mixture at 2.5 percent Ag-concentration. From Fig. 10 it is realized that the influence upon CDm of Ag-admixtures is very remarkable though entirely irreproducible. The fact that it is possible to affect the anisotropy R by the insertion of foreign atoms with no solubility seems very interesting, since such insertion does not influence the lattice con-

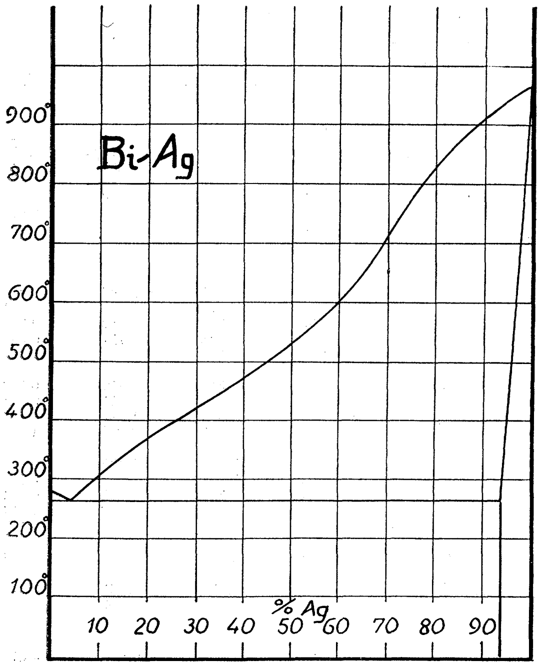

FIG. 9. Equilibrium diagram Bi-Ag (Petrenko).[38] The system is characteristized by the absence of atomic solubility on the Bi-side.

figuration at all. The fact that it is not difficult to grow good single crystals from such mixtures shows that also the macroscopic structure of the crystal is not very much distorted. (For further discussion see Section 7.)

(c) *Complete atomic solubility.* Example, the system: Bi-Sb (Fig. 1) (Table V).[21, 39, *] In this case the effect upon CDm is a simple volume effect and the additive law (Eq. (1)) is valid, also very little discrepancy exists between Endo's and Shimizu's results. Our results show no influence of Sb as far as the anisotropy is concerned, because of the small value of α and the comparatively small concentrations used (Fig. 15). ($\alpha = (\alpha R/dN)$.)

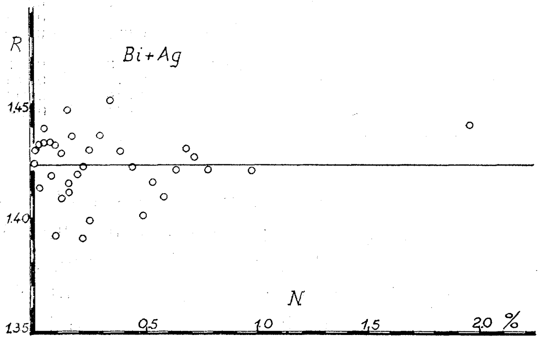

FIG. 10. R-N diagram for Bi+Ag for T=22°C. The full drawn line indicates R for pure Bi crystals. Evidence of the random, i.e., undirectional, influence of an atomically insoluble admixture.

TABLE V. $T=-185°C$.

Bi +	N %	$-\chi_\perp \times 10^6$	$-\chi_{\perp r}$ %	$-\chi_{\|\|} \times 10^6$	$-\chi_{\|\| r}$ %	$lg\alpha_{\perp r}$	$lg\alpha_{\|\| \alpha}$
–	0.0?	1.945	100	1.230	100		
						+2.24	−1.26
Sn	0.01	2.282	117.3	1.207	98.2		
						+1.86	−1.62
	0.03	2.568	132.0	1.104	89.8		
						−1.40	−1.39
	0.09	2.275	117.0	0.925	75.0		
						−0.93	−0.86
	0.81	1.070	55.0	0.286	23.2		
						−0.68	−0.15
	2.43	0.704	36.2	0.065	0.5		
						+1.56	−1.51
Pb	0.01	2.017	103.7	1.189	96.8		
						+1.67	−0.95
	0.03	2.197	113.0	1.169	95.0		
						+1.45	−0.93
	0.09	2.530	130.1	1.108	90.1		
						−0.45	−0.92
	0.27	2.431	125.0	0.927	75.2		
						−0.76	−0.92
	0.81	1.827	94.0	0.752	61.0		
						−0.16	−0.42
	2.43	1.365	70.3	0.498	40.5		
Sb	0.01	2.025	104.1	1.303	105.9		
	0.03	1.920	98.8	1.270	103.2		
	0.09	1.875	96.5	1.330?	108.1		
	0.27	1.978	101.7	1.279	104.0		
						−1.88	+2.08
Se	0.01	1.800	92.5	1.376	112.0		
						−1.54	+1.73
	0.03	1.663	85.5	1.511	122.8		
						−1.06	+0.82
	0.09	1.530	78.7	1.535	124.8		
						−0.87	−0.38
	0.27	1.268	65.3	1.482	120.5		
						−0.40	−0.35
	0.81	1.004	51.6	1.333	108.4		
						−2.13	+2.31
Te	0.01	1.682	86.5	1.478	120.2		
						−1.81	−0.60
	0.03	1.427	73.5	1.468	119.4		
						−1.29	+0.78
	0.09	1.224	62.9	1.474	119.8		
						−0.94	−0.85
	0.27	0.919	47.2	1.490	121.1		

(d) *Limited atomic solubility.* In this case several variations are possible:

α. Limited solubility of pure A in pure B, i.e., limited solubility only on the Bi-side. No example.

β. Limited solubility of B-A-Solution in A, i.e., limited solubility on both sides. Example, the systems: Bi-Sn (Fig. 2) and Bi-Pb (Fig. 3) and according to our results also Bi-Ge.

γ. Limited solubility of A_mB_n+A in A, i.e., existence of an intermetallic compound and limited solubility on both sides. Example, the systems: Bi-Se,[40, 48] (Fig. 11) and Bi-Te,[24, 25] (Fig. 4).

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[*] There is some discrepancy among different authors about the shape of the solidus curve; Fig. 1 was copied from the most recent investigation.

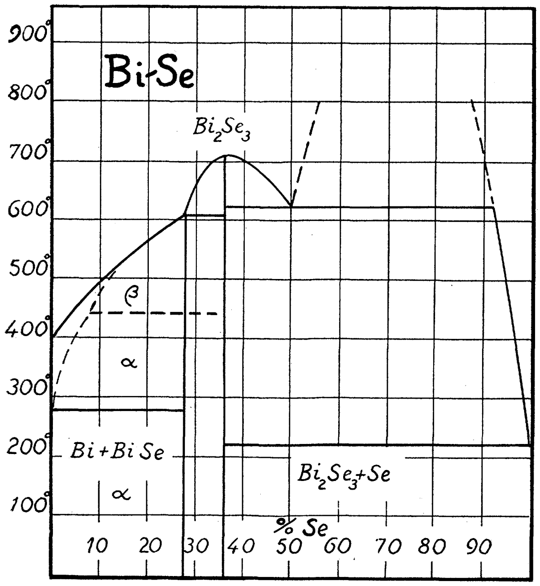

FIG. 11. Equilibrium diagram Bi-Se (Parravano[40] and Tomashige).[41] The full drawn liquidus curve represents the results of Parravano, the dashed curve those of Tomashige indicating the existence of two allotropic modifications for BiSe (α and β). According to our results the diagram should show a region of limited solubility of α-BiSe in Bi<2 percent.

As has been mentioned already (Part A, Section 2) the specific effect of atomically dissolved foreign atoms upon CDm is very large even for polycrystalline material and this investigation of single crystals has supported this fact very largely. According to our results it can be said generally that the specific influence of atomically dissolved atoms (i.e., the effect per inserted atom) is many times larger than that of any other type of admixture and furthermore that among atomically dissolvable admixtures *the specific effect is the larger the smaller the solubility limit.* Thus the atomic effect of Sn and Te upon the CDm is larger than of Pb and Se, corresponding to the solubility of Se and Pb which is larger than of Sn and Te.

Another observation may be mentioned in this connection: It is to be expected that an alloyed metal can only be grown in single crystalline form as long as the concentration does not exceed the solubility limit, because in case the component *B* exists in too large concentration the system disintegrates in two phases which upset the macrocrystalline arrangement. It is however surprising to see that the solubility of Bi in single crystalline form is much larger than for the polycrystalline material if one measures the solubility limit by the concentration beyond which it is impossible to grow single crystals without inclosures of crystal elements of different orientation or observable heterogeneous deposits. The solubility of a dissolvable admixture seems therefore to depend upon the size of the crystal complexes in such a manner that the solubility is larger for large than for small complexes. This dependence is analogous to the observations of previous authors[42, 43, 44] for the solubility of Ag in Cu. (The phase-relations of Ag-Cu are similar to Bi-Pb (Fig. 3).) In the case of the system Bi-Sn this difference is of particular importance since the solubility of Sn in Bi was not known before the magnetic researches of Endo and was made again doubtful by the observations of Shimizu.[20] We have made therefore a precision determination[29, 30] of the lattice spacing in Bi along [111] as function of the Sn-concentration and found an increase of the atomic distance up to the highest concentrations for which a single crystal still could be obtained, i.e., approximately 5 percent atmos., whereas the solubility limit for polycrystalline material is given as 1.7 percent.[18] We consider this as a proof that Sn is partially soluble in Bi and hence the phenomena observed by the insertion of Sn in Bi crystals must be due to atomically dissolved Sn.

2. The effect of the nature of the dissolved atom upon the magnetic anisotropy

If a section of the periodic system is chosen with the Bi-metals in the center it is to be considered most fortunate (and certainly not accidental) that all neighbors of the Bi metals form limited solutions with the latter. Accordingly all such combinations with Bi with its immediate neighbors have been investigated with the exception of Po, in order to study the variation of the effect upon the CDm with the electron configuration of the dissolved admixture. The arrangement is seen from Table VI and the valency configuration from Table VII.

The present investigation has shown that *all dissolved neighboring atoms which possess one valency electron less than Bi* (left (electropositive) neighbors) *increase the anisotropy* $\chi_{\perp}/\chi_{\parallel}=R$,

TABLE VI.

32 Ge	33 As	34 Se
50 Sn	51 Sb	52 Te
82 Pb	83 Bi	84 Po

TABLE VII.

