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.*

ROBERT B. JACOBS† AND ALEXANDER GOETZ
Cryogenic Laboratory, California Institute of Technology, Pasadena, California

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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. α_{11} 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 α_{11} 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.

of those volume elements of the crystal which contribute to the diffraction. As an actual crystal ("Realkristall") does not necessarily consist entirely of elements of sufficiently well aligned atomic configuration, it is conceivable that the results of both types of measurement can differ.

For a number of reasons this problem seems to be particularly interesting in the case of Bi crystals. Here the integral expansion has been measured by a number of authors, whose results are given in Table I, as far as the coefficient of the thermal expansion parallel to [111] is concerned. These measurements are in fair agreement (with the exception of Bridgman's value) and give a nearly constant value for $\alpha_{\parallel}$ between room temperature and 30°–50° of the melting point of the metal; certain detailed differences, however, will be discussed later. Goetz and Hergenrother[1] were the first to measure the lattice expansion systematically and compare them with the dilatometric (integral) values of $\alpha_{\parallel}$ obtained previously. Their results indicated that there exists a considerable difference between the microscopic (lattice) and the integral expansions. Jay,[2] in a later paper, performed similar measurements on a number of crystalline substances (Ag, SiO_2, Bi) and concluded that his lattice expansion coefficients agreed quite well with the known values for the integral expansion.

Differences between Jay's work and that of Goetz and Hergenrother are immediately evident: The latter authors find a continuous variation of $\alpha_{\parallel}$ from room temperature to a temperature slightly below the melting point of Bi (271°C), i.e., from 14.4×10^{-6} to 20.3×10^{-6}, whereas the former finds a value of $\alpha_{\parallel}$ which is essentially invariant with the temperature between 20° and 150°C, i.e., $16.9\pm0.5\times10^{-6}$. Beyond 150° Jay's x-ray lines overlap with control lines, making further measurements of $\alpha_{\parallel}$ impossible. He was, however, able to determine the values of $\alpha_{\perp}$ (expansion coefficient normal to [111]) for the whole region between the melting point and room temperature, which are of considerable value, as an approximate proportionality between $\alpha_{\parallel}$ and $\alpha_{\perp}$ for higher temperatures can safely be assumed. These values are:

20°– 70° $=11.0\times10^{-6}$
80°–160° $=11.9\pm0.2\times10^{-6}$
160°–240° $=12.1\times10^{-6}$.

TABLE I. *Integral expansion of bismuth crystals parallel to 111 axis as measured by various authors.*

OBSERVER	$\alpha_{\parallel}\cdot10^6$	TEMPERATURE INTERVAL
H. Fizeau[1]	16.4	20°– 80°C
P. W. Bridgman[2]	13.96	20°C
J. K. Roberts[3]	16.2	20°–220°C
T. L. Ho and A. Goetz[4]	16.6	20°–150°C

[1] H. Fizeau, Comptes rendus **68**, 1125 (1869).
[2] P. W. Bridgman, Proc. Nat. Acad. **10**, 411 (1924).
[3] T. K. Roberts, Proc. Roy. Soc. **A106**, 385 (1924).
[4] T. L. Ho and A. Goetz, Phys. Rev. **43**, 213 (1933).

Two points are of special interest in Jay's observations: The existence of a discontinuity in the region of 75°C and the occurrence of an actual contraction of the lattice for the last 25° before the melting point, which would necessitate a negative expansion coefficient. Whereas these results are in fair agreement with dilatometric values up to about 248°C, they disagree with the dilatometric observations for higher temperatures, since no observer has found a contraction. Recent investigations by Buchta and Goetz[3] concerning this particular temperature range showed only a decrease in $\alpha_{\parallel}$, but always a positive value for the expansion coefficient. The size and the nature of this decrease was found to depend to a large extent upon the presence of small traces of impurities in the metal. In the light of these discrepancies it appears that Jay's results cannot be offered as complete proof of the equality of the integral and the lattice expansion coefficients.

In addition to the question of whether the integral expansion of a single crystal is identical with the lattice expansion, another problem needed investigation concerning the validity of the Grüneisen rule[4] (predicting a constancy of the ratio between the expansion coefficient and the specific heat (c_p) of a metal) which obviously does not hold for the integral expansion coefficient (as a decrease of the specific heat in the

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

[2] A. H. Jay, Proc. Roy. Soc. **143**, 465 (1934).

