Second Series *April 15, 1932* *Vol. 40, No. 2*

THE

PHYSICAL REVIEW

X-RAY STUDIES ON BI SINGLE CRYSTALS

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(Received February 2, 1932)

Abstract

An x-ray analysis of different types of Bi single crystals is described in order to decide whether or not the difference in density, electric conductivity and thermal e.m.f. observed between Bi crystals grown within (M), or outside (N) of a transverse magnetic field were caused by a change in lattice spacing or due to an alteration of the lattice parameter.

Determination of the interplanar spacing along $(11\bar{1})$. The Bi crystals were grown by the method described by Goetz, and the cleaved planes (111) and $(11\bar{1})$ were used. By means of the precision method of Siegbahn the interplanar spacing along (111) was determined with Mo $K\alpha$ radiation as 3.9453 ±0.0002A at 23°C. No difference larger than 0.003 percent of $d_{(111)}$ was found to exist between N and M crystals hence the former conjecture was proved that the changes caused within the crystal by its formation in a magnetic field affect only its mosaic structure and do not influence the lattice.

Determination of the parameter. Two different methods have been used to measure the integrated reflected intensities for different orders. By means of a new photographic recording method the intensities of the first to the fifth order have been compared and no consistent change of the parameter could be found. In addition to the photographic records an ionization method of high sensitivity has been used involving a new type of x-ray spectrometer—designed by Hergenrother—in connection with a Hoffmann electrometer. The photographic results were verified and the integrated intensities could be measured up to the seventh order, thus permitting much greater accuracy in the determination of the parameter than has been previously reported. Making use of Pauling and Sherman's computation of the atomic structure factor and applying an experimentally determined value of the Debye factor, the parameter along (111) was found to be 0.359A ±0.0006A, which value lies well within the limits of Hassel and Mark and is slightly larger than James' observation.

Conclusion. The non-existence of a change in lattice structure and in parameter for the N and M crystals shows that the electric volume effects which distinguish the two types of crystals can exist in spite of the unchanged conditions for the existence and distribution of the "free" electrons as given by the geometric configuration of the atoms in the lattice. Hence the cause of these effects can only be ascribed to changes of certain variations in the lattice, the period of which must be many times larger than the size of an elementary rhomboheder in order to be undetectable to x-ray analysis. This implies the assumption of very large "mean free paths" for the electrons in a crystal.

INTRODUCTION

IN PREVIOUS papers certain changes have been described by Goetz and Hasler[1] and Goetz and Focke[2] which a bismuth single crystal undergoes, if it is crystallized in a transversel magnetic field. It has been observed that for an orientation in which the principal axis (111) was parallel to the rod and normal to the lines of force a large thermal e.m.f. existed between a section of the crystal grown without and another crystallized within the field, although the two sections did not show a change in orientation larger than 0.5°. The thermal e.m.f. changed sign and magnitude in the opposite orientation, where the (111) axis was normal to the axis of the rod and normal to the lines of force. In addition to this effect a change in conductivity and density was observed, such that in the former case the density decreased (*ca.* 0.3 percent below normal), whereas it was found to increase in the latter orientation (*ca.* 0.2 percent above normal).

Obviously the question arose as to whether or not the genesis of the crystal under the influence of a magnetic field caused a change in the interplanar spacing of the crystal lattice or in its parameter, of which possibilities the former seemed to be indicated by the change in density.

PREPARATION AND ORIGIN OF THE CRYSTALS

The bismuth crystals used were grown one half within and the other half outside of a magnetic field of approximately 13,000 Gauss using the method previously described.[3] The orientation of the crystals was either: (111) parallel or normal to the axis of the rod, the diameter was 3–4 mm, the length 10–12 cm. The metal used was of the origin "B"[4] and showed the largest magnetic effect.

Since it is rather difficult to prepare good cleavage surfaces suitable for intensity measurements—as is necessary for the determination of the parameter—a number of experimental difficulties had to be overcome,* and a large number of cleavages had to be performed in each case before a satisfactory plane could be obtained.

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

[2] A. Goetz and A. B. Focke, Phys. Rev. **37**, 1044 (1930).

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

[4] Reference 1, page 1775, Table IV.
The "B" metal (origin: Hartmann and Braun, Frankfurt a.M. Germany) contains according to a spectroscopic analysis by Mr. M. F. Hasler, approximately the following impurities:

0.01% Cu
0.028% Ag
0.061% Pb
0.0022% Tl
0.0013% Te.

