

Heat Capacity and Entropy of Liquid He³ from 0.23 to 2°K: Nuclear Alignment in Liquid He³††

BERNARD M. ABRAHAM, DARRELL W. OSBORNE, AND
BERNARD WEINSTOCK

Argonne National Laboratory, Lemont, Illinois

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WE have extended our measurements¹ of the heat capacity of liquid He³ to cover the temperature range 0.23 to 2°K, and the results are shown in Fig. 1, along with the values reported by Roberts and Sydoriak.² The data of deVries and Daunt³ have not been included because of their very large scatter. Also shown are calculated curves of C_V for an ideal Fermi-Dirac gas with degeneracy temperatures of 0.45°K (suggested by Fairbank, Ard, and Walters⁴ to fit their susceptibility measurements) and 4.98°K (the Fermi temperature for He³ at the liquid density). A comparison of these curves with the experimental measurements⁵ shows that the ideal Fermi-Dirac gas model is unsatisfactory for liquid He³.

The entropy of liquid He³ between 0.23 and 2°K was calculated from the equation

$$S = 2.52 + \int_{1.5}^T C_{\text{sat}} d \ln T,$$

where the constant 2.52 cal deg⁻¹ mole⁻¹ is the entropy of the liquid at 1.5°K obtained from our vapor pressure data⁶ and from new values of the second virial coefficient⁷ and the liquid density.⁸ The entropy obtained in this way is given in Fig. 2 (curve A), together with the values at 1, 1.5, and 2°K calculated from the vapor

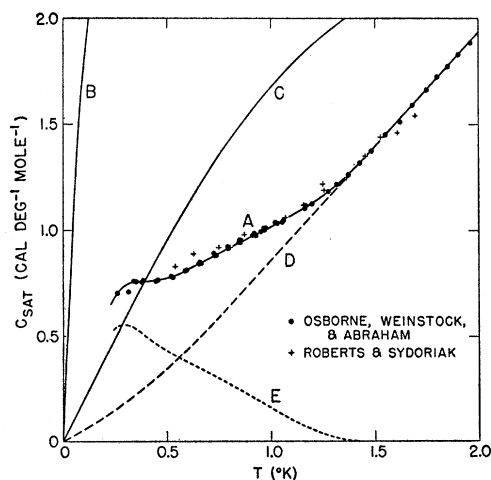


FIG. 1. Heat capacity of liquid He³ at its saturated vapor pressure. (A) Experimental results; (B) and (C), C_V of ideal Fermi-Dirac gas with degeneracy temperatures of 0.45° and 4.98°K, respectively; (D) estimated nonspin heat capacity; (E) estimated spin heat capacity (curve A minus curve D).

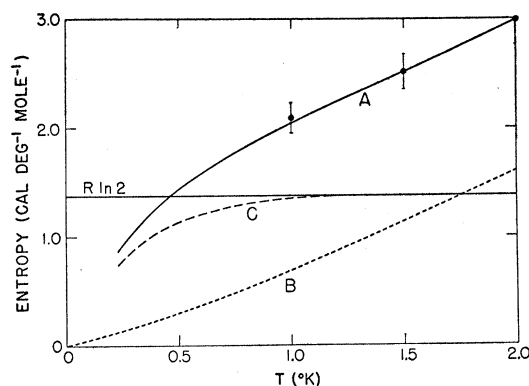


FIG. 2. Entropy of liquid He³. The circles show the entropy calculated from the vapor pressure. Curve A gives the entropy calculated from the heat capacity data and the value 2.52 cal deg⁻¹ mole⁻¹ for the entropy at 1.5°K. (B) Estimated nonspin entropy [from integration of curve D], Fig. 1; (C) estimated spin entropy, S_{spin} , [curve A minus curve B].

pressure. Since there is an estimated uncertainty of 0.17 cal deg⁻¹ mole⁻¹ in the entropy at 1.5°K, the whole entropy curve may have to be shifted up or down when an accurate measurement of the heat of vaporization is obtained.

The entropy at 0.23°K is 0.86 cal deg⁻¹ mole⁻¹, a value significantly smaller than $R \ln 2 = 1.38$ cal deg⁻¹ mole⁻¹, the entropy for random orientation of the nuclear spins. It follows, without any assumption regarding other contributions to the entropy, that the nuclear spins in liquid He³ must be appreciably ordered at this temperature. A similar conclusion was drawn by Roberts and Sydoriak² from their preliminary value of 1.20 cal deg⁻¹ mole⁻¹ for the entropy at 0.4°K.

Fairbank, Ard, and Walters have demonstrated nuclear alignment in liquid He³ more directly by measurement of the nuclear magnetic susceptibility.⁴ In order to make a quantitative comparison between our results and those of Fairbank, Ard, and Walters we have empirically resolved the heat capacity of liquid He³ into two parts, one attributed to the alignment of the nuclear spins and the other to the remaining types of excitation. A striking similarity was noticed between the heat capacity of liquid He⁴ above 2.5°K⁹ and that of liquid He³ above 1.4°K, in that both heat capacities vary linearly with temperature and extrapolate nearly to zero. It seems reasonable to interpret this "high temperature" heat capacity as arising from excitations in which statistics and spin do not play an important role. The linear part of the heat capacity curve was extrapolated to 0°K (Fig. 1, curve D) and was assumed to represent the nonspin contribution to the heat capacity. The difference between this curve and the total heat capacity gives the spin heat capacity, which is plotted in Fig. 1 as curve E. The entropy was resolved by integrating the nonspin heat capacity from 0°K to obtain the nonspin contribution to the entropy (Fig. 2, curve B) and subtracting this from the total

entropy to obtain the spin contribution (Fig. 2, curve C). Actually the extrapolation of the nonspin heat capacity was not strictly linear but rather was curved below 0.75°K so that it would pass through the origin and also would integrate to give $R \ln 2$ for the spin entropy at 1.4°K .

