

HEAT CAPACITY OF THE γ PHASE OF He^4 [†]

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About two years ago Vignos and Fairbank reported a new solid phase, identified as the γ phase, in He^4 ,¹ and soon thereafter Schuch and Mills established that this phase has a body-centered cubic (bcc) structure.² Recently Grilly and Mills established the PVT relations for the transition from the α to the γ phase, and from the α and γ phases to the liquid.³ The α phase in He^4 has an hexagonal close-packed (hcp) structure. Both an hcp and a bcc structure also exist in He^3 , and the heat capacity of both of these phases has been measured by Heltemes and Swenson for this isotope.⁴ The Debye θ of the bcc phase was found to be about 20% smaller than that of the hcp phase at the same density, the isotope effect on θ was observed to be only slightly larger than the $m^{0.5}$ ratio in the hcp phase, and an anomaly of unknown origin was found in the heat capacity of the bcc phase. The work presented here was undertaken primarily to determine if a similar difference in the lattice heat capacity of the two phases also exists in He^4 , to determine the isotope effect in the bcc phase, and to see if a similar anomaly exists in the heat capacity of $\gamma\text{-He}^4$.

Experimental investigations of the properties of the γ phase of He^4 are difficult because of the small volume and temperature range over which this phase exists. In order to measure the heat capacity, temperature increments of (1 or 2) $\times 10^{-3}$ °K had to be used. It was nonetheless possible to obtain a precision of the order of 1% in the heat capacities by using a germanium thermometer which was calibrated against the vapor pressure of He^4 . The sample was introduced into a beryllium-copper container through a stainless steel capillary at 4.2°K. The capillary was then blocked by cooling the bath, to which it was attached, to 1.2°K. Thereafter the sample was cooled by means of a mechanical heat switch.

It is an inherent limitation of this method that only molar volumes less than 20.98 cc are accessible to measurements. For any greater volume there is no freezing in the capillary, and the sample cannot be kept at constant volume. For this reason the data obtained here are limited to the higher density region of the γ phase.

In view of the small range of densities involved in these measurements, it was not possible to make a direct determination of the sample density with meaningful accuracy. Rather the molar volume was inferred from the α -to-liquid or γ -to-liquid transition temperature and the data of Grilly and Mills.³

Some of the experimental results in the α phase and most of the results in the γ phase are presented in Fig. 1. Within experimental accuracy, the Debye θ of the α phase decreases linearly with increasing temperature over the temperature range covered here. The Debye θ of the γ phase is 16.9°K. One set of measurements on the α phase was made at a molar volume of 19.87 cc, at which direct comparison with existing data is possible. The data presented here agree well with those of Keesom and Keesom,⁵ but differ from those of Webb, Wilkinson, and Wilks⁶ by about 12% in the heat capacity. The heat capacity of solid He^4 has also been measured by Dugdale and Simon⁷ and by Heltemes and Swenson.⁴ However, Dugdale and Simon's data are at smaller molar volumes, and comparison is difficult. Heltemes and Swenson's data include the molar volume range studied here, but are supposedly reliable only below 1.1°K. Thus comparison is again not straightforward. Since the θ values reported herein are temperature-dependent and only extend down to 1.3°K or $(T/\theta) \approx 0.052$, an extrapolation to 1.1°K or $(T/\theta) \approx 0.044$ must be made. Comparison with Debye θ values of other substances on which accurate measurements are available over a large temperature range shows that a linear extrapolation in this relative temperature range is not likely to be in error by more than 1 or 2%. This type of extrapolation agrees well with Heltemes and Swenson's data at 20.9 cc/mole, but differs from their data by 4% in θ at 19.87 cc/mole.

In order to compare the Debye θ values of the α and the γ phases at the same molar volume, again an extrapolation is necessary because the two-phase temperature range at constant volume is about 0.2°K. Extrapolation from $(T/\theta) \approx 0.060$ to $(T/\theta) \approx 0.067$ must be made in this case, and again a linear extrapolation for the α phase is not likely to introduce a prohibitive error. This extrapolation yields a difference between the

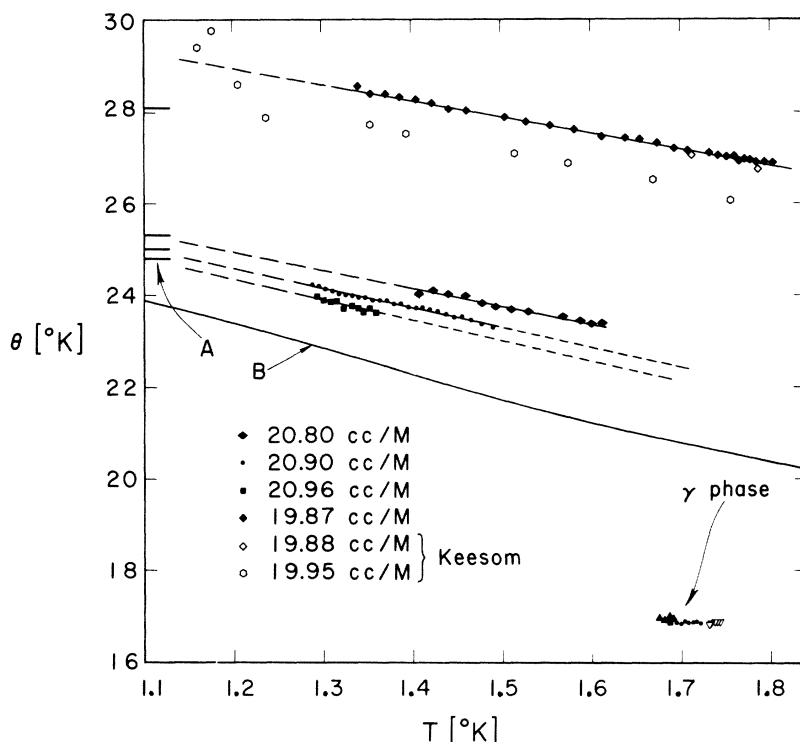


FIG. 1. Debye theta vs temperature for the α and γ phases of solid He^4 . A indicates the values obtained by Heltemes and Swenson for the volumes of He^4 , used in this experiment, and B indicates the Debye θ calculated from Heltemes and Swenson's total heat capacity for bcc He^3 at 20.9 cc/mole.

