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Intensities of X-Ray Reflections from Bismuth Crystals Between 25° and 530° Abs.[1]

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The temperature variation of the "integrated intensities" of reflections of Mo $K\alpha$ radiation from Bi crystals on (111) are reported over a range from near the boiling point of hydrogen to the melting point of the crystal. A modified Bragg spectrometer with stationary ionization chamber was used. The cryostat in which the crystal is mounted for observations at low temperatures is described as well as the thermostatic arrangement used for high temperatures. The observations were taken for the second, third and fifth order. The relative values of the integrated intensities (J_T/J_N) were found to follow the Debye-Waller relation:

$$J_T = J_0 \cdot e^{-2M \cdot \sin^2 \vartheta}$$

for $\Theta \gtrless T$ within the range of the experimental error. Also the $\sin^2 \vartheta$-relation was found to hold well for the three orders used, thus the reduction $\ln (J_T/J_0)/\sin^2 \vartheta = f(T)$ could serve to determine the Debye factor in first approximation. As $f(T)$ is almost linear, M'/T (the slope of the line) was determined to be $1.15 \cdot 10^{-2}$. By an approximation method the characteristic temperatures of Bi were calculated without (Θ) and with (Θ^*) consideration of the zero-point energy. The values obtained are: $\Theta = 92.5°$ and $\Theta^* = 95.9°$ (abs.). Although the scattering of the observations is of nearly the same order of magnitude as the difference between the Debye function with and without zero-point energy, the deviations from the former are smaller and our measurements thus support the assumption of the zero point energy.

No indication of a discontinuity of (J_T/J_0) was found in the region of the pseudoallotropic transformation point at 75°C.

However, a deviation from the relation begins 50° to 80° before the melting point in the direction of an absolute increase of M which finally even becomes positive. Although $(J_T/J_0) = f(T)$ is reversible for $dT/dt \gtrless 0$, a hysteresis of the function over this temperature region indicates a dependence upon the thermal history of the crystal which may be attributed to a temperature dependence of the secondary extinction.

INTRODUCTION

THE purpose of this paper is to describe measurements of the temperature dependence of the intensity of x-rays reflected from Bi crystals over a temperature range extending from the melting point of bismuth down to the neighborhood of the boiling point of hydrogen (25° abs).[2, 3]

The reasons for undertaking this type of investigation are several:

First: previous investigations[4–6] made it probable to assume a process of "decrystallization" beginning 50°–100° before the melting point, that is, a process in which certain parts of the crystal, not arrayed in the perfect lattice configuration (e.g., intermosaic boundary regions, loci of plastic deformation or regions distorted by the segregation of impurities), which can thus be considered to approach an "amorphous"

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[1] Partly contained in R. B. Jacobs, Thesis, Cal. Inst. (1934).

* Now at Harvard University.

[2] R. B. Jacobs and A. Goetz, Phys. Rev. **47**, 94 (1935).

[3] R. B. Jacobs and A. Goetz, Phys. Rev. **47**, 257 (1935).

[4] A. Goetz and R. C. Hergenrother, Phys. Rev. **38**, 2075 (1931).

[5] A. Goetz and R. C. Hergenrother, Phys. Rev. **39**, 548 (1932).

[6] A. Goetz and R. C. Hergenrother, Phys. Rev. **40**, 643 (1932).

state, begin to yield. Such an assumption seems to be natural in view of the fact that distorted lattice sections in contradistinction to regions of perfect array cannot have a sharp melting point. This process of decrystallization, which was previously suggested for the interpretation of the divergence between the thermal macroscopic and the lattice expansion in the neighborhood of the melting point should be revealed in the temperature variation of the integrated intensities of Bragg reflections of the crystal in the temperature range mentioned above; in other words, such a process would prove to be the cause of a temperature dependence of the secondary extinction.

Second: It is of considerable interest to check the validity of the Debye-Waller relation between integrated intensities (J) and temperature (T), over as large a temperature range as possible. This holds particularly for low temperatures where $T<\Theta$ (characteristic temperature) since the relation[7, 8]

$$J_T = J_0 \cdot e^{-2M \cdot \sin^2 \vartheta} \tag{1}$$

defines

$$M = \frac{6h^2}{m \cdot k \cdot \Theta \cdot \lambda^2} \cdot \left[\frac{\varphi(\Theta/T)}{\Theta/T} + 0.25 \right], \tag{2}$$

where $\varphi(\Theta/T)$ is the Debye function and $\frac{1}{4}$ is a correction for the zero-point energy. As $\varphi(\Theta/T)$ shows only small variation for values of Θ/T between 0 and 1, the temperature variation of the [ ] term approaches linearity ($\sim T$), thus M/T can be considered within the range of experimental error to be invariant with temperature for $T>\Theta$. It is obvious that $M(T)$ can only be checked experimentally if temperature independence of other extinguishing factors can safely be assumed. This assumption seems justified (as far as the causes of the secondary extinction are concerned) in temperature ranges sufficiently far removed from the melting point of the crystal.