* The best technique seems to be to cleave at room temperature (liquid air was tried, however, without better success) with a very thin Gillette blade. For this purpose the crystal is held with wax to a piece of hard wood and the blade adjusted to the cleavage plane is struck sharply with a small hammer. Two pieces of rubber as thick as the crystal support the ends of the blade in order to prevent it from cutting deep into the crystal. Hence the blade penetrates into the crystal only to approximately one fifth of its diameter, whereas the rest of the cross-

DETERMINATION OF *D* ALONG [111]

After preliminary measurements with the Bragg method had proved the necessity of high accuracy, the final observations were taken with a Siegbahn spectrometer[5] at which the angle scale could be read to 30 inches with a pair of vernier scales and microscopes. A water-cooled x-ray tube of Müller type with molybdenum target was used as source and was run at 57 kv and 10 m.a. with half-wave rectification (kenetron).

In order to be able to compare the reflections from "magnetic" and normal crystals a special holder shown in Fig. 1 was made. Two cleaved sections of the same crystal, C_1 and C_2,—one of the magnetic and one of the normal half—were cemented onto the holders *a* and *b*. The crystals were adjusted parallel to each other by putting them on a plane glass plate with the faces downward, then the holder was put over the crystals standing with its edges *EE* on the plate. After this the sliding pins *a* and *b* were lowered until they gently touched the crystals. Then the crystals were attached to the tips of *a* and *b* with a drop of a non-shrinking cement. The holder itself could be mounted onto a movable stage in order to align the crystal faces with the axis of rotation of the spectrometer. The final adjustment was checked by optical reflections in the usual way.

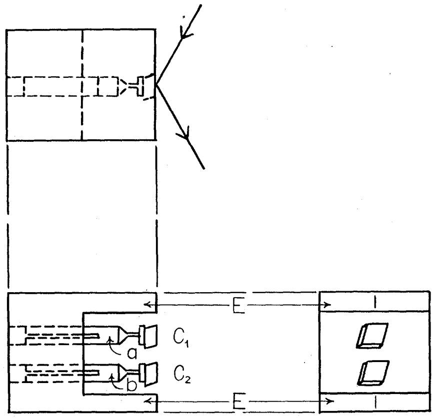

Fig. 1. Design of the double crystal holder for the photographic method in order to compare *M* and *N* crystals simultaneously.

Using a precision method developed by one of us for this purpose (6) on the base of Siegbahn's technique, the reflections were recorded on a photographic plate.

Two reflections of a given order were obtained for each crystal, according to two opposite corresponding positions of the crystal including the known

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section splits without having been touched by the blade. The region which came into touch with the blade is distorted and twinned whereas the large portion of the surface is very flat. This procedure can be applied to the planes (111) and (11$\bar{1}$), though the latter are very difficult to obtain in good perfection.

[5] Siegbahn, Spektroskopie der Röntgenstrahlen p. 64, Berlin 1924.

angle ϕ. The separation of each set of lines on the plate $\delta = R \cdot d\phi'$, is determined by the comparator and by measuring the distance R between the axis of the spectrometer and the plate. The glancing angle θ is then determined by:

$$\theta = \tfrac{1}{4}\left(\phi + \frac{360\delta}{2\pi R}\right) \cdot \cdot \cdot \cdot$$

Fig. 2 shows a reproduction of the 5th order reflection of Mo $K\alpha$ doublet reflected from [111] of a "normal" (N) and a "magnetic" (M) crystal. The separation of the $K\alpha_1$-lines, measured as an average from several plates was 0.799 mm for "normal" and 0.777 mm for "magnetic" crystals. Since this difference was within the uncertainty of the measurement of the center of each line the value 0.778 was chosen as an average. This proves that the interplanar spacing along [111] is *not* different between "magnetic" and "normal" sections of the crystals within the limits of error (0.003 percent).[6]

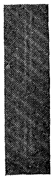

Fig. 2. Reproduction of the 5th order reflection of the Mo $K\alpha$-doublet from (111) of a "normal" and a "magnetic" crystal.

The values measured are:

$$\delta = 0.788 \pm 0.001 \text{ mm}$$
$$R = 172.6 \pm 0.2 \text{ mm}$$
$$\phi = 106.329^\circ \pm 0.004^\circ$$
$$\theta = 26.647_0 \pm 0.001^\circ.$$

Hence the interplanar spacing along [111] is given by:

$$d = \frac{n \cdot \lambda}{2 \sin \theta} = 3.9453\text{A} \pm (0.0002\text{A}) \text{ at } 23^\circ\text{C}.$$

This value is in good agreement with the results obtained by James[7] (3.95A±0.08A) and Hassel and Mark[8] (3.945A).

