

THE
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**X-ray Studies of the Thermal Expansion of
Bismuth Single Crystals**

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Previous observations of several authors have shown certain anomalies of bismuth at higher temperatures of which the thermal expansion is very prominent. In order to decide whether those effects are to be ascribed to changes in the crystal lattice or in the mosaic structure, the *temperature shift of Bragg reflections* has been studied quantitatively between liquid air temperature and the melting point of the metal. A modified Siegbahn method, previously described by Hergenrother, has been used and an arrangement is herewith described which allows the crystal to be maintained during the observation at liquid air temperature, or at any temperatures between 20° and 265°C. The shift of Mo $K\alpha$ radiation reflected from the (111) plane of a Bi crystal has been measured for the first to the fifth order at twelve different temperatures and from it α_{11} —the thermal expansion of the crystal along (111)—was calculated. These results have been compared with the values of the true specific heat of Bi and a surprisingly high degree of constancy of α/c_p has been found up to a few degrees below the melting point. Between room temperature and melting point the thermal expansion coefficient is given by:

$$\alpha_{11} = 14.4 \times 10^{-6} [1 + 1.76 \times 10^{-3} (T_{\text{abs}} - 298^\circ)]$$

whereas:

$$c_p = 2.84 \times 10^{-2} [1 + 1.76 \times 10^{-3} (T_{\text{abs}} - 323^\circ)].$$

The values of the thermal lattice expansion thus obtained are compared with measurements of α_{11} obtained in the usual macroscopic way by several authors and also with values observed on the same crystals in our laboratories. *The macroscopic values are found to differ from the x-ray values many times more than could possibly be explained by experimental errors*, the principal discrepancies being first a much larger value of $d\alpha/dT$ for the lattice expansion, second the absence of a gradual reversible decline of $d\alpha/dT$ at higher temperatures, which decline is typical for the macroscopic crystal. Accordingly it is considered that Grüneisen's relation of the constancy of the ratio of the expansion coefficient and the specific heat does not hold for the macroscopic crystal. The question is raised whether or not one should expect the same values from an x-ray determination of the thermal displacement of lattice points and from a direct measurement of the crystal, when consideration is given to cubic and fourth order terms of the potential. It is to be remembered that Waller's theory predicts such an agreement. Next the conditions for the validity of $\alpha_{11}/c_p = \text{const.}$ are discussed. This relation comes out to be true only in a first approximation. An interpretation of the non-parallelism of the macroscopic and the lattice-expansion is attempted, on the assumption of the coexistence of a regular lattice component in the crystal together with an amorphous component, the latter of which increases relative

to the former with increasing temperatures. This however is not assumed to correspond to a statistical disintegration in view of the existence of a sharp melting point, but an effect being closely related to the mosaic structure. Certain conclusions derived from this idea are verified by experiments.

The "allotropy" of bismuth. The x-ray shift does not show any indication of a discontinuity in the expansion within the temperature range observed. Hence the allotropic transformations at 75°C (Cohen, Wurschmidt, Goetz and Hasler) and close to the melting point (Kapitza) do not exist in the sense of a change of the lattice spacing. A definite discontinuity has been found however in the macroscopic expansion at 75°C. This must be ascribed to a very small but sudden change in a periodicity of a larger parameter than the x-ray wave-lengths.

INTRODUCTION

THE physical properties of a crystalline metal in the neighborhood of its melting point are known to show certain anomalies which are not easily explained by the theories of an ideal crystal lattice. One of these qualities is the thermal expansion which has been studied by Roberts¹ for Bi single crystals from room temperature up to the point of fusion. Robert's results show that the expansion coefficient begins to decline at from 30°–40° before the melting point is reached. Similar results have been found with other metals though they were not studied in the single-crystalline state. Since there is no parallel in the behavior of the true specific heats, Grüneisen's rule as to the proportionality between the expansion coefficient and the specific heat apparently ceases to hold before fusion occurs, although the validity of this semi-empirical relation seemed to be established for ordinary temperatures in the case of a large number of metals.

There is no satisfactory explanation of these effects that does not meet serious objections, which will be discussed later. It seemed necessary therefore to investigate first whether or not this anomalous change of the expansion coefficient is actually a property of the lattice. To do this the linear expansion coefficients of a single crystal must be determined by x-rays and then compared with the true specific heats. This procedure should show whether Grüneisen's rule does actually hold for the lattice expansion near the melting point.

Apparently no specific attempt has ever been made to compare systematically the macroscopic expansion with the lattice expansion. It was thought that if an actual difference were found between these two magnitudes it would throw light on the problem of the mosaic structure of the crystals, especially since the authors could show in a previous paper² that the lattice of Bi crystals grown within and outside of a magnetic field could not be distinguished by x-ray analysis in spite of the fact of certain considerable differences in their physical properties.^{3,4} It was suggested that these effects might be due to the change in periodicities within the crystal, the parameter of which must be large relative to the x-ray wave-length, i.e., to the interplanar spacing of

¹ J. K. Roberts, Proc. Roy. Soc. **A105**, 385 (1924).

² A. Goetz and R. C. Hergenrother, Phys. Rev. **40**, 137 (1932).

³ A. Goetz and M. F. Hasler, Phys. Rev. **36**, 1752 (1930).

⁴ A. Goetz and A. B. Focke, Phys. Rev. **37**, 1044 (1931).

the crystal. It is natural to attempt the identification of this periodicity either with the more general concept of the mosaic structure (of a more or less accidental character) or of the secondary structure proposed by Zwicky^{5,6} and verified to some extent by one of the authors⁷ by observations upon the size of etching figures.

A comparison of the lattice and the macroscopic expansion should also enable a decision to be made about the much discussed "allotropy" of bismuth which occurs around 75°C where Goetz and Hasler⁸ found a Peltier effect³ such as would indicate under normal circumstances a change in phase. The x-ray analysis should reveal a sudden change of the lattice expansion at this temperature (not indicated in Robert's macroscopic observations) in case the allotropy is "true."

In addition one should expect evidence of Kapitza's hypothetical cubic modification of Bi near the point of fusion.⁹

EXPERIMENTAL PROCEDURE

The x-ray spectrometer used to measure the change of reflected intensities from Bi crystals as well as the angular shift of the reflections with temperature within the range of -182° to $+270^{\circ}$ has been described recently by one of us.¹⁰ The method of measurement was the same as previously reported and also there was used the same crystal has been used which served for the determination of the lattice parameter.² Hence it only remains to describe the arrangements for the heating and the cooling of the crystal.