		N	*O*	*P*
Ge	$K-M$ complete	2 2		
Sn		2 6 10	2 2	
Pb		2 6 10 14	2 6 10	2 2
As		2 3		
Sb		2 6 10	2 3	
Bi		2 6 10 14	2 6 10	2 3
Se		2 4		
Te		2 6 10	2 4	
Po		2 6 10 14	2 6 10	2 4

whereas a decrease of the anisotropy takes place for dissolved right (electronegative) *neighbors.* This behavior is definitely different from Ag (see Section 1.b, Part C) where R was decreased or increased at random. Among the great number of crystals with atomically dissolved mixtures such irregularities as to sign or magnitude of the effect upon R were not observed once.

The valency structure of the foreign atom decides upon the sign of the change of R whereas the magnitude of the effect seems to depend upon the same cause as the solubility which is not obvious. (See 1, Part C.) It is certain however that the crystal structure of B has nothing to do with this effect since nearly all neighbors of Bi crystallize differently.* In spite of this fact Ge (of which however only 2 crystals were grown) has the same effect as Pb which again is comparable in magnitude to Se. One should accordingly expect for Po the same magnitude as for Se and Pb. The effect of Sn and Te is however 3–4 times larger. It is thus evident that the atomic radius of the foreign atom with a given valency configuration has no simple relation to the size of the influence caused by it (Section 5.4).

3. The dependence of the anisotropy on temperature

The above relation has to be correlated with the temperature since its influence adds an important factor to the whole phenomenology. Our investigation included the range from liquid oxygen (90°abs.) to the melting point of Bi (543°abs.). The variation of R with the temperature T can generally be stated as follows: *The effect of any dissolved admixture on R irrespective of its sign and magnitude increases with lower temperatures and decreases approaching the melting point.*

(3.1) *Electropositive admixtures.* The dependence of the anisotropy on the temperature can be described more easily if one plots $1/R=\chi_{||}/\chi_{\perp}=\rho$ against T as is done for pure Bi (F) and different concentrations of electropositive admixtures in Fig. 12, illustrating that:

α. The temperature coefficient γ of the anisotropy ρ is positive and increases with the concentration of the dissolved admixture.

β. *The effect for high concentrations can be so large at sufficiently low temperatures that R can become* ∞ *and even negative,* i.e., *the crystal can be paramagnetic in one* ($||$) *and diamagnetic in the other direction* ($\perp$).[3]

γ. *The anisotropy* ρ *is seemingly a linear function of T such that the extrapolation of all* $\rho-T$ *lines beyond the melting point results in an accurate intersection at a temperature* T_0. This relation is not obeyed for the highest concentration of Sn at low temperatures which is apparently due to an instability of the solid solution at low temperatures.* Another deviation which seems to be of more fundamental character occurs in the region below and above the temperature of the pseudo-allotropic transformation of Bi for medium concentrations of Sn and Pb. To what extent a linear inter- and extrapolation of the $\rho-T$ function of small concentrations is

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* Ge—Diamond; Sn—tetragonal; Pb—cubic; Se—hexagonal, special; Te—hexagonal special; Sb—rhombohederal.

* This is already indicated by the fact that the solubility limit for polycrystalline material is given by Endo at 1.7 at percent at room temperature.

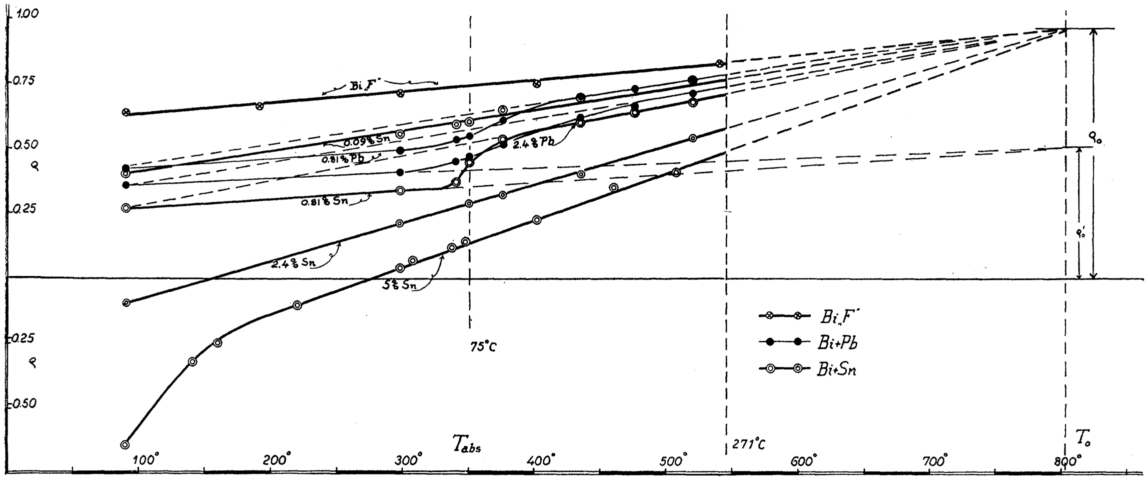

FIG. 12. $\rho-T$ diagram for electropositive admixtures (Tables IV and V). The dashed lines represent linear interpolations across the region of possible anomaly and the extrapolations to T_0, ρ_0 and ρ_0'. Only the large concentrations are shown.

justified cannot be stated since the measurements in the region between 90° and 300°abs. are still missing for these concentrations. However, a considerable number of crystals especially of the larger concentrations (not shown in Fig. 12) justify the linear extrapolation.

The temperature T_0 is characterized by the fact that an (imaginary) crystal at T_0 would have a magnetic anisotropy ρ_0 common to pure crystals as well as to alloyed crystals; in other words: the effect of any of the studied admixtures would have disappeared and their ρ would be identical with that of the pure metal. The analytical relation is accordingly:

$$\chi_{\parallel}/\chi_{\perp}=\rho=\rho_0-\gamma'(T_0-T) \tag{2}$$

where ρ_0 and T_0 are constants independent of the concentration and the kind of dissolved admixture. The temperature coefficient γ' varies with concentration and type of the admixture and is best expressed by its two components, the coefficient of pure Bi (γ_0) and the additional coefficient (γ) which latter is always positive for electropositive admixtures. Accordingly:

$$\chi_{\parallel}/\chi_{\perp}=\rho=\rho_0-(\gamma_0+\gamma)(T_0-T). \tag{2a}$$

The temperature T' at which the change of sign of the scz in one direction within the crystal occurs is thus given by:

$$T'=T_0-\rho_0/\gamma'. \tag{2b}$$

The values of the constants are:

$$\rho_0=0.95, \qquad R_0=1/\rho_0=1.05,$$
$$T_0=803°\text{abs.}, \qquad \gamma_0=4.9\times10^{-4}\ \text{deg.}^{-1}.$$

(3.2) *Electronegative admixtures.* The variation of ρ with the temperature T for electronegative admixtures is in many ways similar to the above relation. Fig. 13 illustrates this in the same scale as Fig. 12 for a different section of the ordinate, the line for pure Bi (F) being used as reference. It is seen that:

α. *The temperature coefficient γ of the anisotropy increases with the concentration of the dissolved admixture* (same as Section 3.1α).

β. *In contradistinction to the electropositive admixtures the temperature coefficient γ is negative.*

γ. Below the pseudo-allotropic transformation point (75°C) the $\rho-T$ functions are linear and the extrapolation for the large concentrations of Te intersect with good accuracy at the values for ρ_0 and T_0 given above. The transformation point, however, is characterized by a discontinuity in the ρ values being negative for large and positive for small concentrations of Te and Se.

δ. Above the transformation point the linearity of the $\rho-T$ function holds still true, at least for larger concentrations whereas the accuracy of the measurements for the smaller concentrations makes the validity of this statement less certain. The extrapolations of the $\rho-T$ line

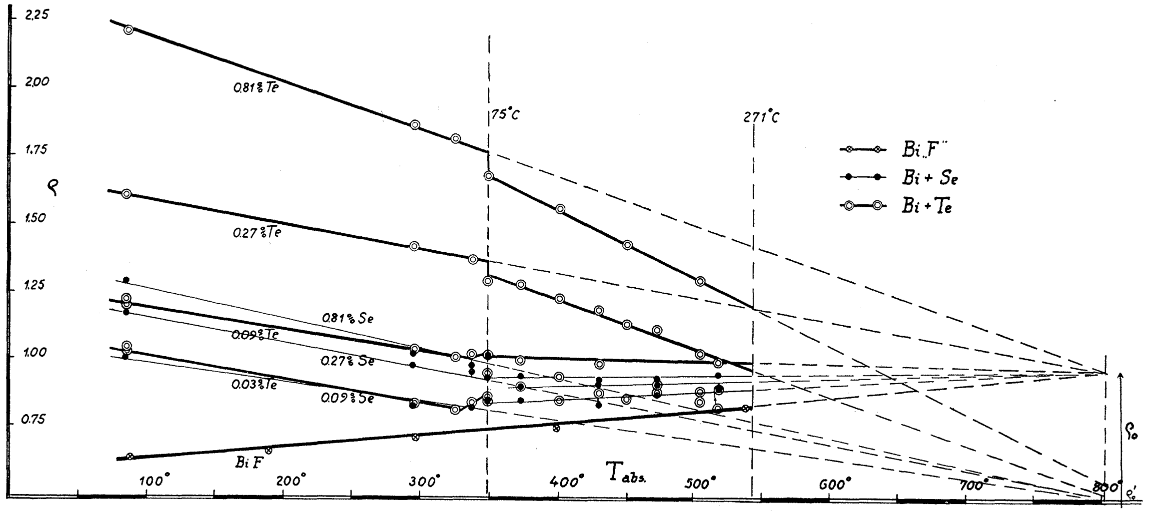

FIG. 13. $\rho - T$ diagram for electronegative admixtures. The dashed lines represent the linear extrapolations beyond the transformation point and the melting point to T_0, ρ_0 and ρ_0'. Only large concentrations of Te and Se are shown.

above 75°C intersect very well at T_0, though, for a different value of $\rho_0 = \rho_0' = 0.5$. The same is apparently true for Se and the small concentrations of Te, in such a manner that only two cases are possible: *If the* $\rho - T$ *line of an electronegative admixture has an extrapolated intersection at* ρ_0 *for* $T < 75°$, *the discontinuity at the transformation point is negative and the extrapolated intersection for* $T > 75°$ *occurs at* ρ_0'. *The other case is the exact opposite: If* ρ_0' *holds for* $T < 75°$, ρ_0 *holds for* $T > 75°$ *and the discontinuity is positive.* (A discussion of the possible nature of the transformation point is to be found in Section 7.)

The first case is only true for large concentrations of Te, whereas the second holds for all concentrations of Se and the small concentrations of Te which is in perfect agreement with the later (Section 4) discussed fact that a much larger amount of Se produces the same effect as a small quantity of Te, the effect produced, however, being almost exactly the same. The alikeness of the influence of Se and Te is so close, especially at higher temperatures, that the measured points cover each other and hence the lines for Te admixtures are not shown in the diagram.

