X-RAY STUDIES OF METALLIC SINGLE CRYSTALS

Thesis

by

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ABSTRACT

Problem (1)

Some improvements in the use of the Siegbahn precision spectrometer employing two crystals (a specimen to be measured and a standard comparison crystal) are described. These enabled the author to ascertain changes in lattice spacing smaller than one part in ten thousand. Two series of bismuth single crystals containing impurities up to five atomic percent were studied. These were bismuth-tin and bismuth-lead. Roughly, up to these concentrations of impurities the change in lattice spacing went linearly with the amount of added impurity. However, the accuracy was still not sufficient to decide whether or not the first few foreign atoms (first tenth of a percent or so) go into the crystal lattice as do the subsequent atoms, there being reasons to believe that they do not.[1]

Problem (2)

A new X-ray cryostat is described which enables one to keep a crystal at any desired temperature down to about 25 degrees absolute using liquid hydrogen. The method of temperature control is by regulation of the flow of the heat-transfer gas (helium) which is circulated through the apparatus. A fast ionization method for measuring small changes in the Bragg angle of reflection and hence small changes in the crystal lattice is explained. This

makes it possible to measure coefficients of expansion by the x-ray method in these low temperature regions. A series of measurements (in three orders for purposes of counterchecking) of lattice changes and coefficients of expansion are given covering the temperature range from 25 to 535 degrees absolute. A test of the Grueneisen rule is made, values of the specific heat at low temperatures being extrapolations from the extremely low temperature values taken at Leiden. The rule is found to have only limited applicability, failing above 100 degrees absolute, and failing to show similar discontinuities in specific heat values where discontinuities occur in expansion coefficient values. The question as to whether or not there is a difference between x-ray and macroscopic expansion values is believed to be settled.

Problem (3)

A method for using the apparatus described in problem (2) for intensity measurements is outlined, the chief feature being the automatic integration of the intensity under a given line. Measurements are taken throughout the same temperature region as in problem (2), namely from 25 - 535 degrees absolute. The exponential form of the Debye heat factor is found to be obeyed below 480° absolute. Above that point there is noticeable hysteresis and an increased intensity with increasing temperature. No discontinuities in intensity occur where they are found in the coefficient of expansion measurements.

PROBLEM I

THE EFFECTS OF SMALL AMOUNTS OF IMPURITIES
ON THE BISMUTH LATTICE SPACING

Introduction

The results of studies made by Goetz and his co-workers[2] on bismuth single crystals containing small amounts of impurities (generally one or two atomic percent or less) made an x-ray investigation of the same very desirable. Hergenrother[3] had previously made measurements on single crystals containing several atomic percents of impurities, employing a Siegbahn method which gave the required accuracy at the time. However, in view of the fact that very small amounts of impurities (of the order of a tenth of a percent) seemed to give the most interesting effects, while the addition of larger amounts of the same impurity had diminishingly smaller effects, it was felt that a systematic x-ray investigation of these crystals might give some clew as to the position of the foreign atoms in the crystal lattice. At the same time, since the problem now centered on smaller amounts of impurities, it was necessary to improve the accuracy of the method.

Experiment

The camera employed was of the Siegbahn type. Two crystals replaced the usual one. For purposes of comparison alone, the pre-

cision scale of the usual camera is not necessary, since the difference in lattice spacing between the two crystals employed (let us say the pure and impure metal) can be directly calculated from the x-ray plate measurement, of course, providing that the lattice spacing of the standard crystal is known. Since this method has been fully described by Hergenrother, it is useless to go into detail here. Suffice it to say that the greatest source of error in the method had previously been in the incorrect alignment of the crystals on the axis of rotation of the spectrometer. In the present work a new double crystal holder was employed which allowed the crystals to be adjusted to within 5×10^{-5} cms. of the axis or better. The adjustment was made by setting a microscope with a special base directly over the axis of rotation of the instrument. Then, with the aid of a long focal length objective (2.0 cm) the crystals could be aligned individually on the axis of rotation by properly focussing the microscope and making the necessary adjustment on the crystal holder. With this arrangement the error in adjustment was now comparable in effect with the uncertainty in measuring the position of the lines upon the x-ray plate, and hence it was felt that a limit in accuracy for a camera of this size (radius 17 cm.) had been reached. This accuracy was somewhat better than one part in ten thousand.

Two series of metals were studied, namely bismuth-tin and bismuth-lead. The percentages (atomic) of the added metals ranged
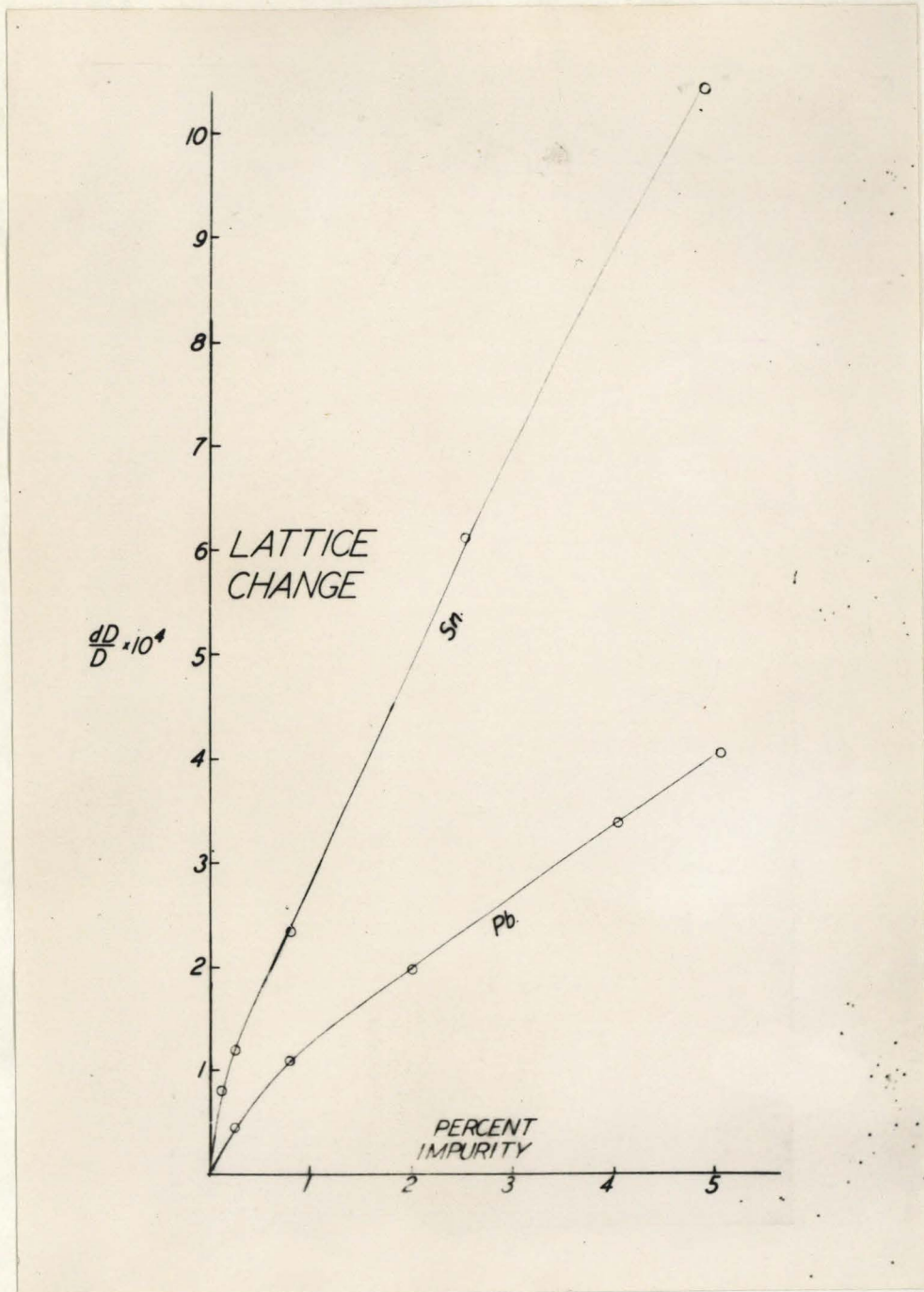
Fig. 1.

Fractional lattice change for Bi - Sn and Bi - Pb
plotted against atomic percents of the added metal.

from one-tenth of a percent to five percent. The results of these measurements are shown graphically in figure I. Each point is itself obtained from the results of measurements taken in at least three different orders of interference. Generally the first, second and fifth orders were employed; the (1,1,1) that is, the natural cleavage plane of bismuth was used. The calculations are made by first performing a logarithmic differentiation of the fundamental Bragg equation:

$$n \quad = 2 \, D \, \sin \Theta$$

yielding as a result:

