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DENSITY AND CONDUCTIVITY OF BISMUTH SINGLE CRYSTALS GROWN IN MAGNETIC FIELDS WITH RELATION TO THEIR MOSAIC STRUCTURE

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Abstract

In continuation of the study of the thermoelectric effect, previously described by Goetz and Hasler, existing between the two halves of the same bismuth single crystal, of which one has been crystallized within, and the other outside of a strong magnetic field (21,000 gauss), the density and the specific resistance of different sections of these crystals, grown by the discontinuous method, have now been measured.

The change of density of "magnetic" crystals. The density of perfect crystals grown under normal conditions was found to be between 9.82 and 9.83 i.e., 0.2 percent higher than the values of other authors. Furthermore, it was found that any crystalline imperfection such as twinning, etc., decreases the density; that, further there exists a difference of density between the "normal" and the "magnetic" half of the same crystal, the sign of which depends on the orientation with which the crystal entered the field: In case the trigonal axis is normal to the axis of the rod and normal to the lines of force, the "magnetic" half shows an increase of density, whereas the opposite is true in case the principal axis is parallel to the rod (and therefore parallel to the direction of growth and to the heat-flow). The difference of density is ca. 0.3 percent but can be several percent in imperfect crystals. The purity of the metal affects the change of the density. The results indicate that the ideally pure metal would not be affected by the magnetic treatment.

The specific resistance of "magnetic" crystals. The values of the specific resistance obtained on "normal" single crystals agree approximately with the results obtained by Bridgman and Kapitza and also with those obtained by spectroscopic analysis. The value of $\rho_{\parallel}/\rho_{\perp}$ was found to be much larger for bismuth, being sensitive to the "magnetic" treatment. There is a small change of resistance between the normal and the magnetic half, depending on the orientation of the crystal to the field: In case the orientation is such as to decrease the density the resistance increases and *vice versa*. The accuracy necessary for the satisfactory quantitative determination of the change could not yet be reached, since the change is of the magnitude of 0.5 percent.

An attempt is made to combine the phenomena of the magnetic effect thus far known. It seems probable that the influence of the magnetic field upon the formation of a crystal consists of a change within the mosaic structure of the lattice. The investigation is being continued.

Introduction

A THERMOELECTRIC effect within one and the same Bi single crystal of which one half had crystallized under normal conditions, the other within a strong transverse magnetic field has recently been described by A. Goetz and M. F. Hasler.[1] It was found that the size as well as the sign of the e.m.f. depends on the orientation of the crystal with respect to the lines of

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[1] A. Goetz and M. F. Hasler, Phys. Rev. 36, 1752 (1930).

force and on the method of growth; also that the e.m.f. depends largely on traces of impurity within the crystal.

Due to the fact that this magnetic effect is altogether new, very little information as to the cause of the observed e.m.f. can be obtained from the observations themselves and accordingly additional measurements of another type have been here undertaken.

Although we realized in advance that the thermoelectric effect would be by far the most sensitive indicator, and other volume effects should be very minute if at all measurable, there seemed to be encouraging indications in the observations of previous authors concerning the density and the electric conductivity of Bi crystals.

THE DENSITY OF "MAGNETIC" BI CRYSTALS

The density of bismuth has been measured very frequently by different authors and it seems quite remarkable that there is no other common element for which the different observers differ so largely though they seem to have worked with great care. A study of the literature[2] shows that the measured density of Bi varies between 9.66 (Marcus, Giebe) and 10.055 (Zavaffiero), a difference of more than 5 percent. There can be no doubt that part of this variation is due to fissures and inclosures of gas within the metal which falsify the measurement of the volume. It is quite remarkable that the average value of a perfect single crystal is far below the maximum density measured on specimens consisting of compressed powder, thus indicating that the bismuth lattice is *not* the closest possible packing of Bi atoms.

For the present measurement of densities the usual hydrostatic method was improved only in that thin transformer oil was used for the immersing liquid instead of water. In the case of water, it was found that shortly after boiling (a process which is necessary to prevent the formation of gas-bubbles on the surface of the specimen) the absorption of air gradually changes the density until saturation is reached again. In case of oil dried artificially this trouble does not occur and its density can be kept constant for months if one works carefully. The density of the oil was measured in a pyknometer.