The existence of two values for ρ_0 is probably not restricted only to electronegative admixtures, since it is possible to describe the deviation from the straight line relation for electropositive admixtures (Fig. 12) in terms of ρ_0', though the much smaller accuracy of the measurements in the region of higher temperature for those admixtures did not seem to justify such a procedure. For comparison it has to be realized that these are not strictly commensurable since Bi forms with its right neighbors only solutions with the compounds BiSe and Bi_2Te_3 (Fig. 11 and Fig. 4) whereas the left neighbors go into atomic solution.

4. The dependence of the anisotropy on the concentration of the admixture

For a closer understanding of the mechanism of the insertion of the foreign atom within the crystal it is necessary to study the dependence of ρ on the concentration of the admixture (N). The observations of Spencer and John[10] as well as of Endo[18] (Figs. 1–4) indicate in their concentration diagrams a linear dependence of the total susceptibility on N. Since the number of different concentrations studied within the region of solubility by these authors is much too small for the accurate determination of this function we have prepared a great number of single crystals with different concentrations of the elements under consideration. Some of the results are shown in Fig. 14 representing the run of ρ with N for the electropositive elements Pb and Sn for room temperature. It is immediately

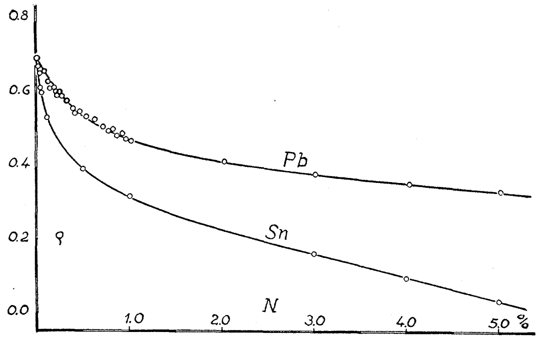

FIG. 14. $\rho - N$ diagram for electropositive admixtures for room temperature.

realized that the *dependence is not linear and approaches more a parabola*. Both curves are of the same character with the difference that the absolute influence of the Sn atom is larger than of the Pb atom. The relative effects of different impurities for different temperatures is seen more easily in Fig. 15. Here ρ is plotted in the same manner against the concentration N, the values for room temperature being represented by dashed curves, the corresponding values for liquid air temperature by full drawn lines. ρ_p—the anisotropies of the pure metal for the two temperatures—is taken as axis of reference and is seen to coincide with the admixtures Cu (see Part C, 1a), Sb (see Part C, 1c) and the average of the Ag crystals (see Part C, 1b). In order to show the dependence for small concentrations, the left side of the diagram is repeated in a large scale in the right upper corner. One realizes that the curves for room temperature for electro-

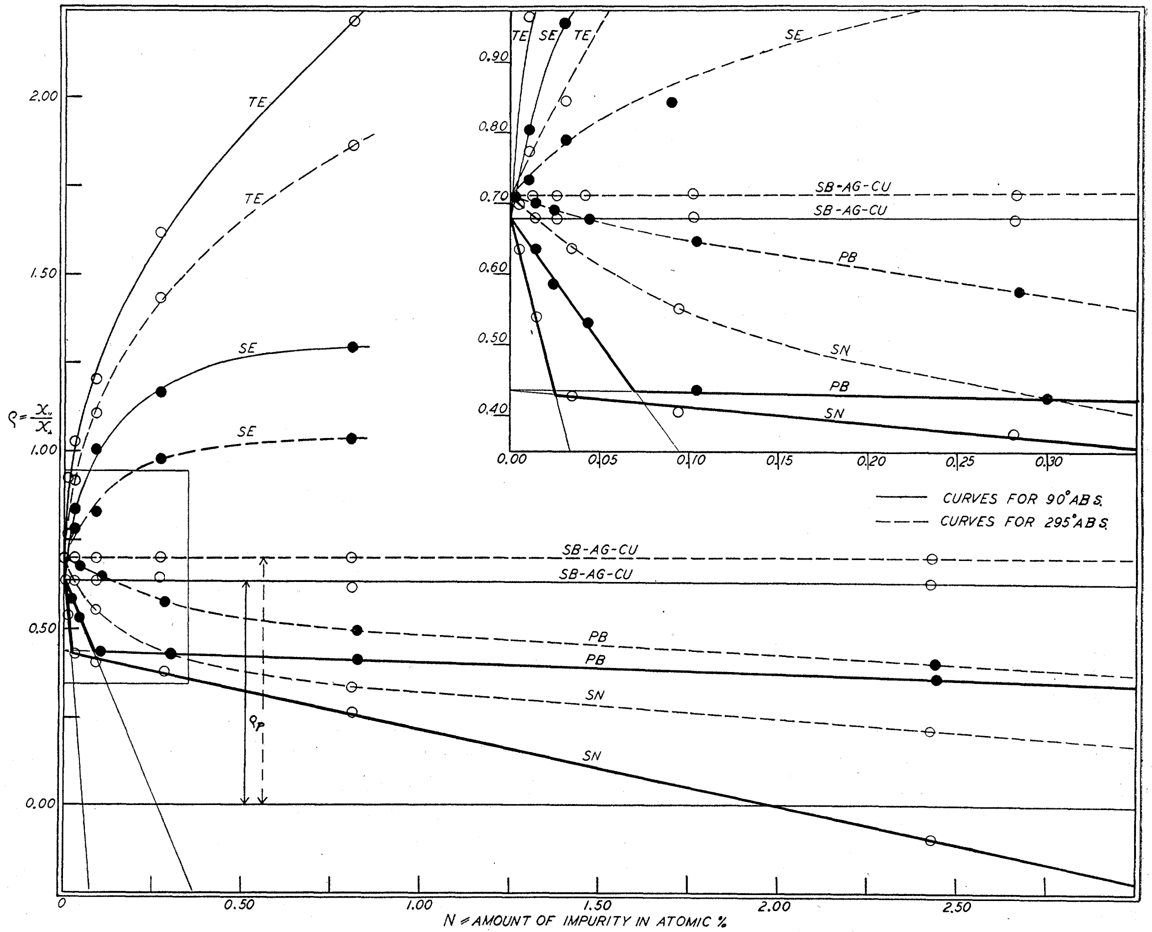

FIG. 15. $\rho - N$ diagram for electropositive and electronegative admixtures at liquid air and room temperature. The diagram in the right upper corner represents only small concentrations on a magnified scale.

positive admixtures lie almost perfectly symmetrical to the curves for electronegative atoms if taken with reference to the pure metal. Pb and Ge correspond to Se and Te to Sn as indicated by their position in the periodic system (see Section 2).

This symmetry as well as the general parabolic shape of the curve disappears at liquid air temperature where the electropositive curves are changed into two linear dependences which change their direction abruptly at a certain "critical" concentration which occurs for both elements at very small values: approximately 0.027 percent for Sn and 0.08–0.09 percent for Pb. This relation is illustrated by the derivative curves of Fig. 15 in Fig. 16 for both temperatures. This sudden change of $d\rho/dN$ indicates already the fact that the mechanism of the insertion of foreign atoms in a very small concentration is different from larger concentrations, suggesting evidently the existence of two different types of solid solution. It is also important to note that this "critical" concentration, being three times larger for Pb than for Sn, occurs for almost exactly the same value of ρ. In other words: the *magnitude of the effect, admixtures of a certain valency configuration are able to inflict upon* ρ *for a certain (low) temperature, is definite; to produce this effect three times as many Pb (and probably also Ge atoms) atoms are necessary as Sn atoms.*

The dissimilarity of the curves in Fig. 15 on the electronegative side is only apparent and is caused by the much less distinct discontinuity of $d\chi_{||}/dN$ (see Section 5.2). These relations are discussed more thoroughly after the treatment of the directional scz's (Section 7).

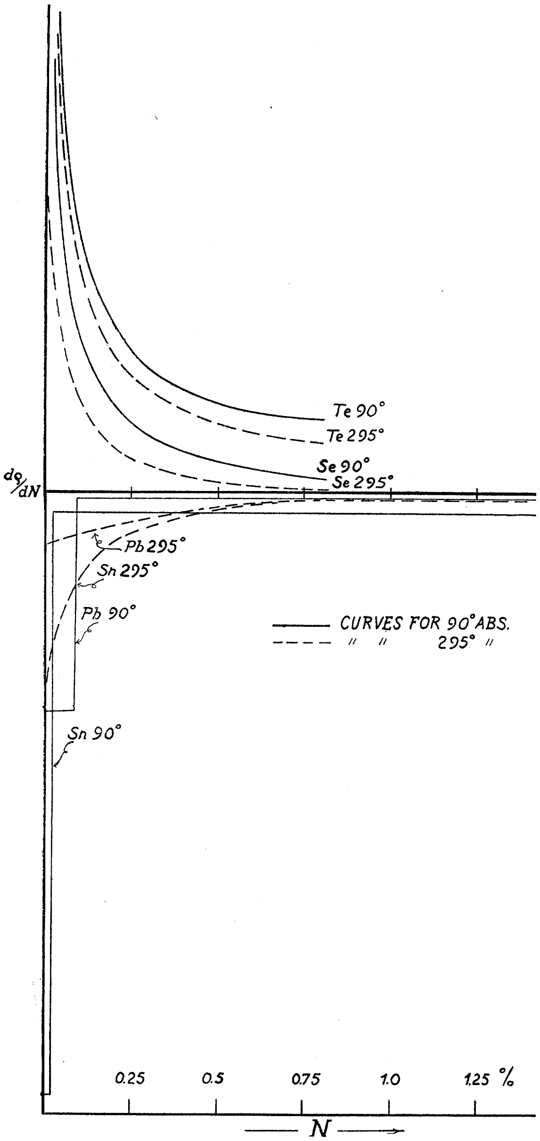

FIG. 16. $d\rho/dN=f(N)$ diagram for electropositive and electronegative admixtures. The values for room temperature are indicated by dashed, for liquid air temperature by full drawn lines.

5. The dependence of the susceptibilities $\chi_{||}$ and $\chi_{\perp}$ on the concentration and the type of admixture

The described peculiar dependence of the anisotropy on the temperature and the concentration of the admixture proves beyond doubt that the insertion of an atomically soluble foreign atom follows very definite laws, in other words, there must be a definite equilibrium condition for the insertion in the two principal directions within the crystal. It was therefore very desirable to measure in addition to the ratio of the susceptibilities the absolute value of the susceptibility in at least one direction. The absolute determination of χ involves, however, the destruction of each single crystal in order to determine its exact cross section. Since this cross section, however, was of a shape not easily to be determined, the mass of the section of the crystal which was exposed to the field gradient had to be measured. Only one susceptibility was determined and the other calculated from the known values of the anisotropy.

