LOW TEMPERATURE SPECIFIC HEATS
OF LAYERED LATTICES

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The Debye law which relates specific heat at low temperatures
to $T^3$ was derived on the basis of a three dimensional elastic con-
tinuous medium. Although a large number of solids have been
found to fit this $T^3$ law, many solids have shown "anomalous"
behavior. However, it cannot be expected that the specific heats
of anisotropic solids should agree with a theory based on an
isotropic model. The $T^3$ law has been used extensively to ex-
trapolate specific heats below the lowest measured temperature in
order to obtain entropies. As the entropy at these very low
temperatures is a small portion of the total entropy, this ex-
trapolation has proved satisfactory for most substances. If one
wishes to relate the temperatures dependence of the low tem-
perature specific heats to the structure of the solid, another
approach is required.

Recently, low temperature specific heat equations have been
derived for highly anisotropic substances. The Debye approach
was used but one and two dimensional models replace the three
dimensional model of Debye. It has also been found necessary
to take into consideration interaction between the atoms. We
have measured the specific heats of BN (Dworkin, Sasmor and
Van Artsdalen, 1954) and CdI$_2$ while other investigators have
measured the specific heats of graphite (DeSorbo and Tyler,
1953), gallium (Adams, Johnston and Kerr, 1952), antimony
(DeSorbo, 1953b), selenium (DeSorbo, 1953a), and tellurium
(DeSorbo, 1953d). The low temperature specific heats of these
highly anisotropic substances may be used to check the validity
of these equations.

In the course of our investigations of the thermodynamics of
boron-nitrogen compounds we have measured the heat capacity
of BN from 20°K to 300°K. BN is very similar in structure to
graphite in that it consists of layers of hexagonal rings. The
distance between layers in both substances is more than twice
the distance between atoms within the layers. Low temperature
heat capacity equations have been derived for the graphite type
structure by Gurney (1952) and by Krumhansl and Brooks
(1953).

Gurney has derived a $T^2$ law for graphite using the concept of
a two dimensional lattice in an otherwise conventional Debye

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Science in Oak Ridge, November, 1953.
treatment of low temperature heat capacity. For a monatomic lattice he derives the expression:

$$C_v = 9.6 \, R \left( \frac{T}{\Theta} \right)^2$$  \hspace{1cm} (1)

Krumhansl and Brooks have considered the problem in more detail. With the use of lattice vibration theory they derive the limiting expression for low temperatures:

$$C_v = 14.4 \, R \left( \frac{T}{\Theta} \right)^2$$  \hspace{1cm} (2)

It can be shown that equation (2) can also be derived using the two dimensional approach. Krumhansl and Brooks show this $T^2$ dependence to be an intrinsic property of the layer like lattice and therefore BN and other solids with layered structures as well as graphite should show a departure from the usual Debye $T^3$ law.

DeSorbo and Tyler (1951) have measured the specific heat of graphite down to $13^\circ K$. They find that the $T^2$ dependence of the specific heat is verified from $13^\circ K$ to $54^\circ K$. According to the theory of Krumhansl and Brooks, the specific heat should follow a $T^3$ law at sufficiently low temperatures. Measurements have not been made at low enough temperatures for graphite or any of the other substances to be mentioned to decide this point.

BN (Dworkin, Sasmor and Van Artsdalen, 1953) also obeys the $T^2$ law at low temperatures. When a graph of $C_v$ vs. $T^2$ is made, a straight line is obtained from $20^\circ K$ to $66^\circ K$. This line extrapolates to zero calories at absolute zero. To obtain a value for the two dimensional Debye type characteristic temperature, equation (2) must be modified to account for the fact that BN is diatomic whereas equation (2) is derived for a monatomic substance. The modified equation is:

$$C_v = 14.4aR \left( \frac{T}{\Theta} \right)^2$$  \hspace{1cm} (3)

where $a$ is the number of atoms per molecule. The value of $O$ for BN obtained from equation (3) is $598^\circ K$ with a mean deviation of $\pm 7^\circ K$. ($C_v$ is taken to be equal to $C_p$ at these low temperatures.)