To reduce the inaccuracies to a minimum, two pieces of equal length were cut out of one crystal, one belonging to the normal, one to the magnetic side of it. It goes without saying that the crystal had to be free of imperfections—these could be tested for by the thermoanalyser[1]—and also that its surface had to be etched in order to free it from any layer of oxide.

But in spite of the care taken in the measurements and in producing the crystals, the results obtained are not as uniform as expected. Furthermore, according to the thermoelectric results, only measurements on crystals of the same orientation and grown by the same method can be compared. Crystals of the P_1 and P_3-type grown by the discontinuous method, have been investigated, since these orientations show the largest magnetic effects, whereas the P_2-type is almost neutral. In addition to this, it was found that even in the

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[2] Gmelin's Handbuch der Anorg. Chem. Vol. 8, page 35.

measurement of density only crystals of the same sort of bismuth[2] could be compared. Thus most attention had been paid to crystals of the "B" bismuth due to the large "magnetic" effect observed on it in the thermoelectric measurements.

Results. In toto, the density of 76 different specimens was measured. These belonged to 29 different crystals grown in general especially for these measurements. Of these specimens, 15 were of the orientation P_1, 6 of P_2, 16 of P_3, 2 of P_{1-2}, and 2 of P_{2-3}**. Several specimens of the magnetic (M) and the normal (N) halves of the same crystal were cleaved into several pieces, each being measured separately in order to determine the influence of local irregularities and to reveal the accuracy of the method. Table I shows part of the results obtained. The section "number of measurements" in Table I indicates how many different measurements of the same crystal or of its different parts were taken, each measurement consisting of the necessary number of readings.

TABLE I.

Crystal	Orientation	Kind	Treatment	Density	Number of measurements
48/00/0	P_1	*B*	N	9.820	Two
62/00/0	"	"	"	9.815	One
62/00/0	"	"	M	9.845	Two
65/20/0	"	"	N	9.824 (+)	One
65/20/n (×)	"	"	"	9.818 (++)	"
65/20/g (××)	"	"	"	9.819 (†)	"
65/20/0	"	"	M	9.844 (+)	"
65/20/n (×)	"	"	"	9.849 (++)	"
65/20/g (××)	"	"	"	9.838 (†)	"
73/00/0	"	*C*	N	9.833	"
"	"	"	M	9.827	"
83/21/1	"	*B*	N	9.830	Two
"	"	"	M	9.842	"
49/00/0	P_2	*B*	N	9.822	Three
59/00/0	"	"	N	9.813	One
"	"	"	M	9.813	"
60/00/0	P_{1-2}	"	N	9.807	"
"	"	"	M	9.825	"
49/00/1	P_3	"	N	9.826	"
61/00/0	"	"	N	9.835	Two
"	"	"	M	9.805	"
96/31/1	"	"	N	9.837 (*)	?
"	"	"	M	9.817 (*)	?
96/21/1	"	"	N	9.847 (Δ)	?
"	"	"	M	9.836 (Δ)	?
69/00/0	"	"	N	9.803	One
"	"	"	M	9.781	"
70/00/0	"	"	N	9.809	"
"	"	"	M	9.798	"

(××) The specimen included a small twinned region.
(×) The same specimen after removing the twinned region.
(+) Probable error 0.005
(++) Probable error 0.008
(†) Probable error 0.01
(*) N Field strength 17,000 Gauss
(Δ) N Field strength 13,000 Gauss

** The designation of the latter two orientations indicates mean intermediate orientations between P_1 and P_2 etc.

With regard to the absolute value of the density it is apparent that *the average value for single-crystals is between 9.82 and 9.83*, slightly higher than the result obtained by Kapitza (9.80).[3] This result was checked by measurements made upon normal crystals in distilled water immediately after its separation from the absorbed air.

The density of Bi, generally speaking, appears to be abnormally sensitive to crystallographic imperfections, since polycrystals for instance as well as crystals with large twinned regions showed abnormally low values, this probably being due to the enclosure of gas at the intercrystalline borders, as was verified several times by the microscope. This sensitivity is also indicated by the fact that the highest values of the density on our best crystals (9.83) are still below the value to be expected from the x-ray data (9.86).

Nevertheless the values given in Table I have but relative importance (with the exception of the crystals 48/00/0, 49/00/0 and 49/00/1) since they are obtained in oil, the density of which could not be checked in the pyknometer as accurately as the values taken with the balance, though the accuracy indicated by the data given is justified for one and the same crystal because these values were obtained in immediate succession and under similar conditions.