Third: Whereas the theories had originally been restricted to elastically isotropic crystals (cubic systems) they have recently been extended by Zener and Jauncey[9] to anisotropic systems assuming the same $M(T)$ function to be valid. As the temperature function of crystals belonging to such systems have not been measured previously, the use of Bi (rhombohedral) served this purpose as well as previous considerations. With regard to the latter point, it seemed advisable to measure the intensities of as many as possible orders from the same plane for the test of the validity of the $\sin^2 \vartheta$—relation for the case of an irregular system.

Fourth: A number of authors[10, 11] have described the occurrence of discontinuous changes of certain physical and chemical[12] properties of Bi crystals in the region of 75°C whereas others[13, 14] could not find such changes in properties generally known to accompany an allotropic transformation. Since it has been shown[6] that the atomic distances along [111] do not change discontinuously in this region, one is forced to ascribe the alleged change to a case of pseudo-allotropy. Thus the determination of the temperature function of the x-ray reflections in this particular region was another aim of this investigation.

Experimental work done previously in the line of the temperature variation of reflections is described in numerous papers.[15–18] It is, however, almost entirely restricted to crystals of the cubic system of nonmetallic substances and also to temperatures above the boiling point of liquid air, that is $T \geq \Theta$.

In the high temperature range, the melting point of the crystal was in no case approached within a few degrees. The latter fact is easily explained by the predominant use of rocksalt crystals for these experiments, the vapor pressure of which is so large near its point of fusion that the evaporation changes the crystal surfaces sufficiently to cause changes of intensity.

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[7] P. Debye, Ann. d. Physik **43**, 49 (1914).

[8] I. Waller, Zeits. f. Physik **17**, 398 (1923).

[9] C. Zener and G. E. M. Jauncey, Phys. Rev. **49**, 17, 122 (1936).

[10] For a bibliography before 1930 see A. Goetz and M. F. Hasler, Phys. Rev. **36**, 1777 (1930).

[11] A. Goetz and A. B. Focke, Phys. Rev. **45**, 170 (1934).

[12] J. A. Hedvall, R. Hedin, E. Anderson, Zeits. f. anorg. allgem. Chemie **212**, 84 (1933).

[13] A. Schulze, Zeits. f. tech. Physik **11**, 16 (1930).

[14] S. Aoyama and G. Monna, Rep. Tohoku Un. **23**, 52 (1934).

[15] W. H. Bragg, Phil. Mag. **27**, 881 (1914).

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2. Method

For a Bragg spectrometer an instrument with stationary ionization chamber previously described by Hergenrother[19] was used in a modified form. In order to make the whole assembly safe for the application of liquid hydrogen in cooling the crystal, it was mounted in a station of the Cryogenic Laboratory, the construction of which has been described elsewhere.[20]

All measurements described in this paper were performed with Mo-$K\alpha$ radiation. The procedure for obtaining the integrated intensity values was as follows: after the crystal was adjusted by means described below, the x-ray tube (Müller) was swung to the proper angle with respect to the ionization chamber for the particular order under observation. The cryostat, and with it the crystal, was then turned by means of an electrometer *once* through an angle $\Delta\vartheta$ larger than the rocking angle with a velocity $v\sim d\vartheta/dt = \text{const}$. The total charge Q_t collected by the electrometer during the time interval t consists of:

$$Q_t\sim\int_0^t (Q_s+Q_t)dt\sim\int_\vartheta^{\vartheta+\Delta\vartheta}(Q_s+Q_r)d\vartheta\cdots$$

as $dt\sim d\vartheta$, where Q_s and Q_r represent the scattered (background) and reflected intensity components respectively. The $\int_0^t Q_s dt$ is determined by a control exposure of the ionization chamber for the length of t in the neighborhood, though in safe distance from the reflection.

3. Apparatus

The greatest technical difficulty lay in the construction of the cryostat for the crystal. A semischematic vertical cut through it is shown in Fig. 1: The outer circumference of the apparatus is formed by a cylindrical brass tube three inches in diameter (1). Two large windows are cut into its base in order to make the crystal holder accessible (1*a*). The container for liquid air or liquid hydrogen (3) is mounted concentrically inside of (1). It is suspended adiabatically in (1) by means of the thin-walled German silver tube (3*a*). The upper lid of (3) carries isothermically mounted the protective shield (2) which extends over and beyond the whole length of (3).