The fraction of the spins which are not aligned was then calculated from the ratio $S_{\text{spin}}/(R \ln 2)$.¹⁰ These values were found to be in satisfactory agreement with the measurements of $\chi T/C$.⁴

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¹ Osborne, Abraham, and Weinstock, Phys. Rev. **94**, 202 (1954).

² T. R. Roberts and S. G. Sydorak, Phys. Rev. **93**, 1418 (1954).

³ G. deVries and J. G. Daunt, Phys. Rev. **92**, 1572 (1953); **93**, 631 (1954).

⁴ Fairbank, Ard, and Walters, Phys. Rev. **95**, 566 (1954).

⁵ Strictly speaking, the difference between C_{sat} and C_V should be taken into account before making this comparison. Although data are not available for a precise calculation of this difference, the correction is in the direction of making the discrepancy even greater than that shown.

⁶ Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950).

⁷ Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).

⁸ E. C. Kerr, Phys. Rev. **96**, 551 (1954).

⁹ W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 212.

¹⁰ L. Goldstein, Phys. Rev. **96**, 1455 (1954), has independently suggested a similar resolution of the heat capacity and entropy of liquid He³ and has presented a theoretical basis for the relation $S_{\text{spin}} = (\chi T/C)R \ln 2$.

Effect of Oxygen Gas on the Photoconductivity of BaO

M. SAKAMOTO, S. KOBAYASHI, AND S. ISHII

Tokyo College of Science, Kagurazaka,
Shinjuku-ku, Tokyo, Japan

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WHEN a barium-oxide coated cathode with a probe electrode, as shown in Fig. 1, is irradiated by ultraviolet light, a remarkably steep peak is observed at about 3.7 ev.^{1,2} The author has proposed that this peak might be due to a level of surface origin, since it was observed only in powders and not in single crystals.² To test this idea, we have observed the change of the photocurrents before and after the breaking of an oxygen ampule, which was inserted in the vacuum

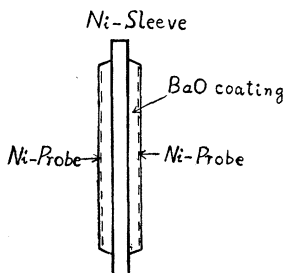


FIG. 1. BaO cathode specimen.

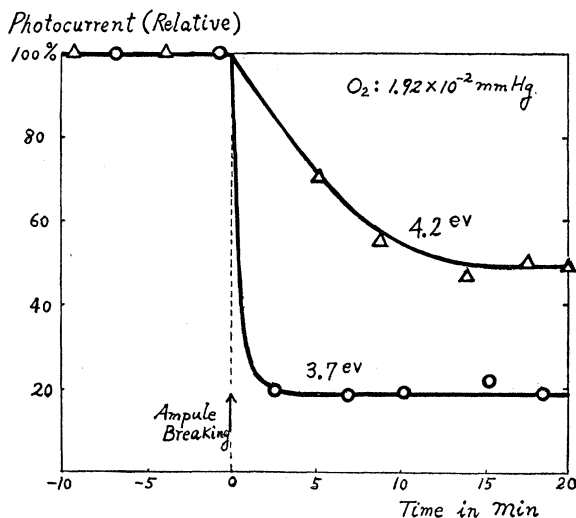


FIG. 2. The effect of oxygen gas on the photoconductivity of BaO. The relative photocurrents are shown to facilitate comparison.

tube. These observations were made especially at the 3.7-ev peak and at the 4.2-ev hump which was thought to be due to the thermal dissociation of the excitons.³ According to the results shown in Fig. 2, the photocurrent at 3.7 ev decreases rapidly with a time constant of several tens of seconds after exposure to the oxygen gas and finally reaches about 20 percent of the initial value. On the other hand, the photocurrent at 4.2 ev decreases slowly with a time constant of about 5 minutes, and the final total decrease is only about 50 percent. The author has repeated this experiment with argon gas, but did not find in this case such a difference in behavior between the 3.7-ev and 4.2-ev photocurrents.

Therefore, the decay phenomena of the two currents are of essentially different types. As one possibility, the decay at 4.2 ev may be interpreted as the scattering of the conduction electrons by the oxygen molecules which diffused into pores existing between the powdered small crystals. The calculated value of the time constant for the simple model shown in Fig. 3 (Knudsen's formula) was reasonable in comparison with the observed value. The decay at 3.7 ev may, on the other hand, be considered as supporting the proposition of a surface level.

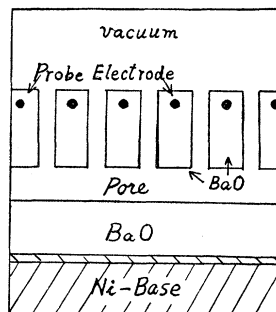


FIG. 3. Simple model for the calculation.