$$\frac{dD}{D} = \frac{dl}{4 \, R \, \tan \Theta}$$

where dl is the difference in the measured distances between the lines from each of the samples on the x-ray plate. Hence if 4 R tan Θ is plotted against dl and the slope of the straight line (fitting the points given by the various orders) measured, that slope serves to give an average value of $\frac{dD}{D}$ for the measurements in the various orders of interference. Since the lines drawn should pass through the origin of coordinates, the intercept on the dl axis serves as a measure of the error in adjusting the crystals on the axis. In cases where this was too large, the crystals were re-adjusted, and another set of measurements were taken. In Figure 2 this method is illustrated for the bismuth-tin series.
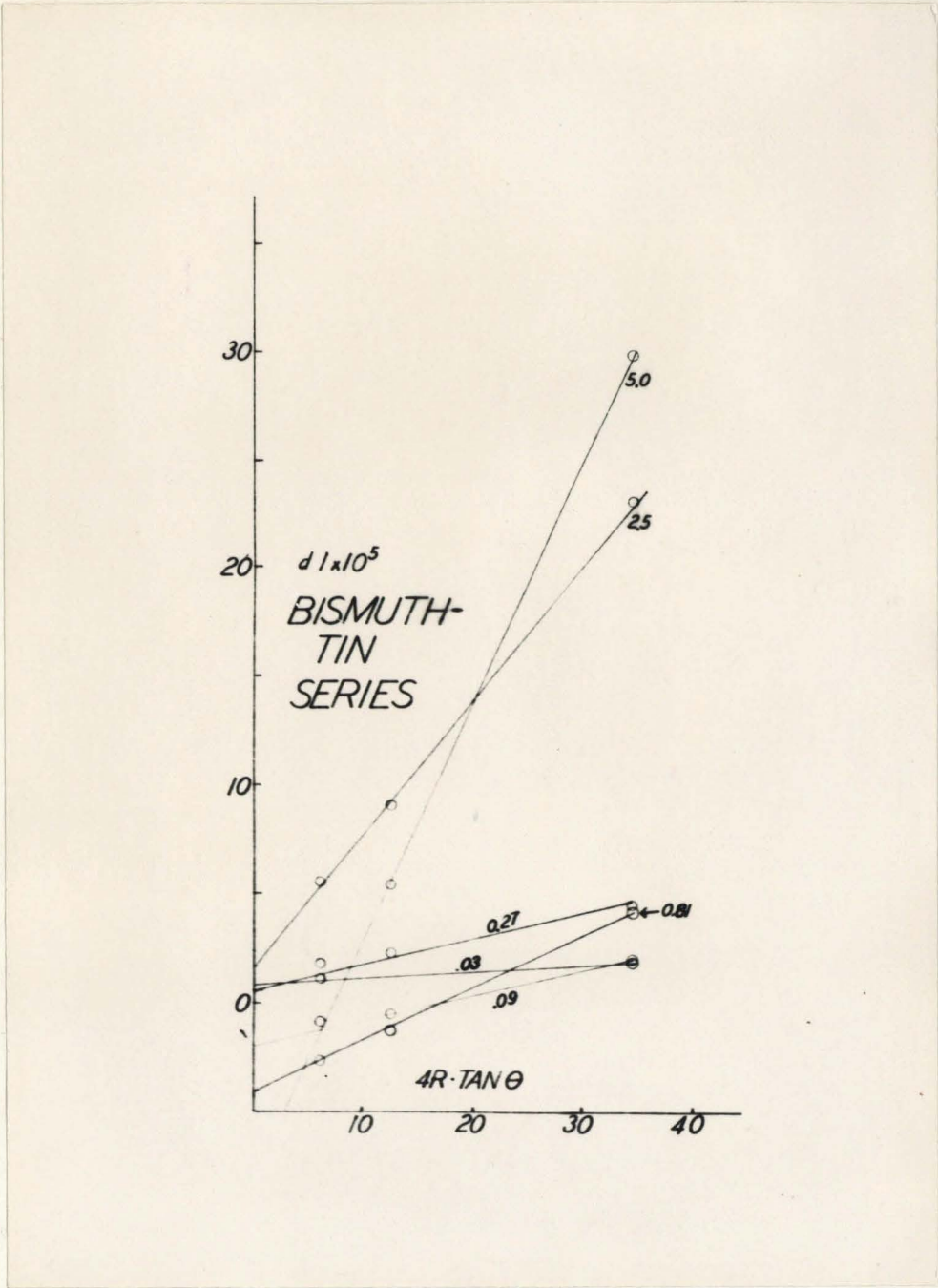
Figure 2.

The slope of these lines is a direct measure of
the fractional lattice change along the 1,1,1 axis.

Conclusion

As was mentioned at the offset, the purpose of this investigation was to ascertain whether or not the first small amounts of impurities went into the bismuth lattice in some way different from that in which the larger amounts did. This is important because it serves as an explanation for some of the results obtained by Goetz and Focke in their measurements on diamagnetism. They have postulated that the first few foreign atoms arrange themselves in "crevices" about the pure crystal blocks, and only after such desired positions are filled do these atoms take up positions throughout the entire crystal mass. In such a way they are able to explain their results. Now, if such is the case, an x-ray analysis should show for the first small amounts of impurities no effect, and after a certain limit (about a tenth of a percent) a more or less linear change in lattice spacing up to a few percent. This latter condition is fulfilled as Fig. 1 clearly shows. Concerning the former there is no contradiction, but no definite proof. The accuracy of the method is still insufficient for a positive proof, and plans are now under way for an extremely accurate camera with a radius of at least one meter. With the new instrument, this question should be definitely settled.

PROBLEM (II)

X-RAY DILITATION MEASUREMENTS ON THE BI LATTICE FROM 30° - 530° K.

Introduction

Although the problem of x-ray determinations of coefficients of thermal expansion is not new[4,5] attention was recently refocused on the problem by Goetz and Hergenrother[6] who reported that between room temperature and the melting point of the metal they found a substantial difference in the x-ray measurements from the ordinary optical measurement. Three essential differences were emphasized: First, no sharp discontinuity at 75°C as was found in the optical measurement. Secondly, a more or less gradual rise in the coefficient from about 15×10^{-6} to 20×10^{-6} in the range investigated, as against a nearly constant value of about 17×10^{-6} in the optical measurement of Ho[7], and, thirdly, no decline after 250° as was shown in the measurement of Ho. Recently, Jay[8], using a powder camera, has found almost complete agreement between his x-ray measurements and the accepted macroscopic values.

A definite agreement on this question seemed important, because, if the work of Goetz and Hergenrother proved valid, bismuth would again appear to be the "exception" among metals in view of the agreement between x-ray and microscopic measurements on a number of other metals.[9]

Another point seemed interesting, namely the question of the validity or non-validity of the Grueneisen[10] rule stating a constancy in the ratio of the specific heat to the coefficient of expansion in the different temperature regions.

Apparatus

The same Bragg spectrometer used by Hergenrother[11] was employed in the present investigations, with **two** important additions. First of all, the apparatus (spectrometer and electrometer) were mounted firmly on the same concrete bench in order to secure absolute stability, and an adjustable lead slit carried on a micrometer screw was placed before the window of the ionization chamber. This served to measure the small displacement of the reflected beam when the crystal was subjected to temperature changes. The crystal itself was set at the center of the "rocking" angle"; the tube and its slit system were fixed for the correct order of reflection, and the measurements were taken by moving the slit in steps of one-thousandth of a centimeter in order to ascertain the maximum position of the line. It should be noticed that with this arrangement the danger of a systematic error can be entirely avoided by using more than one order of reflection and checking the results of the several independent sets of measurements. In this way, a movement of the crystal, for example, caused by a thermal distortion of the crystal support, can be immediately found and eliminated in the calculations.
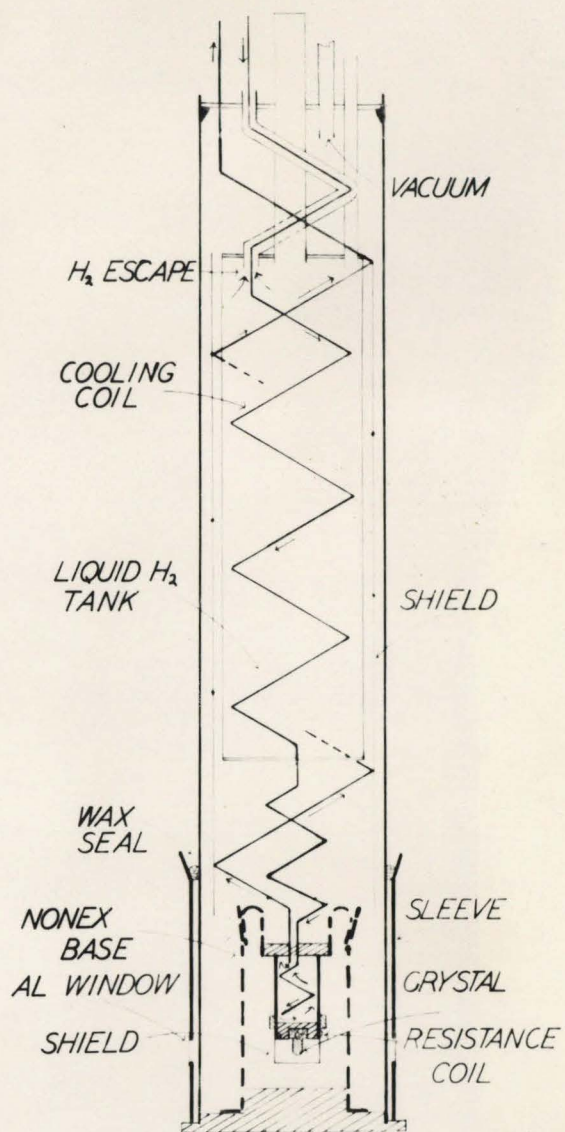
Figure (3).

X-ray cryostat allowing the crystal to be
kept at any temperature down to 25°C.