The measurements thus obtained indicate the following connection between the normal and the "magnetic" part of the same crystal: *If the crystal has an orientation in which the principal axis is normal to the lines of force* (P_1 and P_3) *the density of both halves differs considerably, whereas no change can be found if the axis is parallel to the field.* (P_2).

Furthermore with relation to the first part it is evident that the *density of the "magnetic" half is larger than that of the normal, in case the trigonal axis is normal to the axis of the rod,* (P_1), *whereas the opposite is true if the axis is parallel to the axis of the rod* (P_3).

In intermediate orientations (P_{1-2}) where P_2 is unaffected, the resulting change is the same as it is in the case of P_1, but one should not rely too much upon it, since there exists only the measurement of one crystal (orientation ca. 30°). Concerning the measurement of the crystal 73/00/0 which has the P_1-orientation but consists of the kind C (i.e., the purest metal[1]) it is striking that *no change of density could be observed.*

In consideration of the large experimental difficulties connected with density measurements of this kind, one should not put too much stress on the absolute value of the differences of the density between the normal and the "magnetic" parts, since an almost invisible layer of oxide or grease and small enclosures, difficult to detect, affect the results fatally by fogging the whole effect. Thus a number of observations had to be discarded among which were a few whose sign was not in agreement with the above statement. Nevertheless the discarding was done only after it was evident that the crystals were imperfect.

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[3] P. Kapitza, Proc. Roy. Soc. **A119,** 358 (1928).

The Electric Resistivity of "Magnetic" Crystals

As soon as it was evident that the growing of crystals in a magnetic field affects their density, it was decided to measure their electric resistivity, since it is well known that these qualities are closely related within the same metal.

There are a number of very exact investigations published concerning this subject (Bridgman,[4] Schneider,[5] Borelius and Lindh,[6] Schubnikow and de Haas[7] and Kapitza[3]). It is made quite certain by Bridgman that the Voigt-Thomson law holds also in case of Bi, whereas concerning the absolute values of the specific resistance, a small discrepancy still remains between the recent authors, a discrepancy which is very probably due to the fact that it is very difficult to obtain bismuth of sufficient purity, or better of equal impurity.

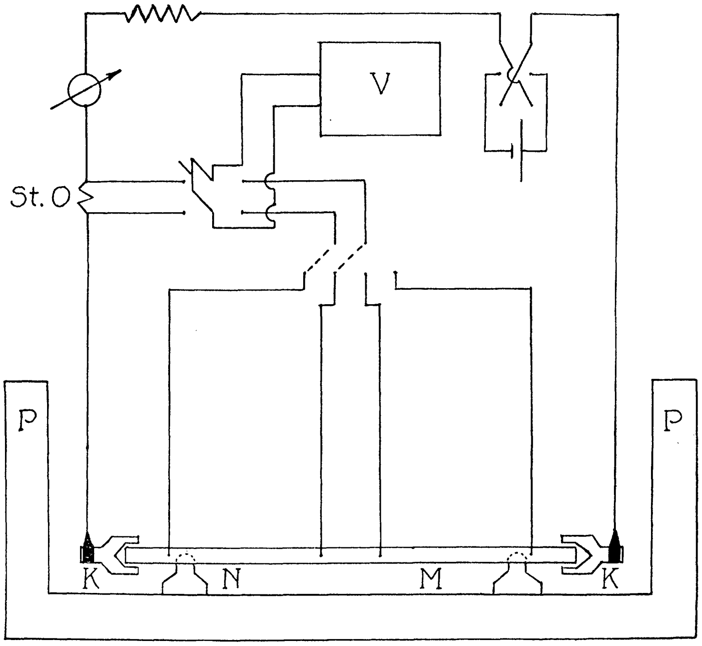

Fig. 1. Diagram of apparatus.

Also the measurements themselves must be performed with special precautions, so as to avoid the large thermoelectric forces due to small changes of temperature as well as any permanent or elastic distortion of the crystal, for these affect the results largely.

We used for our measurements, for the most part, the arrangement already described by Kapitza[3] with certain modifications however, dictated by the much larger size of our crystals and by our special purpose of comparing the values of two different parts of the same crystal. Thus the arrangement was as shown in Fig. 1.

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[4] P. W. Bridgman, Proc. Am. Acad. **63**, 351 (1929).

[5] G. W. Schneider, Phys. Rev. **31**, 251 (1928).

