HEAT CAPACITY OF CaF$_2$ AT LOW TEMPERATURES

by

DONALD R. HUFFMAN

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS

Houston, Texas
May, 1959
TABLE OF CONTENTS

I. Introduction .................. 1

II. Experimental Technique .......... 6
   A. Sample .................. 6
   B. Calorimeter ............... 6
   C. Procedure ................ 8
   D. Measurements .............. 9

III. Analysis of Data ............. 12
   A. Calculation of Specific Heats . 12
   B. Corrections ............... 13

IV. Results ..................... 15

V. Discussion ................... 16

VI. Conclusions .................. 19

Acknowledgments .................. 20

References ...................... 21
Heat Capacity of CaF₂ at Low Temperatures

I. INTRODUCTION

The development of a successful theory for specific heats in solids showed a most important advance in 1912 when the Debye theory\(^1\) was published. The Debye theory considers the atoms of a solid to be coupled together and to vibrate as an elastic continuum, supporting normal vibrations up to a certain maximum frequency. An important feature of this theory was a \(T^3\) dependence of the specific heat on temperature at very low temperatures according to the expression

\[
C_v = \frac{3Nk_b\frac{1}{3} (\frac{T}{\Theta_D})^3}{5}
\]

where \(C_v\) is the specific heat per gram atomic weight, \(N\) is Avagadro's number, \(k\) is the Boltzmann constant, and \(\Theta_D\), the Debye characteristic temperature, is a constant characteristic of the particular solid. In the derivation of formula (1) use is made of the fact that there are \(N\) atoms per gram atomic weight and 3 degrees of freedom per atom to give 3\(N\) degrees of freedom per gram atomic weight. If a substance has a triatomic molecule, as will be considered in this work, there will be 3\(N\) atoms per gram molecular weight and hence 3\(N\) or 9\(N\) degrees of freedom, so that formula (1) will rather be

\[
C_v = \frac{3Nk_b\frac{4}{5} (\frac{T}{\Theta_D})^3}{5}
\]
where \( C_v \) is the specific heat per gram molecular weight. The Debye theory further predicted that the \( T^3 \) dependence should be obeyed to an accuracy of 1\% to a temperature of approximately \( \Theta_D/12 \). This \( T^3 \) dependence at low temperatures differed decidedly from the earlier, successful Einstein theory.

Einstein's model considered all atoms of the solid to vibrate with the same frequency \( \nu \), and with discrete quantities of energy \( (n + \frac{1}{2})\hbar \nu \), \( n \) being an integer, and \( \hbar \) Planck's constant. This gave a specific heat function:

\[
C_v = 3R \left( \frac{\hbar \nu}{kT} \right)^2 \frac{e^{\hbar \nu/kT}}{(e^{\hbar \nu/kT} - 1)^2}
\]

and gave the first correct prediction of the decrease of \( C_v \) to 0 with \( T \) in general, but gave a faster decrease at low temperatures than the later Debye \( T^3 \) relationship.

Early attempts to fit experimental data to the Einstein theory resulted in serious deviations at the low temperature end. The Debye \( T^3 \) law, however, found quick apparent verification in the work of Eucken and Schwers who measured \( C_v \) for flourspar (CaF\(_2\)) and pyrites to as low as 17°K. Calcium fluoride seemed to go as \( T^3 \) from 17° to about 50° or approximately \( \Theta/10 \). The fact that CaF\(_2\) is hardly among the simplest of solids added to the success of the Debye theory.

The complete initial success of the Debye theory was
dimmed slightly by later work which brought out several discrepancies. First, it was found that a single value of $\Theta_D$ would not fit the experimental data at all temperatures, so the custom arose of calculating an effective $\Theta_D$ for each temperature and plotting $\Theta_D$ as a function of temperature. In such a way, $\Theta_D(T)$ is found to be independent of temperature only at low temperatures, often in the liquid helium range, where the true $T^3$ region is reached. Figure 1a displays the data of Eucken and Schwers and Todd for CaF$_2$ plotted in this way. If this data is plotted as $C_V$ vs. $T^3$, as in figure 1b, it appears that the $T^3$ law may be obeyed to about 50 °K. If this were true, the $\Theta_D(T)$ of figure 1a would be temperature independent below 50 °K, and an extrapolation to 0 °K as indicated would be justified to give the value $\Theta_D(0 °K) = 473 °K$.