A new adjustable crystal table of larger dimensions was employed, and most important of all, the crystal was now symmetrically mounted on a cylindrical base of nonex glass inside a vacuum chamber. The new cryostat allowed temperatures down to 25° absolute to be reached with perfect facility and absolute reproducability, showing the absence of permanent or incontrollable distortion in the crystal position. This apparatus is best explained by reference to figure 5. It is seen that the crystal is firmly supported by the nonex base which attaches directly to the bottom of the outer vacuum chamber which in turn is fastened to the adjustable crystal table on the spectrometer. The temperature of the crystal is controlled by the flow of helium gas (precooled with liquid air before entering the apparatus) which is there further cooled by the vapours escaping from the liquid hydrogen in the apparatus, and finally is run through the hydrogen liquid cooling coils and into the crystal cooling tank system, to which the crystal is attached by direct metallic contact. By varying the flow of gas through the system any desired temperature between liquid hydrogen and room temperature may be reached. Above $100^{\circ}K$ liquid air is used instead of liquid hydrogen. Temperatures are measured by means of a copper resistance which is wrapped about that part of the crystal tank to which the crystal is directly attached. In calibrating the copper resistance, certain fixed points were used, namely the ice
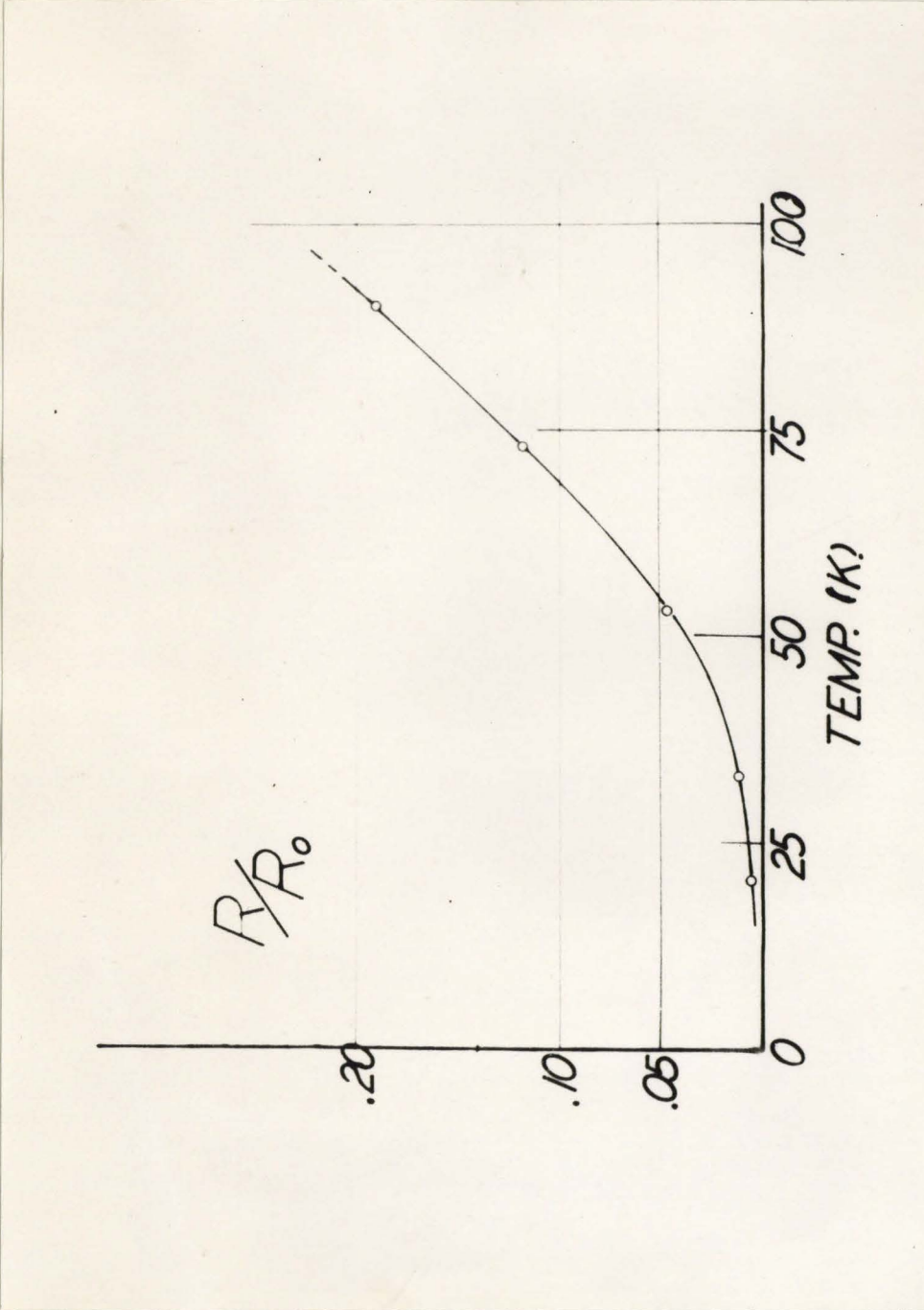
Figure (4)

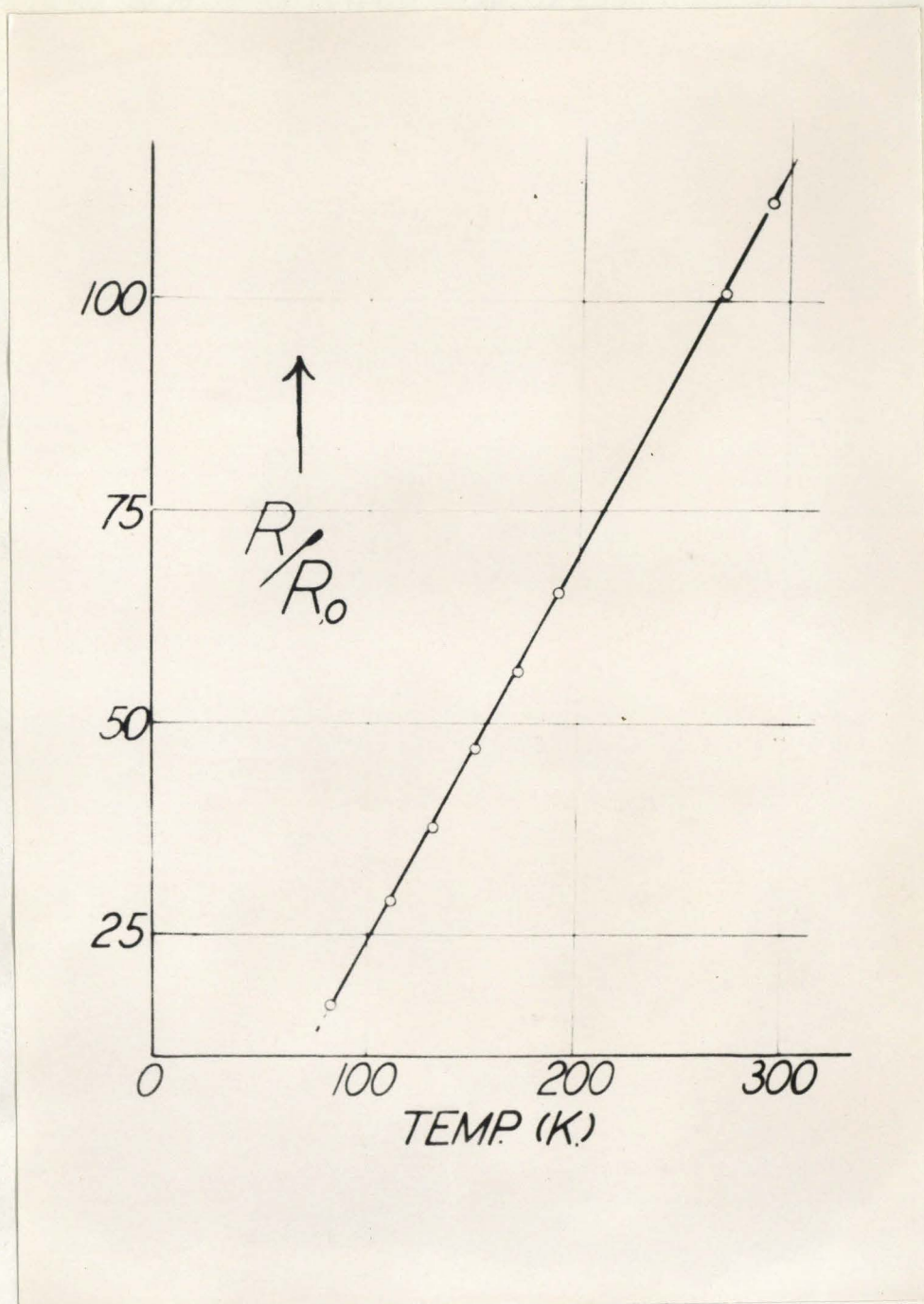Copper-resistance calibration range 0 - 100° Abs.

Figure (5).

Copper-resistance calibration range 0 - 300 Abs.

point, and the boiling points of liquid nitrogen and liquid hydrogen. These were checked against the same points at Leiden[12] and certain intermediate points were taken from their data. These calibrations are shown in figures (4) and (5). Attention might be called to the fact that the crystal is thermally shielded on four sides by a shield attached directly to the crystal tank, and further since the crystal is in a high vacuum, the gradients throughout the crystal should be small indeed. Use of the returning cold gas is made by wrapping the return line around a shield which is consequently cooled by the gas. Care was taken to reduce radiation to a minimum by keeping the interior walls of the apparatus brightly polished or nickel plated. The tubes connecting the hydrogen chamber directly to the outer wall were of .005 inch nickel-silver. Cooling coils were of copper of about 0.1 inch in external diameter. For the purpose of maintaining a low heat capacity the hydrogen tank walls were constructed of 0.005" nickel silver. Provision is made for changing crystals by having the entire assembly (except the nonex base) removable from the outer brass cylinder by merely loosening the top seal which is of Wood's metal. This is possible since the crystal tank-nonex base connection is made by means of a ground glass joint which slips apart when the crystal assembly is lifted. The crystal can then be removed by simply screwing it (by its holder in which it is fixed with Wood's metal) out of the tank part. Several

crystal holders are available so that a new crystal may be immediately installed. As is indicated in the diagram an optical adjustment of the crystal can be easily made since the brass outer wall of the cryostat is cut away at those parts which would intercept the optical beam. When this adjustment is made the apparatus is made vacuum tight by the sliding cylinder to which the aluminum windows are attached. This is waxed in place at top and bottom.

As a safeguard against possible accidents due to the considerable amount of hydrogen gas escaping from the evaporating liquid, the apparatus is so arranged that the spectrometer, x-ray tube and accessories are in one room, while the top of the crystal (from which the gas escapes) projects through a specially constructed partition into a gas hood in the adjoining room. The vapours are swept from the hood at a considerable rate by a large exhaust fan. Great care was taken in making electrical connections with sparkless switches etc in the hydrogen hood. Direct connections to the helium supply are permanently installed at the hydrogen hood as are the ordinary utilities plus vacuum mains, hydrogen gas mains, etc. Liquid hydrogen is introduced into the apparatus by means of vacuum insulated tubes made in the shape of L's. One half is attached to the hydrogen Dewar bottle and the other half slips into the upper part of the cryostat. The L's are slipped

together and the hydrogen "pushed" across by the pressure gen-
erated by the evaporating hydrogen. The flow of helium re-
quired to maintain a given temperature varies from 0 - 50 cc.
per second. The flow is throttled by a needle valve and
measured by a simple manometer which registers the pressure
drop over a given coil resistance which is placed in series
with the helium flow on the low pressure side. The pressure
of the entering gas is only two or three atmospheres. Consider-
able care in properly removing moisture and other easily conden-
sable impurities must be taken to avoid "freezing" in the
hydrogen tank coils. This purification is accomplished by
connecting a charcoal trap cooled by liquid air in series with
the apparatus on the high pressure side.