(5.1) *Electropositive admixtures*

The variation of the absolute values of the scz's in different directions within the crystal for electropositive admixtures is shown in Figs. 17–20. In each diagram a family of curves describes the variation at a series of temperatures from liquid-air temperature to 25° before the point of fusion. The curves for $T<75°$ are full drawn and are dashed for $T\geqq 75°C$.

(5.11) *Electropositive admixtures and scz parallel to [111].* The almost perfect analogy of the influence of Sn and Pb is realized from comparison of Figs. 17 and 18. Since the only

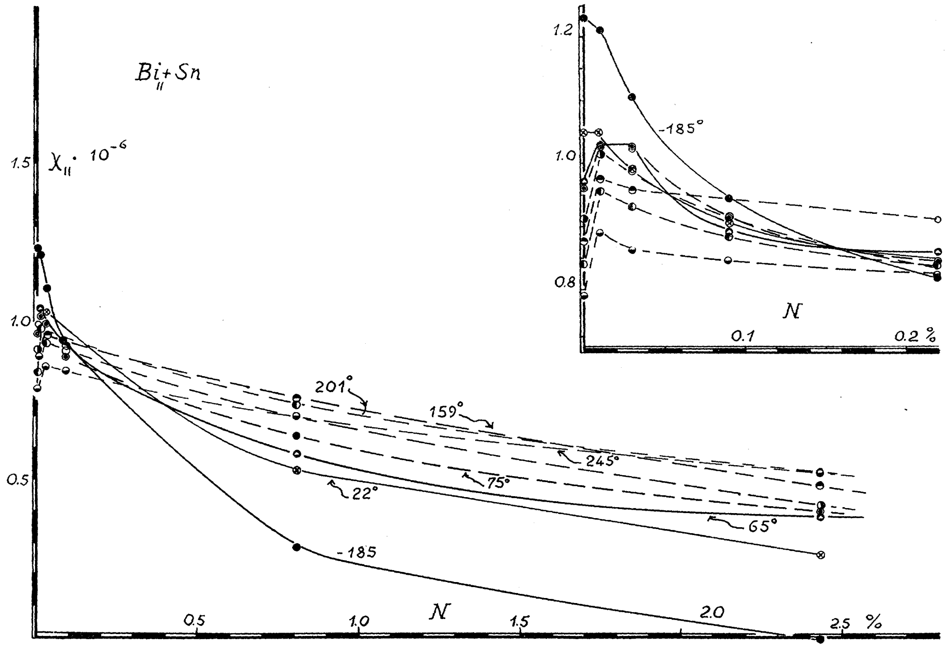

FIG. 17.

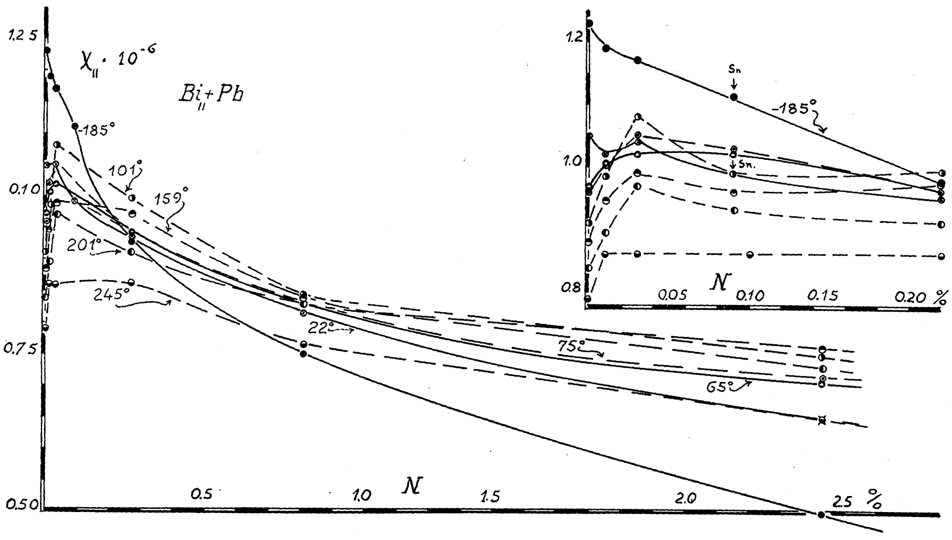

FIG. 18.

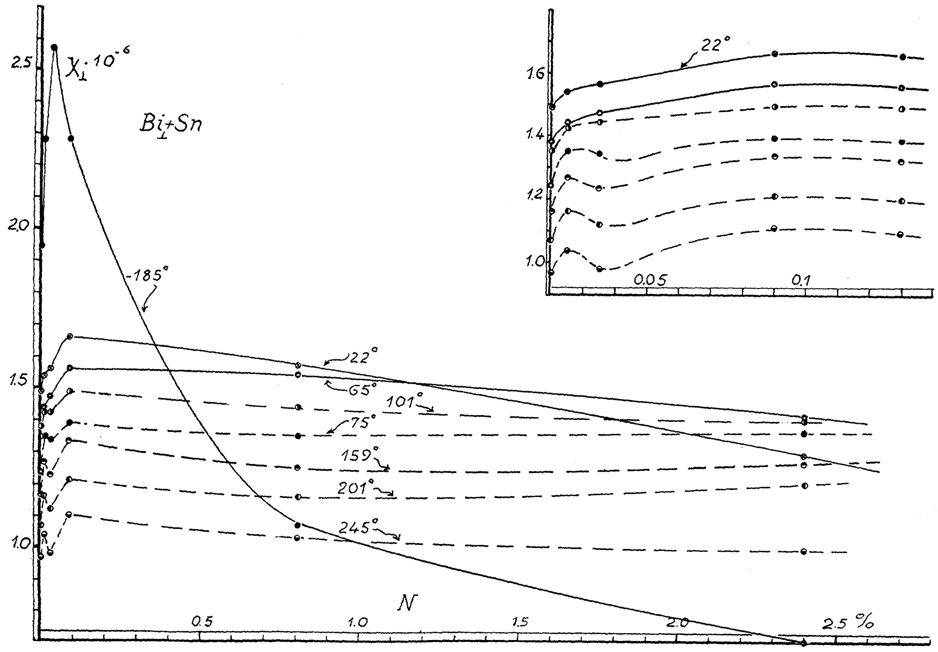

FIG. 19.

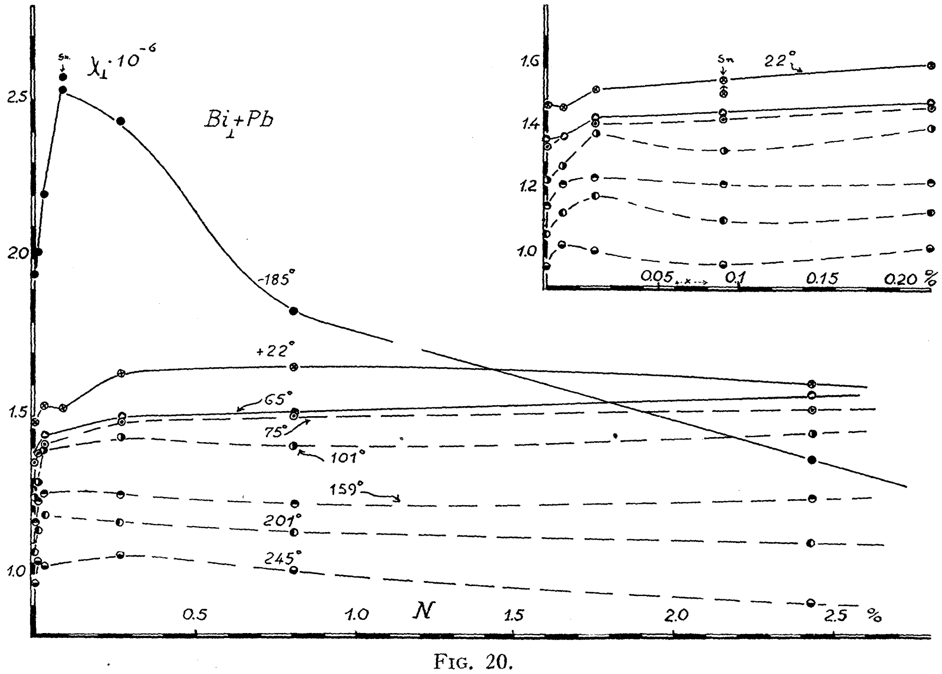

FIG. 20.

FIGS. 17–20. $\chi-N$ diagrams for electropositive admixtures (Table IV). The scale of the abscissae in all main diagrams is the same, whereas the zero point of the ordinates is different and also the scale for Fig. 18. The diagrams in the right upper corner are enlarged representations for small N; in Fig. 20 a specially large scale was chosen for the small values of the abscissa. Observations for different temperatures are indicated by points of different pattern, this being the same throughout all $\chi-N$ diagrams. The curves for $T<75°\text{C}$ are indicated by full drawn lines, for $T\geqq 75°\text{C}$ by dashed lines. In Figs. 18 and 20 certain observations missing in Table IV are replaced by observations for Sn according to $\alpha_{\text{Sn}}/\alpha_{\text{Pb}}=3$.

difference between these two admixtures is the value of $\alpha_{||}=d\chi_{||}/dN$, it was even possible to replace several missing Pb-observations (Table V) for 0.09 percent with Sn observations for 0.03 percent since $\alpha_{||\mathrm{Sn}}/\alpha_{||\mathrm{Pb}}=3$. In case both observations are present, the Sn point is marked as such.

The rather complicated relations between the different types of crystals shall be described in the following by an analogous enumeration of the four most prominent characteristics ($\alpha-\delta$) in the $\chi-N$ relation for different orientations and admixtures:

α. For *large* concentrations $\chi_{||}$ decreases with increasing concentration, i.e., $\alpha_{||}=d\chi_{||}/dN$ is negative. This holds for all temperatures.*

β. For *small* concentrations $\chi_{||}$ increases with N for temperatures larger than 75°C, i.e., $\alpha_{||}$ is positive.

γ. For *low* temperatures the sign of $\alpha_{||}$ does not show a difference between large and small concentrations.