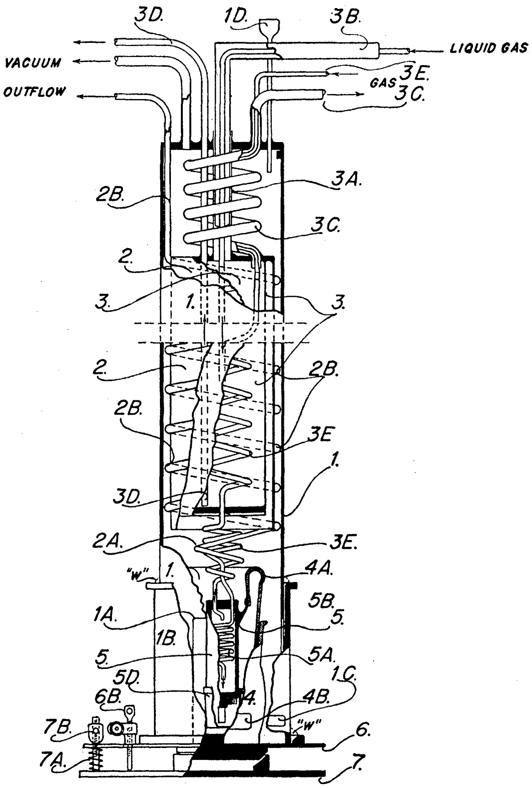

FIG. 1. Semischematic view of cryostat. The numbers designate isothermal parts of the system: 1. Outer shell; 2. shield of gas container; 3. container for liquid gas; 4. glass-support of crystal holder; 5. crystal holder; 6. base attached to cryostat; 7. base attached to spectrometer.

The windows (1*a*) of the outer wall can be closed by the lowering of the outer sleeve (1*b*), which itself carries two small windows (1*c*), which are covered with aluminum foil in a vacuum-tight fashion. As the outer assembly remains at room temperature, (1*b*) can be sealed vacuum-tight to the base and to (1) with Picein at the places indicated by "*W*." All leads to the inside of the cryostat enter the top plate of (1) and as they are soldered, (1) forms a vacuum-tight system which can be exhausted to vacuum of the order necessary for thermal adiabacy. The container (3) is supplied with liquid gas through the metal-Dewar-syphon (3*b*) inserted into (3*a*). The evaporated gas is led to the outside through the vent (3*c*). The liquid gas can be blown out of (3) through the drain tube (3*d*), which leads to the bottom of (3) and is operated by closing (3*b*) and (3*c*). (This device is used while changing from liquid air over to liquid hydrogen: in this

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[19] R. C. Hergenrother, Physics **2**, 211 (1932).

[20] A. Goetz, Rev. Sci. Inst. **7**, 307 (1936).

case (*3b*) is closed and hydrogen pressure of 0.5 atmos. is applied to (*3c*), and the liquid hydrogen is admitted only after the last drop of liquid air has left (*3d*).)

The type of measurements described in this paper made it necessary to have the possibility of cooling the crystal to any intermediate temperature between 25° and 300° abs. It was for this reason that the constant flow of a gas independent of the gas in the cryostat was used, He or H_2. The obvious advantage of this arrangement is that one can adjust the temperature by the rate of the flow of the gas; also that one can maintain a certain temperature by adjusting the flow so as to compensate for the influx of heat from the outside. A further advantage of this method is that no part of the cryostat has to be dimensioned for high pressures. Thus the danger of clogging fine capillaries and the nuisance of large heat capacities is avoided.

The gas to be used for the cold transfer enters at (*3e*), and joins (*3c*) for a preliminary heat exchange before entering the container (3), where it is cooled down to the boiling point of the liquid gas. (*3e*) leaves the bottom of (3) and brings the cooled gas through a coil (in order to provide mechanical flexibility) into the crystal holder (5). After a heat exchange with the latter, it leaves (5) through (*2a*) (coiled for the same reason) and enters a long coil (*2b*), which is mounted isothermally upon the shield (2). Thus a protection against radiation losses of (3) against (1) is afforded without waste of liquid gas. Finally the gas is led through the top of (1).

The considerable danger of thermal distortion of the crystal holder and its mountings inside such a complex apparatus as this cryostat was avoided—as tests have shown—by mounting the crystal holder (5) into a cylinder of Nonex glass (4). The crystal holder consists of a fairly heavy-walled, closed, copper cylinder, into which the gas is led from (*3e*) where it passes a spiral (*5a*). After the gas has left the latter, it returns through the tube (*5b*), connected with (*2a*). The heavy bottom of (5) carries a recess (*5c*), upon which a resistance coil is wound for the measurement of the temperature. At the center of the bottom a tapped hole is bored, which receives a small copper cylinder, the outside of which carries a corresponding male thread, into the inside of which the crystal is soldered. The latter is shielded against radiation from outside by a cylindrical shield (*5d*) which is equipped with windows. The shield (*5d*) is held in close contact with (5) and consists of copper. The windows are uncovered, the bottom is of massive copper.

The Nonex cylinder (4) is sealed with wax to the base of the cryostat. Opposite to the crystal it carries the windows (*4b*). Its upper end consists of a ground female cone. Into it fits the male cone (*4a*), which is bent inward in order to provide for sufficient elasticity of the ring seal with respect to the cylindrical copper rim, which latter forms an integral part of the copper tank of the crystal holder. The ground surfaces are covered with colloidal graphite for a smooth fit. The inner part of (4) communicates with the vacuum in the outer container through the windows (*4b*). The separation of the Nonex cylinder into two parts by means of the cone is necessary for the facilitation of the assembly of the apparatus; also for changing the crystals.

