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HEAT CAPACITY OF SMALL PARTICLES OF MgO
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William H. Lien and Norman E. Phillips

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HEAT CAPACITY OF SMALL PARTICLES OF MgO BETWEEN 1.5° AND 4°K*

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

At low temperatures the principal contribution to the heat capacity of dielectric solids comes from the excitation of long wave length lattice vibrations. At liquid helium temperatures the important wave lengths are of the order of 1000 \AA . It follows that the heat capacity at liquid helium temperatures of particles with linear dimensions of 1000 \AA or less must differ considerably from that of macroscopic crystals of the same material. Montroll¹

(1) E. W. Montroll, J. Chem. Phys., 18, 183 (1950)

has given a treatment based on the elastic continuum model and the continuous frequency spectrum approximation. This approximation is valid only for wave lengths which are small compared to the particle size. Jura and Pitzer² have pointed out that for still

(2) G. Jura and K. S. Pitzer, J. Am. Chem. Soc., 74, 6030 (1952)

smaller particles or lower temperatures a contribution from the external degrees of freedom of the individual particles can be expected to be important. They have calculated the heat capacity of a material which has a Debye characteristic temperature of 400°K and which is in the form of cubes 100 \AA on edge. The

calculated heat capacity consists of two contributions: a constant term of $6k$ per particle for the degrees of freedom associated with the motion of the particle as a whole, and a sum of harmonic oscillator functions for the internal degrees of freedom. The two terms are of comparable size at 3°K but the constant term dominates the heat capacity below 1.5°K .

The measurements described here were made on magnesium oxide prepared by the dehydration of magnesium hydroxide at 350°C . Nitrogen adsorption isotherms gave a surface area of $166 \text{ meters}^2/\text{gm}$ corresponding to an edge length of 100 \AA if it is assumed that the particles are in the shape of cubes.

Because of the high surface area it was impractical to use helium exchange gas to obtain thermal equilibrium in the powder and so an experiment was carried out to determine the time necessary for thermal equilibrium without exchange gas. The experiment consisted of introducing heat into the interior of a loosely packed, thermally isolated sample of the powder and observing the temperature changes at the surface of the sample. The surface temperature followed changes in heater power with a time lag of 3 to 5 minutes. This time lag was considerably less than had been expected and has led us to speculate on the possibility that motion of the individual particles may have contributed to heat transport as well as to heat capacity. The thermal conductivity estimated from the equilibrium times is about $5 \times 10^{-8} \text{ watt cm}^{-1} \text{ deg}^{-1}$.

For the heat capacity measurements the powder was sealed in a thin walled copper calorimeter to which was attached a carbon resistance thermometer and a heater. Apart from the time that had to be allowed for the attainment of thermal equilibrium, the experimental method was the same as that which has been described in connection with other measurements³, a more complete account of

(3)

N. E. Phillips, Proceedings of the Fifth International Conference on Low Temperature Physics, Madison Wisc., Aug. 1957 (to be published).

which will appear shortly. Fig. 1 shows the heat capacity C as a plot of C/T^3 vs T . This plot emphasizes the difference between the small particles and macroscopic crystals, for which C/T^3 would be a constant equal to about .003 millijoules mole⁻¹ deg⁻⁴ as estimated from measurements at higher temperatures.^{4,5}

(4)

