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Thermal Anomaly in Anhydrous Copper Sulfate

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IN connection with an investigation of the application of the third law of thermodynamics to paramagnetic substances, measurements have been made of the heat capacity of anhydrous copper sulfate. The heat capacity curve shows an anomalous behavior at low temperatures, exhibiting a maximum at 34.8°K. The data are shown in Fig. 1. The first series of measurements, indicated by solid circles, extended from 15°K to room temperature. In order to investigate more carefully the shape of the curve in the neighborhood of the anomaly, a series of short heat capacity measurements, indicated by open circles, was made between 27 and 41°K. The calorimeter was then cooled to 34°K and a third series, indicated by triangles, was taken. In the last two series each measurement in the anomalous region covered a temperature interval of about 0.6°K. There is no evidence of supercooling in the third series of measurements and in all measurements the resistance thermometer readings after the introduction of energy showed no slowness in the attainment of thermal equilibrium.

The copper sulfate was in the form of a fine powder prepared by dehydrating the hydrated salt at a temperature of 250°C. The measurements were made with a vacuum calorimeter and apparatus similar to that described by Giauque and Archibald.[1]

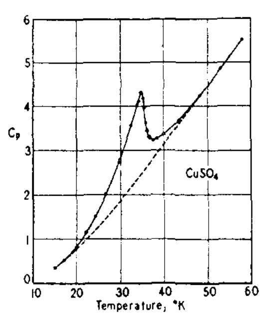

FIG. 1. Heat capacity in cal. deg.$^{-1}$ mole^{-1} of anhydrous copper sulfate.

The magnetic susceptibility of anhydrous copper sulfate has been measured at low temperatures by de Haas and Gorter.[2] The magnetic measurements indicate that at the temperatures of liquid hydrogen the magnetic ions have reached some ordered arrangement corresponding to zero entropy while at higher temperatures they approach a random distribution between the two states available for each ion and so have a magnetic entropy of $R \ln 2$. The hump in the heat capacity curve is associated with the loss of the magnetic entropy. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve, shown by the dotted line in Fig. 1, was drawn. The entropy above the dotted curve is 0.48 cal. deg.$^{-1}$ mole^{-1} rather than $R \ln 2 = 1.377$. Apparently the magnetic entropy increases gradually above 40°K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

Recently Van Vleck[3] has presented a theory of antiferromagnetism in which the magnetic interaction is taken as a Heisenberg exchange coupling favoring antiparallel alignment of the spins. The theory is based on a model similar to that in the Weiss theory of ferromagnetism. According to this model the magnetic heat capacity should rise gradually to a maximum of 2.98 cal. deg.$^{-1}$ mole^{-1} at the Curie temperature and then drop abruptly to zero. At the Curie temperature the complete magnetic entropy of $R \ln 2$ has been acquired. The measured heat capacity curve of copper sulfate does not resemble that calculated for the model used in Van Vleck's theory. The use in the theory of an inner field, vanishing at the Curie temperature, to represent the magnetic interactions is probably the reason for the discrepancy. The entropy calculation mentioned in the last paragraph shows that the magnetic interactions must affect the heat capacity at temperatures well above that of the maximum in the curve.

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[1] Giauque and Archibald, J. Am. Chem. Soc. **59**, 561 (1937).
[2] de Haas and Gorter, Comm. Phys. Lab. Leiden, 215*a* (1931).
[3] Van Vleck, J. Chem. Phys. **9**, 85 (1941).