Fig. 1 shows the crystal mounting used for measurements either above or below room temperature. The crystal *c* is cemented in the brass cup *B* which

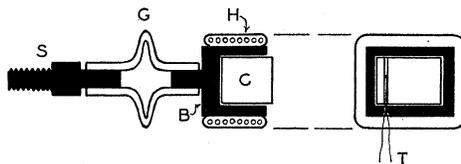


Fig. 1. Heat-insulated mounting of the crystal *c* in the metal cup *B* surrounded by the heating coil *H*. *T* is a thermocouple imbedded within the crystal.

is in turn attached to the heat insulating glass bushing *G*. The brass screw *S* serves to fasten the ensemble to the goniometer. An electrical heating coil *H* surrounds the cup *B*. The temperature of the crystal is measured by means of the fine wire thermocouple *T*, cemented into a narrow groove at one side of the crystal. The cold junction is placed into a constant temperature bath, the potential is measured with a potentiometer. In order to protect the crystal surface of the crystal from air currents it was surrounded by a shield con-

⁵ F. Zwicky, Proc. Nat. Acad. **15**, 253; 816 (1929).

⁶ F. Zwicky, Hel. Phys. Acta **3**, 269 (1930).

⁷ A. Goetz, Proc. Nat. Acad. **16**, 99 (1930).

⁸ A. Goetz and M. F. Hasler, reference 3, footnote page 1777.

⁹ P. Kapitza, Proc. Roy. Soc. **A119**, 358 (1930).

¹⁰ R. C. Hergenrother, Physics **2**, 63 (1932).

sisting of a metal frame which was covered on both sides with cellophane. With this air tight cover protecting the crystal it was possible to maintain the crystal surface at a temperature constant to 0.1° at any predetermined point. Fig. 2a presents a schematical view of the arrangement.

The method used for maintaining the crystal at liquid air temperature is illustrated in Fig. 2b. From a Dewar container the liquid air is forced through the heat insulated glass tube *T* upon the crystal surface by means of adjust-

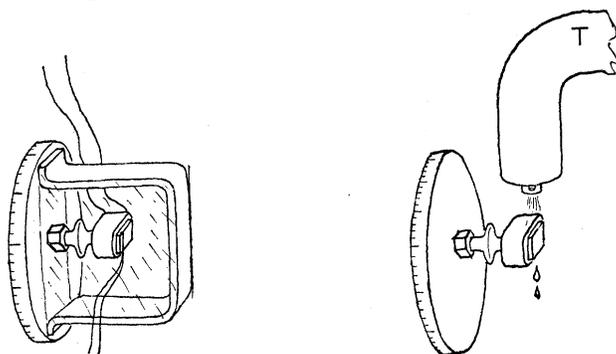


Fig. 2a and b. 2a shows scheme of cellophane hood around the heated crystal. 2b shows arrangement of cooling the crystal with liquid air.

able air pressure. This pressure being properly adjusted the liquid air leaves the nozzle in a fine spray which wets the surface of the crystal with a thin uniform film and keeps the surface free from water and CO_2 crystals.

EXPERIMENTAL RESULTS

The results obtained in the range of temperature used are presented in Figs. 3 to 7. Each diagram represents the intensities reflected from the (111) plane for one order for different temperatures.

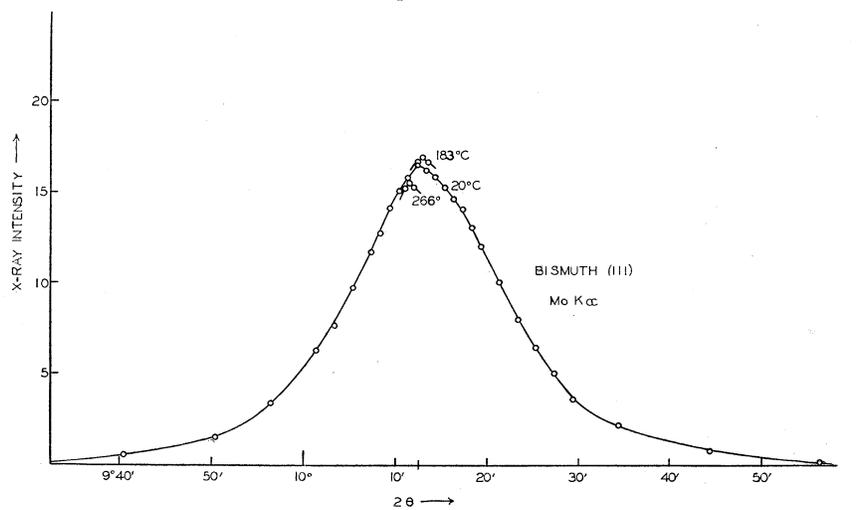


Fig. 3.

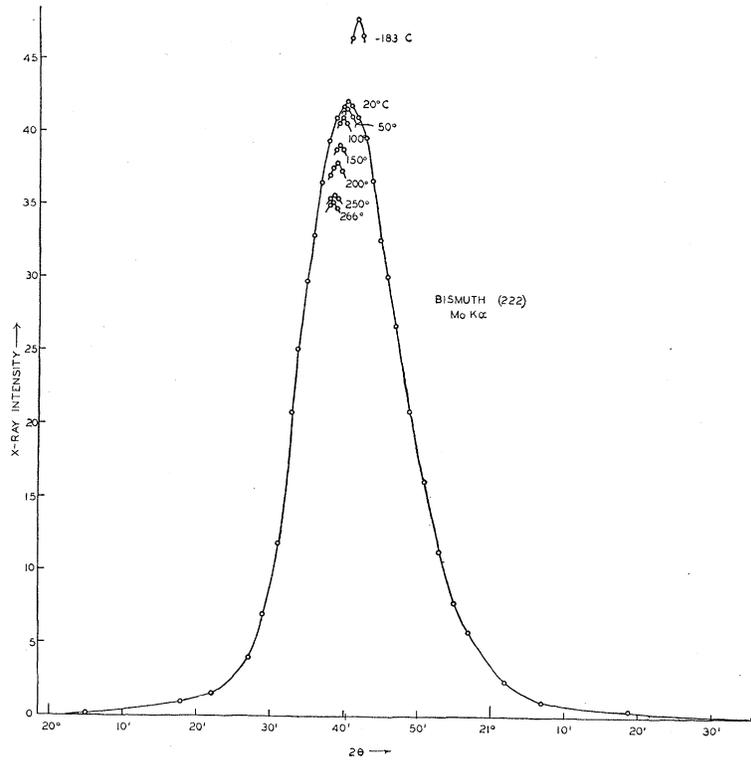


Fig. 4.