The possibility of a lattice deformation in another direction to the principal axis was checked also although the oriented thermal e.m.f. of "magnetic" crystals made such an effect less probable.[1] Reflections from $(11\bar{1})$ planes measured in the same manner gave also no change between two different sections. For these measurements the accuracy obtained was, however, only 0.5 percent due to the imperfect cleavage of such planes.

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[6] R. C. Hergenrother, Physics **2,** 63 (1932).

[7] R. W. James, Phil. Mag. **42,** 193 (1921).

[8] O. Hassel and H. Mark, Zeits. f. Physik **23,** 269 (1924).

The conjecture already presented in a previous paper[1] that the change in density caused by the crystallization in the magnetic field be due to a change in the mosaic structure of the crystals seems therefore justified.

DETERMINATION OF THE PARAMETER

The identity of the lattices of the two types of Bi is however not established as long as the parameters are not compared, although a change in this magnitude would not account for the observed change in densities. A determination of the parameter involves an exact method to determine the reflected integrated intensities of different orders, and a photographic method as well as the direct measurement by means of ionization have been applied.*

The photographic method

The first attempt to determine the reflected integrated intensities by photometry of photographic records for different orders (1 to 5) showed a distinct difference between "magnetic" and "normal" portions of the crystal; the results however were too inconsistent to be relied upon in spite of a qualitative agreement with James' results. Table I presents the intensities in arbitrary units standardized for the second order (=100), for the first five orders of the simultaneous measurement of a "magnetic" and a "normal" section of the same crystal from three different plates in comparison with James'[7] values. Since this author used Rh $K\alpha$-radiation an exact agreement is not to be expected.

TABLE I.

Order	James'[1] $\lambda=0.612$A	Plate *A*		Plate *B*		Plate *C*		Average *A*,*B*,*C*.	
		N	*M*	*N*	*M*	*N*	*M*	*N*	*M*
1	29	47	17.6	32.7	26.7	—	—	39.8	22.2
2	100	100	100	100	100	100	100	100	100
3	24	20.5	37.6	25.8	37.7	27.3	28.6	24.5	38.2
4	Not given	0.0	2.1	1.3	1.5	0.0	3.0	1.3	2.2
5	Not given	0.0	6.5	0.0	5.1	0.0	4.5	0.0	5.36

With the wide range of reflected intensities for different orders the disadvantage of the usual photographic recording method is obvious and therefore a new technique was developed. Although the quality of the cleaved surfaces was not sufficient to permit a direct measurement of integrated intensities for the final determination of the parameter of Bi, the new method, which uses the photographic plate only as zero-instrument, shows certain general advantages, that may justify its description.

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* The source of the x-radiation as well as the high tension arrangement used was essentially the same as described above, with the only difference that the filament of the x-ray tube was heated by a storage battery of large capacity, the constancy of the current being regulated manually by a micrometer rheostat of special design and being checked by the emission current accurate to 0.02 percent. Because of the large range of reflected x-ray intensities for different orders, two standard emission currents were use: 1 m.a. for low (first to third) and 10 m.a. for high orders (fourth to seventh). This made it possible to cover all ranges of intensity without necessitating a change in sensitivity of the electrometer for the ionization measurement nor requiring extremely short or long exposures for the photographic method. It involved however a correction for the leakage currents, since the batteries were on the high tension side.

The Siegbahn spectrometer as mentioned above was used for this purpose, though any spectrometer arranged for adjusting crystal as well as plate accurately in a predetermined position can be used. The method involves the following procedure. (Fig. 3.)

(a) In order to record a given order of Bragg reflection, the plate *P* is fixed at a predetermined position and the crystal *C* is turned at a definite angular speed through the Bragg-angle from a position $\theta-\phi$ to $\theta+\phi$ by means of a motor driving a threaded shaft over a transmission, thus pushing the arm *A* of the crystal holder through the range 2ϕ. The motor has to be adjustable over a large range of speeds. The angle 2ϕ is slightly larger than the experimentally determined rocking angle of the crystal.