The base plate (6) of the cryostat is adjustable in all directions: *a*. The crystal can be tilted over a solid angle of 6° by moving the cryostat on the spherical surface between (6) and (7). As the center of the sphere lies in the center of the crystal, no lateral displacement of the crystal takes place with this adjustment. The position thus obtained can be fixed by the compression of each of three coil springs with the nuts (*7b*) (only one of which is shown in the figure). After the final adjustment is reached, the fixation of the position can be insured with three adjustment screws (*6a*) (only one of which is shown in the figure).

The plate (7) rests upon a large-based cross-stage built similar to the construction used in a microscopic table. This arrangement permits the motions necessary for centering the crystal to the axis of the spectrograph.

The leads for the thermometer coils (*5c*) are brought through a German silver tube (*1d*) which ends in a cup at several inches distance from the top of (1). The wires are led through the cup and afterwards the cup is filled with Picein, insuring a vacuum-tight lead of the wires into the cryostat. The cup has to be kept at room temperature in order to avoid cracking of the wax.

The chief controlling factor of the temperature of the crystal—the flow rate of the gas—is measured with a flow meter[20] connected with (2*b*), whereas the inlet of the gas (3*e*) is connected with a sensitive pressure gauge. The thermometric measurements were taken with the potentiometric arrangement described previously.[20]

Although the method of changing and maintaining a temperature of the crystal used in this cryostat could be extended to temperatures above room temperature (by filling container (3) with heated oil, etc., and preheating thus the transferring gas), the temperature range in this direction is limited by the unavoidable use of soft solder in the instrument. Thus a different device for holding and heating the crystal was used for the range between room temperature and the melting point of Bi (271°C). It consists chiefly of a thermally isolated holder of the crystal, a heating and a thermometer coil around the base of the crystal. A hood of light material with Cellophane windows permitted one to surround the crystal with an atmosphere of carbon dioxide in order to avoid oxidation of the surface. A similar arrangement has been described previously by Goetz and Hergenrother.[16]

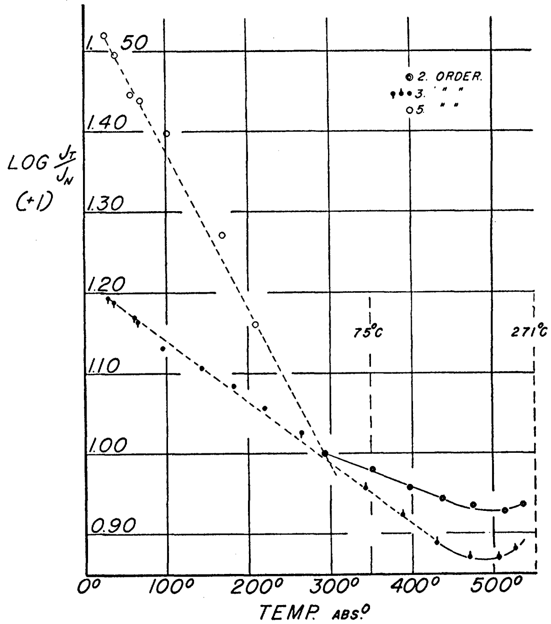

FIG. 2. Diagram of the logarithms of the relative integrated intensities of the 2nd, 3rd, 5th orders against temperature. The room temperature (=294° abs.) is taken for reference.

TABLE I. *Relative integrated intensity values for various orders.*

ORDER	T(abs.)	J_T/J_N	lg J_T/J_N	lg (J_T/J_N) +1	$\sin^{-2}\vartheta$	lg $J_T/J_N \cdot \sin^{-2}\vartheta$
2	537.0	0.861	−0.064	0.936	30.3	−1.94
2	514.5	0.839	−0.076	0.924	30.3	−2.31
2	475.5	0.860	−0.064	0.936	30.3	−1.94
2	438.0	0.878	−0.056	0.944	30.3	−1.70
2	397.0	0.922	−0.042	0.958	30.3	−1.27
2	353.5	0.956	−0.020	0.980	30.3	−0.608
2	294.5	1.000	0.000	1.000	30.3	0.00
3	527.0	0.770	−0.120	0.880	13.9	−1.67
3	507.0	0.741	−0.130	0.870	13.9	−1.81
3	470.5	0.741	−0.130	0.870	13.9	−1.81
3	431.5	0.774	−0.111	0.889	13.9	−1.54
3	389.5	0.837	−0.077	0.923	13.9	−1.07
3	344.5	0.906	−0.042	0.958	13.9	−0.58
3	294.0	1.000	0.00	1.000	13.9	0.00
3	221.0	1.140	+0.057	1.057	13.9	+0.78
3	182.5	1.215	+0.084	1.084	13.9	+1.17
3	143.0	1.279	+0.107	1.107	13.9	+1.48
3	95.8	1.351	+0.131	1.131	13.9	+1.82
3	266.0	1.060	+0.026	1.026	13.9	+0.36
3	66.0	1.292	+0.164	1.164	13.9	+2.28
3	62	1.474	+0.170	1.170	13.9	+2.37
3	36	1.539	+0.188	1.188	13.9	+2.62
3	29	1.563	+0.194	1.194	13.9	+2.70
5	294.5	1.000	0.000	1.000	4.95	0.000
5	210.0	1.44	+0.160	1.160	4.95	+0.792
5	165.0	1.82	+0.270	1.270	4.95	+1.36
5	103.0	2.50	+0.398	1.398	4.95	+1.97
5	71.0	2.68	+0.428	1.428	4.95	+2.12
5	58.5	2.84	+0.452	1.452	4.95	+2.23
5	43.0	3.16	+0.500	1.500	4.95	+2.47
5	27.5	3.30	+0.519	1.519	4.95	+2.57