[3] J. W. Buchta and A. Goetz, Phys. Rev. **46**, 1042 (1934).

[4] Strictly speaking, the volume coefficient is implied, but owing to the apparent constancy of $\alpha_{\parallel}/\alpha_{\perp}$ for Bi, either of the latter may be substituted.

neighborhood of the melting point would have to be postulated). Goetz and Hergenrother, however, found the validity of this rule by introducing the lattice expansion coefficient instead of the integral α_{11}. Nevertheless, this agreement would be considered substantiated only over the comparatively small temperature range over which c_p values were available. Meanwhile, the range from helium temperatures to the point of fusion has been covered with the exception of 40°.[5–7]

2. Method and Apparatus

In the work being reported in this paper, the values of the lattice expansion coefficient (α_{11}) are determined over an extended temperature range, that is, from near the boiling point of hydrogen to within a few degrees of the melting point of the crystal (30°–537° abs.).

In order to ensure the identity of the crystal material used in the dilatometric measurements, the Bragg method was employed for the determination of the change of the lattice spacing whereas the Debye-Scherrer method used by Jay necessitates the use of powdered crystals, the integral α values of which cannot be determined for the sake of comparison with the lattice values of α.

The spectrometer is the same as the one described in the preceding paper,[6] likewise the cryostatic and the thermostatic crystalholders. The only alteration introduced for a more sensitive and accurate determination of the position of the maximum reflection consists of providing the ionization chamber with a movable slit. A schematic view of the assembly is given in Fig. 1, where C is the cryostat, J the ionization chamber, S the aforementioned slit guided by an accurate micrometer spindle M, facilitating a measurable displacement of the former with respect to the chamber and thus also to the beam of the reflected x-rays. The exact position is given by the reading of the micrometer head. The (adjustable) width of the slit is kept small compared to the width of the beam. The record of a line profile $[J=f(\vartheta)]$ is thus taken in the following manner: When the crystal (Cr) has reached thermal equilibrium at the desired temperature, it is set together with the tube (T) somewhere near the center of the rocking angle corresponding to the order of reflection under observation. The slit system of the incident beam is then rigidly fixed in position. Now slit S is moved across the path of the reflected beam and the current in J is recorded for different slit positions. From this record the exact position of the maximum is found by interpolation. The temperature of the crystal is then changed, the procedure repeated and a new maximum found. The shift of the latter is then a measure of the change in ϑ, that is, in the lattice spacing.

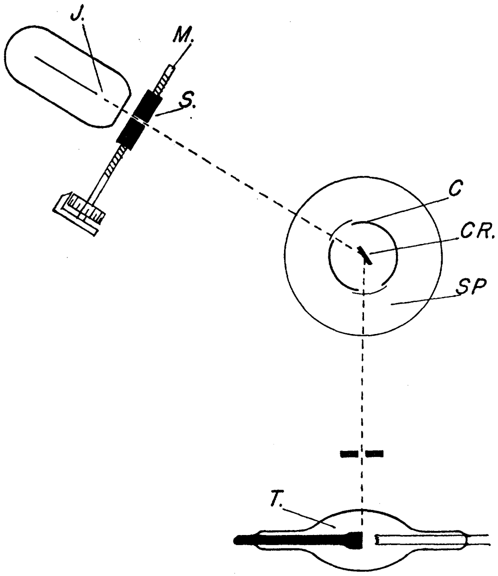

Fig. 1. Scheme of spectrometer assembly: SP, Spectrometer; CR, cryostat; C, crystal; T, x-ray tube; J, ionization chamber; M, micrometer spindle; S, movable slit.

The increase in accuracy of these experiments compared with previous work at this laboratory is partly due to the use of the movable slit in front of the ionization chamber instead of moving the crystal through the full rocking angle, the former technique making it possible to use several orders of reflection for comparison. Although Goetz and Hergenrother took observations of all of the first five orders, the resolving power of their method was not sufficient to permit the application of any but the fifth order. The present apparatus, however, resolves well

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[5] L. G. Carpenter and T. F. Harle, Proc. Roy. Soc. **A136**, 243 (1932).

[6] A. Goetz and R. B. Jacobs, Phys. Rev., preceding paper.

[7] W. H. Keesom and S. N. van der Ende, Kgl. Acad. Amsterdam **33**, 243 (1930).