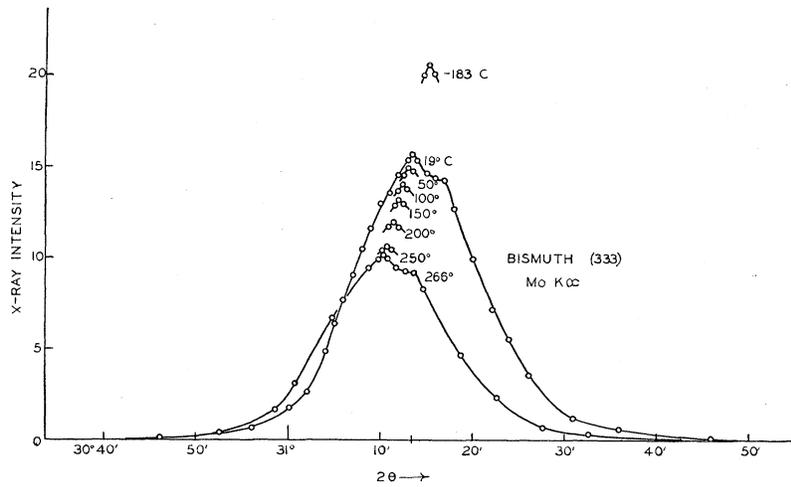


Fig. 5.

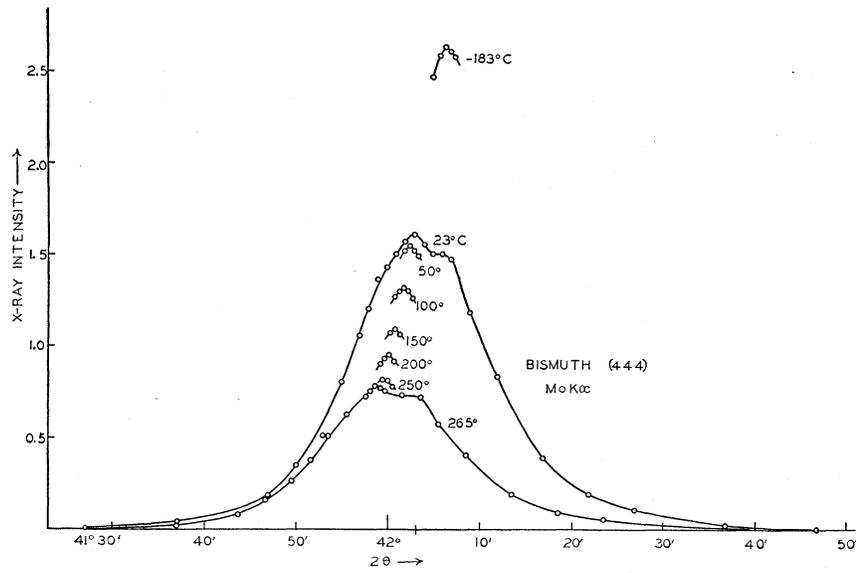


Fig. 6.

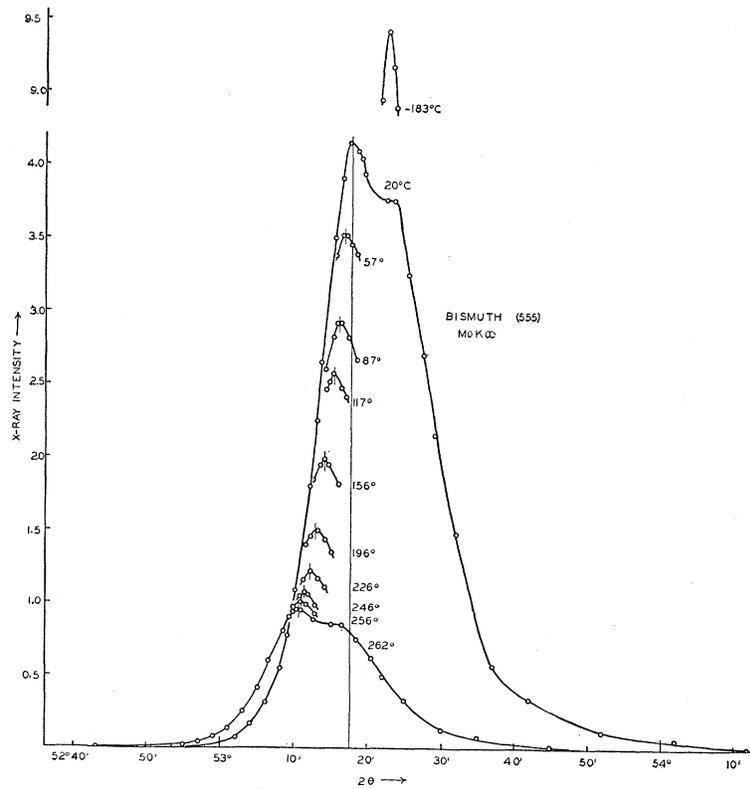


Fig. 7.

Figs. 3-7. Intensity curves of Mo K α radiation for (111) to (555) at different temperatures. A complete curve is drawn for only one temperature for the first two orders, in order to simplify the diagrams.

The area of each curve was determined with a planimeter and the comparison with the maximum intensities showed in each case that the ratio between the integrated intensities and the maximum intensity remained constant. Hence it was considered sufficient for the final measurements to determine only the shape of the curve in the neighborhood of the maximum as shown in the diagrams. This had the advantage of shortening the time necessary for keeping the crystal at constant temperature.

Only the first five orders were used, since the intensity of the seventh order was too weak to measure accurately at high temperatures. The fifth order is best suited for the exact location of the maximum intensity and accordingly the angular values of this order were taken with special care* and they were used exclusively for the determination of the thermal expansion, whereas the values of other orders served for the determination of the Debye factor.

THE THERMAL LATTICE-EXPANSION ALONG (111)¹¹

The thermal expansion of the Bi lattice parallel to the principal axis (111) can be determined from the shift of the maximum intensities towards smaller angles with increasing temperature. From Fig. 7 this shift can be seen to be rather large and the subsequent calculations proved that the accuracy of this type of measurement approaches that of the usual "macroscopic" expansion measurement.

TABLE I.

1	2	3	4	5	6	7	8	9	10
$T(^{\circ}\text{C})$	ΔT	$\frac{1}{2}(T_1+T_2)$	$\Delta\theta$ observed	$D(\text{A})$ observed	$c_p \cdot 10^2$	α_T	$1+\alpha(T_1-T_2)$	$D^*(\text{A})$ calculated	$D-D^*$ $\times 10^4(\text{A})$
21°			0' 0''	3.9453	270			3.9452	-1
56°	35°	38°	0' 46''	3.9475	279	14.72	1.00052	3.9473	-2
87°	31°	71°	1' 20''	3.9492	298	15.68	1.00048	3.9492	± 0
117°	30°	102°	1' 48''	3.9506	302	16.32	1.00049	3.9510	+4
156°	39°	137°	2' 47''	3.9534	309	17.22	1.00067	3.9535	+1
196°	40°	176°	3' 49''	3.9564	314	18.20	1.00073	3.9561	-3
226°	30°	211°	4' 30''	3.9584	323	19.10	1.00057	3.9584	± 0
246°	20°	236°	4' 57''	3.9598	332	19.72	1.00039	3.9599	+1
256°	10°	251°	5' 20''	3.9608	343	20.10	1.00020	3.9607	-1
262°	6°	259°	5' 35''	3.9616	353	20.30	1.00012	3.9612	-4

* This means that the temperature of the crystal was changed slowly and that the points near the peaks of the curves were checked from 4 to 8 times. It seems furthermore to be of importance that the complete set of readings was taken without interruption. The position of the maximum was found the same at the beginning and at the end of the run for room temperature. The lower orders however were not measured over an uninterrupted interval and it was found that the angle scale reading would change slightly from day to day. Although those spurious shifts were corrected as well as possible for the smaller orders, the values of the lattice expansion derived from them are not sufficiently reliable.

