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RESEARCH OBJECTIVES

The program summary of this group is given in the Quarterly Progress Report of July 15, 1954, page 17.

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A. MEASUREMENT OF THE THERMODYNAMIC EQUATION OF STATE OF PARAMAGNETIC SALTS

The measurements required for determining the properties of potassium chromium alum in the demagnetization region have been completed. Since the entropy is constant in a demagnetization and may be determined in the helium region of temperature, magnetic measurements easily give us $M(B_e, S)$, where M is the magnetization, and B_e is the external field. The thermodynamic temperature, $T(B_e, S)$, is not so easily measured, but this information is needed to complete our knowledge of the thermodynamic properties of the salt.

This information is obtained as follows. We have the magnetic Maxwell relation $(\partial T/\partial B_e)_S = -(\partial M/\partial S)_{B_e}$. The final temperature, T_f , achieved in a demagnetization from temperature T_i and field B_i is then integrated as

$$T_{f} = T_{i} + \int_{0}^{\bullet B_{i}} \left(\frac{\partial M}{\partial S}\right)_{B_{e}} dB_{e}$$
(1)

where the integral is along an isentrope. Since T_f may be quite small compared to T_i , this direct method is quite inaccurate. We use an indirect method based on the well-known property of an ideal paramagnetic (1) that the entropy and magnetization are both functions of B_e/T alone. Then we see that, along an isentrope, the magnetization, M_I , is constant and that the temperature goes to zero in a demagnetization. We define a quantity M_C with respect to the magnetization, M, of the real salt, appearing in Eq. 1, by $M(B_e, S) = M_I(S) - M_C(B_e, S)$. Since an actual salt approaches the behavior of an ideal salt at large fields, M_C approaches zero at large fields. Equation 1 then becomes

$$T_{f} = T_{i} + \int_{0}^{\bullet B_{i}} \frac{d M_{I}}{d B_{e}} d B_{e} - \int_{0}^{\bullet B_{i}} \left(\frac{\partial M_{C}}{\partial S}\right)_{B_{e}} d B_{e}$$
(2)

By the properties of an ideal salt, the first two terms on the right cancel, leaving



Fig. IV-1

Magnetization as a function of magnetic field at different entropies (specified by Curie temperature).

$$T_{f} = -\int_{0}^{\bullet B_{i}} \left(\frac{\partial M_{C}}{\partial S}\right)_{B_{e}} d B_{e} = -\frac{\partial}{\partial S} \int_{0}^{\bullet B_{i}} M_{C} d B_{e}$$
(3)

Values of T at other values of B_e than $B_e = 0$ may then be obtained from Eq. 1 by interchanging the roles of T_f and T_i .

The motivation for the use of Eq. 3 and then Eq. 1 is that theoretical interest is greatest in the region of low fields, where the interactions among the elementary dipoles outweigh that between each one and the external field. It is desirable to investigate the properties of paramagnetic salts at temperatures so low that the dipolar interactions are not masked by thermal agitations. Since such low temperatures are available only through the use of a large magnet, we decided to investigate the applicability of Eq. 3 before this step was taken.

Although the theoretical interpretation is more difficult than for other salts (2), potassium chromium alum was chosen for the paramagnetic sample because a great deal of thermometric work has been done on it. A 7-mm spherical crystal, aligned with a cubic axis along the magnetic field, was demagnetized to approximately 0.07°K. The solenoid described in the Quarterly Progress Report, July 15, 1954, was used. Measurements of the differential susceptibility were made alternately at a given field and at zero field and were continued until the sample warmed up to approximately 0.2°K (about one hour). The zero-field susceptibility, $\chi_0^{}$, was used to determine $T^* = \lambda/\chi_0^{}$, which was used as a measure of the entropy. From time to time the sample was remagnetized to a large field to ensure thermal equilibrium. The constant, λ , was determined from measurements in the helium region of temperature letting $T^* = T$, by the application of Curie's law, with g = 2, J = 3/2. This data sufficed to determine the curves of M vs. B_c at constant S of Fig. IV-1. The entropy is labeled with the value of T^* . An extrapolation carried out for $B_e > 2000$ gauss yielded the values M_{∞} of Table I for $M_{\infty} = M(B_{e} = \infty)$; M_{∞} equated to $M_{I}(S)$ yielded the values of S of Table I and Fig. IV-2. As representative of the values of other workers, obtained by computation of the entropy in the helium region before demagnetization, we give the curves of Ambler and Hudson (3) and of Bleaney (2). Temperature values were computed from Eq. 3. They are plotted against T^{*} in Fig. IV-3. Bleaney's curve is included for reference. His temperatures were computed from T = dQ/dS, where dQ was obtained by gamma ray heating.

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T^{*}	0.10	0.11	0.12	0.13	0.14	0.15	0.16	0.17	0.18
$M_{\infty}/N\beta$	2.221	2.110	2.013	1.926	1.846	1.771	1.700	1.633	1.568
\widetilde{S}/R	0.8176	0.8817	0.9336	0.9766	1.0134	1.0461	1.0748	1.1010	1.1246





Fig. IV-2 Entropy as a function of Curie temperature for potassium chrome alum.

Fig. IV-3

Thermodynamic temperature as a function of Curie temperature for potassium chrome alum.

We note that there is good agreement for the temperature measurements, but not for the entropy measurements. We cannot explain the deviation of our entropy values from those of other workers. Our method of measurement excludes irreversibilities in the magnetizing process. For this reason our entropy cannot be raised. It has been suggested that the g value for this salt might be as low as 1.96 (see ref. 4). This change would only bring our points about 10 per cent closer to those of Ambler and Hudson, although the raising of our points would be greater at the lower entropies. This deviation would tend to make our temperatures agree more closely with those of Bleaney. It is possible that the computation of Ambler and Hudson of the entropy in the helium region is in error because of the lack of understanding of the low-lying energy levels (2). L. D. Jennings, Jr.

References

- 1. C. G. B. Garrett, Magnetic Cooling (Harvard University Press, Cambridge, 1954).
- 2. B. Bleaney, Proc. Roy. Soc. <u>A204</u>, 216 (1950).
- 3. E. Ambler and R. P. Hudson, Phys. Rev. <u>95</u>, 1143 (1954).
- 4. A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. A205, 135 (1951).