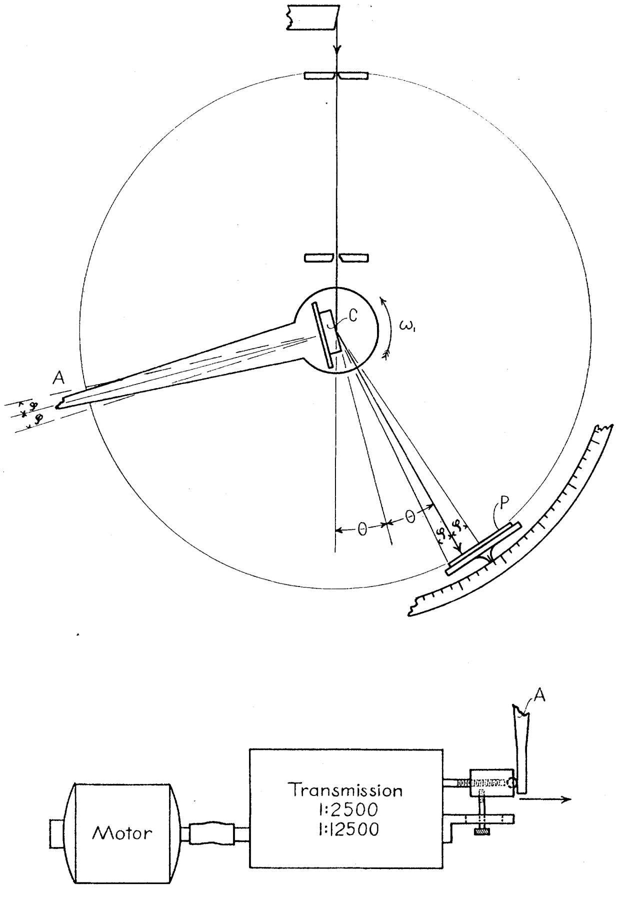

Fig. 3. Scheme of photographic recording method of intensities. θ = Bragg angle; $2\theta >$ rocking angle.

(b) To record successive orders of reflection, the plate is set at a series of successive positions which are chosen so that the respective reflected images are adjacent on the photographic plate.

(c) For different orders, the x-ray tube voltage and current are maintained the same, but the angular speed of turning of the crystal is set for each case so that the blackness of the recorded lines of the different orders are nearly the same on the photographic plate. (It is assumed that the relative intensities are known roughly from a previous measurement.) These angular speeds are so adjusted that the blackness of the line corresponds to the linear part of the plate characteristic.

(d) The plate is calibrated by turning the crystal to the order of reflection which is most intense and adjusting the crystal to a fixed position, where it gives a strong reflection. A number of exposures of this line are made for a series of different time intervals at successive positions of the plate.

The advantages over the usual photographic methods are the following ones:

(a) The total angular turning distance of the crystal is very small compared with the total Bragg angle (usual method) thus giving a great economy of time of exposure.

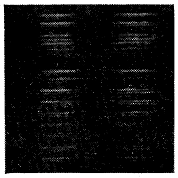

Fig. 4. Reproduction of the $K\alpha$-doublet reflections of the first five orders for N and M crystals on the (111) plane with monochromatic calibration lines.

(b) The lines of successive orders are close together, which insures uniform characteristics of the plate and uniform treatment in development and fixing of the photographic plate. Having the lines close together also allows quicker and more accurate microphotometer measurements.

(c) The adjustment of the angular speed of turning of the crystal can be done accurately by adjusting the speed of the driving motor. The relative opacities of the lines on the photographic plate can be determined with greater accuracy if the opacities are nearly alike and in the linear part of the plate characteristic than if they are widely different.

(d) The calibration of the plate is made with the same wave-length as the lines to be measured. The width and intensity distribution of the calibration lines is the same as that of the lines to be measured, which makes the measurement independent of response characteristics of the microphotometer.

Fig. 4 is a reproduction of a plate obtained with this method for the two types of crystals from (111). The different orders can easily be recognized by the increasing resolution by the $K\alpha$-doublet. In addition to the two sets of the first five orders there are the calibration lines. The results obtained from photometric measurements taking into account the speed ratios for the different orders and standardizing again for the 2*d* order for 4 different plates obtained from three different crystals are shown in Table II.

TABLE II.

Order	Plate *D*		Plate *E*		Plate *F*		Plate *G*	
	N	*M*	*N*	*M*	*N*	*M*	*N*	*M*
1	39.3	37.6	40.6	40.6	34.3	51.8	69.0	47.0
2	100	100	100	100	100	100	100	100
3	41.2	43.0	48.6	41.0	28.7	27.2	26.1	41.1
4	2.05	2.13	—	—	1.99	1.88	2.9	4.3
5	6.80	7.64	9.6	7.8	4.82	9.55	5.6	7.3

Although the data obtained are not sufficient for an exact determination of the absolute value of the parameter, the absence of a systematic difference supports the conclusion of its invariance with the two types of crystals.