δ. For *high* temperatures the transition from small to large concentrations is characterized by a critical concentration N_c' at which $\alpha_{||}=0$. For $N<N_c'\alpha_{||}$ is always positive, for $N>N_c'\alpha_{||}$ changes generally to negative values. The observations available at present make an independence of N_c' of the temperature probable for $T>75$°C. The most probable value of N_c' for Sn is around 0.01 percent and for Pb 0.03 percent, although it has to be realized that the uncertainty of the exact amount of the residual impurity in the Bi metal used as well as the lack of observations on very small concentrations renders this statement quantitatively uncertain.

(5.12) *Electropositive admixtures and scz normal to [111]*. Figs. 19 and 20 represent the $\chi_\perp-N$ relations analogous to Figs. 17 and 18. The relation can be described as follows:

α. Except for the lowest temperature where $\alpha_\perp$ is negative $\chi_\perp$ is practically independent on N for *large* concentrations, $\alpha_\perp\sim 0$. (Different from 5.11α.)

β. For small concentrations $\chi_\perp$ increases for all temperatures and is especially large for low temperatures. (Different from 5.11β.)

γ. For low temperatures the values for $\alpha_\perp$ are positive for concentrations smaller than a critical concentration N_c, the existence of which proves to be independent of N_c' (5.11δ). Whether or not N_c exists only for low temperatures cannot be decided yet: it is obviously much less prominent for high temperatures. The value for N_c is for Sn around 0.03 percent and for Pb 0.09 percent; these values coincide obviously with the critical concentration for the anisotropy.[4] (Different from 5.11γ.)

δ. The critical concentration N_c' for high temperatures exists with the same values in analogy to 5.11δ.

(5.2) *Electronegative admixtures*

Figs. 21 and 22 represent the variation of $\chi_{||}$ and $\chi_\perp$ with the concentration N of the electropositive admixtures Se and Te. Since the atomic solubility of Bi_2Te_3 and BiSe (see Figs. 4 and 11) are very different, abscissae of different scales were chosen.

(5.21) *Electropositive admixtures and scz parallel to [111]*. The comparison of Figs. 21 and 22 shows the very perfect analogy between the effect of Se and Te, the only difference being that the value of $\alpha_{||\mathrm{Se}}$ is smaller than the value of $\alpha_{||\mathrm{Te}}$. Since the production of an homogeneous crystal containing this type of admixture is very difficult, the observation especially for the high concentrations seems to be less trustworthy than the previous ones. The pattern of the points and lines follows the same system as in the previous diagrams. The results can be described as follows:

α. Except for the lowest temperature where $\alpha_{||}$ is apparently negative* it is nearly independent of N for *large* concentrations. (Same as 5.12α, different from 5.11α.)

β. For small concentrations $\alpha_{||}$ has a large positive value for all temperatures. (Same as 5.21β, different from 5.11β.)

γ. For *low* temperatures $\alpha_{||}$ is positive and the existence of N_c is definite, but it is doubtful if it holds for all temperatures. The value for N_c for Se lies at 0.09 percent, for Te around 0.01 percent. (Same as 5.12γ, different from 5.11γ.) Since the transition of $d\alpha/dN$ is much less marked, a discontinuity of $d\rho/dN$ (Figs. 15 and 16) could not be found.

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* The details of the temperature dependence (χ, $\alpha=f(T)$) for this and all other types of crystals are treated separately in 6.

* The largest Te-concentration at −185° gives probably too large a value for $\chi_{||}$.

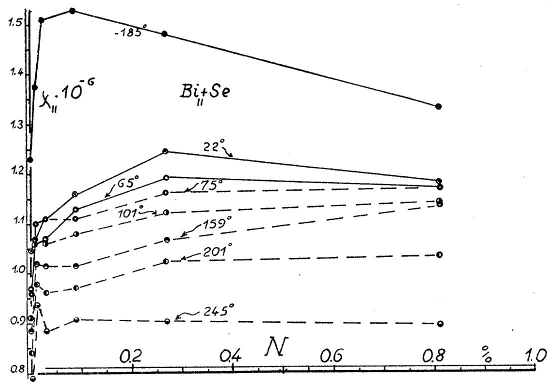

FIG. 21.

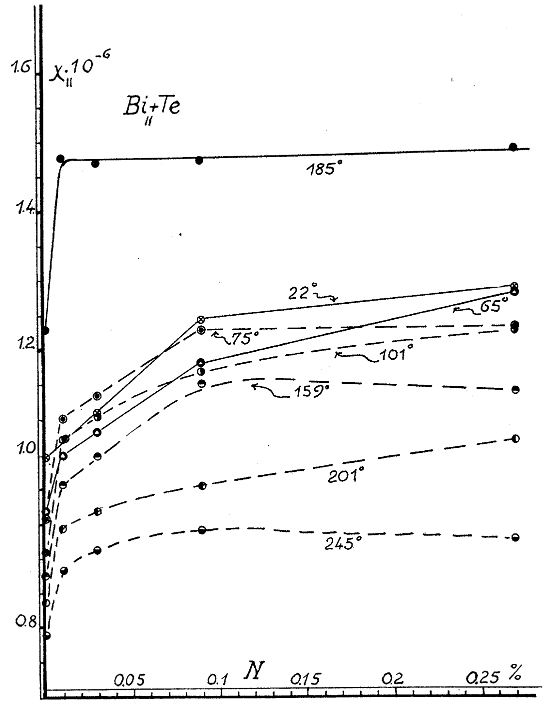

FIG. 22.

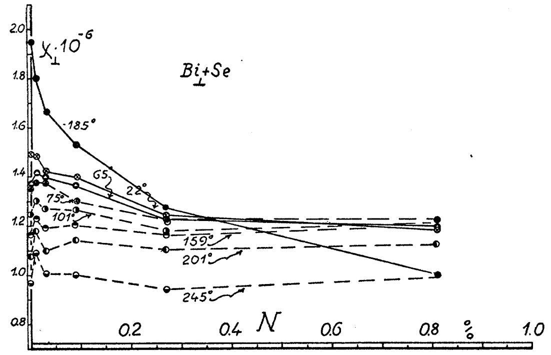

FIG. 23.

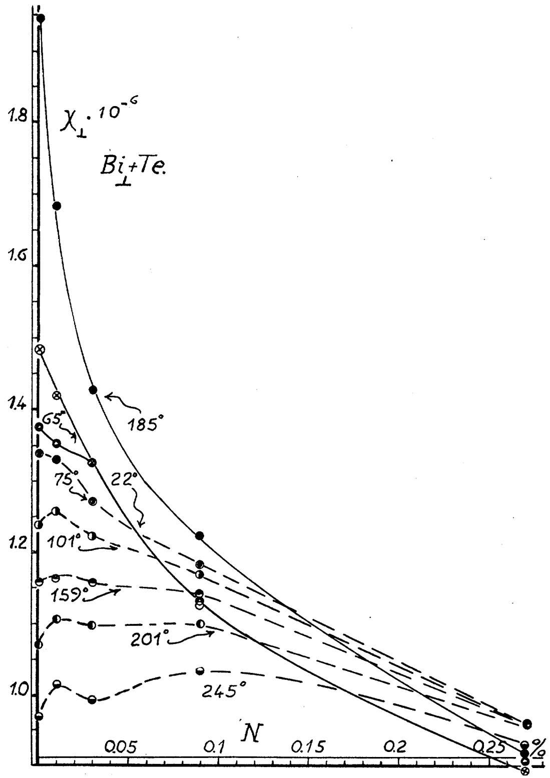

FIG. 24.

FIGS. 21–24. $\chi-N$ diagrams for electronegative admixtures (Table IV). The scale of the abscissae differs for Se and Te; the scale of the ordinate is the same for Te, but different for Figs. 21 and 23. The same pattern of observation points as in Figs. 17–20 is used and the same distinction between dashed and full drawn lines.

δ. For *high* temperatures the existence of $\overset{\circ}{N}_c'$ is obvious for Se and is indicated at least for Te. (Apparently same as 5.11δ and 5.12δ.)

(5.22) *Electronegative admixtures and scz normal to [111].* Figs. 23 and 24 represent the variations of $\chi_\perp$ with N analogous to previous diagrams; the results are:

α. $\chi_\perp$ decreases for *large* concentrations for *all* temperatures for Te and probably also for Se. (Same as 5.11α at least for Te, different from 5.12α and 5.21α.)

β. For *small* concentrations $\alpha_\perp$ is positive for $T > 75°C$. (Same as 5.11β, different from 5.12β and 5.21β.)

γ. For *low* temperatures $\alpha_\perp$ has the same sign for large *and* small concentrations, i.e., N_c does not exist within the measured range of concentrations. (Same as 5.11γ, different from 5.12γ and 5.21γ.)

δ. N_c' exists for high temperatures for Se and Te. The value of N_c' is apparently the same for both admixtures at 0.01 percent. (Same as all previous δ-statements.)

(5.3) *Isomorphous admixture*

Of the two existing admixtures isomorphous to Bi—As and Sb—only Sb was measured. Fig. 25 represents the $\chi - N$ relation in the same scale (0/00) for both abscissae of which a section (from 0.04 percent to 0.25 percent) has been cut out. The scale of the ordinate varies in the usual manner.

(5.31) *Isomorphous admixtures and scz parallel to [111]*

α. For *large* concentrations $\alpha_{||}$ is very little depending upon N, being possibly positive only for high temperatures. (Almost perfect analogy to Te in 5.21α and similar to 5.12α, different from 5.11α and 5.22α.)

β. For *small* concentrations $\alpha_{||}$ has positive values for low and high temperatures. (Similar to 5.12β and 5.21β, different from 5.11β and 5.22β.)

γ. The existence of N_c is marked for the lowest temperature, although the value of $\chi_{||}$ for $N \leqq N_c$ is much smaller than in previous cases. The value of N_c is around 0.01 percent. (Analogous to 5.12γ and 5.21γ, different from 5.11γ and 5.22γ.)

δ. The critical concentration N_c' exists for high temperatures at 0.01 percent, being identical with N_c. (Same as all previous δ-statements.)

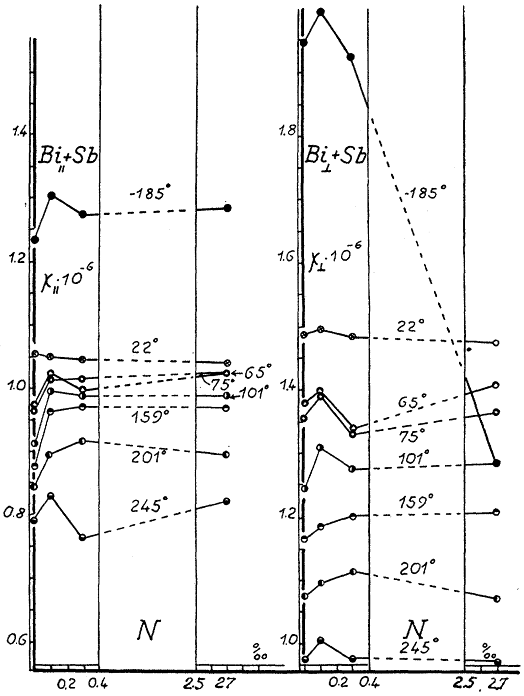

FIG. 25. χ—N diagram for the isomorphous admixture Sb (Table IV). The scales for the abscissae and the ordinates are identical, though the zero for the latter is different. The concentration between 0.04 percent and 0.25 percent is omitted, the N scale is marked in per mil. The pattern of the points is the same as previously, no distinction between lines is made.