Another discrepancy between the Debye theory and experiment is the difference observed in the values of the Debye temperature from low temperature specific heats, $\Theta_D$, and those calculated from elastic constants measurements, $\Theta(\text{el.})$. In the $T^3$ region the two should agree. The lack of agreement between the two in some cases where the specific heat has been measured to temperatures less than $\Theta_D/12$, according to a suggestion by Blackman, may be due to the fact that the $T^3$ region has not been reached. Blackman has used the work of Born and Born and von Karman to show that the $T^3$ region may be attained
FIGURE 1A

○ EUCKEN & SCHWERS
× TODD

\( \Theta (^\circ K) \)

TEMPERATURE (\(^\circ K\))
only at values of \( T \) of the order of \( \Theta_D/50 \), varying somewhat from case to case. For calcium fluoride the only elastic constants measurements previously available were at room temperatures and gave a value \( \Theta(\text{el.}) = 510^8 \). This is seen to be significantly different from the specific heat value of \( \Theta_D = 473 \) determined as mentioned previously.

Measurements\(^9,10\) have been made previously at this laboratory on some alkali halide crystals to check the agreement between the \( \Theta_D \) and \( \Theta(\text{el.}) \) at low temperatures and to determine at what temperature the \( T^3 \) region is reached. These measurements and similar work on other crystals elsewhere\(^11,12\) gives the following indications:

1. The two \( \Theta \) values are in good agreement when the \( T^3 \) region is definitely attained.
2. The Blackman criterion for the upper limit for the \( T^3 \) region, \( \Theta_D/50 \) appears to be obeyed rather than the Debye criterion \( \Theta_D/10 \).

In the light of these studies, we have questioned whether or not the \( T^3 \) region was really reached in the specific heat work on \( \text{CaF}_2 \). We have questioned whether the low temperature limit of \( \Theta_D = 473 \ ^0\text{K} \) determined from this data is correct because it does not agree with elastic constant \( \Theta(\text{el.}) = 510 ^0\text{K} \). With reference to figure 1a, this would mean that the \( \Theta_D(T) \) values may not be available at low enough temperatures for a confident extrapolation to \( 0 ^0\text{K} \), although the \( \Theta_D(T) \) appears
to have become temperature independent. Since no low temperature elastic measurements had been made, an accurate comparison of $\Theta_D$ and $\Theta(\text{el.})$ for CaF$_2$ with a possible indication as to whether or not the $T^3$ region had been reached in the specific heat work was not possible. Clearly more data were needed.

For these reasons specific heat measurements have been made on CaF$_2$ from 2.3 °K to 20 °K in the present work. These results are to be compared with elastic constants measurements just completed by Mr. M. Norwood in our laboratories. From a broader viewpoint we would emphasize that the research program, of which these heat capacity studies are an important part, has begun a study of single crystals with a lattice structure slightly different from the simple alkali halides studied previously.
II. EXPERIMENTAL TECHNIQUE

A. Sample

The sample used for these measurements was a single crystal of optically clear CaF$_2$ obtained from the Harshaw Chemical Company. It was cylindrical in shape, about three inches long and one inch in diameter. After a groove was made in one end for embedding the resistance thermometer the mass measured 123.119 grams.

B. Calorimeter

The calorimeter is essentially the same one that was used for previous heat capacity measurements at this laboratory. It employs direct mechanical contact between the salt and the bottom of the brass calorimeter can which is in contact with the liquid helium bath. With provision for raising the salt until hanging freely within the highly evacuated interior of the can, this arrangement circumvents the need for helium exchange gas which might adsorb upon the sample. For very low specific heat values this adsorbed helium could cause a significant error in heat capacity measurements.

Plate 1 is a diagram of the apparatus showing the salt inside the calorimeter hanging freely by threads from a brass supporting plate. This supporting plate is attached to the lowering screw at the room temperature end.
Plate 1

MONEL TUBING

LOWERING SCREW

BELLOWS

"O" RING SEAL

TOP PLATE

ROD TO BELLOWS

SOLDER JOINT

RADIATION SHIELD

SALT

HEATER

DEWAR WALL

KOVAR SEAL

COPPER WIRES

THREADS

CARBON THERMOMETER

BRASS CAN
of the gear by a small stainless steel rod. A Lucite tip on the lower end of the rod helps protect the crystal as it is pressed against the bottom. The lowering screw is mounted on a metal bellows which gives a vacuum tight connection by means of an O-ring to the top of the gear, but still permits enough vertical freedom for the salt to be lowered and raised through approximately one inch. An ion guage and thermocouple guage at the top of the apparatus permit a constant check on the high vacuum part of the gear.