Tarassov (1945, 1946, 1950) also suggested the application to specific heat data of a one and two dimensional frequency distribution function based on a Debye type of continuum model. He applied this anisotropic model to the then existing data for a number of elements and compounds among which were graphite, gallium, arsenic, antimony, bismuth, ferrous chloride, magnesium chloride, and molybdenum sulphide. Most of the data he used, however, extended only as low as $50^\circ K$. At this high temperature no conclusions can be reached concerning a $T^2$ dependence. Since Tarassov's work, the heat capacities of a number of the above substances have been measured down to liquid hydrogen temperatures. Agreement with prediction has been found in some

\[\text{The O is used here to represent the Debye theta.}\]
cases while in others the simple model does not account for the experimental results.

Gallium also has a layered structure. The low temperature heat capacity of gallium has been measured by Adams, Johnston, and Kerr (1952). The $T^2$ dependence from $15^\circ K$ to $34^\circ K$ has been pointed out by DeSorbo (1953c). Such anisotropic substances as antimony, selenium, tellurium, and cadmium iodide have layered or chain structures which are not as pronounced as those in graphite, BN, and gallium. These substances do not follow a $T^2$ or a $T^3$ law. The deviations are explained in terms of an anisotropic continuum theory accounting for the interaction between the layers or chains.

Antimony offers an example of a layered structure for which the anisotropic continuum theory agrees with the measured heat capacities at low temperatures better than does the simple two dimensional theory. Selenium and tellurium are examples of long chain structures for which the anisotropic theory agrees better than does the one dimensional theory. If the log of the heat capacity is plotted against the log of the temperature, a straight line is not obtained at low temperatures but rather a curve with a slope approaching three at the lowest measured temperature. This would seem to indicate that the frequency-distribution function following a one or two dimensional form at the higher temperature is going over to a three dimensional form at the very low temperatures. This would occur if the higher frequencies, which are associated with the strong forces within the layers or chains, become less highly excited at lower temperatures leaving waves of longer wave lengths as the only ones excited. At a sufficiently low temperature, the isotropic three dimensional continuum model should apply to these longer waves. The anisotropic continuum model used by DeSorbo (1953a, 1953b, 1953d) to obtain calculated heat capacities which show good agreement with his measured values for antimony, selenium and tellurium differentiates between these "soft" and "hard" modes of vibration.

Our heat capacity measurements of cadmium iodide show that at $15^\circ K$ not even a $T^2$ dependence has been reached. However, its heat capacity at this temperature is still very high (almost three calories per mole) and it is not unusual for the heat capacity of such heavy molecules to be dropping rapidly with temperature even at temperatures as low as $15^\circ K$. We believe, therefore, that nothing of theoretical significance can be implied from these measurements until the heat capacity is obtained at liquid helium temperatures.

Heat capacity data at liquid helium temperatures is lacking for all of the above mentioned substances. These measurements should be made if one is to investigate further the behavior of the heat capacity of anisotropic solids at low temperatures.
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LITERATURE CITED


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are actively engaged in teaching science in secondary schools, (2) supervisors whose duties include those of working with secondary school science teachers, (3) representatives of departments of education of colleges or other workers in science education at college level whose interest is in college science courses. The course will include lectures, laboratory work, discussions, films, and field work related to the problem of presenting nuclear science in the secondary school program.

At the Medical Units of the University of Tennessee in Memphis, it has been announced that fellowships will be available for the year 1955-56 to assist college graduates in securing advanced training in those fields of biological sciences which are related to medicine. These include Anatomy, Biological Chemistry, Physiology, Pharmacology (effect of drugs on living cells) and Bacteriology. Application blanks for these fellowships may be secured from the Dean of the Graduate School in Memphis.

The Fifth Annual Fisk University Infrared Institute brought scientists from 18 states and 10 foreign countries to Nashville for a week, beginning

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