(5.32) *Isomorphous admixtures and scz normal to [111]*

α. For *large* concentrations $\alpha_\perp$ is negative for low temperatures and very small (perhaps 0) for higher temperatures. (Same as 5.12α and 5.22α, different from 5.11α, 5.21α (?) and 5.31α.)

β. For *small* concentrations $\alpha_\perp$ is positive for high and low temperatures. (Similar to 5.12β, 5.21β and 5.31β, different from 5.11β and 5.22β.)

γ. The existence of N_c is marked, although the value of $\chi_\perp$ for $N \leqq N_c$ is much smaller than in previous cases. N_c lies around 0.01 percent. (Analogous to 5.12γ, 5.21γ and 5.31γ.)

δ. N_c' exists for high temperatures at 0.01 percent. (Same as all previous δ-statements.)

(5.4) *Summary concerning the $\chi - N$ relations*

It appears from the above statements that the effects of different types of admixtures in different directions within the crystal show a number of characteristic similarities and differences. These relations are seen easily from Table VIII.

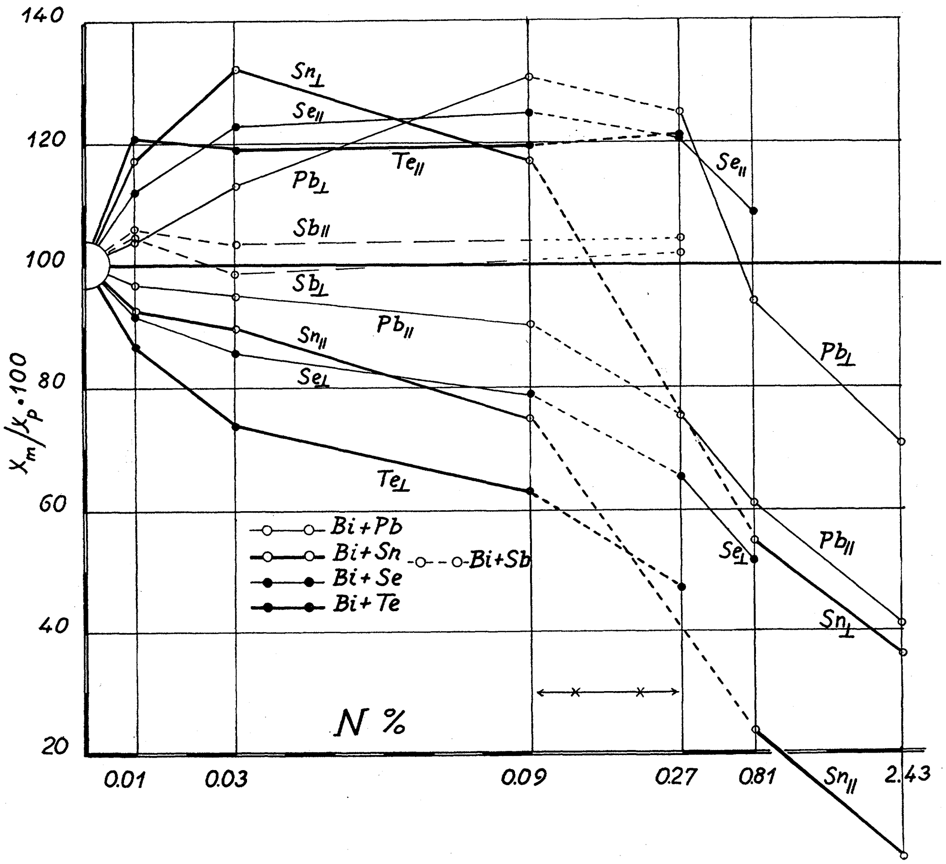

FIG. 26. The values of the relative scz's $\chi_r=\chi/\chi_p$ is plotted against N for all types of admixtures and all orientations. The abscissa consists of two different scales for $N<0.09$ percent and $N>0.27$ percent. The values refer to $T=-185°$C. (Table V.)

TABLE VIII. $\chi-N$ *relations.*

No.	large N	small N	N_c	N_c'	0_r to [111]	Admixture
5.11	$\leqq 0$	<0	none	0.01% Sn 0.03% Pb	$\parallel$	electro-positive
5.12	$\leqq 0$	>0	0.03% Sn 0.09% Pb	0.01% Sn 0.03% Pb	$\perp$	
5.21	$=0$	>0	0.09% Se 0.01% Te	0.01%	$\parallel$	electro-negative
5.22	$=0$	<0	none	0.01%	$\perp$	
5.31	$=0$	>0	0.01%	0.01%	$\parallel$	iso-morphous
5.32	$\leqq 0$	>0	0.01%	0.01%	$\perp$	

Certain similarities of the effects of different admixtures at *high* temperatures are apparent; here α is either slightly negative or zero for *large* N: the CDm is very little affected by a large concentration, the scz is generally slightly larger than of pure Bi.

All *small* concentrations increase the CDm up to a critical concentration N_c' which is apparently for all admixtures the same (0.01 percent) except for Pb (0.03 percent) which observation may be uncertain due to the fact that the most prominent residual impurity in Bi (F) and (G) is Pb (Table I).*

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* The existence of N_c' depends of course on the correctness of the measurement of pure Bi at different temperatures and since the purity was not absolute the α-values for small concentrations are not quite correct, i.e., it could be that N_c' did not exist at all if the observed temperature coefficients $\gamma_{||}$ and $\gamma_\perp$ were too large. It is however seen easily that the values of χ at N_c' for different admixtures vary to a much larger extent as γ_p (γ for pure Bi) could vary, which fact would then result in the existence of a minimum for χ at N_c' in some cases and in a maximum in others.

The main similarity at *low* temperatures is best illustrated by plotting the relative scz's χ_r (in percent) against N for all types of admixtures, (Table V, Fig. 26). It is seen that here the CDm is very much affected by all types of admixtures (except by the isomorphous type), the effect being the *same* for *large* concentrations for both directions within the crystal, such that the scz *decreases* considerably.*

The most striking difference between electropositive and electronegative types of admixtures for *small* concentrations is their effect in different directions within the crystal, apparent from the varying occurrence of the critical concentration N_c. The relation can be summarized: *An electropositive admixture acts upon the CDm in the same way normal to the axis as an electronegative admixture parallel to it and vice versa.* A small concentration of an *electropositive* admixture *increases* the CDm *normal* to [111] to almost the same extent as an electro*negative* does *parallel* to [111], whereas the CDm is *decreased* by an electro*negative* admixture *normal* to [111] to approximately the same values as is done parallel to [111] by an electro*positive* admixture. Accordingly N_c exists in the cases 5.12 and 5.21 and is missing in 5.11 and 5.22. The magnitude of the effect produced on χ_r at N_c (Fig. 26) is almost the same (30–32 percent) for electropositive admixtures and seems to be slightly smaller for electronegatives (20–25 percent). Whether this difference is true or only apparent due to lack of a sufficient number of concentrations neighboring N_c cannot yet be decided. The values of N_c range as follows: Te, Sn, Se= Pb.

This commensurability does not hold for the *isomorphous* admixture Sb. First, the absolute magnitude of the influence is much smaller (only 1/8 to 1/10 of the previous effects), second, it stands in the middle between the two previous types because of the existence of N_c normal *and* parallel to [111]. Also for *large* concentrations the resemblance to electropositive admixtures is indicated *normal* to [111] and to electronegatives parallel to [111] (5.32 = 5.12, 5.31 = 5.21). Though the effects are close to the range of experimental error it seems thus probable that *normal to [111] the isomorphous admixture behaves electropositive and parallel to [111] electronegative.*

In order to illustrate the variation of α for large and small concentrations for the different types of admixtures and different orientations, the dependence of $d\chi_r/dN - \alpha_r$ on N obtained by differentiation of the curves in Fig. 26 is shown in Fig. 27 for electropositive and in Fig. 28 for electronegative admixtures for liquid air temperature. The value of this representation is only on the qualitative side since the number of observations is not by far sufficient for a quantitative evaluation. Accordingly the presentation is chosen such that the logarithms of α_r for $\alpha_r > 1$ and $\alpha_r < (-1)$ are plotted in opposite directions against $\log N$, thus neglecting the small values of α_r. The analogy of $\alpha_r(N)$ in Fig. 27 for Sn and Pb is obvious: $\alpha_{r\perp}$ has large positive values for $N < N_c$ and changes its sign for $N > N_c$, *at a certain concentration (approximately 0.09 percent for Sn, 0.81 percent for Pb) the difference between* $\alpha_{r\parallel}$ *and* $\alpha_{r\perp}$ *disappears*, i.e., the directional influence of the admixture ceases to exist. This fact can be realized already from the parallelity of the $\alpha_r - N$ curves for large N in Fig. 26. The function $\alpha_r(N)$ for electropositive admixtures in Fig. 28 shows a similarity to the above as far as the change of sign of α_r at N_c is concerned, the difference consists in the values of $\alpha_{r\perp}$ for small N which indicate a straight line relation. Since the larger concentrations for Te were not reliable it is uncertain whether or not Te behaves similar to Se as far as the disappearance of the difference between $\alpha_{r\parallel}$ and $\alpha_{r\perp}$ is concerned. Se shows in any case the same analogy to Pb as was seen before in Table V. From the fair parallelity of the Pb and Se lines in Fig. 26 for large N results also that the absolute values of α_r in this region for both admixtures are the same.

The differences between the α_r-values become much smaller for high temperatures for the directional effect as well as for different elements.

Considering the different influences of admixtures of the same valency configuration the following can be said: The fact that the specific influence is largest (N_c smallest) for Te and Sn indicates that the disturbance within the crystal is largest by atoms of a structure $\nu - 1$ where ν

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* It does not seem probable that Te is an exception (see 5.21) mainly since Te could not be admixed in sufficiently large concentrations.