The calorimeter can is made of brass and is about 6 inches long with a 2\(\frac{1}{4}\) inch diameter. A thin-walled monel tube attaches the calorimeter can to the top plate. Low melting point solder is used to seal the can closed at the top so that it may be opened easily without injury to its delicate contents or nearby Kovar seals.

A double Dewar flask arrangement surrounds the calorimeter. The inner flask is attached to the top plate with an O-ring connection, and can be filled with either liquid helium or liquid hydrogen to form a constant temperature bath. By pumping on the contents of the inner Dewar with a National Research Corporation Type 6-S rotary gas ballast pump, temperatures as low as 1.5 °K for helium and 14 °K for hydrogen could be obtained.

Several precautions were taken to minimize heat leaking into the sample. First, the electrical leads were brought through the bath, entering the calorimeter through
individual Kovar seals in its top. A concentric cup radiation shield placed inside the calorimeter at the bottom of the monel tube minimized the radiation reaching the salt. In order to divert the heat leaking down the rod as quickly as possible to the bath, braided copper wire was used to connect the rod and the supporting plate to the calorimeter.

Inside the calorimeter the leads of No. 38 manganin wire were made as long as was considered practical. The leads to the thermometer were about 50 cm in length, but the heater leads were shortened from 50 cm used previously by Scales to 20 cm. This was considered to be a helpful compromise in order to reduce the effect of the troublesome correction due to ohmic heating in the leads, at the cost of very slightly worse thermal isolation of the salt. Due to the very low current through the thermometer circuit, causing a negligible amount of heating, these leads were used at the original length.

C. Procedure

Initial cooling of the calorimeter from room temperature to liquid air temperature was slowed down to at least 8 hours. This was to minimize danger of injuring the Kovar seals, which several times developed minute cracks while undergoing quick temperature changes.

The required high vacuum for thermal isolation of the
crystal was obtained by pumping out the chamber before cooling, then allowing the liquid helium or hydrogen to freeze out the remaining air to a pressure of the order of $10^{-6}$ mm of mercury. Occasionally a diffusion pump was used for the pre-cooling period pump-out, but this was observed to be an unnecessary precaution if the system was perfectly leak free.

Helium was transferred into the inner Dewar using a bottom filling transfer tube mounted so as to extend just below the bottom of the calorimeter. It was rebuilt to permit a snug fit with the tip of the exterior transfer tube and succeeded in correcting a former tendency for the transfer line to become blocked with solid air at this connection during transfer.

Usually, the salt was in contact with the bottom of the calorimeter during helium transfer to allow it to cool more efficiently. From 30 to 40 minutes were required for the salt to reach helium temperatures in this way. Although the salt could be cooled to about $1.5^\circ$ by pumping on the helium bath, a rapid rise in temperature to about $2.4^\circ$ occurred immediately on raising it, thus giving a higher minimum temperature for taking data than was reached with bath contact.

D. Measurements

Temperature measurements were made with a thermometer
consisting of an Allen-Bradley type, 56 ohm, \( \frac{1}{2} \) watt, carbon composition resistor with the ceramic coating ground off. Good thermal contact was insured by embedding it in the salt and covering with a thin coating of red glyptal.

A heater of constantan wire wrapped directly on the salt allowed measurable amounts of heat to be admitted. The heating period was fixed by a small synchronous motor driving a cam to operate a microswitch in the heater circuit. Its period was measured to be 30.83 seconds.

Both heater and thermometer measurements were made using Leeds and Northrup Type K-3 potentiometers. Two such instruments were first used to measure simultaneously the voltage drop across the heater or thermometer and across a standard resistance in the corresponding circuit. It was found, however, that in both circuits the current remained constant enough for an occasional measurement to suffice. Thus one person with one potentiometer and suitable switching circuits was able to take the required data.