¹¹ A brief abstract of this paragraph has been published in a letter to the Editor: A. Goetz and R. C. Hergenrother, Phys. Rev. **38**, 2075 (1931).

Table I shows in column 1 the temperatures T at which the Bragg angle θ has been observed.** The shift $\Delta\theta$ is given in column 4 and from it the absolute value D_T at T of the interplanar spacing along (111) is calculated, based on the previous determination of D for $T=20^\circ$ by the authors.² (Column 5.)

Fig. 8 represents these values as functions of T and it is evident that the deviation of the points observed (O) from the smooth curve is much smaller than the previously estimated errors would allow.

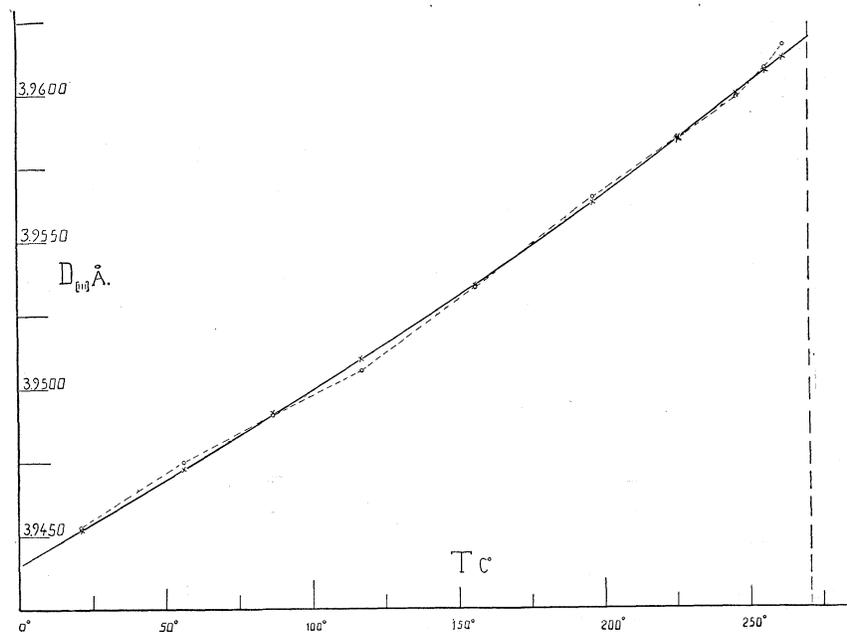


Fig. 8. Diagram of the interplanar spacings D along (111) against temperature T . The observed points are indicated by circles; the points obtained from the β -value of the true specific heats are indicated by crosses.

In order to determine the coefficient of expansion α_{11} and its change with temperature, $d\alpha/dT$, use was made of the following consideration:

If T_1 and T_2 are two neighboring temperatures at which the corresponding spacings D_1 and D_2 have been measured, the expansion coefficient is defined as:

$$\alpha_\tau = \frac{1}{D_\tau} \left(\frac{D_1 - D_2}{T_1 - T_2} \right) = \frac{1}{D_\tau} \left(\frac{\Delta D}{\Delta T} \right)_\tau \quad (1)$$

where $\tau = \frac{1}{2}(T_1 + T_2)$.

In case $d\alpha/dT = \text{const} \neq 0$, the spacing at the temperature τ is:

$$D_\tau = D_0(1 + T\alpha_\tau) \quad (2)$$

** The measurement at liquid air temperature is omitted because of a possible thermal distortion of the crystal holder due to the asymmetrical application of the liquid air.

If:

$$\alpha_\tau = \alpha_0 + b \cdot \tau \quad (3)$$

Eq. (1) changes to:

$$\alpha_\tau = \frac{D_1 - D_2}{(T_1 - T_2)D_0 \cdot (1 + \alpha_0\tau + b\tau^2)} \quad (1a)$$

D_0 is a known spacing for which the previous precision determination² gave $D_{20} = 3.9453\text{\AA}$.

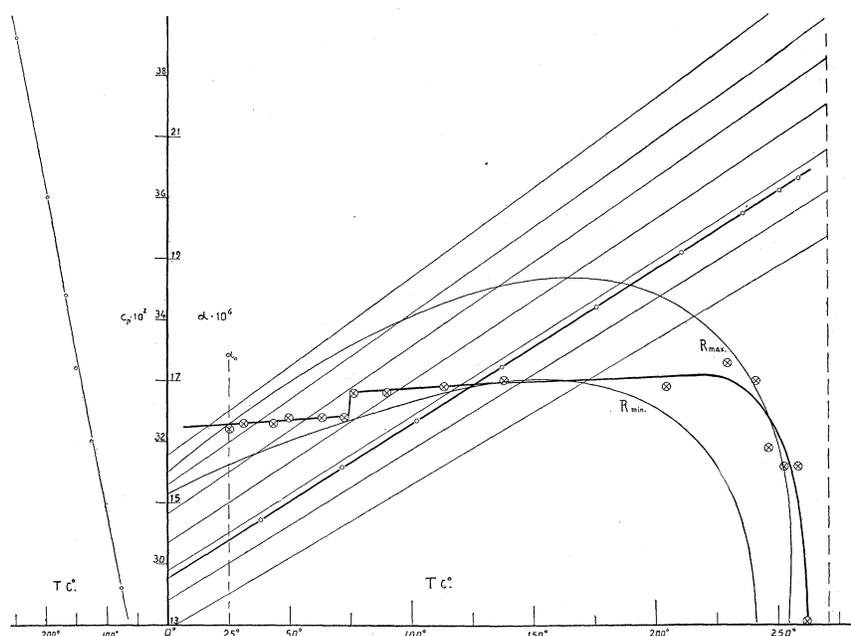


Fig. 9. Diagram of the linear expansion coefficient $\alpha_{||}$ (right) and the specific heat (left) against temperature. The family of straight lines (right) represent the locus for $\alpha_{||} = \alpha_0(1 + \beta\tau)$ varying from $13.5 \cdot 10^{-6}$ to $16.5 \cdot 10^{-6}$ in intervals of $5 \cdot 10^{-7}$. The heavy drawn line represents the accepted value of $\alpha_0 = 14.4 \cdot 10^{-6}$. The curved lines show the limiting values of the macroscopic expansion measured by Roberts (R_{\max} , R_{\min}). The crossed circles indicate the macroscopic expansion coefficients (not averaged) by Ho on crystals of the same stock as the crystal used for the x-ray analysis. The latter curve shows distinct indication of the pseudo-allotropic transformation at 75°C .

