APPENDIX I

Target Preparation

Barium carbonate, enriched to 53.7 percent C^{13}, was obtained from the Eastman Kodak Company, Rochester, New York, and was reduced to the elemental form by means of a technique similar to that used by Anderson *et al.*[16] for the production of C^{14} samples.

The barium carbonate was doubly decomposed with lead chloride, to yield carbon dioxide, by prolonged heating at 360°C in a potassium nitrate and sodium nitrate bath. The fine magnesium turnings and cadmium metal catalyst were contained in a stainless steel reaction boat in a stainless steel furnace. The reduction reaction was initiated by flaming the furnace with a gas-oxygen torch and was completed, over a period of several hours, by maintaining the furnace at about 1000°C with an external electric heater.

The resultant mixture of carbon, magnesium oxide, and magnesium metal was treated with boiling concentrated hydrochloric acid, washed, and the filtrate was removed using a sintered glass filter and aspirator. This was repeated three times with concentrated hydrochloric acid and three more times with concentrated nitric acid. The carbon residue was evaporated to dryness, finely ground in an agate mortar, and weighed. An 80 percent recovery efficiency was found; the 20 percent loss was largely mechanical resulting from the difficulty in completely recovering the charge from the furnace and from the considerable handling which followed.

Tantalum foil of 0.003-inch thickness was used as a target backing because of its availability, high Z, and consequent low yield of neutrons from low energy deuteron bombardment. In preparing the C^{13} target it was found that if the fine carbon powder was made into a slurry with benzene and spread evenly on the tantalum, foil it did not crack or separate from the backing when the benzene was slowly removed by evaporation. This method was used to prepare a target of areal density 20 mg/cm². The Be^9 target consisted of a sheet of beryllium metal $\frac{1}{16}$-inch thick. The F^{19} target consisted of a 0.012-inch sheet of Teflon (CF_2).

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[16] Anderson, Arnold, and Libby, Rev. Sci. Instr. **22**, 225 (1951(.

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Properties of the Cr^{+++} Ion in the Paramagnetic Alums at Low Temperatures*

RALPH P. HUDSON
National Bureau of Standards, Washington, D. C.

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Formulas for the entropy and magnetic moment as functions of temperature and magnetic field are derived for the paramagnetic chromic alums at liquid helium temperatures, taking into account the Stark splitting of the magnetic energy levels by the electric field of the crystal lattice. A comparison is made between values of the magnetic moment derived therefrom and the results of recent experimental work on paramagnetic saturation in potassium chromic alum by Henry.

I. INTRODUCTION

In experiments on the magnetic properties of matter below 1°K it is often necessary to calculate the entropy of the paramagnetic salt as a function of external magnetic field at constant temperature, the adiabatic-demagnetization starting temperature. One makes use of the thermodynamic relation $(\partial S/\partial H)_T = (\partial M/\partial T)_H$, whence

$$S = S_0 - S_m = S_{0,T} - S_{H,T} = R\log_e(2J+1) + \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \quad (1)$$

and for M as a function of T and H it is customary to use the Brillouin formula,

$$M = NgJ\mu\left[\frac{2J+1}{2J}\coth\frac{2J+1}{2J}a - \frac{1}{2J}\coth\frac{a}{2J}\right], \quad (2)$$

where $a = gJ\mu H/kT$, the symbols having their usual meanings. Since the orbital quenching is practically complete in the magnetic alums at liquid helium temperatures, we have $J = S = 3/2$ (for Cr^{+++}) and g has the value 2. Combining (1) and (2) we obtain, for Cr^{+++}

$$S/R = x\coth x - 4x\coth 4x + \log_e \sinh 4x - \log_e \sinh x, \quad (3)$$

where

$$x = \mu H/kT.$$

The fact that the ion, in zero field, is not in a $(2J+1)$-fold degenerate state but has its degeneracy partly lifted by the Stark splitting due to the crystalline electric field, is taken into account by correcting S_0 to $S_0 - S_c$. Here, S_c is simply related to the Stark splitting δ, if the temperature is sufficiently high to bring one into the region of the "tail" of the zero-field specific heat curve. Thus, in the case of potassium chromic alum $\delta/k \sim 0.25$ degree,[1] and if $T = 1$°K or higher $C_c/R = \frac{1}{4}(\delta/kT)^2$ and $-S_c/R = -\frac{1}{8}(\delta/kT)^2$. At 1°K, therefore, $-S_c/R = -0.00781$; actually, use of this approximation still introduces a small error, and exact calculation gives 0.00775.