[6] G. Borelius and A. E. Lindh, Ann. d. Physik **51**, 607 (1916).

[7] A. Goetz, Phys. Rev. **35**, 193 (1930).

After a crystal of 13 to 15 cm in length, of the desired orientation, was grown within a graphite trough previously described,[7] one half of which (*N*) was grown under normal conditions, the other (*M*) within a magnetic field, both ends including the transition between the seed crystal and the main crystal were carefully cleaved off so as to obtain the standard length of 12 cm. Then the crystal was etched and searched for imperfections or twin lamellae. In case it proved satisfactory two copper cups (*K*)—the current leads—were soldered to the crystal with Wood's metal. This method has the advantage of avoiding the necessity of heating the crystal long enough to produce an alloy between bismuth and Wood's metal, which makes the further use of the bismuth impossible, whereas here one has only to heat the cup filled with Wood's metal up to its melting point and then to put one end of the crystal into it, after which the liquid metal solidifies shrinking around the crystal. Thus a reliable contact for comparatively large currents is made.

The potential leads consisted of 0.1 mm silver wire which was spark-welded on to the crystal at 4 different points as shown in Fig. 1 to allow the measurement of the specific resistance separately across the normal and the magnetic parts of the crystal. In order to keep the temperature constant the whole arrangement was immersed in a bath of oil within a container of paraffin (*P*).

The current was measured by means of a standard ohm (St. O) and a precision potentiometer *V*, whereas the voltage across one pair of silver wires was measured directly with the potentiometer. There were furthermore the usual precautions for balancing the thermoelectric effects etc.

The largest difficulty consisted in the exact determination of the cross section of the crystal, since it could not be taken from direct measurement because of the peculiar shape of the trough. Thus it was necessary to calculate the specific resistance from the length (*L*), the weight (*G*) and the density (*D*) by means of the relation:

$$\rho = \frac{E \cdot G}{J \cdot D \cdot L^2}$$

where J and E are current and voltage and ρ the specific resistance. Since it was impossible to obtain any better accuracy by this method than 1—2 percent the variation of density between *N* and *M*, as described before, was not considered. For *D* the value of 9.82 was taken.

The reason for the inaccuracy of this method is found in the assumption that the cross section over the length used is constant. This becomes less true the larger this length is chosen. This distance between the potential leads on the other hand has to be large enough to avoid the influence of the unequal current distribution in the neighborhood of the leads and the uncertainty of the distance due to the cross section of the welding spot, which was in the present case at least 0.5 mm. The distance used was in general between 30 and 40 mm so as to decrease the uncertainty of ρ to about 3 percent.

Results. It is well known that the specific resistance parallel to the trigonal axis of a Bi crystal is larger than normal to it, furthermore, that the ratio between these two values increases with the increasing amount of impurity, since in this case, the resistance along the trigonal axis increases faster than perpendicular to it. The minimum values of $\rho_\parallel/\rho_\perp$ are 1.27 (Bridgman[4]) and 1.30 (Kapitza[3]), whereas Schneider[5] finds 1.62 using a metal with 0.04 percent silver. Table II gives the results which seem the most reliable ones. No reliable values for bismuth D[1] could be obtained, since this kind is very hard to obtain in single-crystalline form without inclosed air-bubbles.

TABLE II.

Crystal	Orientation	Kind	Part	Resistance
83/21/1	P_1	B	M+N	1.395
"	"	"	M	1.384
"	"	"	N	1.407
83/11/?	"	"	M+N	1.395
"	"	"	M	1.343
"	"	"	N	1.438
96/31/1	P_3	"	M_1	2.085
"	"	"	M_2	2.088
"	"	"	N_1	2.030
"	"	"	N_2	2.030
91/41/1	P_1	C	M+N	1.109
"	"	"	M	1.122
"	"	"	N	1.090
91/33	P_3	"	N	1.358 (?)
"	"	"	N	1.428
"	"	"	N	1.419
91/51/1	"	"	M+N	1.438
"	"	"	M	1.493
"	"	"	N	1.393
86/11	P_1	A	N	1.334 average
85/21	P_3	"	N	1.745 "

The values for $\rho_\parallel/\rho_\perp$ in Table II are taken at temperature of 25°C which is slightly higher than the temperatures used by Bridgman and Kapitza (20°). This difference makes it necessary to decrease our values about 2 percent to compare them with the values of these authors.