4. CRYSTALS

The crystals used were made from highly purified Bi (Braun Corporation) used in previous work and were tested for impurities by magnetic methods.[11] They were grown in "P_1" orientation ([111] ⊥ to rod) after methods described previously.[21, 22] In order to increase the degree of purity the material was subjected to the process of repeated recrystallization, first developed by Schubnikow and de Haas.[23] Then the crystals were cleft on the cleavage goniometer and by optical methods the best cleavage was selected. The size of the cleavage planes approximated in width: 6–8 mm, in breadth: 4–5 mm.

5. RESULTS

The relative integrated intensity values (J_T/J_N) for the 2nd, 3rd, and 5th order obtained from Bi (111) with Mo-$K\alpha$ are given in Table I

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

[22] M. F. Hasler, Rev. Sci. Inst. **4**, 356 (1933).

[23] L. Schubnikow and W. J. de Haas, Kgl. Acad. Amsterdam **33**, Nr. 4 (1930).

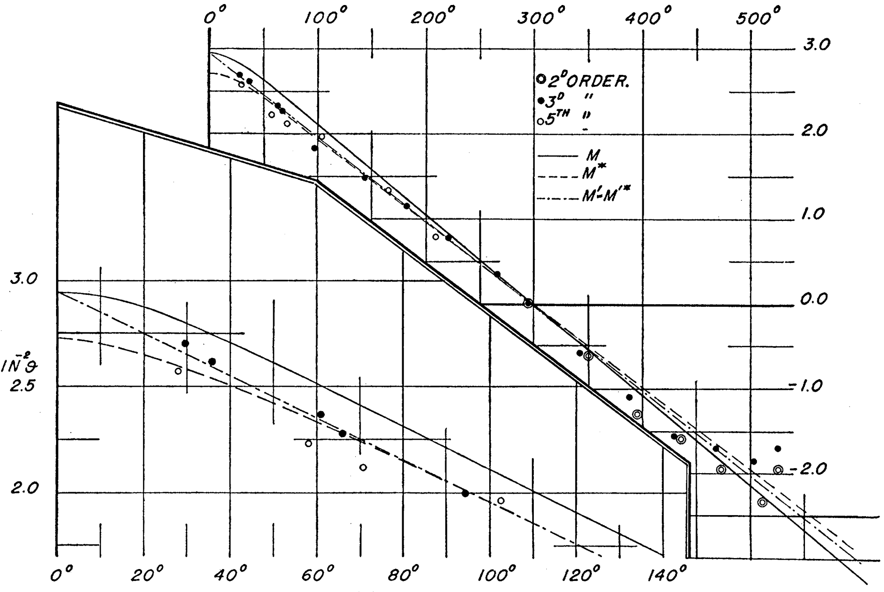

FIG. 3. Diagram of the reduced logarithms of the relative integrated intensities (lg $(J_T/J_0)\sin^{-2}\vartheta$ of the 2nd, 3rd, 5th order against temperature. The straight line extrapolation is marked —·—·—·—, the Debye function without zero-point energy is drawn full (for $\Theta=92.5°$), the same with zero-point energy is drawn dashed (for $\Theta^*=95.9°$). The auxiliary diagram on the left represents the range of $\Theta<T$ on an enlarged scale.

together with their algebraic modifications used in the diagrams. In Fig. 2 J_T/J_N is plotted in the usual logarithmic form against T. The different orders are indicated with different demarkations, the room temperature (T_N) is taken as reference temperature for J_N. (Some of the J_T/J_N values were taken at different dates—almost two years apart—and are marked as such in order to demonstrate the magnitude of error.)

In general the points for the 2nd, 3rd and 5th orders fall well on straight lines for the whole range of temperature except for the concave deviation beginning about 70° before the point of fusion. Disregarding this range of the highest temperatures for the moment it is thus well established that the exponential relation (Eq. 1) for $M=M'T$ holds over a temperature range of at least 400° even down to $T=0.27\Theta$ within the limits of experimental error.