Strictly speaking, however, the application of this correction is valid only up to quite small external fields, such that $\mu H \ll \delta$. In large fields, where $\mu H \gg \delta$, the effect of the Stark splitting is negligible and the

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[1] de Klerk, Steenland, and Gorter, Physica **15**, 649 (1949).

"Brillouin entropy curve" is correct to a high order of accuracy.[2]

In the following, the entropy in a magnetic field at 1°K is calculated taking into account the initial splitting δ and also the magnetic moment as a function of H and T. The latter is of interest in the light of recently reported small deviations from the Brillouin curve in potassium chromic alum, etc.[3]

II. ENERGY LEVELS

The energy levels of the Cr^{+++} ion as a function of magnetic field have been given by Broer:[4]

$$W^4+2\delta W^3+W^2(\delta^2-10\mu^2H^2)-2\delta\cdot W\mu^2H^2(7-6c)+9\mu^4H^4-\delta^2\mu^2H^2(4-3c)=0, \quad (4)$$

where $c=\cos^2\theta$ and θ is the angle between the direction of the field and the trigonal axis. The four Cr^{+++} ions in unit cell have different values of θ for an arbitrary direction of the magnetic field and Eq. (4) only has a simple solution for the case $c=1$. If H is applied along a trigonal axis (111), $c=1$ for one in four ions and $c=1/9$ for the other three; if the magnetic field is applied along a crystal cubic axis (100), $c=1/3$ for all ions. For $c\neq 1$, one can develop W in a power series for the two cases $\mu H\ll\delta$ and $\mu H\gg\delta$,[4] or graphical solutions may be obtained[5] by treating (4) as a quadratic in H^2.

It may be noticed, however, that with $c=1/3$ the pattern of energy levels is symmetrical about a line $W=-\delta/2=-\Delta$. By transferring to the origin $W=-\Delta$, $H=0$, we find

$$W^4-(2\Delta^2+10\mu^2H^2)W^2+\Delta^4-2\Delta^2\mu^2H^2+9\mu^4H^4=0, \quad (4a)$$

and the solutions are

$$\begin{aligned} W_{4,\,1}&=\pm[\Delta^2+5\mu^2H^2+2\mu H(3\Delta^2+4\mu^2H^2)^{\frac{1}{2}}]^{\frac{1}{2}}, \\ W_{3,\,2}&=\pm[\Delta^2+5\mu^2H^2-2\mu H(3\Delta^2+4\mu^2H^2)^{\frac{1}{2}}]^{\frac{1}{2}}. \end{aligned} \quad (5)$$

III. ENTROPY

We take $\delta/k=0.25°$, i.e., $\Delta/k=0.125°$, as derived from specific heat measurements, assuming that this is the unique value of δ (see below). Values of μH (in "degrees") may now be inserted in (5) and the partition function Z may be written down. Making use of the relation $S=Nk(\partial/\partial T)(T\log_eZ)$, we find

$$S/R=\log_e 2\left(\cosh\frac{W_4}{kT}+\cosh\frac{W_3}{kT}\right)-\frac{1}{kT}\cdot\frac{W_4\sinh(W_4/kT)+W_3\sinh(W_3/kT)}{\cosh(W_4/kT)+\cosh(W_3/kT)}. \quad (6)$$

Values of S/R have been calculated for $T=1$°K and μH varying between 0 and 1.5 "degrees" (0–22 kilogauss), and some of these are shown in Table I. The difference S_c/R between the "Brillouin entropy" $(S/R)_B$ and that calculated from (6) decreases steadily as a function of increasing magnetic field, or decreasing entropy. (Over the range of entropy $0.2<(S/R)_B<1.3$ the variation is represented quite closely by the relation

$$S_c/R=0.00574[(S/R)_B-0.046].$$

TABLE I. Entropy for $J=3/2$.