In addition to D_0 the coefficients α_0 and b have to be known. Although previous authors have claimed α to be invariant with temperature over the region considered, the curvature of the $D = f(T)$ in Fig. 8 relation disproves this statement and consequently a linear relation was assumed.

This supposition was also based on the linear relationship of c_p —the true specific heat—with temperature, as shown by Umino¹² for a range from 50° to 250°C . The values for c_p —interpolated, where necessary—are given in column 6 of Table I and Umino's original values are shown in the left part of the diagram Fig. 9.

Since the physical reason of the parallelism of α and c_p will be discussed below it will only be stated here that the determination of α_0 and b is obviously correct only if the relation is valid; the observed values of D however permit an accurate check for each temperature due to their small deviations, in other words: *as soon as the values of D calculated from α_0 and b (i.e., from the temperature variation of c_p) coincide with the observed values of D , α and $d\alpha/dT$ are determined as well as the validity of the above assumption is proved.*

If c_{p1} , c_{p2} , $c_{p\tau}$, α_1 , α_2 , α_τ are the true specific heats and the expansion coefficients at T_1 and T_2 and τ , b is determined by:

$$\frac{c_{p1} - c_{p2}}{c_{p0}(T_1 - T_2)} = \frac{\alpha_1 - \alpha_2}{\alpha_0(T - T_2)} = \frac{b}{\alpha_0} = \beta. \quad (4)$$

From the values of Table I β is determined to be $1.76 \cdot 10^{-3} \text{ deg.}^{-1}$, and the quantitative equation of c_p is calculated as:

$$c_{pT} = 2.84 \cdot 10^{-2}(1 + 1.76 \cdot 10^{-3}(T_{\text{abs}} - 323^\circ))^{13}$$

Thus the expansion coefficient should follow:

$$\alpha_\tau = \alpha_0(1 + \beta\tau). \quad (5)$$

The evaluation of the best fitting value of α_0 was done graphically as shown in Fig. 9, where α is plotted against T . The straight lines show the locus of α_τ for $\beta = 1.76 \cdot 10^{-3}$ and different values of α_0 , (α_0 being taken as α_{25°) varying from $13.5 \cdot 10^{-6}$ to $16.5 \cdot 10^{-6}$ in intervals of $0.5 \cdot 10^{-6}$.

The observed D values in Fig. 8 were then joined in an approximately fitting smooth curve and small corrections for D were made. These values were then used for a rough determination of α_τ using Eq. (1) and taking for simplicity $D_\tau = \text{const.}$ Those values were plotted in the diagram (Fig. 9) and the best fitting of the β lines was interpolated. Thus α_0 came out to be $= 14.4 \cdot 10^{-6}$. This locus is indicated by the heavy drawn line in Fig. 9.*†

With α_0 , β and b known, the values for D_T could be calculated from Eq. (1a). Since however the α_τ values could be read directly from the graph (column 7 in Table I) the simpler relation was used namely:

$$D_{T1} = D_{T2}(1 + \alpha_\tau(T_1 - T_2)) \quad (6)$$

which had the advantage of giving D_T instead of D_τ . This renders a direct comparison with the observed values possible. The values thus calculated of (D_T^*) are given in column 9 of Table I and are shown as crosses in the diagram in Fig. 8.

The differences between the observed (D) and calculated (D^*) values are given in column 10 of Table I showing that in no case the deviation reaches

* The preliminary corrected D values are not shown in Figs. 8 and 9.

† The values for the temperature relation of c_p in older papers vary considerably for the value of β . Umino's measurement was chosen as being the most recent work with the largest number of observations in the temperature range under consideration.

¹² S. Umino, Sc. Rep. Tohoku University 15, 604 (1926).

¹³ Gmelin's Handb. d. anorg. Chem. Nr. 19, 46 (1927).

more than 0.01 percent. This however is the case only twice: once at 117°, where the measurement was obviously not perfect and again just before the melting point. The deviation of the latter observation is probably real, as will be discussed later. Excluding the last value for this reason the mean total deviation regarding size and direction is only $-1.10 \cdot 10^{-5}$ Å or 0.00025 percent of D . Taking the average value of α_{\parallel} for this temperature range to be $18 \cdot 10^{-6}$ deg.⁻¹ and the average ΔT to be 30°, α_{\parallel} has been determined within 1.9 percent.

The quantitative equation for α_{\parallel} is:

$$\alpha_T = 14.4 \cdot 10^{-6} (1 + 1.76 \cdot 10^{-3} (T_{\text{abs}} - 298^\circ)) \quad (7)$$

or:

$$\alpha_T = 14.4 \cdot 10^{-6} + 2.54 \cdot 10^{-8} (T_{\text{abs}} - 298^\circ). \quad (8)$$

The quantitative agreement between the temperature function of the true specific heat and the lattice expansion was taken as evidence for the validity of the original assumption for the whole range of temperature investigated excepting for the last 10°–15° below the melting point. With regard to this the following suggestions may be made.

It has been found by many authors, for example,¹⁴ that the specific heat ceases to be constant before the fusion sets in and shows an increase, an effect which is in general ascribed to impurities. Dickinson and Osborne¹⁵ found a gradual disappearance of this effect for ice with increasing purity. In the case of metals however a large part of this change seems to be independent of admixtures, since Carpenter and Stoodley¹⁶ in very carefully conducted experiments have found the existence of the increase of c_p even for the purest Hg. Unfortunately the values of c_p in this temperature region are not known since Umino's values which reach from 50°–800°C are taken in intervals of 25°–50° and hence our values are obtained by linear extrapolation. If Bi shows such an increase in c_p , as is most probable, the last point would show less or no deviation from the straight line relation.

COMPARISON WITH THE MACROSCOPIC EXPANSION

It is of interest to compare the lattice expansion as determined above with the macroscopic expansion obtained in the usual way by the direct measurement of the change of length of the crystal as a whole with temperature.

The anisotropy of Bi crystals was very early considered to be an interesting subject. In 1869 Fizeau¹⁷ measured α_{\parallel} and α_{\perp} ; α_{\parallel} was determined to be $16.4 \cdot 10^{-6}$ between 20° and 80°C. Within the last few years the coefficients have been redetermined by Roberts¹ and Bridgman.¹⁸ The latter author obtained $\alpha_{\parallel} = 13.96 \cdot 10^{-6}$ at 20°C, whereas Roberts made a study of α_{\parallel} and α_{\perp}

¹⁴ R. Ladenburg and E. Minkowsky, *Zeits. f. Physik* **8**, 137 (1922).