The ionization method

In order to verify this and to determine the value of the parameter quantitatively with a higher degree of accuracy as had been reached before in previous investigations, the photographic method was abandoned and a special construction of an x-ray spectrometer was designed in order to record the reflected intensities by means of an ionization chamber and a Hoffmann electrometer as described separately by Hergenrother.[9]

With this method only one crystal at a time could be used which was either of the "normal" or the "magnetic" type and special great care had to be taken in order to obtain good cleavages.*

The intensities of the reflected $K\alpha$ doublet as a function of θ were measured repeatedly with different sets of crystals with great care, the values agreeing within *ca.* 1 percent for each set. Table III gives the data of the areas of the intensity curves together with the standardized values.

TABLE III.

Order	Normal		Magnetic	
	Area	Standardized	Area	Standardized
1	780	66	487	40.5
2	1180	100	1201	100
3	400	33.9	417	34.7
4	36.8	3.11	45.1	3.75
5	65.0	5.50	90.1	7.50

Comparison with the values of Table II show a still smaller variation of the intensities of *N* and *M* crystals, although the shape of the intensity curves showed evidently the presence of few facets, the existence of which affects the integrated intensities. The large difference in the first order is obviously

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[9] R. C. Hergenrother, Physics **2**, April (1932).

* Since it is very difficult to obtain sufficiently flat surfaces for this kind of measurement it was tried to use natural surfaces of (111) by solidifying liquid Bi in a test tube until the first crystals appeared, then separating the liquid from the solid. The crystal-filigrane thus obtained was examined for individual crystals showing perfect (111) planes—a rare occurrence since the preferred growing plane of Bi is (100). Few perfect specimens could be found, but the operation of separating them from the neighboring crystals caused sufficient distortions to spoil them for intensity observations and all final measurements were therefore taken from cleaved crystals.

caused by surface distortion, being very influential due to the exceedingly small penetrating depth of the radiation for small angles. If only the respective maximum intensities are taken, their standardized values are found to agree within 2 percent.

It seems to be impossible to account for the remaining variations of the intensities by a change in parameter, since the variation is not systematic—neither in direction nor in size. Hence the conclusion was drawn definitely that *the parameter for "magnetic" and "normal" crystals is the same.*