Results

Measurements were made in the second, third, and fifth
orders on pure bismuth crystals. The range covered was from
25 degrees absolute to the melting point of the metal. The
natural cleavage plane was always employed. In the following
table the results of these measurements are given.

Date	Order of Refl.	Temp.(Abs.)	dD x 10" (change in lat-tice spacing)
6/10/32	2	294.2 (Room)	0
"	"	323.0	1.44
"	"	350.0	2.88
"	"	371.2	4.94
"	"	391.3	6.35
"	"	416.4	7.79
"	"	434.5	9.11
"	"	454.6	10.70
"	"	472.3	11.63
"	"	514.9	14.32
"	"	533.4	15.51
8/9/34	3	30.2	-18.00
"	"	35.0	-17.85
"	"	56.1	-16.88
"	"	63.9	-16.60
"	"	75.2	-15.55
"	"	96.3	-14.12
8/2/34	"	123.0	-13.15
"	"	154.6	-10.03
"	"	162.1	- 9.98
"	"	189.7	- 7.56
"	"	247.0	- 2.96
"	"	294.2	0.0
7/5/32	"	323.5	+ 1.46
"	"	346.3	2.90
"	"	349.5	2.97
"	"	373.0	4.48
"	"	395.5	6.08
"	"	435.1	8.97
"	"	472.0	11.80
"	"	511.3	14.08
"	"	531.2	15.28
8/21/34	5	32.7	-17.55
"	"	42.6	-17.20
"	"	48.5	-16.90
"	"	56.0	-16.35
"	"	64.5	-15.90
"	"	71.8	-15.48
"	"	81.2	-14.65

Date	Order of Refl.	Temp.(Abs.)	dD x 10^n (change in lattice spacing)
8/17/34	5	97.0	-13.35
"	"	123.9	-11.50
"	"	151.2	-9.65
"	"	186.3	-6.72
"	"	216.8	-5.14
"	"	226.0	-4.22
"	"	236.3	-3.32
"	"	256.1	-1.84
"	"	294.2	0.0
"	"	348.2	+2.88
"	"	394.5	5.92
"	"	430.8	8.20
"	"	461.3	11.3
"	"	505.9	13.7
"	"	536.7	15.9

The figures 6, 7, 8 give the complete data plotted for the second, third, and fifth orders respectively. Figures 9 and 10 are plotted on a larger scale to show the region from zero to one hundred degrees absolute for the third and fifth orders. By measuring the slopes of these lines the following results concerning the coefficients of expansion are obtained. (Table 2)
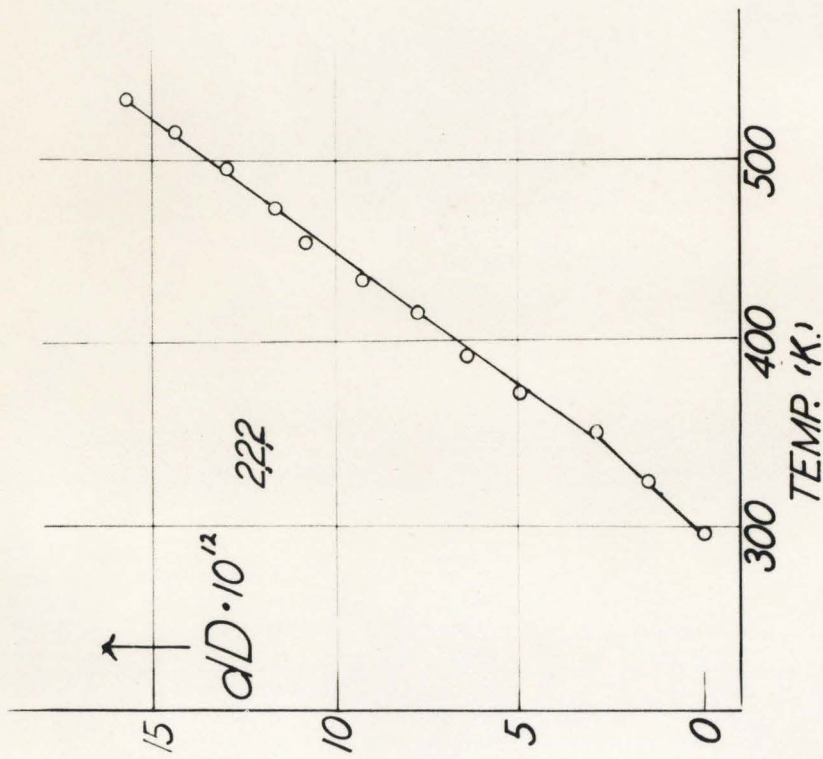
Figure (6)

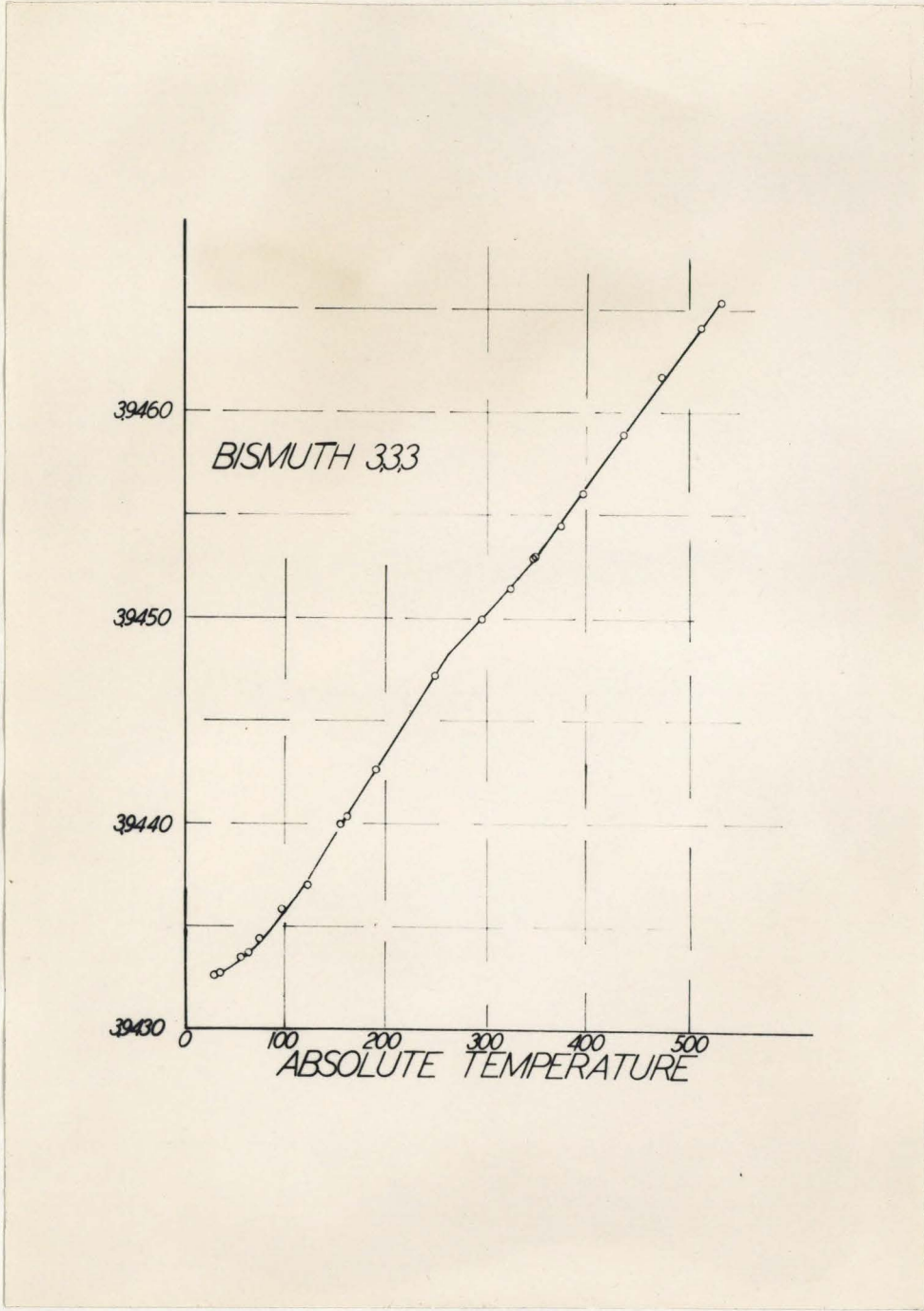Change in lattice spacing as a function of temperature.