¹⁵ H. C. Dickinson and N. S. Osborne, *Bull. Bur of Stand.* **12**, 49 (1915).

¹⁶ L. G. Carpenter and L. G. Stoodley, *Phil. Mag.* **10**, 249 (1930).

¹⁷ H. Fizeau, *C. R.* **68**, 1125 (1869).

¹⁸ P. W. Bridgman, *Proc. Nat. Acad.* **10**, 411 (1924).

for the whole range between room temperature and melting point, and taking special care of determining $d\alpha/dT$. He concluded from a large number of observations that α_{\parallel} as well as α_{\perp} are *constant* to approximately 35° below the melting point. Within the region of constancy α_{\parallel} was computed to be $16.2 \cdot 10^{-6}$. Roberts drew furthermore the conclusion as to the constancy of α_{\parallel}/c_p , by extrapolating the approximately constant values of c_p by Richards and Jackson¹⁹ taken between -188° and $+20^{\circ}$, for higher temperatures, (Umino's paper had not yet been published and the author apparently did not rely on the older determinations). It is obvious now that the statement was erroneous.

The most astonishing fact is the decline of α_{\parallel} as well as α_{\perp} beyond *ca.* 240°C to such an extent that α_{\parallel} reaches one half of its original value at *ca.* 255°C . The possibility of a plastic deformation of the crystal so close to the melting point must be excluded because of the reversibility of the process and thus the decrease of α_{\parallel} must be taken as a natural property of the crystal.

Although Robert's mean values show a satisfactory constancy for the lower temperatures ($16.2 \pm 1 \cdot 10^{-6}$) the single observations, though taken with all precautions, are scattered over a large range. His maximum and minimum values are approximately indicated by the two curves (R_{\max} , R_{\min}) crossing the β lines in Fig. 9. It is obvious that the deviation between the macroscopic and lattice expansion is such that it cannot be explained by experimental errors.

In order to be certain that neither the small imperfection of the crystals used by Roberts nor the different kinds and amounts of impurities caused the difference, Mr. T. L. Ho of this Institute performed macroscopic expansion experiments with a method similar to Roberts'. As a specimen, Bi of the same stock as the metal used in the x-ray experiments was taken, and the crystals were grown by the same method described previously.²⁰ Hence one should expect them to be commensurable. Since the technique as well as the results of this work will be published separately, further details are omitted and only the α_{\parallel} -values of one typical crystal are shown in Fig. 9 in crosses in circles points. Since no averaging was done the data are rather scattered, though less so than are Roberts'. An approximately best fitting line is drawn through the points and it is evident that except for the highest temperatures these values lie within the limits of Roberts' values. The reversible decline of α_{\parallel} is also present, though the beginning of it is at slightly higher temperatures. The value of α_{\parallel} up to 75° is *ca.* $16.3 \cdot 10^{-6}$, which is in good agreement with Roberts' and Fizeau's values. We should consider it premature however to place much importance upon the absolute values of α_{\parallel} at the present state of this experiment. Nevertheless the qualitative values of $d\alpha/dT$ could be reproduced on a number of different crystals as well as the discontinuity at $75^{\circ} \pm 2^{\circ}$, i.e., at the temperature of the pseudo-allotropic transformation, which will be discussed below.

¹⁹ Th. W. Richards and F. G. Jackson, *Zeits. f. physik. Chem.* **70**, 414 (1910).

²⁰ A. Goetz, *Phys. Rev.* **35**, 193 (1930).

The results of the last paragraphs can therefore be summarized in the following statement:

The actual thermal expansion at higher temperatures of a Bi crystal is entirely different from the lattice expansion. Whereas $d\alpha/dc_p = dc_p/dT = \text{const.}$ from room temperature to the immediate neighborhood of the melting point, the macroscopic (actual) expansion varies much less (if at all) with T and begins to decline 30° – 40° before the melting point; accordingly $d\alpha/dc_p$ is not constant in this case.

Fig. 10 shows this difference schematically, $\alpha_{||}/c_p$ being plotted in arbitrary units against T . The full line represents the values of the lattice expansion, the dashed line represents the macroscopic expansion.

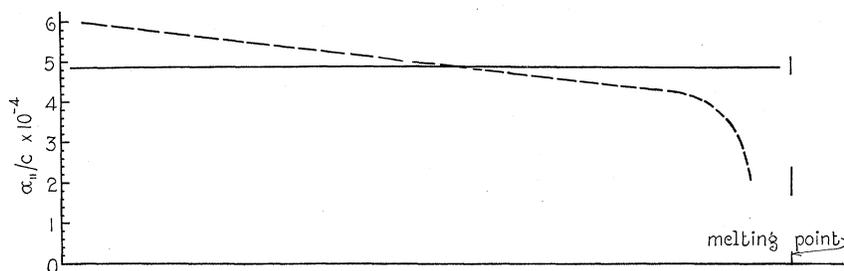


Fig. 10. Diagram of $\alpha_{||}/c_p$ in arbitrary units plotted against temperature. The full drawn line represents the lattice coefficient, the dashed one the macroscopic expansion.

THE "ALLOTROPY" OF BI

In addition to the determination of thermal expansions our observations in combination with the macroscopic measurements give some information about the much discussed allotropy of Bi.

From the x-ray investigation it is evident that no sudden change takes place either at 75° or in the neighborhood of the melting point within the limits of our experimental uncertainty. It seems to prove definitely that there is no allotropic i.e., lattice transformation in Bi in the range of temperature between 20° and 269° .^{*} In view of this Kapitza's hypothesis⁹ of the existence of a cubic modification near to the melting point does not seem to be supportable, as has already been pointed out previously from a different line of argument.²¹ This agrees also with the results of Webster²² who recently performed very careful measurements on the change of the diamagnetic susceptibilities of Bi immediately below and above the melting point with special regard to its coincidence with the heat of fusion and the change of rigidity. Since Kapitza ascribed the large crystal diamagnetism to the rhombohedral modification one should expect a decrease at a change into a cubical modification.

^{*} Although the shift of the Bragg angle was only observed to 262°C for the fifth order (Fig. 7), the third (Fig. 5) was taken up to 269°C and though not considered accurate enough for the determination of the lattice expansion, shows no deviation which should account for a sudden change of spacing.

²¹ A. Goetz and A. B. Focke, reference 4, footnote page 1054.

²² W. L. Webster, Proc. Roy. Soc. **A133**, 162 (1931).

Hence the change of the susceptibility should not coincide with the process of fusion; whereas Webster could prove a coincidence to 0.3°C , thus rendering the existence of such an allotropy highly improbable.