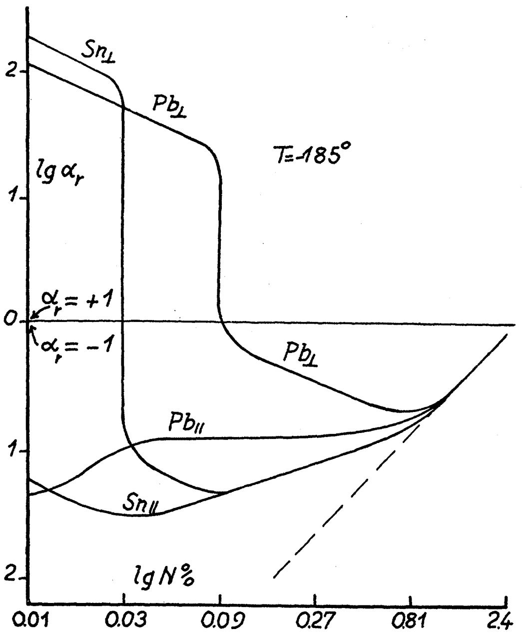

FIG. 27.

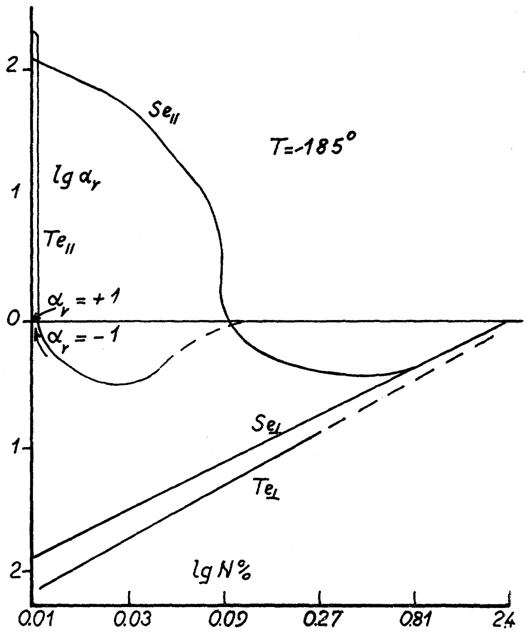

FIG. 28.

FIGS. 27–28. $\alpha_r - N$ diagram for electropositive[27] and electronegative[28] admixtures (Table V). The ordinates are arranged in such a manner that the logs of $\alpha > 1$ are plotted above the zero line and for $\alpha < (-1)$ are plotted below; the abscissa represents log N. The diagram is only a schematic representation of the most probable values of $\alpha_r = f(N)$ at $T = -185°\text{C}$.

is the level of the outermost completed shell of the crystal atom, i.e., the 0-shell for Bi. (See Table VII.) If the structure is the same as the structure of the crystal atom ($=\nu$) the inserted foreign atom is apparently too similar to cause a disturbance as large as in the previous case. This is indicated already by the fact that the solubility of Pb in Bi is larger than of Sn in Bi. (See Figs. 2 and 3.) One should thus expect that the specific influence of Po would be smaller than of Te. If, on the other hand, the structure is of the type $\nu - 2$, the actual size of the atom seems to be too small to affect the crystal as is the case for Se and Ge where the last completed shell is on the M-level. Here the effect is smaller in comparison with the $\nu - 1$ type and commensurable with the ν-type. One should accordingly also expect that in case of a Sb-crystal the maximum influence should be found for Ge and Se instead of Sn and Te for a Bi crystal.

6. The dependence of the susceptibilities $\chi_{||}$ and $\chi_{\perp}$ on the temperature

The dependence of the scz of pure Bi on the temperature is *linear* within the limits of experimental error, such that in both directions the CDm *increases* with *decreasing* temperature.*

If γ (see Eq. (2)) is the temperature coefficient in the usual definition:

$$\gamma = (1/\chi_0)(\chi_T - \chi_0)/(T - T_0) \tag{3}$$

and if χ_0 is taken for $22°\text{C} = T_0$

$$\gamma_{||} = -1.1 \pm 0.05 \times 10^{-4} \text{ deg.}^{-1},$$

$$\gamma_{\perp} = -1.5 \pm 0.08 \times 10^{-3} \text{ deg.}^{-1}.$$

Hence the dependence of CDm on the temperature is 40 percent larger normal to [111] i.e., in the direction of the densest packing then parallel to [111], the direction of the least dense packing.

This simplicity of the temperature dependence is changed very much by an admixture as is seen easily from the $\chi - N$ diagrams. The data of Table V were used for plotting the scz against the temperature for a number of characteristic

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* The fact that ρ is also a linear function of the temperature (see Part C, Section 3) is caused by the small magnitude of the temperature coefficient which renders a deviation from linearity unobservable.

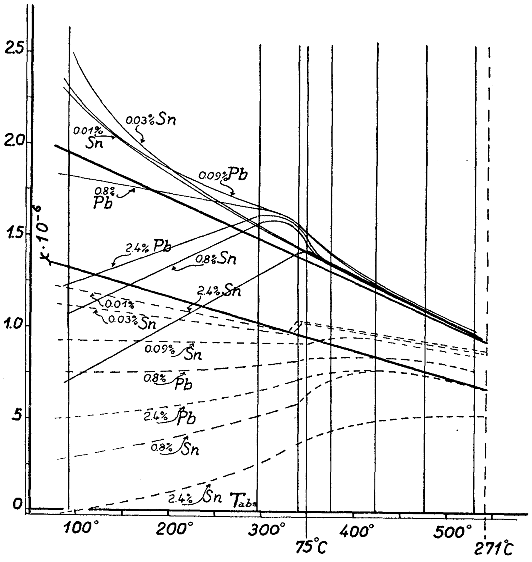

FIG. 29.

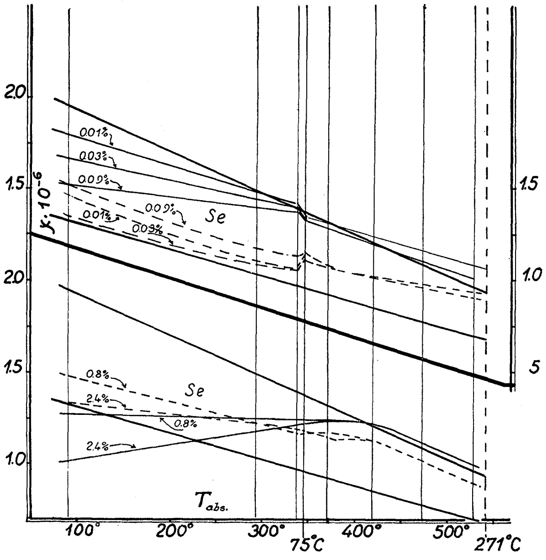

FIG. 30.

FIGS. 29–30. $\chi-T$ diagrams for electropositive[29] and electronegative[30] admixtures (Table IV). The scales of the coordinates are the same in both figures. The heavy drawn lines indicate χ_p (Bi "F") for both directions. The observed points are indicated by the intersection of the curves with the lines of equal temperature. The diagram Fig. 30 is divided into two: the upper (right and upper left scale) for $N \leqq N_c$, the lower (lower left scale) for $N > N_c$. In both figures the direction normal to [111] is indicated by full drawn, parallel to [111] by dashed lines.

concentrations for electropositive and electronegative admixtures in Figs. 29 and 30. The isomorphous admixtures were omitted on account of their very small temperature dependence.

(6.1) *Electropositive admixtures*

Fig. 29 represents the $\chi-T$ relations for electropositive admixtures from $-185°$ to $+245°$C for both principal directions in the crystal, the *normal* direction being drawn in *full* lines.

(6.11) *Electropositive admixtures parallel to [111]*

α. For *small* concentrations (N_c does not exist according to 5.11γ) and $T < 75°$ the temperature coefficient γ of $\chi_{||}$ is smaller than for χ_p (χ_p of pure Bi) but still negative. Around 75° a positive discontinuity takes place, the exact temperature of which cannot be determined due to lacking observations. For $T > 75°$C $\chi_{||}$ becomes larger than $\chi_{p||}$ whereas γ does not change appreciably. Below 75°C the admixture decreases the CDm, above it the opposite is true.

β. The behavior for *large* concentrations does not show typical differences. With increasing N γ decreases still further for $T < 75°$ and becomes for very large concentrations positive. Here the discontinuity at 75° is marked much *less* and disappears finally in a point of inflection. At high temperatures $\chi_{||}$ is larger than $\chi_{p||}$ for the smaller concentrations and considerably smaller than $\chi_{p||}$ for the highest concentration; γ is slightly smaller than γ_p.

(6.12) *Electropositive admixtures normal to [111]*

α. For $N < N_c$ and $T < 75°$ the scz is larger than χ_p, the same being true for γ. Hence the effect of the admixture decreases fast with the temperature towards χ_p as an asymptote. The transformation point at 75° is *not* marked.

β. For $N > N_c$ the temperature coefficient grows smaller with increasing N and reaches positive values for the highest concentrations analogous to 6.11 β, although the magnitude of γ is much larger. The difference with 5.11 β consists mainly in the occurrence of a maximum between 20 and 100°C. The transformation point is *marked* by a negative discontinuity beyond which all χ-values approach closely the values of the pure metal.

(6.2) *Electronegative admixtures*

The $\chi-T$ relations of the electronegative admixtures are represented in Fig. 30 in the same scales. Since the effects of these admixtures go in the opposite direction, the diagram was divided in two: one for $N \leqq N_c$ and one for $N > N_c$, the abscissa being the same for both.

(6.21) *Electronegative admixtures parallel to [111]*

α. For $N < N_c$ and $T < 75°$ γ stays practically unchanged similar to 6.11 α. At $T = 75°$C the discontinuity is *positive*. Above 75°C χ becomes considerably larger than χ_p and γ slightly smaller than γ_p.

β. For $N > N_c$ and $T < 75°$C γ approaches zero with increasing N and is positive for the large concentrations. The transformation point is less distinct. For high temperatures the analogy with 6.11 β holds also with the only difference that $\chi_{||}$ is apparently only for the largest Te concentrations smaller than χ_p.

(6.22) *Electronegative admixtures normal to [111]*

α. For $T < 75°$ χ decreases with decreasing γ. The transformation point is marked by a negative discontinuity and the approximate equality of $\chi_\perp$ and χ_p. For higher temperatures γ is smaller than γ_p and $\chi_\perp$ is but slightly larger.

β. For *large* concentrations γ becomes more positive with increasing N. Though the discontinuity at 75°C is doubtful, it is of interest to see that in the neighborhood of this point the reversal of $\chi_\perp$ and $\chi_{||}$ takes place, such that above 75° $\chi_\perp$ is always larger than $\chi_{||}$, i.e., above 75° a dissimilarity of the anisotropy of the crystal does not exist regardless to the effect of the admixture. For $T > 75°$ $\chi_\perp$ approaches χ_p and $\gamma = \gamma_p$ in close analogy to 6.12 β.