In Fig. 3, lg $(J_T/J_N)/\sin^2\vartheta$ is plotted against T. The demarkation of the observations at different orders is the same as in Fig. 2. The fair coincidence of the observations of different orders proves the validity of the $\sin^2\vartheta$ relation, the small magnitude of a systematic experimental error and a good verification of the above relation.

This simple exponential relation being only a rough approximation used for higher temperatures it has been attempted to compare the data with the exact relation predicting

$$J_T=J_0\cdot e^{-2M\cdot\sin^2\vartheta}\cdots, \qquad (1)$$

where J_0 is the reflection at the absolute zero and

$$M=c\cdot\sin^2\vartheta\cdot\Theta^{-2}(\phi(\Theta/T)\cdot T), \qquad (2a)$$

$$M^*=c\cdot\sin^2\vartheta\cdot\Theta^{*-1}[T/\Theta^*\cdot\varphi(\Theta^*/T)+0.25] \qquad (2b)$$

with and without assuming zero-point energy, where

Θ = characteristic temperature (proportional to the maximum elastic frequency),

ϑ = Bragg angle,

$c=6h^2\cdot m^{-1}\cdot k^{-1}\cdot\lambda^{-2}$,

λ = the x-ray wave-length used $(=7.1\cdot 10^{-9}$ cm for Mo-$K\alpha$),

m = mass of a Bi atom $=3.45\cdot 10^{-22}$ g,

$h=6.55\cdot 10^{-27}$ erg. sec.,

$k=1.37\cdot 10^{-16}$ erg. deg.$^{-1}$.

Accordingly, $c=1.05\cdot 10^2$,

$$\varphi(\Theta/T)=T/\Theta\int_0^{\Theta/T}\xi d\xi/e^{\xi}-1 \text{ (Debye-Function).}$$

TABLE II. *Value of M for different temperatures.*

T	Θ/T	$\frac{\varphi(\Theta'/T)\cdot c}{\Theta^2/T}$	Θ^*/T	$\frac{C}{\Theta^*}\left[\frac{\varphi(\Theta'^*/T)}{\Theta^*/T}+\frac{1}{4}\right]$
0	∞	0	∞	0.238
10	9.25	0.0177	9.59	0.252
20	4.63	0.0692	4.79	0.304
30	3.08	0.144	3.19	0.377
40	2.31	0.237	2.40	0.459
50	1.85	0.324	1.92	0.544
60	1.54	0.436	1.60	0.638
70	1.32	0.538	1.37	0.731
80	1.16	0.636	1.20	0.834
90	1.02	0.735	1.06	0.918
100	0.92	0.831	0.96	1.014
200	0.46	1.875	0.48	1.990
294	0.32	2.902	0.33	4.842
400	0.23	4.038	0.24	3.900
500	0.19	5.075	0.19	2.938

As for practical purposes J_N for $T_N=294°$ is used for reference, Eq. (1) is changed into

$$J_T/J_N=J_0/J_N\cdot e^{-2M\cdot\sin^2\vartheta}. \tag{1a}$$

It has been shown above that our observations are represented in sufficient first approximation by assuming the Debye function ($\varphi(\Theta/T)$) to be invariant with T. Thus Eqs. (2a) and (2b) change into

$$M'=c\cdot T_N\cdot\Theta'^{-2}\cdots;\quad M'^*=c/\Theta'^*\cdot(T_N/\Theta'^*+0.25)$$

or in combination with Eq. (1)

$$M'=M'^*=\lg\,(J_0/J_T)\cdot\alpha/2\,\sin^2\vartheta\cdots,$$

where α is the modulus of the natural logarithms.

The value of $\lg\,(J_0/J_N)\,\sin^{-2}\vartheta=2.95$ is obtained by linear extrapolation according to Fig. 3 (—·—·—). This results in $M'=3.38$ and in the value for the inclination of the straight line

$$M'/T=c\cdot\Theta'^{-2}=1.15\cdot10^{-2}\cdots.$$

Thus: $$\Theta'=(c\cdot T_N/M')'=95.6°\cdots. \tag{3b}$$

In the same way the value of Θ'^* with consideration of the zero point energy is derived according to Eq. (2b):

$$\Theta'^*=\frac{c}{8M'}\left[1+\left(\frac{64M'\cdot T_N}{c}+1\right)^{\frac{1}{2}}\right]=99.5°\cdots. \tag{3b}$$

The exact solution is now derived by considering $\varphi(\Theta'/T)$, for the numerical evaluation of which the obtained approximate values of $\Theta\sim\Theta'$ and $\Theta^*\sim\Theta'^*$ can be used. Thus the second approximations of Θ and Θ^* are derived from Eqs. (3a) and (3b) as follows:

$$\Theta=\left(\frac{c\cdot T_N\cdot\varphi(\Theta'/T)}{M}\right)^{\frac{1}{2}}=92.5°\cdots, \tag{4a}$$

and analogously:

$$\Theta^*=\frac{c}{8M}\left[1+\left(\frac{64M}{c}\cdot T_N\cdot\varphi(\Theta'^*)/T)+1\right)^{\frac{1}{2}}\right]$$
$$=95.9°\cdots. \tag{4b}$$

It is interesting to compare these values for Θ with values obtained hitherto by other methods (specific heat measurements or elastic constants).