The nature of the other allotropic transition at 75°C is much more puzzling, because of an almost equal amount of experimental evidence against and in favor of it. The literature on this subject as given previously⁸ was augmented recently by a careful investigation of Schulze²³ concerning the temperature coefficient of the electric resistivity and of the volume expansion in this range of temperature which did not show a discontinuity at any point. His expansion measurements were taken however at intervals of *ca.* 10° , i.e., in the critical region at 70.0°C and 79.8°C , hence a very small discontinuity may have been left unobserved.

The shift of the x-ray reflections with temperature (Fig. 8) shows definitely that *there is no such discontinuous change in the lattice spacing along (111) as one should expect in case of an allotropic modification.*

A careful study of the macroscopic expansion however shows that a small actual change takes place (Fig. 9) which is of the same order of magnitude as Cohen's observations. This proves definitely *that a rearrangement occurs within the crystal at 75°C which is not characterized by a change in the lattice.*

It may be anticipated from a detailed report about the studies of macroscopic expansion that this change can be reproduced in all crystals of different degrees of purity and that it is independent of the thermal history, i.e., its occurrence and size depends neither on the number of times, nor the length of time the crystal was heated above this temperature. Hence the effect can seemingly not be ascribed to recrystallization or to reaction with impurities which latter effect could be conjectured from the transformation point of the ternary system of Bi-Sn-Pb at 76°C which has been recently discovered by Isihara.²⁴

INTERPRETATION OF RESULTS

The purpose of this paragraph is to discuss the nature of the validity of the α/c_p relation together with the discrepancy between the macroscopic and lattice expansion and to present a tentative hypothesis from which these phenomena may be explained.

First the question may be discussed, whether or not one is entitled to compare the temperature shift of the Bragg reflection with the macroscopic measurement of the thermal expansion; in other words: Is the average of the atomic displacements, effective for the x-ray interference, equivalent to the mean sum of the displacements, effective in the length-determination of the crystal?

Waller²⁵ has shown in a calculation regarding the cubic terms of the potential energy of atomic displacements in a lattice, that classical as well as quantum-statistics result in an agreement of both types of summation, i.e., the

²³ A. Schulze, Zeits. f. tech. Physik **11**, 16 (1930).

²⁴ T. Isihara, Sc. Rep. Tohoku Univ. **18**, 715 (1929).

²⁵ I. Waller, Ann. d. Physik **83**, 153 (1927).

difference between the shift of x-ray reflection with temperature and the corresponding macroscopic thermal expansion of a three-dimensional crystal is negligible. In addition to this the same author also introduces a fourth order term for the potential of a one-dimensional lattice:

$$\Phi = \sum_{L=2}^L u_T \text{ for } u_T = A\frac{1}{2}\xi L^2 + B\frac{1}{3}\xi L^3 + C\frac{1}{4}\xi L^4. \quad (9)$$

The second-order approximation for the cubic term together with the first-order approximation of the fourth order term results in an expression for the spacing $D_{T'}$ effective for x-rays:

$$D_{T'} = D_0' \left[1 + \alpha T - \frac{kT^2\pi^2\alpha}{3A} \frac{(\theta - \theta_0)^2}{\lambda^2} \right] \quad (10)$$

where λ is the wave-length of the radiation and θ, θ_0 the cosines of the reflected and incident radiation respectively. Since:

$$\frac{(\theta - \theta_0)^2}{\lambda^2} \sim n^2 \text{ (order)}$$

one should expect, that $D_{T'}$ measured by x-rays would be smaller than the macroscopic

$$D_T = D_0(1 + \alpha T)$$

furthermore $D_T - D_{T'}$ should increase with higher orders as well as with temperature. Waller states that these effects are small and probably negligible for the three-dimensional case, and since our experiments have shown exactly the opposite deviation ($D_{T'} > D_T$) it seems impossible to ascribe the observed deviation to effects inherent in the difference of the two methods of observation.

The theoretical reasons for the existence of an approximate proportionality between α and c_p were discussed for monatomic crystals by Grüneisen,²⁶ Born,²⁷ Debye and implicitly in Waller's paper.²⁵ The conclusion at which the authors arrive is that the constancy of α/c_p is only an approximate one, the validity of its relation for temperature beyond the T^3 -region is only to be expected for monatomic crystals.²⁷ It is interesting to note that in Waller's treatment of the one dimensional lattice (Eq. (9)) the expression for the mean potential energy contains the term:

$$\frac{5B^2}{6A^3} - \frac{3C}{4A^2}, \text{ whereas } \alpha = -\frac{Bk}{A^2D}.$$

The constancy of α/c_p can only hold if:

$$\frac{5B^2}{6A^3} - \frac{3C}{4A^2} \sim \frac{Bk}{A^2D}, \text{ or if } C = B \cdot \left[\frac{B}{A} - 1 \right].$$

²⁶ E. Grüneisen, Ann. d. Physik **39**, 257 (1912).

²⁷ M. Born, Enz. d. Math. Wiss. **3**, 663, ff. (1925).

Since B has to be negative in order to have $dD/dT > 0$, the condition $dc/dT > 0$ prescribes:

$$\frac{3B^2}{4A^3} \left[1 + \frac{A}{B} \right] < \frac{5B^2}{6A^3} \text{ or } \left| \frac{A}{B} \right| < 0.1111.$$

If C is neglected completely one obtains $(B/A^3) \sim (B/A^2)$ which is obviously not true, though it has to be remembered that these expressions are only valid for one-dimensional lattices.

Grüneisen and Goens^{28,29} proved the validity of the α/c_p relation in their classical experiments on Zn and Cd crystals for a range of temperature from -160° to $+100^\circ$ and Borelius and Johansson³⁰ did the same for polycrystalline Cu between -182° and $+20^\circ$. The experiments prove however the validity of the relation only for α_v , the volume expansion coefficient; they indicate also definite deviations of the relation below *ca.* -160°C . α_v [being synonymous with the linear expansion coefficient for the cubic Cu] is defined for hexagonal crystals (Zn, Cd, Bi, etc.) as:

$$\alpha_v = \frac{1}{V} \frac{dV}{dT} = \alpha_{\parallel} + 2\alpha_{\perp}. \quad (11)$$

The experiments on Zn and Cd showed α_{\parallel}/c_p to be distinctly different from α_{\perp}/c_p , especially for low temperatures. The first author to test the relation at high temperatures—i.e., $+20^\circ$ to $+270^\circ\text{C}$ —was Roberts,¹ as has already been seen. The discrepancy between his results and Grüneisen's relation cannot be understood from the difference between the Zn and the Bi lattice, since both metals belong to the same fundamental type of symmetry. In view of the reported observations it seems evident that the linear expansions of Bi also do not show a simple relation to the specific heats as far as macroscopic measurements go, which is also obviously true for the macroscopic α_v .