(6.3) *Summary concerning the* $\chi - T$ *relation*

In realization of the fact that the number of observations as well as the accuracy of the measurements is not sufficient to ascribe a reality to the smaller variations the results are much simpler than for the $\chi - N$ relation; they can be summarized as follows:

α. In contradistinction to the $\chi - N$ relation *the* $\chi - T$ *function does not show any fundamental difference between electropositive and electronegative admixtures.*

β. *The effect of admixtures is different above and below 75°C. Above 75°C the influence is much smaller, though different for the two directions:* it is smallest (if existing at all) normal to [111] and comparatively large parallel to [111]. In the latter case the CDm is always increased except for the largest concentrations of electropositive admixtures (see 6.12 β). Otherwise there is no difference between different types.

γ. *The transformation point at 75°C is marked in the same way for all admixtures for small concentrations* by a discontinuity which is *positive for* $\chi_{||}$ *and negative for* $\chi_\perp$. No discontinuity was found for pure Bi in either direction, neither is it present (or at least so distinct) for $N \gg N_c$. The existence of a discontinuity for large concentrations seems improbable.

δ. For temperatures *below* 75°C the differences between different types of admixtures become increasingly larger with decreasing temperature: with it increases the influence of the temperature. *The effect of temperature in this range works always toward a greater similarity with the pure crystal regardless of the sign of the influence of the admixture, i.e., the absolute value of* α *is always decreasing with increasing temperature.*

7. Hypothesis regarding the influence of admixtures upon the CDm

The interpretation of the influence of admixtures upon the CDm is only possible along two lines: the assumption of a *volume*—or a *surface* effect. For the volume effect one has to assume a superstructure caused by the admixture similar to the many other systems of intermetallic solutions already studied. The existence of a critical concentration (N_c) indicating a certain saturation of the crystal with B atoms, means the completion of such a superstructure. If one considers however the values of N_c one obtains for the "effective radii" of the B atoms $= (1/N_c)^{\frac{1}{3}}$ expressed in A atoms the values: Te = 21.5; Sn = 14.9; Se = Pb = 10.3 and one arrives at elementary units in a crystal which contain 10^3–10^4 atoms which is highly improbable. Furthermore if such B atoms should cause a gradual distortion of the A lattice, one should have a periodicity equivalent to those radii, i.e., of the order of the depth of penetration of normal x-rays (e.g., in Bi for Mo $K\alpha$), which however should affect the intensity of the directed scattered radiation considerably. Such effect has not been observed.

A much more probable interpretation seems to be the following one which has the advantage of accounting for almost the entire phenomenology of the effect. Following the hypothesis of Ehrenfest-Raman (see Part A, Section 1) concerning the CDm we assume large orbits of "free" electrons within the crystal. Since the scz is proportional to the areas circumscribed by these orbits, it must be proportional to $\lambda^2(\lambda = \text{m.f. path})$: only the largest paths contribute to the CDm. There is furthermore sufficient evidence that in a crystal certain directions are preferred for the propagation of the electrons, such that in an anisotropic crystal the components of the paths in different directions are different. Hence $\chi_{||}$ equals the sum of components of all electron orbits normal to [111] etc.

If for *low* temperatures and *small* concentrations the assumption is made that the B atoms are not scattered at random throughout the crystal but are adsorbed in certain crystallographic planes which reoccur periodically over the whole volume of the crystal the smallness of N_c is easily understood. Such a superstructure of planes will cause potential barriers to the "free" electron owing to the different nature of the B atom; consequently the paths larger than the parameter of such a structure will be shortened and the electron will be scattered in different directions. The number of such scattered electrons will depend on the "opacity" of the wall, which in turn depends on the type and the density of the adsorbed B atoms. It is reasonable to assume that the capacity of the planes is filled if a mono- or bimolecular layer of B atoms is present, this being identical with the critical concentration N_c. It is obvious that such a mechanism can only shorten the path, i.e., *decrease* the CDm.

In case of an anisotropic crystal there are no planes of the same order parallel and normal to the principal axis, hence the stability of an atom adsorbed in a plane normal to [111] is different from its stability in any other plane. From this follows that the growing opacity of one type of planes will not necessarily affect the opacity of other types. Such a process results in the shortening of only *one* path-component, the other path-component is not affected: the number of electrons with the latter component will however increase: the CDm will *decrease* in one and *increase* in the other direction for approximately the same amount, which actually occurs. Furthermore: this latter component cannot be increased indefinitely as a complete opacity of the plane will only scatter a limited number of electrons. This means that for N_c the increase and the decrease must be independent from the type of B atoms, which is the case for Pb and Sn. (Figs. 15 and 26.) The fact that, e.g., 3 times as many Pb as Sn atoms are used for reaching N_c can be interpreted by the geometrical arrangement of the atoms in the plane, of which a suggestion is made in Fig. 31. The same result could be reached by assuming a different periodicity of the planes, but it is obvious that in this case the previous condition of equal increases or decreases for N_c would not be fulfilled.

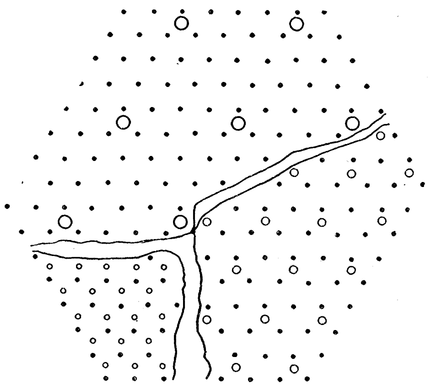

FIG. 31. Scheme of three different types of adsorption of B atoms on a (111) plane. The black dots represent Bi atoms, the smallest circles are B atoms adsorbed at the rate 1 : 1, the medium circle B atoms 1 : 3, the large circles for B atoms 1 : 9.

An anisotropic crystal has a polarity asymmetric with respect to the principal axis, hence it can be understood that electropositive B atoms are more stabile in planes of a certain direction than in another. Accordingly α is quantitatively the same in opposite directions for admixtures of opposite type. With regard to the actual situation of these planes the following conclusion has to be drawn:

Since for $N = N_c$ the scz increases $\substack{\textit{normal}\\\textit{parallel}}$ to [111] for electro$\substack{\textit{positive}\\\textit{negative}}$ B-atoms, the number of electrons with path-components $\substack{\textit{parallel}\\\textit{normal}}$ has increased by scattering on a wall $\substack{\textit{parallel}\\\textit{normal}}$ to [111].

Since there is no prominent plane on Bi which is parallel one has to assume three with a large component in this direction which is either $(11\bar{1})$ or perhaps (110), both planes being predominant in the formation of the etch figures.[26] It may be added that sufficient evidence for such a difference between crystals containing electropositive and electronegative admixtures has been found in etch figures by one of us (G) and the existence of Te in (111) planes seems to be proved.

If one assumes the pseudo-octahedral planes to be equal to each other and also that N_c characterizes a concentration where each Bi atom on the wall is covered by a B atom one obtains for the distance between the (111) plane 0.4–0.5 micron which is in very good agreement with the measured depth of a primitive etch figure. It is also well within the magnitude of the critical sizes of the CDm of fine powders (see Part A, Section 1).[9–12]

An *isomorphous* atom (Sb) causes a much smaller disturbance because of its similarity with A. The small dissimilarity will also for small concentrations cause a higher stability in a plane than in the volume, though the difference of stability for different planes is probably exceedingly small which is a satisfactory reason for the statement in Section 5.4.

For $N > N_c$ one has to assume that gradually other planes with lower affinities are filled which destroy the increase gained by blocking the paths also in this direction. Thus the gain of CDm will be lost and α becomes negative. If admixtures are added even after all planes are filled (indicated probably by $\alpha_\perp = \alpha_{||}$ (Fig. 27)) they distribute themselves over the volume until also this is saturated (limit of the metallographic solubility). For this region a general decrease of the CDm and small values for α should be expected which agrees with the observations.

Analogous to similar hypotheses the authors have given in an earlier paper,[48] one should expect that at higher temperatures the boundaries become less sharp and the effect of the B atoms becomes much smaller: the difference between the stabilities of the B atom in the volume and in the plane becomes less.

Very little can be said about the nature of the concentration N_c' as long as the theoretical analysis of the CDm is as little developed.

The above hypothesis leads one to postulate similar effects though smaller in magnitude $(\sim\lambda)$ for the conductivity and the thermal e.m.f. in Bi crystals containing B atoms. One has to realize though that these phenomena must be affected in the *opposite* direction within the crystal. One of us (F) has measured an *increase* of the conductivity *parallel* to [111] for small concentrations of Te and a *decrease* in the *same* direction for Sn admixtures. Dr. M. F. Hasler could prove a similar relation for the thermal e.m.f.'s.

In case of a macroscopic solubility (Ag) (see Part C, Section 1), the dissimilarity between A and B atoms is so large that their insertion will work completely at random, i.e., increasing or decreasing the anisotropy (Fig. 9).

Finally something remains to be said about the pseudoallotropic transformation point at 75°C. The question of its existence has been discussed by many authors, though no definite interpretation of its nature has yet been obtained. Goetz and Hergenrother[31] proved by x-ray analysis that the lattice structure does not undergo a change, whereas the observation of a Peltier heat[28] as well as of a change in the macroscopic thermal dilation[45] seems to prove the existence of a discontinuous change in the electron configuration over crystal complexes too large to be seen by x-rays (mosaic structure). Recently J. A. Hedvall and his collaborators[46] have confirmed the existence of a discontinuity of the macroscopic expansion of pure Bi and in addition to this they have found a distinct change in the tendency of chemical reaction (*chemische Reaktionsfähigkeit*) between 74° and 76°C.* For the CDm this point is characterized by a negative discontinuity normal and a positive discontinuity parallel to [111], being absent for pure Bi and for high concentrations (Section 6.3). One is probably not far from reality by assuming that the plane structure above this point becomes unstable, which breakdown of the walls causes the surface effect to disappear in a volume effect. Hence the existence of the point is only marked for a large surface effect, i.e., not for large concentrations and not for pure metal. Furthermore

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* Through the kindness of Professor Hedvall the senior of the authors had a chance of a discussion on this subject by letter before the article appeared, for which courtesy he wishes to express his sincere obligation.

the influence of admixtures is small above this point and exists practically only parallel to [111], suggesting the possibility of the disappearance of only one type of plane.

A more detailed discussion of the possible nature of this transformation point in connection with this hypothesis will be published soon.

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