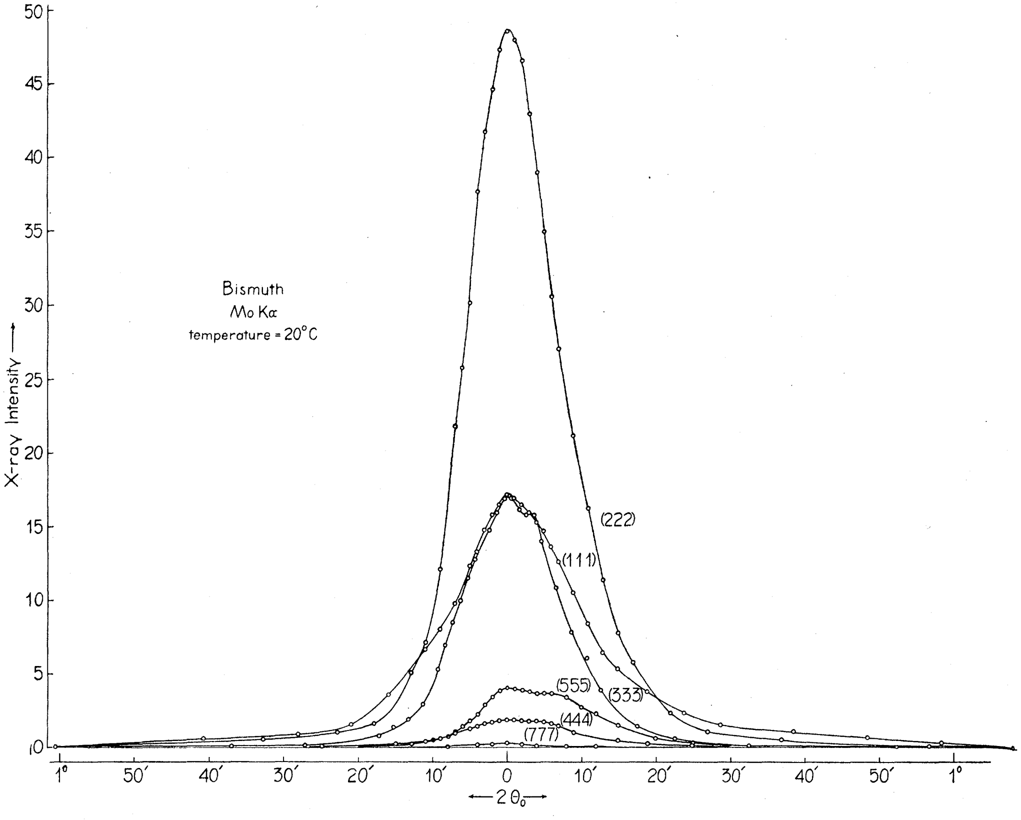

Fig. 5a represents the 1st to 7th order of the $K\alpha$-doublet reflection on (111) shifted in such a manner that the maximum intensities of $K\alpha_1$ coincide at 0°. Abscissa in minutes.

The Quantitative Determination of the Parameter

In order to determine the absolute value of the parameter an exceptionally good cleavage of a "normal" crystal (111) was selected, which permitted one to measure the intensity curves very accurately up to the seventh order. Fig. 5 a, b represent the diagrams obtained from which the quality of the crystal can be judged. Fig. 5a gives the first seven orders shifted in such a manner that the maximum intensities of $K\alpha_1$ coincide at 0°, the abscissa is shifted to the level of the background. Fig. 5b shows the last four orders again for a tenfold ordinate scale. It appears that the 6th order is zero within experimental error.

In order to compute the parameter the following procedure has been used. First the atomic structure factor, defined as

$$F = z\int_{-\infty}^{+\infty} p(z)\cos\left(4\pi z/\lambda\cdot\sin\theta\right)dz$$ [10]

has to be known. The function $p(z)$—the probability of an electron being between the planes the distances of which from the atomic midplanes are respectively z and $z+dz$, has been recently calculated by Pauling and Sherman[11] assuming hydrogen-like eigenfunctions for each of the component electrons of the atom. Those values of F are shown in Table IV for values of sin θ/λ from 0 to 1.

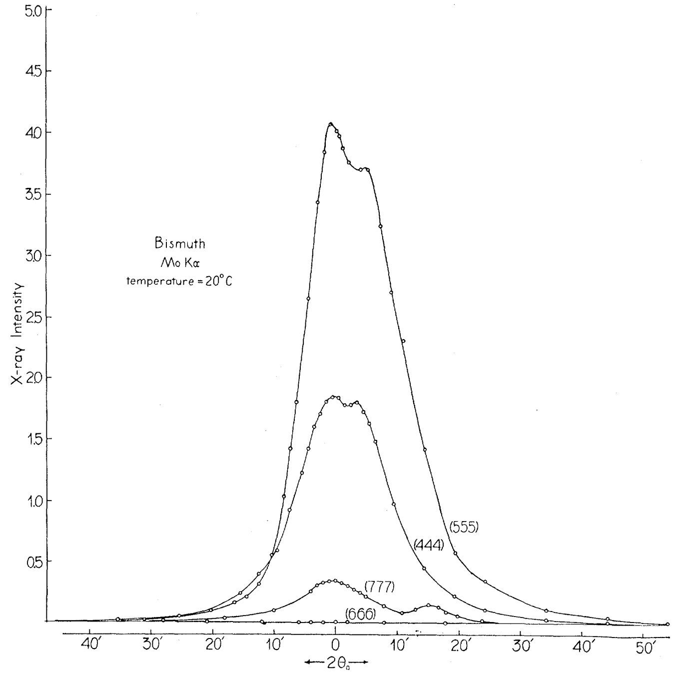

Fig. 5b represents the 4th–7th of Fig. 5a on a tenfold ordinate scale.

TABLE IV.

sin θ/λ	F	sin θ/λ	F
0.0	83.00	0.6	41.55
0.1	75.53	0.7	37.15
0.2	65.83	0.8	33.03
0.3	56.92	0.9	29.24
0.4	50.59	1.0	26.18
0.5	46.11		

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[10] A. H. Compton, X-rays and Electrons, page 122.

[11] L. Pauling and J. Sherman, Zeits. f. Kristallographie **8**, 1 (1932).