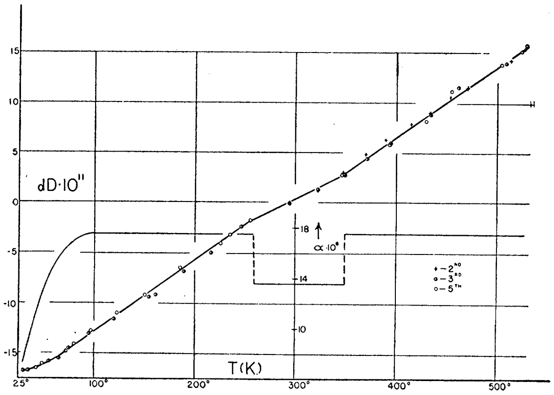

FIG. 2. The temperature function of the lattice spacing along [111] of Bi and of the expansion coefficient α_{II}. The abscissa is common to both, the ordinate of the latter is indicated in the center.

enough even the second order. The advantage obtained thus is obvious, as a simple geometrical consideration shows that any displacement of the crystal due to thermal distortion in its mountings, etc., will to a first approximation result in an *equal* angular displacement for *each* order of reflection. However, a change in the lattice spacing will give *different* angles for *different* orders in accordance with the Bragg equation. It is thus easily possible to distinguish between a $\Delta\theta$ caused by a displacement of the crystal as a whole or one caused by the thermal dilatation within the lattice.[8]

The wave-length used was that of Mo-$K\alpha$ radiation. Only the [111]-direction in the crystal was used as only (111) produces a plane satisfactory for this type of work.

3. MATERIAL

Most of the crystals used in this work are identical in origin with the crystals used in previous work.[6] The metal used for measurements above room temperature comes from stock identical to the crystals used by Ho (reference 4, Table I). The crystals used below room temperature were produced in a vacuum and are identical with those used by Buchta and Goetz.[3] No essential difference between the two different stocks is known.

4. RESULTS

In Table I the experimental data are given. The change in the lattice spacing ($dD\times10^{11}$) for each temperature is calculated with reference to the room temperature (294° abs.). Measurements of the 2nd, 3rd, and 5th order of reflection have been used, as the first is too much influenced by the surface condition of the cleavage plane, and the 4th is not sufficiently intense. In Fig. 2 the values of dD (Table II) are plotted against the temperature, observations of different orders being marked by different designations. The small scattering of the observations of different orders demonstrates the smallness of a systematic error.

The curve reveals two distinct changes of inclination, occurring at about −15° and +75°C,

TABLE II. *Expansion data.*

ORDER OF REFL.	ABS. TEMP.	$dD\times10^{11}$	ORDER OF REFL.	ABS. TEMP.	$dD\times10^{11}$
2	294.2	0.0	3	395.5	6.08
"	323.0	1.44	"	435.1	8.97
"	350.0	2.88	"	472.0	11.80
"	371.2	4.94	"	511.3	14.08
"	391.3	6.35	"	531.2	15.28
"	416.4	7.78	5	32.7	−16.8
"	434.5	9.11	"	42.6	−16.55
"	454.6	10.70	"	48.5	−16.15
"	472.3	11.63	"	56.0	−15.60
"	514.9	14.32	"	64.5	−15.20
"	533.4	15.51	"	71.8	−14.95
3	30.2	−16.85	"	81.2	−14.15
"	35.0	−16.75	"	97.0	−12.85
"	56.1	−15.80	"	123.9	−11.0
"	63.9	−15.70	"	151.2	− 9.20
"	75.2	−14.60	"	186.3	− 6.41
"	96.3	−13.20	"	216.8	− 4.21
"	123.0	−11.65	"	226.0	− 4.03
"	154.6	− 9.41	"	236.3	− 3.16
"	162.1	− 9.25	"	294.2	0
"	189.7	− 6.85	"	348.2	2.88
"	217.2	− 5.0	"	394.5	5.92
"	247.0	− 2.4	"	430.8	8.20
"	294.2	0	"	461.3	11.3
"	323.5	1.46	"	505.9	13.7
"	346.3	2.90	"	536.7	15.9
"	349.5	2.97			
	373.0	4.48			