In any case the most important point seems to be the proof that α_{\parallel} of the lattice satisfies the relation up to the melting point and we hope to prove this soon for α_{\perp} also, in which case the same is established for α_v .

This new effect can seemingly only be explained by the existence of *two* components of the macroscopic expansion coefficient: α and α' , of which α is the expansion coefficient of the ideal lattice and α' the expansion of a disintegrated portion of the crystal. Of these the first and *only* the first component is accessible to the x-ray measurement, whereas the macroscopic method integrates over both components, thus the expansion of the ideal lattice follows Grüneisen's relation whereas the disintegrated part does not do so.

The question arises as to the cause of such gradual disintegration which disagrees completely with our usual concept of the sharp melting point of a crystalline substance, accompanied by a sudden change of the physical quali-

²⁸ E. Grüneisen and E. Goens, Phys. Zeits. **24**, 507 (1923).

²⁹ E. Grüneisen and E. Goens, Zeits. f. Physik **29**, 141 (1924).

³⁰ G. Borelius and C. H. Johansson, Ann. d. Physik **75**, 23 (1924).

ties typical for a solid body. The explanation which several authors have advanced to explain phenomena similar to the decrease of the macroscopic α , is the assumption of a gradual dissociation of the crystal into a semi-liquid; near the melting point a crystal would therefore be considered as a solid solution of the liquid substance in the remains of the lattice. However any theory assuming a statistical distribution of dissociation atoms over the crystal is untenable in view of the existence of a sharp melting point, as Roberts¹ has already indicated.

However, if one accepts the picture of a mosaic crystal, consisting of units of rather definite size, one does not encounter the above objection. In an ideally pure crystal the boundaries of the mosaic units consist of atoms the spacing of which is slightly different from the interior as has been pointed out by Zwicky.⁶ If enantiomorphous impurities are present, the probability of their deposition in those boundaries is more probable than inside the unit⁴; they cause however an additional distortion within these boundaries. At higher temperatures one must assume a farther reaching distorting influence of the boundary upon the intact lattice of the unit, with the effect that a "decrystallization" starts with increasing temperature. The total volume of the crystal existing in a "decrystallized" state increases therefore with the approach to the melting point at the expense of the truly crystalline volume; hence the macroscopic qualities will be increasingly influenced by the qualities of the amorphous substance. It may be emphasized that such a system can very well be in a perfect thermodynamic equilibrium and have a sharp melting point due to the fact that sufficiently large complexes of atoms in an undisturbed spacing exist to grant the interaction necessary for a sharp melting point. In a recent paper Zwicky³¹ has pointed out the necessity that cooperative phenomena of such kind are necessary to understand a sharp melting point which after all is the most characteristic quality of a crystal. One has to assume apparently that the cooperation of a definite number of atoms is necessary in order to cause fusion; in other words a *definite minimum number of atoms able to cooperate since coexisting within an ideal lattice configuration*. Since however the number able to stay in such configuration at high temperatures depends on the degree of decrystallization, which itself depends to a certain extent on the number of foreign atoms, the lowering of the melting point by comparatively small admixtures may be understandable.

This suggestion seems to gain probability in view of the expansion phenomena. If N_c is the number of atoms per unit volume of a large crystal existing in a perfect lattice configuration, N_d the corresponding number of decrystallized atoms, the macroscopic expansion coefficient is given by:

$$\alpha_m = \frac{N_c\alpha + N_d\alpha'}{N_c + N_d} \quad (12)$$

where α and α' have the same meaning as before. Furthermore:

$$\frac{N_d}{N_c + N_d} = f(T). \quad (13)$$

³¹ F. Zwicky, Proc. Nat. Acad. 17, 524 (1931).

Combining Eq. (12) and (13) one obtains for the degree of decrystallization

$$\frac{N_d}{N_c + N_d} = \frac{\alpha_m - \alpha}{\alpha' - \alpha} = f(T) \quad (14)$$

which can easily be determined from Fig. 9, showing $f(T)$ to be an exponential function as expected.*

To account for the large difference between α and α' one has to remember the well-known fact that the expansion coefficient of solids in the amorphous state is generally much smaller than in the crystalline, [as for instance, SiO_2 shows only one thirtieth of the linear crystal expansion in the amorphous state]. A plausible physical explanation of this fact can be found in a balancing effect of the irregular spacing of the atoms on the dislocating action of the anharmonic oscillations.

Three of the numerous consequences accessible to experiment to be drawn from the above suggestions may be mentioned, though their detailed discussion shall be left to later publications:

(1). If the impurities in a crystal assist the process of decrystallization without being entirely responsible for it, one should expect: (a) that the purest obtainable metal would show the effect as well as metals with impurities; (b) that for slightly impure crystals the decline of α_m would begin at lower temperatures compared with the pure crystal.

The experiments of Mr. Ho and the senior of the authors on the macroscopic expansion have actually proved these postulates.

(2). If the macroscopic crystal at higher temperatures actually consists of an ideally crystalline and of an amorphous component, the intensities of reflected x-rays should decline faster with increasing temperatures than is predicted by the theory of Debye and Waller which accounts only for the the increased undirected scattering caused by the thermal agitation of lattice atom. The presence of an amorphous component should increase the scattered radiation by an additional amount proportional to $N_d/(N_c + N_d)$.

In fact our intensity measurements at different temperatures (Figs. 3-7) show a large deviation from Debye's law at higher temperatures, such that the measured intensities grow increasingly smaller than the theoretical values. A similar effect has been found previously for NaCl and Al crystals.

(3). Grüneisen's relation can be expected to hold only for the lattice expansion and not for the macroscopic one, as long as $\int_0^T u \alpha T$, the atomic heat contents for the decrystallized and the ideal part of the crystal, do not differ greatly.

Although the suggested hypothesis seems to describe the observed effects satisfactorily without assuming too much *ad hoc*, our experiments cannot be considered as definite proof of it. Whereas there already exists certain direct

* The quantitative evaluation of this function needs more systematic observations of the macroscopic expansion, which however will be published soon; an estimate shows however that more than 30 percent of the crystal is decrystallized in the neighborhood of the melting point.

experimental evidence of the periodic absorption of impurities in a metal crystal^{32,33} it will be exceedingly difficult to decide by experiment whether or not the strict periodicity of the mosaic structure assumed by Zwicky is present *a priori* or is due to impurities, since so far no crystal containing an insufficient number of foreign atoms (including gases) to fill the internal surface has been available.

Further experiments on this subject, soon to be published, are expected to bring additional information to the problem of the effects of foreign atoms in a homopolar lattice.

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³² M. Straumanis, Zeits. f. anorg. Chem. **180**, 1 (1929).

³³ M. Straumanis, Zeits. f. physik. Chem. **148**, 112 (1930).