In his first paper already, Debye[24] gives an estimated value for Bi as $\Theta=111°$ derived from elastic measurements. Later Anderson[25] found from specific heat measurements $\Theta=147°$; his measurements, however, were not extended far into the $T<\Theta$-region. The best values so far are given by Keesom and van den Ende[26] with $\Theta=92.3°$ for $T=10°$, and $\Theta=104.1°$ at $T=20°$. Thus the difference with our Θ^* value and that of Keesom is less than 10 percent which agreement is satisfactory especially in view of the fact that a single Debye function is strictly not sufficient to describe an irregular system—in fact a simple consideration shows that in case of Bi the resulting function:

$$\phi=(\varphi_{\shortparallel}+2\varphi_{\perp})/3.$$

According to the existence of different maxima of the elastic spectrum in different directions of the crystal there exist different Θ values. This fact is reflected in the results of Keesom[26] who finds at sufficient low temperatures a dependence of Θ on T.

In order to demonstrate the agreement of our observations with the theory, both functions (Eq. (1)) were calculated for Θ and Θ^*, i.e., without and with considering zero point energy, and plotted in Fig. 3 (the former full drawn, the latter dashed). Table II gives some of the numerical values. The lower left side of the diagram presents the range of the last 120° on an enlarged scale.

Although it is obvious that more measurements should be available and the scattering of the points should be less, it is easily seen that a better agreement exists with the lower than with

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[25] C. T. Anderson, J. Am. Chem. Soc. **52**, 2720 (1930).

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the upper curve, i.e., *with* the assumption of the zero point energy. For $T > T_N$ the observations fall systematically below the M^* curve and are better, but not sufficiently fitted by the M curve. There are several tentative explanations possible if one does not wish to ascribe the deviation to a systematic error. The assumption of a change of the value of Θ^* with higher temperatures is unlikely as Θ^* had to be smaller (Eqs. (2a) and (b)) and our value is already smaller than that of other authors. For the same reason the above mentioned superposition of several functions should not alter the curve in the desired direction.

It seems more likely that an increase of secondary extinction sets in at higher temperatures which should be very influential, in view of the strong tendency of Bi towards mosaic malformation, this effect would support the assumption of the process of decrystallization (see Section 1).

Concerning the aforementioned pseudoallotropic transformation point at 75°C, the diagrams indicate neither a discontinuity in $J_T/J_N(T)$ nor a change of M, although we are to report[27] a change of the thermal expansion coefficient of the lattice as observed at the same crystals in a following paper. The absence of a change of the integrated intensities at this point seems to speak against the implication that the alleged allotropy of Bi was just due to the triple-eutectic point of the system Bi-Pb-Sn. The high purity of the crystals used in our experiments excludes the presence of Pb or Sn in larger concentrations than 10^{-4} and it could hardly be assumed that these small traces of impurities could form eutectic segregations. But even if this were the case and certain sections of the lattice consisting of such eutectic segregations of minute size would melt at 75°C, one should assume a discontinuous change of the extinction of the crystal and with it a change of the integrated intensity.

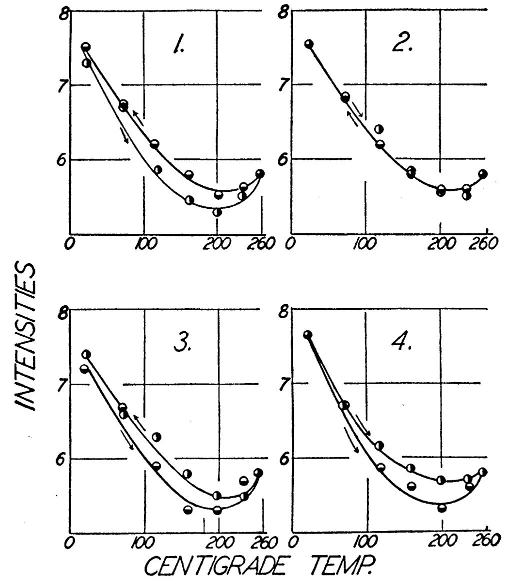

FIG. 4. Diagram of the relative intensities against temperature in the neighborhood of the melting point for different thermal histories of the crystal. (3rd-order only.) In cases 1 and 3 the crystal was "quenched" before measurements were taken. In case 2 the crystal had been annealed. In case 4 the crystal was heated after annealing (upper curve), then "quenched" and reheated (lower curve). The arrows indicate the temperature direction of the measurement. Points of equal demarcation belong to the same direction of measurements.