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[8] Aside from the aforementioned possibility of using large individual crystals instead of powder, the above method should be capable of higher accuracy than the Debye-Scherrer method employed by Jay. Owing to the larger intensity required in a photographic method, the practical limit of the distance between crystal and film is around 4–5 cm. These factors are limited to a much less degree in the Bragg method and 5–10 times larger distances can easily be used. (The distance in these investigations varies between 21.5 and 31.5 cm.) Furthermore, the obvious advantage of the D.-S. method in using extremely high orders with a large displacement corresponding to an increment of the lattice spacing is, in our opinion, outweighed by the indeterminacy of the position of the photometric maximum of the reflection on the photographic record—in addition to the gain of the above factor due to the increased distance.

aside of which it approaches except for the lowest temperatures a fairly straight line. The decline of the expansion in the $T<\theta$ region is obvious and to be expected—it shall be discussed below in connection with the validity of the Grüneisen rule.

It is noteworthy that in agreement with Jay's values for $\alpha_\perp$ and in discrepancy with Goetz and Hergenrother the pseudoallotropic transformation is found to be marked in the lattice expansion, whereas it could not be found in the intensities-temperature function.[6] Also, new to our knowledge is the existence of a change in direction at -15°C which appears to be the reversal of the change at $+75$°C. Hence the curve suggests the existence of a separate phase within this temperature interval, which phase is, however, not a case of normal allotropy, as the lack of a discontinuity in the temperature function of the lattice spacing proves.[9] Since this problem has been discussed already in the preceding paper it may suffice to call attention to the fact that within the range of this phase the expansion rate is abnormally low.

This point is made more obvious by the temperature-function of the expansion coefficient $\alpha_{\parallel}$ derived from the previous curve by differentiation. The function is plotted also in Fig. 2 on a separate ordinate, the numerical data are given in Table III.

The temperature function of $\alpha_{\parallel}$ has therefore three distinctly different sections: The range where $T<\theta-(0°\text{–}100°)-$, where $\alpha_{\parallel}$ shows large variation with temperature, the range where $T>\theta-100°\text{–}538°-$ where $\alpha_{\parallel}$ does not vary appreciably with T. Within this region lies the interval of a separate "phase" within which $-258°\text{–}348°$—$\alpha_{\parallel}$ is apparently constant but considerably smaller than in the range bordering this "phase."

TABLE III. *Values of coefficient of expansion.*

TEMP. (ABS.)	$\alpha_{\parallel}\times10^6$
30°	7.2
35°	8.3
45°	11.2
55°	14.0
70°	15.6
80°	17.0
90°–258°	17.4
258°–348°	13.8
348°–538°	17.4

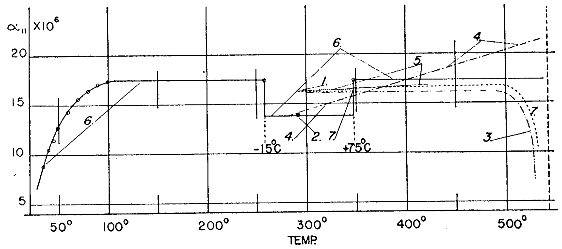

FIG. 3. Compilation of $\alpha_{\parallel}$ values of different authors: "*1*" Fizeau; "*2*" Bridgman; "*3*" Roberts; "*4*" Goetz and Hergenrother; "*5*" Jay; "*6*" authors; "*7*" Ho and Goetz.

5. DISCUSSION

As there exists considerable disagreement among the different observers a compilation of the data so far available is presented in Fig. 3. It is seen that even at room temperature the agreement is not good but that the results fall into two groups:

The dilatometric values of Fizeau ("*1*"), Roberts ("*3*"), Ho ("*7*"), and the x-ray value of Jay ("*5*") are consistent in giving a value of α for room temperature which is between 16.2 and 16.9×10^{-6}. The other group comprises Bridgman's value ("*2*") for the integral expansion and for the expansion of the lattice the observations of Goetz and Hergenrother ("*4*") and of the authors ("*6*") ranging from 13.6 to 14.4×10^{-6}. It appears difficult to explain this discrepancy. Furthermore: at 75°C Ho's dilatometric values and our x-ray values give indications of a discontinuity in $\alpha_{\parallel}$, whereas other authors fail in finding it, as does Jay. This is all the more surprising when it is remembered that in measuring $\alpha_\perp$ Jay found a definite indication of a sudden change in lattice spacing (i.e., $\alpha=\infty$) at 75°C. Beyond this temperature and up to about 240°C there is considerably better agreement among the various observations, with the exception of the results of Goetz and Hergenrother which indicate a continually increasing value of $\alpha_{\parallel}$ from 16.2 to 19.4×10^{-6}, respectively. In view of the present results which were taken by the same method, the quantitative results of the former paper for higher temperatures have to be dis-

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[9] The apparent reversibility of this "transformation" establishes a certain analogy to the $\alpha\rightarrow\gamma$ and $\gamma\rightarrow\delta$ transformation of Fe which is an almost perfect reversal. Of course these transformations are *not* analogous with respect to the true allotropy of Fe.