Figure (7)

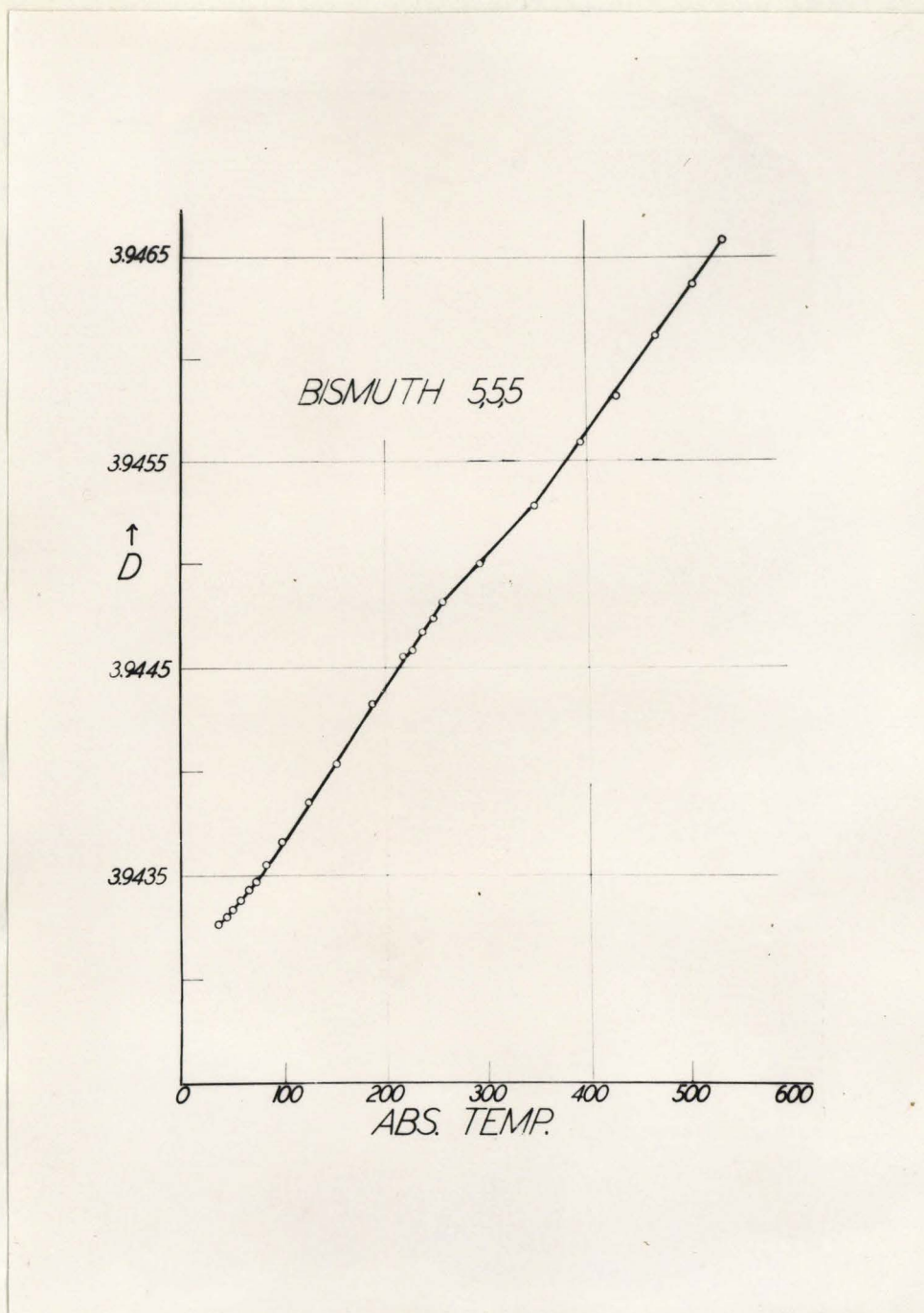Change in lattice spacing as a function of temperature.

Figure (8)

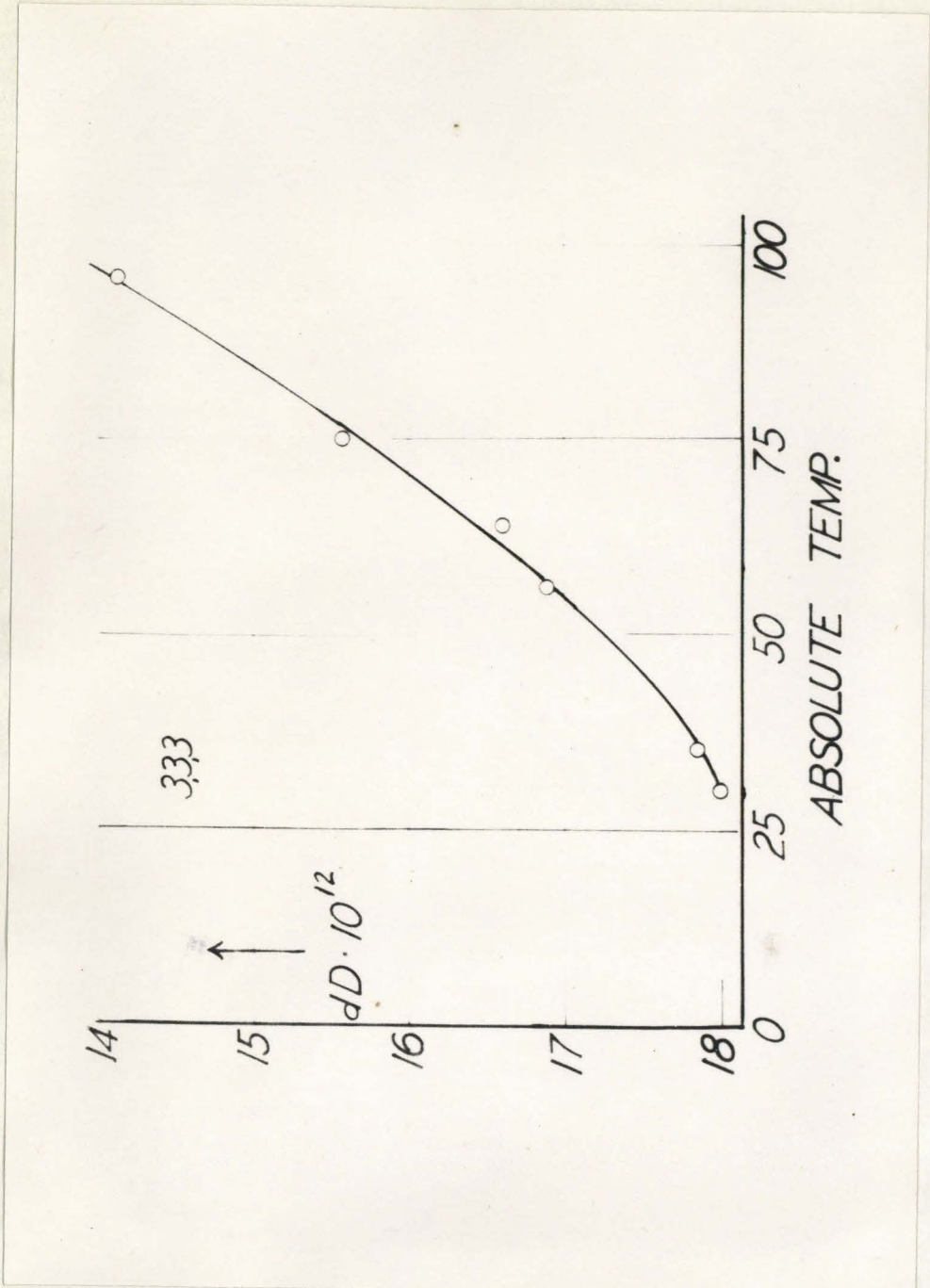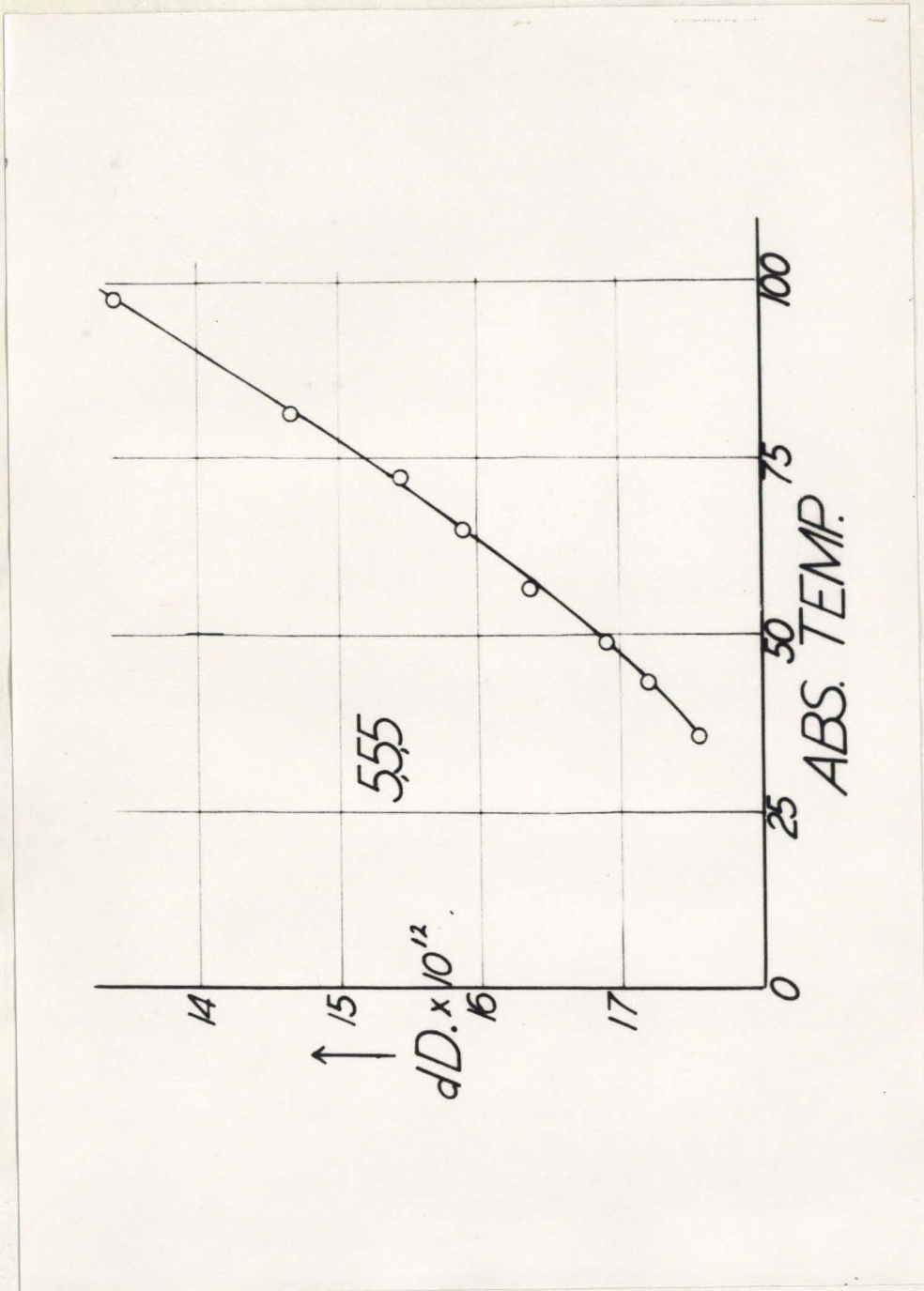Change in lattice spacing as a function of temperature.