The main reason why our values are not as consistent as Kapitza's and Bridgman's is probably the indeterminancy of the cross section of the crystals. Nevertheless these observations (which are not considered to be final) indicate the following facts.

The variation of the specific resistance of the different kinds of bismuth used is in agreement with the spectroscopic analysis published previously[1] showing that C is the purest metal with a resistance $\rho_\perp = 1.09 \times 10^{-4}$ and $\rho_\parallel$ 1.36(?) to 1.43×10^{-4}. The latter value is slightly larger than Bridgman's (1.38×10^{-4}) but can be easily explained by the lack of longitudinal compression in which case Kapitza obtained values up to 1.5×10^{-4}. Bismuth A can be easily recognized as impure and B is still worse, agreeing with the measurements of Borelius and Lindh. Fig. 2 shows the results for the three different kinds of Bi used; the hatched line below C shows Bridgman's best values,* the dotted line crossing *B* gives the conductivity for *B* crystals grown in the magnetic field in the corresponding orientation, the abscissa is given in the usual terms of $\cos^2$ of the angle of orientation.

The most important fact suggested by the results consists in the influence

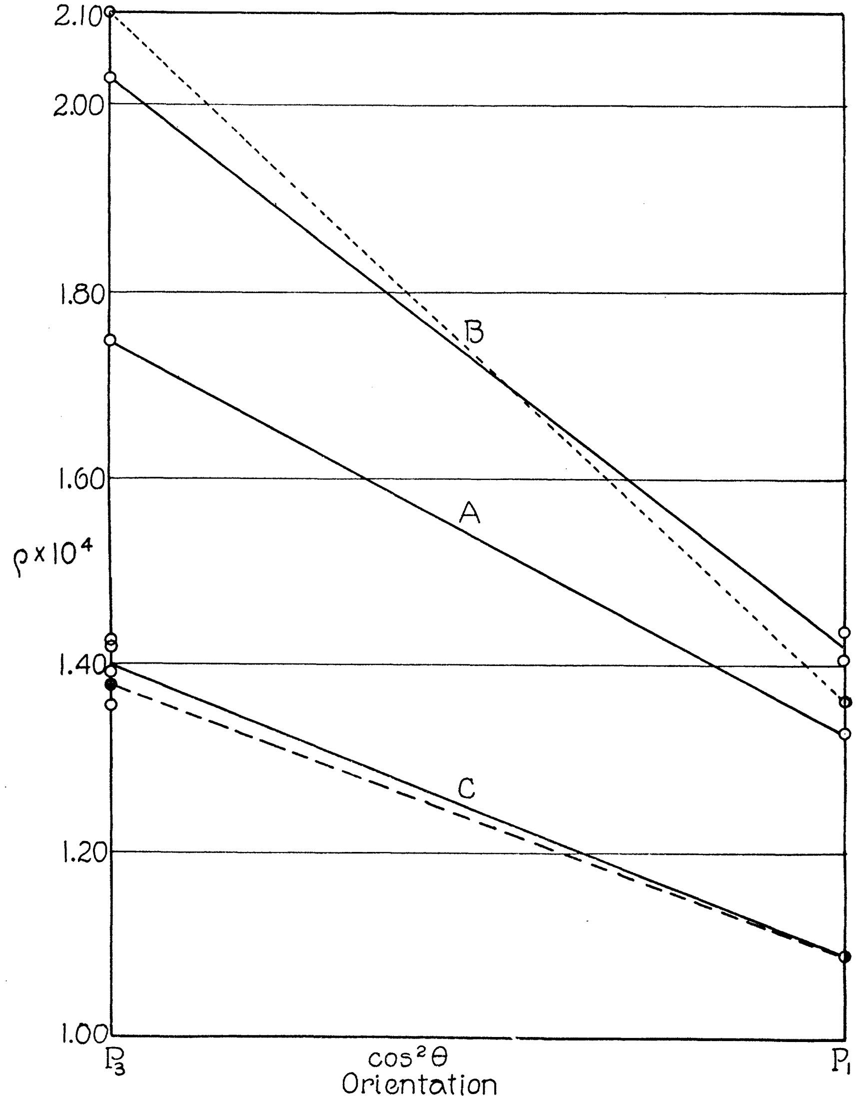

Fig. 2. Results for the three different kinds of Bi used. The hacked line below *C* shows Bridgman's best values. The dotted line crossing *B* gives the conductivity for *B* crystals grown in the magnetic field in the corresponding orientation.