From these values the structure factor for the Bragg angles of the orders in question here interpolated. F being known, the relative values of the integrated reflected intensities at zero temperature J_{r_0} can be calculated for different orders by the relation:

$$J_{r_0} \sim J_i\, F^2\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right)$$

where J_i is the intensity of the incident radiation. The exceedingly small depth in which Mo $K\alpha$ radiation can penetrate into Bi ($Z = 83$) seemed to justify the assumption of the absence of primary extinction and therefore of the direct dependence of J_{r_0} on F^2. The numerical values for J_{r_0} are given in Table V. The existence of a displacement b of atoms along (111) defined by the parameter b/d, introduces a certain phase relation which superimposes another function on $J_r = f(F, \theta)$. The modified integrated intensity at zero temperature is given by:

TABLE V.

n	θ	$\sin \theta/\lambda$	F	$F^2 \dfrac{1+\cos^2 2\theta}{\sin 2\theta} 10^{-3}$
1	5.105°	0.1226	73.20	59.50
2	10.335°	0.2535	60.80	19.67
3	15.612°	0.3800	51.60	8.880
4	21.025°	0.5070	45.80	4.850
5	26.647°	0.6330	40.00	2.710
6	32.560°	0.7600	34.60	1.557
7	38.900°	0.8862	29.70	0.932

$$J_{rm_0} = J_{r_0}(2(1 + \cos 2\pi nb/d))^{1/2}$$

Fig. 6 shows the curves of relative intensities for the first seven orders as function of parameter values from 0.35 to 0.5.

In order to compare the measured intensities from Fig. 5 a and b, which had been integrated by a planimeter, it was necessary to find the Debye factor:

$$D = e^{-B\sin^2\theta}$$

for the (111) direction in Bi. This was done by measurements at liquid air temperature[12] from where the $J_r = f(T)$—curves were extrapolated to 0° K.

Table VI gives the values of intensities, measured at room temperature (J_{296}) and the reduced values (J_0).

TABLE VI.

Order	$1/\sin^2\theta$	$J_2{}^{92}$	J_0
1	125.0	2205	2308
2	31.1	4400	5235
3	13.85	1590	2355
4	7.78	190	383
5	4.97	408	1217
6	3.45	0	0
7	2.54	32.0	272

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[12] A. Goetz and R. C. Hergenrother, Phys. Rev. in press.

In Fig. 7 the relative intensities are plotted on a logarithmic scale against the parameter similar to Fig. 6; the parameter is marked where the intensities values determined by experiment fit best, thus b/d comes out to be 0.409 ± 0.0007. The agreement is obviously good except for the first order where the nature of the crystal surface plays too large a rôle and for the second order where the value of the reflected intensity is largest and hence the effect of secondary extinction is greatest. Since a correction for this could not be made this deviation had to be expected.

Since several definitions of the parameter are used by different authors, the comparison can be made as follows: Using James'[7] definition our value is:

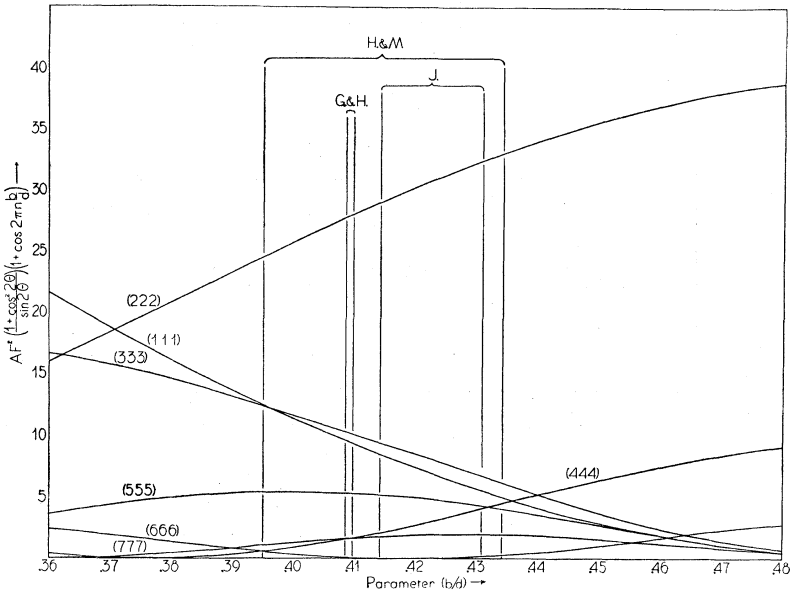

Fig. 6. Curves of relative intensities for the first seven orders as function of parameter values (b/d). The curly brackets include the possible parameter values of Hassel and Mark (H and M), of James (J), and of the authors (G and H).

$$b' = \tfrac{1}{2}d - b = 0.359\text{A} \pm 0.0006\text{A}$$

which is slightly larger than the value of this author $= 0.307 \pm 0.033$A. Hassel and Mark express their parameter in terms of $c = 3 \cdot d = 11.85$A as 0.0285 ± 0.0065. Our value is then:

$$b'' = b'/c = \tfrac{1}{3}(0.5 - b/d) = 0.0303 \pm 0.00005$$

which is well within the order of their experimental error.