The thermometer was calibrated after each run. Helium exchange gas was admitted to the calorimeter to insure good thermal contact of salt and bath. With the vapor pressure of the bath held constant for several minutes to insure thermal equilibrium, thermometer resistance readings were taken to compare with temperatures determined from measuring the vapor pressure with a mercury manometer and
cathetometer. The experimental points were fitted to the following formula suggested by Clement and Quinnell:  

$$\log R + \frac{K}{\log R} = B + \frac{A}{T}$$  

$R$ is the resistance, $T$ the temperature, and $A$, $B$, and $K$ are constants with $K = (\frac{B}{2})^2$. Extrapolation to all intermediate temperatures was then made.

Heat capacity data was taken using the discontinuous heating method. With the specimen hanging freely, the steady drift in temperature was observed. Electrical energy was then admitted to the crystal at a measured rate during the known time. The pre- and post-heating drift curves were then extrapolated to the middle of the heating period. The change in temperature, $T_2 - T_1$, determined in this way, taken to be due to the measured heat input $Q$, gives a heat capacity point $C = \frac{Q}{T_2 - T_1}$.
III. ANALYSIS OF DATA

A. Calculation of Specific Heats

Figure 2 is an example taken from the run of April 1, 1959 to show the type of data taken. The temperature drift of the specimen was followed during a "fore-period" from 2 to 10 minutes long, in which a minimum of 5 temperature-time points were taken. Heat was then admitted for the set time interval with careful note taken of the starting time. The amount of power was regulated to give a rise in temperature of a few hundredths of a degree. Following the heating period the temperature drift was again followed as in the "fore-period".

To obtain the actual temperature rise due only to the measured heat input, the drift curves were extrapolated to the mid-point of the heating cycle, $T_2$ and $T_1$ in the figure. The extrapolations were made by fitting a straight line through the data points as indicated. Although some of the data was analyzed by hand, other points were computed by fitting least squares straight lines to the drift curves and making the other computations on an IBM 650 computer made available through the kindness and generosity of the Shell Development Company.

The heat $Q$ was calculated from the heater current $I$ and the voltage drop across the heater $V$ by the expression

$$Q = V I_{th}$$
FIGURE 2

T (°K)

TIME (MIN)

TYPICAL DATA

HEAT

ON

OFF
where \( t_h \) is the heating period. The specific heat was then calculated from the heat input and the temperature rise.

B. Corrections

Two corrections were considered to be of sufficient size to require adjustment of the specific heat values determined by the above analysis. The first was a correction due to the rather high specific heat of Glyptal at the temperatures used. An approximate formula for the low temperature specific heat of Glyptal due to Pearlman and Keesom is

\[
C_v = 0.22 \, T^2 \times 10^4 \, \text{erg/gm} \, \text{°K}.
\]

From this formula corrections were made to each heat capacity point. At the lowest temperatures, this correction amounted to about 0.7%, decreasing to less than 0.1% at the highest temperatures.

The second correction concerns the heat developed in the manganin leads inside the calorimeter which carry electrical power for heating to the sample. These leads had a resistance of about 0.4 ohm per cm, giving a total resistance of about 16 ohms for the 40 cm of heater leads as compared to 478 ohms for the heater. The heat values \( Q_h \) developed in the heater and \( Q_L \) developed in the leads
are given by

\[ Q_h = I^2 R_h t_h \]

and

\[ Q_L = I^2 R_L t_h \]

where \( R_h \) and \( R_L \) are resistance values for heater and heater leads respectively. Then,

\[ Q_L = \frac{R_L}{R_h} Q_h = \frac{16}{478} Q_h = (0.033) Q_h. \]

If we should make the assumption that half this heat goes into the salt and half into the bath, a 1.67% correction to \( Q \) and hence to the heat capacity would be required. We have, however, taken advantage of the work of Scales\textsuperscript{13}, who has experimentally determined that 19% is more accurately the percentage of lead heating entering the sample. Thus the true \( Q \) to be used in determining a specific heat value is

\[ Q = Q_h + 0.19 Q_L = (1.0063) Q_h. \]

Since the change in heater resistance is only of the order of 1% for the temperature range covered, the resistances and hence the correction for lead heating has been considered to be constant.

The combined effect of these two corrections results in a negligible correction at the lowest temperature due to cancellation; at higher temperatures where the lead heating correction dominates the addition to the heat capacity amounts to about 0.6%. 
IV. RESULTS

Values of the specific heat and the Debye Theta with their corresponding temperatures as determined by this study are tabulated in table 1. The data are displayed graphically in figures 3 and 4 which represent derived quantities. Figure 3 presents the values of $\Theta_D(T)$ obtained from the present work along with some values from previous work mentioned earlier. A difference of 2% to 4% is noted between the lowest temperature points of previous work and our data in the same temperature range. This may not be unreasonable in view of the fact that these lowest temperature points in the work of Eucken and Schwers were subject to a correction of as much as 31.6% for the heat capacity of the addenda to the sample.