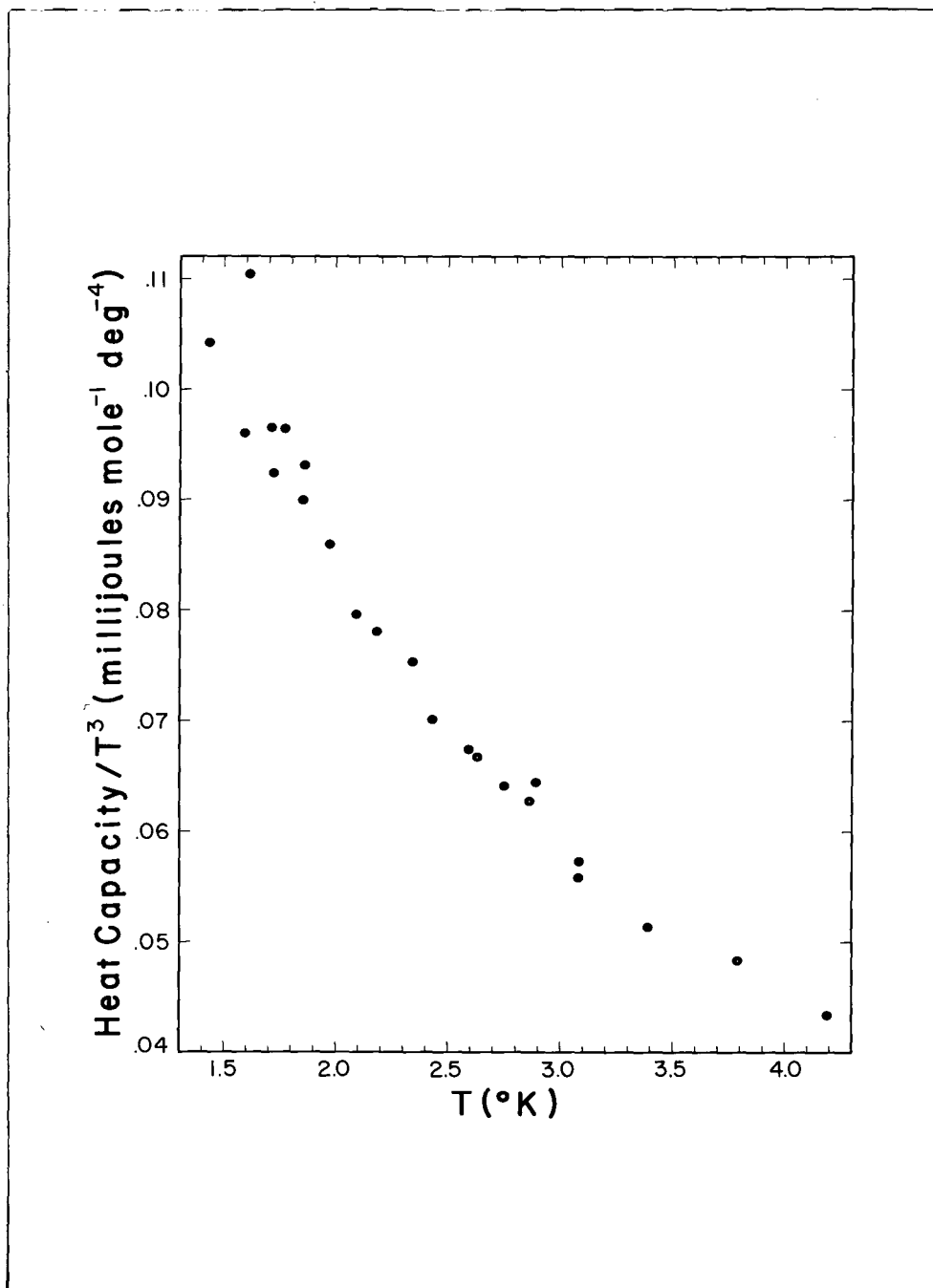
W. F. Giaugue and R. C. Archibald, J.A.C.S. 59, 561 (1937).

(5)

G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926).

Qualitatively the results are consistent with the treatment of Jura and Pitzer in that the heat capacity is appreciably greater than that of macroscopic crystals and shows a slower temperature variation, particularly at the lowest temperatures. The narrow range of temperatures covered by the measurements and the absence of measurements below 1.5° K introduce considerable uncertainty into any estimate of the constant term in the heat capacity but

Figure 1 - Heat Capacity of MgO. The surface area of the sample was 166 meter²/gm



it is possible to fix an upper limit of about one-third of the value calculated for 100 \AA^3 cubes. This discrepancy could be accounted for by the particles having an irregular shape or surface roughness which would lead to an overestimate of their number. In addition, the uncertainty in particle size and shape precludes a quantitative comparison of the temperature dependent part with theory since that part also depends on size and shape.^{1,2}

The measurements are being extended to higher, and to lower temperatures.