ABSOLUTE TEMP.

333

dD · 10¹²

Figure (9)

Change in lattice spacing as a function of temperature.

Figure (10)

Change in lattice spacing as a function of temperature.

Table 2.

Order of Refl.	Temperature (Abs.)	Coefficient x 10^6
3	30	7.8
3	35	8.5
5	35	9.4
3	45	11.6
5	45	12.5
3	55	15.2
5	55	15.2
3	70	16.9
5	70	17.0
3	80	18.6
5	80	18.7
3	90 - 260	19.2
5	90 - 260	18.8
3	260 - 348	12.7
5	260 - 348	12.7
2	273 - 348	12.9
2	348 - M P	17.6
3	348 - M P	17.45
5	348 - M P	17.45

As is immediately observed the only region in which there is
a steady change in value of the coefficient is that below 100
degrees absolute. Beyond that point two changes appear, namely
the definite break which shows up in all orders (and hence can-
not be the result of distortion in the apparatus) at 348° abs.
or 75°C., and secondly, the even sharper break at about minus 15
degrees Centigrade. In figure 11 the values below 100 absolute
taken from the third and fifth order reflections are plotted,
and a smooth line is drawn through the points. In this region
it was thought advisable to test the Grueneisen rule since only
here did the expansion coefficient curve resemble the customary
specific heat curve. Since no direct values of specific heats
were available in the region interested, it seemed best to take
the characteristic temperature for bismuth obtained by specific
heat measurements at Leiden[13] in the region below 20° Abs.
Since their values of the specific heat there conformed remark-
ably well to the Debye theoretical values, an extrapolation up
to 100 Abs. appeared to be in order. The results of these
calculations appear in table 3 along with the ratio of the coeffi-
cient of expansion to the calculated specific heat values. It
is immediately evident that this relation is satisfied only in
the lower temperature regions, but begins to fall off slightly
below 100° absolute, where the specific heat continues to rise
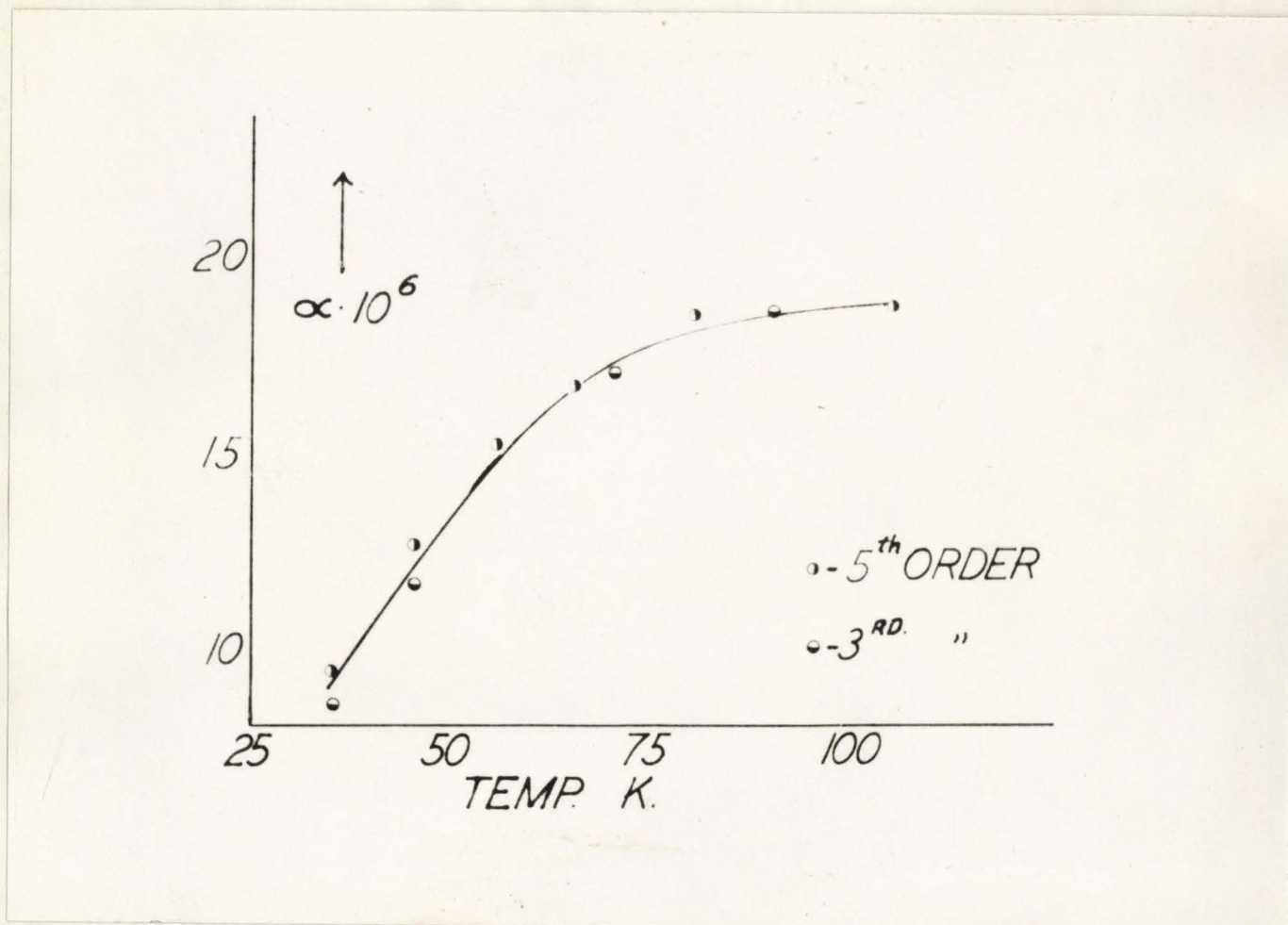and the expansion coefficient remains very nearly constant up to

Figure (11)

Coefficient of expansion plotted against temperature.

Table 3.

Temp.(Abs)	35	40	45	50
Specific Heat (calc)	1.812	2.124	2.406	2.646
(Expansion coeff. along 1,1,1 axis) $\times 10^6$	9.0	10.8	13.9	13.9
Ratio $C_p/\alpha \times 10^{-6}$	2.01	1.96	1.95	1.93

Temp.(Abs)	60	70	80	90	100
Specific Heat (calc)	3.066	3.384	3.648	3.864	4.044
(Expansion coeff. along 1,1,1 axis) $\times 10^6$	15.8	17.0	17.8	18.6	18.9
Ratio $C_p/\alpha \times 10^{-6}$	1.94	1.99	2.05	2.06	2.13

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260 degrees. At the two points at which the expansion coefficient takes sharp breaks, similar breaks would be expected in the specific heat values if the Grueneisen rule is to be obeyed. At the 75°C. point no break has been reported in the specific heat literature,[14,15] and it appears that there is a definite failure of the thermodynamic rule at this point. Concerning the point at -15°C., only preliminary results are available on specific heat measurements. Since these are not sufficiently reliable to base conclusions upon, it might only be mentioned that there seems to be evidence for a break in the specific heat curve at this point, as would be predicted by the Grueneisen rule. At

this time it should be mentioned that one should only expect the
Grueneisen rule to be valid in the present connection providing
that the ratio of the volume expansion coefficient to the coef-
ficient along the hexagonal axis is itself a constant. This
is observed in the optical expansion measurements, and in the
case of zinc this ratio is maintained throughout a considerable
temperature range according to measurements by McLennan and
Monkman.[16] Hence it seems quite reasonable to expect no failure
of the Grueneisen rule from this point; and to attribute the
failure to a more fundamental cause.

Discussion

In view of the rather good agreement in all three orders
in showing a break at 75°C. and constant values beyond there up
close to the melting point, it can be said that there is no sub-
stantial difference between the x-ray and the optical measure-
ments in the 75° - 265° centigrade region. From room temperature
to 75° the x-ray value (about 13×10^{-6}) seems to be definitely
lower than the optical value (about 15×10^{-6}). It is unfortun-
ate that the optical measurements have not been carried on below
room temperature in order to see whether or not a similar break
occurs there at minus 15°, since the region from -15 to +75°
seems to be a "transitional" region between two larger regions
of rather constant expansion values, and it may be possible that
in this transitional area alone there is a real difference between

the two types of expansion. Earlier measurements by the optical
method by Mr. Ho of this laboratory showed a rather rapid de-
cline in the expansion coefficient around 250°C. whereas the
x-ray measurements failed to show this. This was at first re-
garded as a real difference between lattice and macroscopic
expansions, but subsequent work on more pure crystals has failed
to reveal this break, making the agreement between the micro-
and macroscopic work quite good from 75° centigrade to the melt-
ing point. Below room temperature no values are available, for
a comparison with the macroscopic work. The sudden change in
expansion values at -15°C has not previously been recorded to
the author's knowledge, and since the 75°C point has already
yielded interesting results in other properties of the crystal,
the point below zero should likewise prove interesting.

In regard to the Grueneisen rule it should be said that
it has a limited region of application only; namely, that below
100° absolute; that it fails at such points at which the
expansion coefficient takes sudden breaks, such as 75° centigrade,
unless the values of the specific heat are not sufficiently
accurate to show the break.

PROBLEM III

X-RAY INTENSITIES AS A FUNCTION OF TEMPERATURE

(from 25° - 530° absolute)

Introduction

In this portion of the work, the interest was centered
only on the total integrated intensity in a certain order of
reflection as the crystal was turned through its rocking
angle. The temperature range covered was practically the
same as that in problem 2, that is, from 25° absolute to a few
degrees within the melting point of the metal. These measure-
ments furnished data to test the Debye heat factor for x-ray
intensities, and besides were of interest because of the exis-
tence of a hysteresis in the higher temperature regions.
Furthermore, it was desirable to see at those points where the
coefficient of expansion took sudden changes, whether or not
similar discontinuities could be found in the integrated inten-
sity-temperature curve.