From the shape of the curve of figure 1 it is now evident that the earlier extrapolation of the Debye Theta to 0 °K is incorrect, as the curve with the current data added rises to a value over 500, rather than the earlier determined value of 473. For all points below 10°, the values of $\Theta_D$ are seen to cluster about a value that appears to be constant in this temperature interval. An average of these values is taken to be the value at $T = 0$ °K. This value, with the average deviation, is

$$\Theta_D(0 \ °K) = 503.6 \pm 4 \ °K.$$
FIGURE 3

TEMPERATURE (°K)

θ (°K)

PRESENT WORK
EUCKEN & SCHWERS
TODD
<table>
<thead>
<tr>
<th>T(°K)</th>
<th>Θ(°K)</th>
<th>C\textsubscript{V}(cal/mole °K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.820</td>
<td>496.9</td>
<td>.2546 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>2.940</td>
<td>495.6</td>
<td>.2908</td>
</tr>
<tr>
<td>4.455</td>
<td>505.4</td>
<td>.9543</td>
</tr>
<tr>
<td>4.455</td>
<td>497.8</td>
<td>.9988</td>
</tr>
<tr>
<td>4.460</td>
<td>499.3</td>
<td>.9930</td>
</tr>
<tr>
<td>3.617</td>
<td>504.6</td>
<td>.5129</td>
</tr>
<tr>
<td>3.666</td>
<td>500.9</td>
<td>.5460</td>
</tr>
<tr>
<td>3.707</td>
<td>502.2</td>
<td>.5600</td>
</tr>
<tr>
<td>3.735</td>
<td>504.9</td>
<td>.5641</td>
</tr>
<tr>
<td>3.764</td>
<td>508.7</td>
<td>.5851</td>
</tr>
<tr>
<td>3.762</td>
<td>507.8</td>
<td>.5655</td>
</tr>
<tr>
<td>3.785</td>
<td>500.4</td>
<td>.6030</td>
</tr>
<tr>
<td>3.783</td>
<td>511.8</td>
<td>.5765</td>
</tr>
<tr>
<td>3.814</td>
<td>510.9</td>
<td>.5807</td>
</tr>
<tr>
<td>4.000</td>
<td>506.2</td>
<td>.6872</td>
</tr>
<tr>
<td>4.270</td>
<td>501.2</td>
<td>.8613</td>
</tr>
<tr>
<td>7.163</td>
<td>497.4</td>
<td>4.159</td>
</tr>
<tr>
<td>7.591</td>
<td>506.8</td>
<td>4.693</td>
</tr>
<tr>
<td>7.914</td>
<td>505.3</td>
<td>5.351</td>
</tr>
<tr>
<td>8.171</td>
<td>508.8</td>
<td>5.766</td>
</tr>
</tbody>
</table>
TABLE I (continued)

<table>
<thead>
<tr>
<th>$T^{(\circ K)}$</th>
<th>$Q^{(\circ K)}$</th>
<th>$C_v^{(\text{cal/mole}^{\circ K})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.456</td>
<td>499.0</td>
<td>0.04207</td>
</tr>
<tr>
<td>15.838</td>
<td>495.5</td>
<td>0.04550</td>
</tr>
<tr>
<td>15.989</td>
<td>499.2</td>
<td>0.04630</td>
</tr>
<tr>
<td>16.123</td>
<td>497.4</td>
<td>0.04750</td>
</tr>
<tr>
<td>16.556</td>
<td>496.1</td>
<td>0.05170</td>
</tr>
<tr>
<td>16.656</td>
<td>500.3</td>
<td>0.05140</td>
</tr>
<tr>
<td>17.091</td>
<td>498.4</td>
<td>0.05623</td>
</tr>
<tr>
<td>17.658</td>
<td>497.1</td>
<td>0.06202</td>
</tr>
<tr>
<td>17.710</td>
<td>497.6</td>
<td>0.06197</td>
</tr>
<tr>
<td>18.058</td>
<td>496.6</td>
<td>0.06651</td>
</tr>
<tr>
<td>19.014</td>
<td>494.5</td>
<td>0.07920</td>
</tr>
<tr>
<td>20.241</td>
<td>496.6</td>
<td>0.09430</td>
</tr>
</tbody>
</table>
V. DISCUSSION