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* There is one discrepancy worth mentioning in the fact that Bridgman used Kahlbaum metal which is the same as our *D*. Kapitza's remark about this metal as well as our analysis shows that it contains a considerable amount of impurity which is different from the con-

the magnetic treatment of the crystal has on the resistance. This runs as follows: *if the crystal has an orientation in which its trigonal axis is normal to the lines of force and normal to the direction of the current the specific resistance of the magnetic half is smaller than the normal one; if the trigonal axis is normal to the lines of force and parallel to the direction of the current the specific resistance of the magnetic half is larger than the normal.*

As to the qualities of the P_2 orientation no exact measurements were yet performed because the thermoanalysis did not show any "magnetic" effect.

DISCUSSION

The results obtained as to the influence of the magnetic field upon the density and the conductivity of Bi single crystals, have a close relation. This is not altogether unexpected. The increase in density is associated with a decrease of specific resistance (P_1) and *vice versa* (P_3). Furthermore, the crystallization within a magnetic field seems to affect the density and conductivity of a metal with small impurities to a much larger extent than a pure one.

Considering the nature of the change within the "magnetic" crystal it is very difficult to say anything that is more than a mere suggestion. Both the thermoelectric effect and the change of conductivity could be explained by a change at the moment of crystallization in the orientation of the crystal when entering a magnetic field. As has been already stated in a previous paper[7] no change in orientation could be detected, furthermore this explanation would account neither for the large influence of impurities nor for the change in density.

Another suggestion would be an allotropic change of the lattice, indicated by the change in density. Hence an x-ray investigation was started after the first indications of a change of density were found. This consisted of Bragg diagrams taken simultaneously from the (111) plane of the normal and the magnetic half of the same crystal, but, as was stated already briefly by Goetz and Hergenrother,[8] not the slightest displacement of corresponding lines was found, thus indicating that *the atomic distance along the trigonal axis does not differ between both parts of the crystal.*

Hence there are obviously only two conclusions left, of which one assumes that the magnetic half undergoes an pseudo-allotropic change of the same type as the $\alpha\rightarrow\beta$-transformation of iron and zinc which cannot be found by x-ray analysis though indicated by electric volume effects. In general one assumes that the transformation of the first metal is only due to an interatomic change of the distribution of electrons and it would be plausible that such an effect occurs more easily if the internal symmetry of the lattice is disturbed by impurities. Nevertheless this suggestion loses probability as it does not account for the change in density in case of Bi.

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tamination of *A* and *B* but much more than *C*. This fact is also indicated by the size of the "magnetic" effect. We were not able to obtain reliable measurements of the specific resistance of this metal whereas Bridgman got the best results yet published.

[8] A. Goetz, R. C. Hergenrother and A. B. Focke, Phys. Rev. **34**, 546 (1929).

Thus there is apparently no mode of explanation left save that which has been suggested in a previous paper as the only way to account for the large effect of minute impurities in a crystal.[1] This way seems indeed to account for the whole phenomenology of these effects, including the change of density and electric conductivity of magnetic Bi crystals. The assumption is of a change in the secondary structure of the crystal as described first by Zwicky.[9,10]

The experimental evidence for the existence of this structure in Bi crystals has already been given by one of the authors.[11] He showed that this structure, superimposed upon the Laue-Bragg lattice, consists of blocks of a definite size which is within the range of microscopic visibility. Our present suggestion is that the arrangement of these blocks is changed under the influence of the magnetic field so as to produce a closer or less close packing. This would not influence the x-ray diagram, since this depends only on the primary structure of the lattice whereas the density of the crystal as a whole would be affected by a change in the mosaic arrangements of the blocks.

This mosaic arrangement of the blocks is thus assumed to be changed by the influence of a field during the formation of the crystal. Such a change, which we have to think of as a systematic distortion, must depend on the crystallographic orientation of the crystal within the field and must disappear if this orientation causes the smallest possible content of free energy upon the crystal as is the case in the P_2 orientation where the direction of the smallest susceptibility is parallel to the lines of force as follows from the measurements of Focke.[12]

This assumption makes it plausible also that the electric conductivity changes with the density, since both depend on the compactness of the crystal.