The mutual relation of the different values are given in Fig. 6, where the curly brackets include the possible parameter values of Hassel and Mark (H&M) of James (J) and of the authors (G&H).

Discussion and Summary

A precision measurement of the interplanar spacing along $(11\bar{1})$ of the bismuth lattice with a modified Siegbahn method has been performed on crystals formed within and outside of a magnetic field, in order to investigate the cause of the differences in density, thermal e.m.f. and electric conductivity, which have been described previously. It was found that the spacing in the most sensitive direction of the crystal does not show a change within 0.003 percent accuracy. No change could be observed either along $(11\bar{1})$, although the accuracy amounts only to 0.5 percent due to the difficulty of obtaining good planes.

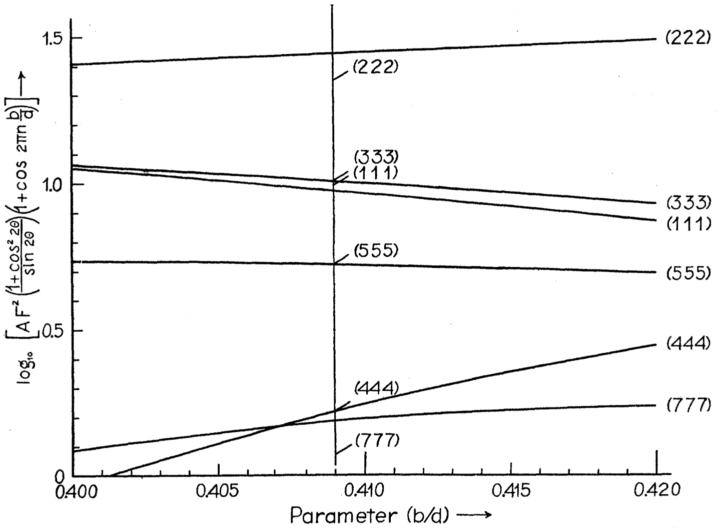

Fig. 7. Curves of relative intensities plotted on a logarithmic scale against the parameter (b/d). The observed J_0 values of the authors are indicated at the best fitting position $(b/d = 0.409)$. The sixth order (666) which cannot be shown on the log scale, agrees within experimental error. The seventh order agrees within the estimated experimental error.

The spacing along (111) was found to be 3.9453A $\pm$ 0.0002A at 23°C. The absence of a change in spacing in spite of the observed change in macroscopic density supports the previous view that the crystallization within a magnetic field affects only the mosaic structure of the crystal and not the lattice, by causing differences in the packing of the mosaic units.

The large thermoelectric effects made it desirable to investigate whether or not a difference in the lattice parameter could be found between the two types of crystals. A new photographic recording method was used and in addition an ionization method of high sensitivity which permitted the quantitative observation up to the 7th order. Pauling and Sherman's wave-mechanical determination of the structure factor being used and the Debye factor being measured between room and liquid air temperature, the parameter along (111) was computed to 0.359 $\pm$ 0.0006A. No change of the parameter between "magnetic" and "normal" crystals could be found within a possible error estimated to less than 1 percent. This proves that the conditions for the existence and the distribution of the "free" electrons as given by the geometric configuration of the atoms in the lattice stay unchanged. The large thermoelectric volume effects can therefore only be caused by variations in the lattice, the period of which must be many times larger than the size of an elementary rhomboheder in order to be undetectable by x-ray analysis. This implies the assumption of very large "mean free paths" for the "free" electrons responsible for the thermoelectric effect. This conclusion is in agreement with the well-known large structure sensitivity of these effects in bismuth crystals.

In conclusion the authors wish to express their indebtedness to Dr. J. W. M. DuMond of this Institute for a number of technical advices and to Dr. L. Pauling and Mr. J. Sherman of the Gates Chemical Laboratory for the kind permission to use the results of their calculated values of the atomic structure factor of Bi before publication.

Fig. 2. Reproduction of the 5th order reflection of the Mo $K\alpha$-doublet from (111) of a "normal" and a "magnetic" crystal.

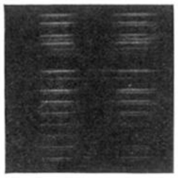

Fig. 4. Reproduction of the $K\alpha$-doublet reflections of the first five orders for N and M crystals on the (111) plane with monochromatic calibration lines.