The fact that the value of the Debye parameter is not independent of temperature below 17.5 °K indicates that the true $T^3$ region had not been reached previously in making heat capacity measurements. Figure 4 uses a method of plotting the data to emphasize the deviations from the $T^3$ law whereby the measured heat capacity, divided by the heat capacity calculated from the $T^3$ law and the $\Theta$ determined above, is plotted as a function of temperature. It is seen that the $T^3$ region is probably not reached above a temperature of 12 to 14 °K. Thus the new implication of this work is that the specific heat of CaF$_2$ does not obey the $T^3$ law to the surprisingly high temperature of $\Theta_D/12$ as concluded earlier, but that it more nearly conforms to the Blackman criterion.

Mr. M.H. Norwood of our laboratories has recently completed measurements to be reported shortly on elastic constants of calcium fluoride from room temperature through liquid helium temperatures. Using the cubic lattice symmetry he calculates two values,

$$\Theta(\text{el.}) = 514.0 \pm 2.5 \, ^°K$$

and

$$\Theta(\text{el.}) = 513.6$$

depending on the type of calculations used. Although
a difference of about 2% still exists between determinations of the Debye temperature by elastic constants and specific heats, the agreement is now quite good.

In the calculations based on elastic constants, it was of interest to note that the CaF$_2$ structure was somewhat different from the NaCl type structure of the alkali halides studied previously at this laboratory. To illustrate this difference, the two structures are sketched in plate 2. The familiar sodium chloride structure can be considered as composed of a face centered cubic lattice of Na$^+$ ions and a similar face centered lattice of Cl$^-$ ions which combine to give a simple cubic lattice with half the lattice spacing of either face centered lattice, with alternating sodium and chlorine atoms on adjacent lattice positions. The slightly more complicated CaF$_2$ structure can be considered as a face centered cubic lattice of calcium atoms with an interlocked, simple cubic lattice of fluorine atoms with half the atomic spacing of the calcium lattice. This gives, therefore, the required twice the number of fluorine atoms as calcium atoms, and results in a Ca$^+$ ion being in the body center of every other fluorine cube. The resulting complete lattice thus has both face centered cubic aspects and body centered cubic aspects, although still possessing cubic symmetry overall.

In view of the fact that CaF$_2$ possesses a more
complicated structure, then, it is gratifying that the θ(el.) calculated in a similar way as is used for the NaCl type lattice is in such good agreement with the θD from specific heat measurements.

The remaining 2% difference bears a noticeable resemblance to the difference observed in similar measurements on LiF10,13, in which the θ(el.) was approximately 2% higher than the specific heat measurements showed. This is of particular interest since two different theories have recently predicted independently just such a difference between values of θ determined in the two ways. The paper by Ludwig17, and the theory of Barron and Morrison18 consider anharmonic terms normally neglected in the crystal potential and in the frequency distribution function to derive the expected difference in θ's. Thus the difference we have observed may be a direct effect of these anharmonic terms.
VI. CONCLUSIONS

The true $T^3$ region has been found in CaF$_2$, and the $\Theta_D$ derived from this is in close agreement with $\Theta(\text{el.})$ from elastic constants data. The triatomic calcium flouride behaves in many ways identical to the alkali halides whose face centered cubic lattice also gave $\Theta_D = \Theta(\text{el.})$ at 0 °K. Thus in spite of the difference in their lattice structure, the cubic symmetry used in the calculation of $\Theta(\text{el.})$ gives the correct value for $\Theta_D$ at 0 °K.
ACKNOWLEDGMENTS

The author wishes to express his thanks to Professor C.F. Squire for suggesting the study and for his continued advice and encouragement throughout its completion.

He also wishes to gratefully acknowledge the advice of Mr. Clarence Belcher concerning the apparatus as well as his assistance in handling the cooling liquids used. Appreciation is expressed to Mr. Mark Norwood for his assistance in using the computer to reduce the data, and to the computing section of the Shell Development Company for the generous use of their IBM 650 computer. A special word of thanks is given to Mr. Tom Adair for many hours of invaluable assistance in taking data.
REFERENCES