The hypothesis as a whole implies a less compact form due to the mosaic structure for the average perfect crystal than for an ideal one.** Although it is perhaps possible to think of accidental fissures within the crystal as the cause of the difference between the theoretical and the actual density (0.3 percent), the fact that one can approach the theoretical density by the crystallization in a magnetic field under the same thermal and mechanical conditions of growth seems to be a strong argument against the presence of such fissures dependent upon imperfect growing conditions. Also the consistency of the density values obtained speaks against such an explanation.

Considering the magnitude of the change of density and conductivity in

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[9] F. Zwicky, Proc. Nat. Acad. **15,** 253, 816 (1929).

[10] F. Zwicky, Hel. Phys. Acta. **3,** 269 (1930).

[11] A. Goetz, Proc. Nat. Acad. **16,** 99 (1930).

[12] A. B. Focke, Phys. Rev. **36,** 319 (1930).

** This conclusion does not contradict Zwicky's assumption[13] for ionic lattices of Na Cl type, where the actual density of a crystal should be larger than the density calculated from the x-ray diagrams due to the contracted Π-planes sandwiched between normally spaced regions. (Hel. acta, page 288.)

magnetic crystals (0.5 percent) one must call these second-order effects in comparison with the magnitude of the thermoelectric changes.[1] This fact also seems to support the suggested hypothesis, since it is well known that thermoelectric effects in general are much more structure-sensitive than density and conductivity known as structure-insensitive.

There are two more arguments in favor of the above explanation: if there is a possibility of a distortion within the mosaic structure, i.e., among the blocks, this can only be possible if during the genesis of the crystal these units possess a larger mobility among themselves than do the molecules of the primary lattice. This is necessary for the following reason: an orienting influence upon the crystal exerted by the magnetic field presupposes the existence of an anisotropic susceptibility. Besides the fact that liquid Bi is almost neutral magnetically and the further fact that the large diamagnetic properties of Bi arise only at the moment* the lattice forms, make it obvious that the magnetic anisotropy cannot exist either before the primary lattice is formed. Hence the orienting influence of the field can only occur if a lattice already exists. As the forces exerted upon the crystal by the fields used are far too small to deform the lattice permanently the only explanation left seems to be the distortion of the secondary structure. This explanation presupposes that the primary structure exists before complete solidification, a fact which former work by one of the authors made highly probable in the case of Bi.[11] The second support of the above hypothesis is found in the observation that a possibility of an orienting influence upon the crystal "*in statu nascendi*" exists in fact, and that it can have mechanical, thermal and

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* This statement is not in harmony with Kapitza's hypothesis according to which the large diamagentism of Bi begins only slightly below the melting point after the metal has already solidified. It seems dubious whether this opinion can be supported by Curie's paper on this subject,[14] for he states emphatically: "· · · la chute (of diamagnetism) est absolutement brusque et correspond exactement avec le phénomène de la fusion · · ·"; and furthermore: "· · · Un curieux phénomène se produit si l'on chauffe le Bi en petits fragments dans une ampoule fermée à une temperature à peine supérieure à celle de fusion. La chute des propriétés magnetiques se produit complètment; cependant si l'on refroidit quelques minutes après, on retrouve les petits fragments qui ont le même aspect qu'avant et se ne sont pas écroulés. Cependant le Bi. a été fondu, car, en cessant les morceaux, on voit que la structure interne a été complètment changée et que les plans de clivage ne sont plus placés comme avant · · · ."

This does not mean necessarily an indication of the existence of a transformation, since similar experiments by us showed that even a thin oxide-coat covering such fragments is very well able to preserve their exterior shape, though a pinch with a needle through this (almost invisible) coat proved the interior to be liquid. Furthermore the change of orientation within those fragments makes a melting more probable than an allotropic transformation, since, as is shown by several authors, the main orientation of a crystal is preserved in general no matter how frequently the transition between two allotropic transformations be passed. It appears also clearly in Honda's paper (16) that the rise of diamagnetism is associated with the process of crystallization and a personal discussion of this matter that one of the authors (G.) had with Professor Honda at Sendai leaves no doubt that the utmost care was taken with respect to this question.

[13] F. Zwicky, Proc. Nat. Acad. **16,** 211 (1930).

[14] P. Curie, Journ. de physique **4,** 206 (1895).

[15] A. Goetz and M. F. Hasler, Proc. Nat. Acad. **15,** 646 (1929).

magnetical causes.[11,17] This proves that the anisotropic qualities do not disappear when the macroscopic crystal melts.