Debye θ values for the two phases of 24%, which is about the same as that found in He^3 for the phases of the same crystal structures. It therefore appears that the larger lattice heat capacity of the bcc phase is not a peculiarity of He^3 , but rather that it is associated with the structure of the lattice.

Heltemes and Swenson pointed out that the ratio of the Debye θ values for the two isotopes below 1.1°K in the hcp phase is 1.19, which is only slightly higher than $(4/3)^{0.5} = 1.16$. A similar comparison for the bcc phase is difficult because the He^4 γ phase can be investigated only at $(T/\theta) \approx 0.1$, and the data on He^3 refer to relatively much lower temperatures. The temperature dependence of θ in He^4 is not established at all. But again comparison with other solids shows that θ is, in general, close to a minimum at $(T/\theta) \approx 0.1$, and that it is between 8 and 15% lower than at 0°K. One can thus estimate that, if the phase were stable, it would have a Debye θ of 18.4 to 19.9°K at 0°K. Comparison with Heltemes and Swenson's value for bcc He^3 gives a ratio of 1.33 to 1.23 for the Debye θ 's of the two isotopes in the bcc phase. Whereas the un-

certainities in the above comparison are rather large, there is a definite indication that the Debye θ ratio is larger than that indicated by simple theory. A similar effect has been observed in solid hydrogen and deuterium, where the ratio is 1.6 rather than 1.4.⁸ It seems reasonable to attribute the effect to the large anharmonicity due to the large zero-point energy.

An anomalous contribution to the heat capacity of bcc He^4 was not observed in this work. Of course, the existence of an anomaly cannot be ruled out entirely, because of the rather small temperature range over which the phase can be investigated. In bcc He^3 at a molar volume of 20.9 cc, Heltemes and Swenson's data do not in themselves establish the existence of an anomaly. The deviation of the heat capacity from a Debye function can, in this case, be adequately explained in terms of the natural deviation of the Debye θ from a constant value and is indeed quite similar to that found in hcp He^4 at the same volume and Debye θ . Only at much larger molar volume does this deviation become larger than would ordinarily be expected, and there is some support for postulating an anomaly. If there

were an anomalous contribution to the heat capacity in both isotopes, then the isotope effect would be more uncertain, and could be closer to the $m^{0.5}$ value. If one attributes the total heat capacity to the lattice for the bcc phase of both isotopes, then the isotope effect as reflected in the θ ratio at 1.70°K is 1.23, which is still considerably larger than the $m^{0.5}$ ratio. The curve for θ vs T corresponding to Heltemes and Swenson's total heat capacity at 20.9 cc/mole is shown in Fig. 1 for comparison.

At present neither the data on He³ nor those on He⁴ are sufficient to establish clearly the relative magnitudes of possible anomalous and lattice contributions to the heat capacity of the bcc phases of the two isotopes. In He⁴ there is not much hope for improvement because of the natural limitations set by the existence range of the phase. The bcc phase of He³ can perhaps be studied more thoroughly, and one would hope that more precise data over a larger temperature range would shed some light on the problem.

Considerable information was gained during this work on the detailed behavior of He⁴ along the various phase boundaries. In particular, the difference between the λ point in the liquid at the

melting line and the upper triple point was found to be 10×10^{-3} °K, in agreement with Vignos and Fairbank¹ and in disagreement with Grilly and Mills.³ Work on the α - γ two-phase region is still in progress, and a comprehensive report on all the work will be given elsewhere.

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ROTATIONAL MAGNETIC MOMENTS OF DIATOMIC ALKALIS*

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Although the diatomic alkali molecules were among the first studied by the molecular beam resonance method,¹ their rotational magnetic moments have never been measured due to the smallness of the gyromagnetic ratios.

However, recent experiments² have demonstrated that small gyromagnetic ratios can be measured by producing a series of quantum transitions of m_J , which lead to large net changes of magnetic moment, and hence to large deflections. Thus it is now possible to pursue the natural continuation of the original rotational moment measurements with hydrogen,³ since the structure of the diatomic alkalis is similar to that of molecular hydrogen.

The apparatus used is the same molecular beam machine that was constructed in 1950 by Kolsky et al.,⁴ primarily for high-precision studies of H₂, and has subsequently been modified by other

workers.⁵ The ovens are a conventional type made of stainless steel, heated by tantalum coils. The detector is of the surface ionization type, and consists of a 1-mil iridium wire which is heated by passing 80 mA of current through it. The ions formed at the wire are accelerated and sent through a mass spectrometer onto an electron multiplier. The output of the multiplier is passed through a high resistance (10^9 ohms), and the resulting voltage is measured by a sensitive electrometer. Typical beam intensities used in these experiments are on the order of 10^6 molecules/second, corresponding to a signal of several volts.

Two rf coils are used for producing transitions, depending on the resolving power desired. One is a 12-inch coil consisting of 72 turns of water-cooled copper tubing; the second is a 3-inch coil of 250 turns of number 22 copper wire, wound