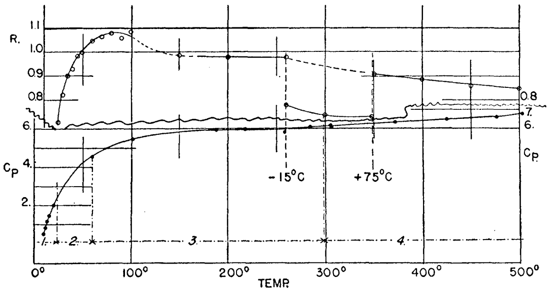

FIG. 4. Lower section: The c_p function of Bi; "*1*" Keesom and van der Ende; "*2*" interpolated; "*3*" Anderson; "*4*" Carpenter and Harle. Upper section: The relative variation of $R=\alpha_{\parallel}/c_p$ for $R_0=3.0$. The dashed line between $-15°$ and $+75°$C indicates R in case of the absence of a "transformation."

carded, probably due to the lack of comparison with other orders and of a sufficient number of readings at different temperatures.

Only four sets of values continue beyond 240°, as Jay's measurement terminated at 150°. The 2 dilatometric values—that of Ho and of Roberts—agree on assigning a decline to $\alpha_{\parallel}$ between 240° and the melting point. However, neither our present values on lattice expansion nor those of Goetz and Hergenrother gave any indication of such a decline. As Buchta and Goetz[3] have shown this anomaly of the dilatometric expansion to be influenced by very small concentrations of foreign atoms in the lattice it appears certain that this anomaly is not a property of the lattice but is caused by those regions of the crystal which do not contribute to the diffraction. (See reference 1.) This is supported by the fact that the anomaly of the temperature function of the integrated intensities begins in the same temperature range as the anomaly of the expansion coefficient.

This, however, leaves Jay's finding of an anomaly of the lattice expansion unsupported.

Finally the relation of our values of the expansion coefficient with the specific heat shall be discussed briefly: The Grüneisen rule postulating $\alpha/c_p=\text{const.}$ (at least for cubic systems) was found by Goetz and Hergenrother to hold remarkably well for their values of the lattice expansion. Since our present values differ considerably from those of the former work and extend over a much larger temperature range—a compilation of the recent c_p values was made which are plotted in the lower section of Fig. 4. The work of three different authors was used, since no measurement extending over the whole of the temperature range is available. Keesom and van der Ende[7] ("*1*") measured from He temperatures to 25° abs., Anderson[10] ("*3*") from 60°–300° and Carpenter and Harle[5] from room temperature to beyond the melting point ("*4*"). Hence the range between 60° and 25° has to be interpolated ("*2*"). Considering the resulting function it is noteworthy that beyond $-15°$C c_p begins to rise with T instead of being constant, although the two "transformation" points are not marked by a discontinuity of c_p. Unfortunately the observations in the range "*4*" are taken over too large intervals of temperature to be decisive about any similar change of dc_p/dT at $+75°$C.

In order to find the relative variation of $\alpha_{\parallel}/c_p$ from constancy, the values of $R=\alpha_{\parallel}/R_0c_p$ are plotted against T. As an approximate *average* value, $R_0=\alpha_{\parallel}/c_p$ was taken as 3.0. A possible systematic variation is indicated by a curve. As a whole this variation amounts to 20–30 percent of R_0, nevertheless the constancy should be considered fair in view of an almost 400 percent variation in c_p and of the uncertainty of the interpolation of c_p in "*2*" and finally of the inaccuracy of the determination of any α value for large $d\alpha/dT$. Thus the validity of the Grüneisen rule as a fair approximation even for the $T<\theta$ region seems to be established. It is obvious that this validity is nonexisting between $-15°$ and 75° due to the absence of a measurable heat of formation. It may be mentioned that the Grüneisen rule would require so large a change in c_p at $-15°$ and $+75°$ that it could not have escaped observation.

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