Apparatus

The apparatus employed in this portion of the work is
essentially that of problem 2. The same x-ray cryostat and
general spectrometer set-up was used. However, to enable the
observer to take integrated intensity readings upon a reflected
x-ray line without the necessity of plotting the line from a

considerable number of observations and then measuring the area
of the same, a small motor with reduction gear was connected
to the axis of the crystal table. This made it possible to
run the crystal at any desired speed through its rocking
angle, the total charge registered on the electrometer then
served as a direct measure of the integrated intensity of the
line. The movable slit mentioned in problem 2 is for these
readings placed at the center of the line and the slit itself
opened sufficiently wide so as to receive the whole line, not
only at room temperature but at the other temperatures at
which the line is naturally displaced. Great care was taken
in these readings to provide sufficient shielding to cut down
background radiation to a minimum. The aluminum windows on
the cryostat, although they decreased the total intensity
somewhat, had the beneficial effect of giving a higher ratio
of integrated line intensity to background intensity than the
apparatus gave before the window assembly was waxed in place.
It should also be mentioned that the readings above room tem-
perature were made before the construction of the vacuum
cryostat had taken place, and for these the crystal was
mounted in a small electric furnace supported by a pyrex holder.
To reduce surface oxidation to a minimum the furnace and crystal
were surrounded by a cellophane windowed enclosure into which a
small stream of carbon-dioxide gas was introduced.

Results

In all of the following readings the integrated intensities are given after the proper correction for general and continuous background have been made. Table 4 below gives some intensity measurements based on room temperature 294° absolute as a reference.

Table 4

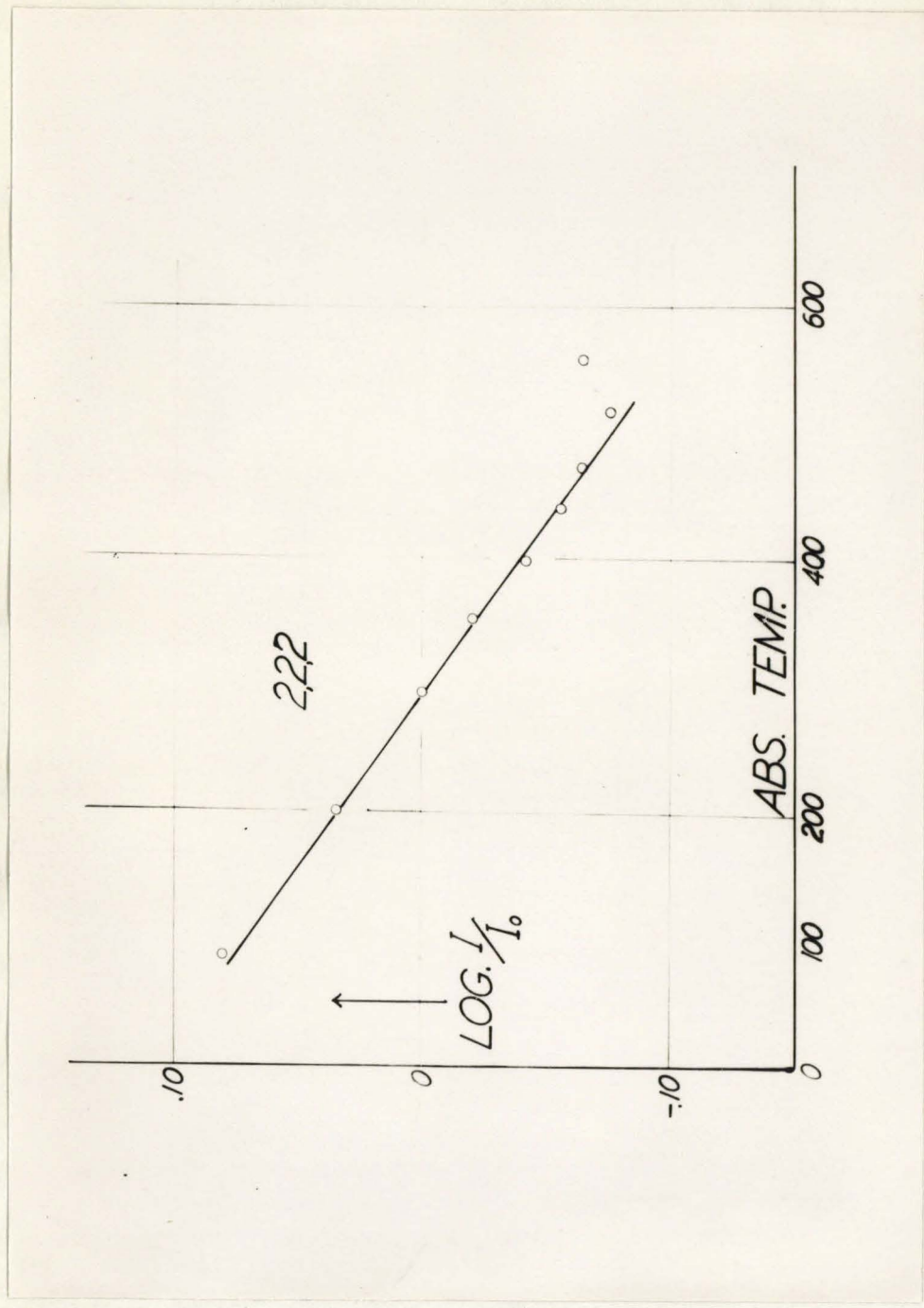| Date	Order	Temp(K.)	I/I_0	$\log_{10} I/I_0$ (+1)
8/12/32	3	527.0	0.770	0.880
"	"	507.0	0.741	0.870
"	"	470.5	0.741	0.870
"	"	431.5	0.774	0.889
"	"	389.5	0.837	0.923
"	"	344.5	0.906	0.958
"	"	294.	1.000	1.000
8/14/34	"	"	1.000	1.000
"	"	221.0	1.140	1.057
"	"	182.5	1.215	1.084
"	"	143.0	1.279	1.107
"	"	95.8	1.351	1.131
8/9/34	"	266	1.060	1.026
"	"	66	1.292	1.164
"	"	62	1.474	1.170
"	"	36	1.539	1.188
"	"	29	1.563	1.194
8/3/32	2	537.0	0.861	0.936
"	"	514.5	0.839	0.924
"	"	475.5	0.860	0.936
"	"	438.0	0.878	0.944
"	"	397.0	0.922	0.958
"	"	353.5	0.956	0.980
"	"	294.5	1.000	1.000
8/31/34	5	294.5	1.00	1.000
"	"	210.0	1.44	1.160
"	"	165.0	1.82	1.270
"	"	103.0	2.50	1.398
"	"	58.5	2.84	1.452
"	"	71.0	2.68	1.428
"	"	83.0	3.16	1.500
"	"	27.5	3.30	1.519

Figure (12)

Intensity logarithms - temperature
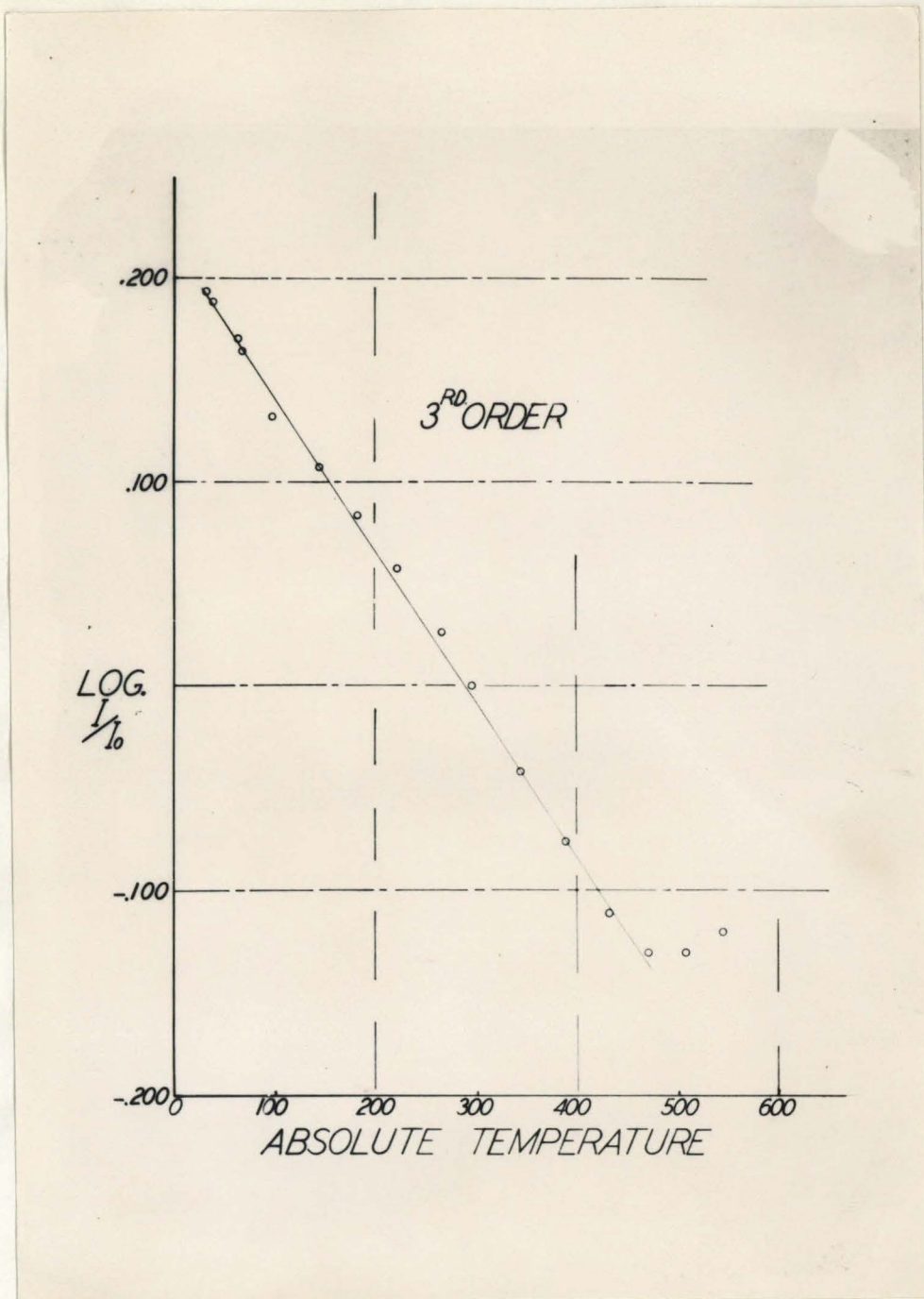
Figure (13)
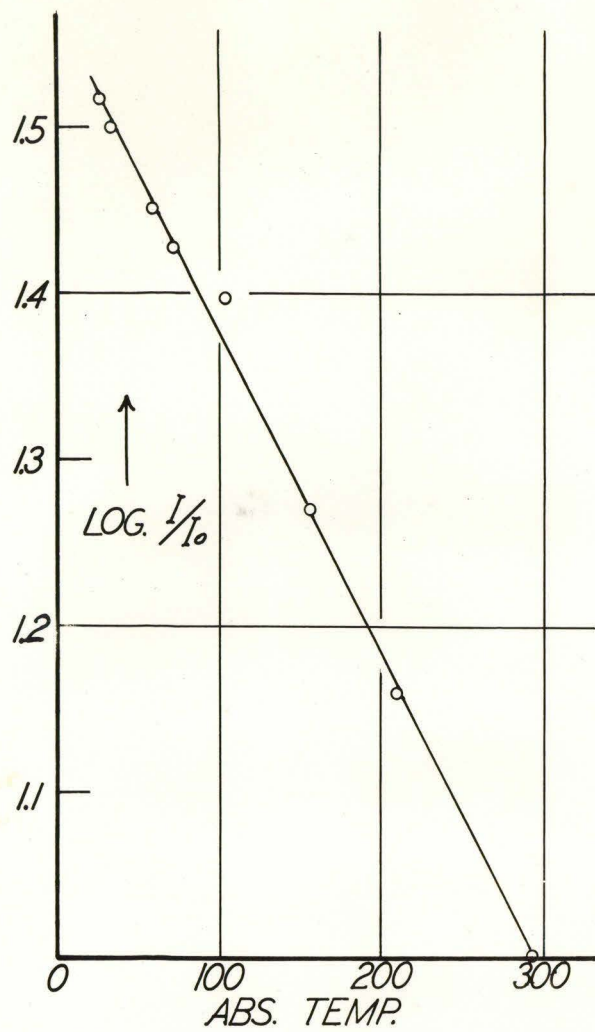
Intensity logarithms - temperature