From Figs. 2 and 3 is seen that the intensities begin to deviate in a positive direction from the straight line relation 50°–80° before the melting point. Contrary to the relatively small negative deviation mentioned above this appears to be a large discrepancy with the temperature function anticipated by the theory which cannot easily be ascribed to an experimental error.[28] A special study of the behavior of the crystal was made by approaching the melting point as closely as possible, that is, up to a temperature at which the crystal began to sag. For these experiments, only the third order was used. As diagram 2, Fig. 4 shows, the integrated intensities do not decline as fast as is expected beyond approximately 180°C. In fact the curve goes through a minimum around 210°C after which the intensities *increase* with increasing temperature in such a way that, for instance, the intensity at 260°C is the same as the intensity around 160°C. As no anomaly of the specific heat or the elastic properties is known to exist in this region a change in the secondary extinction, i.e., in the mosaic discontinuities of the crystal is more likely the cause. In this case, one should expect a dependence of this anomaly upon the thermal history of the crystal and accordingly one should observe an hysteresis between the intensities and the temperature if the crystal is cooled faster

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[27] R. B. Jacobs and A. Goetz, Phys. Rev., following paper.

[28] Against such an error speaks the much tested reproducibility as well as the reversibility with (T) of the phenomenon which excludes, e.g., an oxide layer on the crystal face as a cause.

than is necessary for it to assume a mosaic configuration stable at the particular temperature.

Accordingly intensity measurements were performed on crystals of different thermal history while increasing or decreasing the temperature. The results are presented in the diagrams 1, 3 and 4 in Fig. 4 and it is seen that the expected hysteresis occurs. Whereas the crystal which does not show hysteresis (diagram 2) has been kept at high temperature for a considerable time and cooled very slowly, diagrams 1 and 3 represent crystals which, before the measurement was taken, had been heated to 220°C and were quenched in liquid air before they were heated for the intensity measurement. Both diagrams show that the annealing of the crystal in the neighborhood of the melting point results in a decrease of the extinction, in other words, the crystal is a better reflector after the heat treatment than before. In order to make sure that the hysteresis was not caused by a temperature lag in the apparatus, which would cause lower intensity measurements when the temperature was increased or higher intensity values when the intensity was decreased, a carefully annealed and slowly cooled crystal was reheated while the intensities were measured (upper curve, diagram 4, Fig. 4). Then the crystal was quenched and reheated while another set of intensity measurements was taken. The result proved to be the same as in the other measurements, indicating that *the extinction is largest in a crystal, the mosaic configuration of which is not in temperature equilibrium.* The fact that the "repair" of the crystal sets in only in the neighborhood of the melting point is in agreement with the experience that the recrystallization temperature of bismuth lies very close to the point of fusion. It is easily seen that the increase of J_T/J_N with the temperature is caused to some extent by this "repair." Nevertheless, there remains sufficient curvature even for the perfectly annealed crystal to indicate another phenomenon for which a satisfactory explanation cannot be suggested.

In conclusion the authors wish to express their indebtedness to Dr. A. B. Focke and Dr. M. F. Hasler for growing the crystals and refining the metal used, to Dr. E. Donat and Dr. C. Gregory for assistance in the production of liquid hydrogen and in the temperature measurements and Mr. Charles Edler for a great deal of technical assistance.

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The Thermal Expansion of the Bi Lattice Between 25° and 530° Abs.*

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The thermal expansion of the lattice of Bi crystals between 25° and 530° abs. is measured with a Bragg spectrometer equipped with a movable slit between crystal and ionization chamber. The 2d, 3d and 5th orders of Mo $K\alpha$ reflections on (111) were used. $\alpha_{\|}$ thus obtained varies from 8.3×10^{-6} to 17.4×10^{-6} at 25° abs. and 120° abs., respectively, beyond the latter temperature it stays unchanged until the melting point. Only the range between -15°C and $+75$°C forms an exception where the expansion coefficient drops to 13.8×10^{-6}. This seems to indicate the existence of a separate "phase," not characterized by a change of the lattice configuration and confirms certain previous findings of discontinuities at $+75$°. A definite divergence between the lattice and the integral expansion beginning 30° before the melting point was found. The Grüneisen rule ($\alpha/c_p=$const) is found to hold in first approximation for the whole temperature range. The relation of the $\alpha_{\|}$ values obtained to those of other authors is discussed.

1. INTRODUCTION

THE thermal expansion of a crystalline substance may be measured by two distinct methods. The first is the usual optical method which sums the thermal expansion of every volume element over the whole length of the crystal. In the second type of measurement, x-ray diffraction is employed to measure the change of the crystal lattice spacing due to change of temperature, and the values of the expansion so obtained present the expansion only

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* Partly contained in: R. B. Jacobs, thesis 1934, Cal. Inst.

† Now at Harvard University.