Thus one is forced to assume that the distortion of the mosaic structure is the result of two different influences: The orienting influence of the field and the orienting influence of the crystal grown already in an orientation enforced upon it by a seed crystal such as was always used in our experiments. As long as both influences work in the same direction (P_2) there is no distortion, whereas in case they work in different ways a distortion must occur, depending on the orientation (P_1 and P_3), as is indicated by the different signs of the described volume effects. The magnitude of these effects can obviously be ascribed partly to the degree of the distortion. Since the conditions in our experiments were kept as constant as possible the different magnitudes (Bi A, B, C, and D) especially of the thermoelectric effects of the same orientation can but indicate different degrees of distortions due to the same cause. This makes it probable that the impurities within the crystal determine the energy necessary for a certain change of the mosaic structure.

With regard to such a relation one has to go back to one consequence of Zwicky's theory of the mosaic crystal which has already been suggested by him implicitly: In case a perfect crystal contains a small amount of impurity, too small to form a homogeneous solid solution of the whole crystal, the strange atoms will accumulate in a region where their presence causes the smallest disturbance of the lattice, i.e. within the II-planes. The chance that a certain part of the foreign atoms present in the liquid will accumulate within the II-planes depends on the expression

$$S = \frac{\alpha}{A} \cdot [E_p - E_\pi]$$

which by applying the Boltzmann principle gives for the probability the expression:

$$P = \text{const} \cdot e^{-\alpha(E_p - E)/AkT}$$

where E_p and E_π are the respective energy contents of the same crystal first when the foreign atoms are put into the lattice at random and second when they are arranged within the II-planes. A represents the affinity of the strange atoms for the formation of a solid solution in the crystallographic constellation under consideration and α stands for the "perfection" of the crystal, including the conditions of crystallisation, absence of external disturbances, inverse speed of growth, etc. It is apparent that the above will only hold for an amount of foreign atoms smaller than or equal to that amount necessary to fill the II-planes with a mono- or bimolecular layer and only for one kind of atoms at the same time. Under the assumption that S is sufficiently large in our crystals one is led to think that the units of the secondary lattice are surrounded by a more or less dense hull of impurities. It is obvious that atoms

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[16] K. Honda, Magnetic properties of matter, Tokyo, p. 131, (1928).

[17] L. Schubnikow and W. J. de Haas, Comm. Phys. Lab. Leiden, Nr. 207 c p. 15 (1930).

of different metals should have different effects due to different A's, i.e., similar atoms should have smaller effects than an equal number of dissimilar ones, the correctness of which conclusion is attested for example by the negligible influence of small amounts of Sb within Bi crystals, (Sb forms the same lattice as Bi with only slightly different dimensions) and also by the surprising effect of traces of Ag and Pb (0.02 percent) as already stated by Bridgman, Goetz and Hasler.

The presence of such dissimilar impurities may greatly change the stability of the secondary lattice and thus make it more sensitive to the influence of a magnetic field applied during the formation of the crystal. The large influences that small impurities have on electric volume-effects within Bi crystals make the assumption of a two-dimensional accumulation of impurities (as in the Π-planes) necessary since it is difficult to understand that a homogeneous distribution of minute impurities over the whole crystal can produce such large effects, as have been observed by Kapitza for example in the change of conductivity in strong magnetic fields.[3]

It would be interesting to investigate whether or not the diamagnetic properties of these crystals are affected by impurities and also by their formation within strong magnetic fields. Assuming the correctness of Ehrenfest's hypothesis[18] namely that the large diamagnetic susceptibilities are due to electronic orbits extending around more than one nucleus, a change of the mosaic constellation of a crystal would be expected to affect its magnetic qualities, i.e., one should expect that the large diamagnetic susceptibilities are structure sensitive properties. Experiments of this kind are started and the results seem to point in this direction.

Besides the investigation of the intensity distribution of the x-ray reflections on "normal" and "magnetic" crystals which has already been published[8] briefly, another experiment should be mentioned which could throw light on the nature of the suggested distortion of the mosaic structure: namely an experiment upon the magnetostriction of perfect magnetic and normal crystals, for it is to be expected that this effect must be largely influenced by any systematic change of the secondary structure. Experiments of this kind are planned.

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[18] P. Ehrenfest, Physica, 388, (1925); Phys. Zeits. **58,** 719 (1929).