Figure (14)

Intensity logarithms - temperature

The data given in the above table appears graphically in figures 12, 13, 14 in which the logarithm of the intensity ratio is plotted against the absolute temperature. It will be seen that except for the region within approximately forty degrees of the melting point that the resulting plots are straight lines as would be predicted from the exponential form of the Debye heat factor:

$$I = I_o e^{-k \sin^2 \theta T}$$

In these plots the absolute absence of discontinuities at -15 degrees and +75 degrees centigrade (the points at which the discontinuities in the expansion took place) is evident. Perhaps the most unusual and wholly unexpected feature is the actual increase in intensity beyond 200 degrees centigrade. This as indicated before, as accompanied by a hysteresis effect which is best seen by reference to figure 15. In this figure four plots are given. Plot 1 shows the effect of raising the temperature of a previously "quenched" crystal and then lowering the same. In plot 2 the crystal had preciously been in an annealed condition and its temperature raised, then lowered; it accordingly showed no hysteresis. Plot 3 is similar to plot 1. The crystal in plot 4 is heated after annealing (upper curve) then immediately quenched and reheated. In all cases,
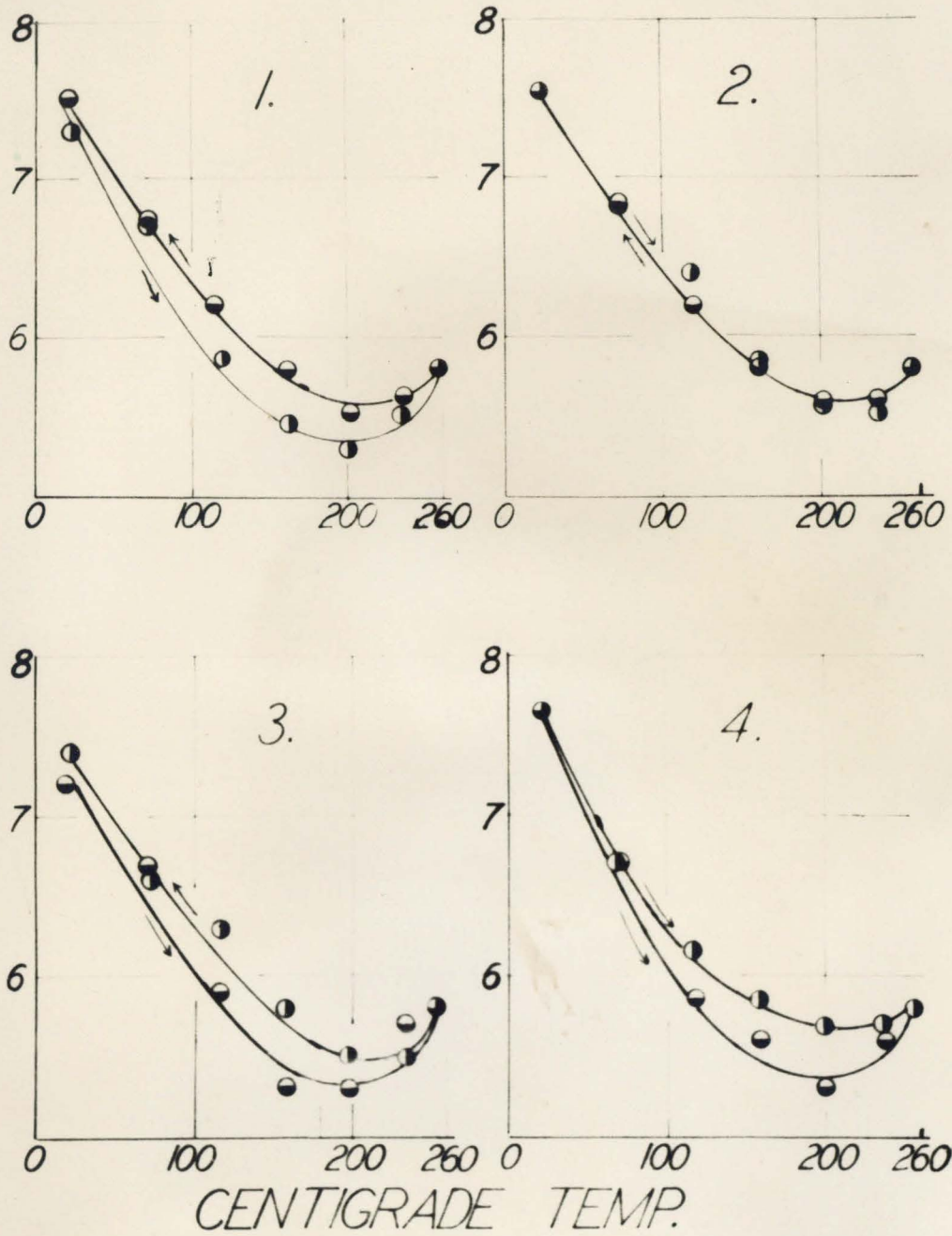
Figure (15)

it will be noticed a crystal being cooled or an annealed crystal being heated follow the same (upper) type of curve, while the non-annealed crystal follows the lower type of curve.

DISCUSSION

The results of this section confirm the theoretical Debye heat factor for x-ray intensities even beyond the limitations of the original theory,[17] which was for simple cubic crystals alone. However, from the work of Waller[18] one would expect bismuth to follow the exponential law. The agreement is, however, much better than any previous work[19,20,21,22] familiar to the author. It was interesting to see how far the results of the theory for the cubic case could be carried over for the hexagonal bismuth crystal. With this in mind, a test for the $\sin^2 \theta$ factor mentioned above was made. The θ here is, of course, the Bragg angle. The results of this test are briefly this:

Table 5

Order	$\sin^2 \theta$	$\sin^2$ ratio	ratio of exponential factors
5	.202	2.63	2.79
3	.072	1.00	1.00
2	.033	0.51	0.46

It is immediately seen that the law is approximately obeyed,

the deviation being in the direction of higher exponential ratios than $\sin^2$ ratios. This would indicate a greater crystal 'disorder' in the bismuth crystal with rising temperature than would be found in a cubic crystal. Mention should also be made of the type of deviation from the Debye law above 200° centigrade. James, employing Na Cl found a greater diminution of intensity than is called for by the Debye law. In this work the intensity is greater. The existence of the hysteresis perhaps lends a clear picture as to the cause. Certainly it cannot be explained by any perfect crystal picture. A certain type of crystal "repair" must take place. This is itself hard to explain even though one uses mosaic crystal ideas, for an increase in temperature should only result in greater disorder of the blocks themselves. It then seems reasonable to attribute the cause to changes which are known to take place in bismuth at this temperature. Namely, there seems to be a reorganization of the impurities around this point, as is evidenced by the difference in dilation measurements made on almost pure bismuth and vacuum distilled bismuth.[23] If then, the impurities break away from the crystal block crevasses where they are supposed to be lodged and redistribute themselves in some fashion about the crystal, it may happen that the "secondary extinction" may be sufficiently changed so as to make possible this rise in

intensity. The time factor involved in the redistribution of the impurities then might explain the hysteresis effect. The final decision of this problem then awaits new measurements on purer crystals if they can possibly be obtained.

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