$\mu H/k\cdot 1°$	Brillouin	This paper ($\delta/k=0.25°$)	Difference
0	1.3862_9	1.3785_4	0.0077_5
0.05	1.3800_7	1.3723_6	0.0077_1
0.10	1.3617_1	1.3441_1	0.0076_0
0.20	1.2926_6	1.2854_8	0.0071_8
0.40	1.0717_9	1.0659_2	0.0058_7
0.50	0.9475_4	0.9423_8	0.0051_6
1.00	0.4554_3	0.4530_7	0.0023_6
1.50	0.2081_8	0.2072_1	0.0009_7

IV. MAGNETIC MOMENT

Since we are here concerned with a differentiation of (5) with respect to H $[M=NkT(\partial/\partial H)(\log_eZ)]$, the rather complicated form of these expressions for the energy W_1, etc., results in a somewhat unwieldy final reltion for M as a function of H and T. It is

$$\frac{M}{N\mu}=\frac{\left[\dfrac{5\mu H+A+4\mu^2H^2/A}{W_4}\sinh\dfrac{W_4}{kT}+\dfrac{5\mu H-A-4\mu^2H^2/A}{W_3}\sinh\dfrac{W_3}{kT}\right]}{\cosh(W_4/kT)+\cosh(W_3/kT)}, \quad (7)$$

where $A=(3\Delta^2+4\mu^2H^2)^{\frac{1}{2}}$.

The labor of calculation is much reduced again, however, by choosing "simple" values of μH and also by making use of some of the computation already made in III.

In Table II we list corresponding values of $M/N\mu$ for the Brillouin treatment and for the above method, calculated for a temperature of 1°K. Since the modified formula (7) is not a simple function of H/T, we have also calculated $M/N\mu$ in a few cases for 2°K. It may be seen that the deviations from the Brillouin curve are very small, e.g., a maximum of -0.2 percent at $\mu H/kT=0.10$, and the deviations are considerably smaller for 2°K than for 1°K.

V. SUSCEPTIBILITY

For very small magnetic fields, such that $\mu H\ll kT$, the Brillouin formula reduces to an expression of

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[2] Casimir, de Haas, and de Klerk, Physica **6**, 365 (1939).

[3] W. E. Henry, Phys. Rev. **85**, 487 (1952); Phys. Rev. **87**, 229 (1952).

[4] L. J. F. Broer, Physica **9**, 547 (1942).

[5] D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) **204**, 193 (1950).

TABLE II. Magnetic moment for $J=3/2$.

$M/N\mu$ $\mu H/kT$	Brillouin	This paper $T=1°\mathrm{K}$	$(\delta/k=0.25°)$ $T=2°\mathrm{K}$
0.05	0.2493_0	0.2487_8	0.2491_8
0.10	0.4944_2	0.4934_3	0.4941_6
0.20	0.9572_7	0.9553_9	0.9568_1
0.40	1.7080_2	1.7050_9	···
0.50	1.9853_1	1.9821_1	1.9845_0
1.00	2.6896_5	2.6868_1	···
1.50	2.8952_6	2.8932_4	···

Curie's law $\chi_0=M/H=a/T$, where a is the Curie constant. Specifically, $\chi_0=N\mu^2g^2J(J+1)/3kT$ and for $J=3/2$, $g=2$ we have $\chi_0=5N\mu^2/kT$. The effect of the crystalline field splitting δ is to cause deviations from the Curie law (unless $T\gg\delta/k$), and this has been studied in detail by Hebb and Purcell[6] for the temperature range below 1°K. Taking H to be of the order of a few oersteds or less and assuming $\delta\ll kT$, we may expand the hyperbolic functions in (7) and approximate to obtain the result

$$\chi_0\approx(5N\mu^2/kT)[1-\delta^2/30T^2]. \tag{8}$$

The same expression may be derived as a high temperature approximation of the pertinent Hebb and Purcell formula.

The expressions for the magnetic moment in the foregoing take no account of the magnetic coupling between ions which reinforces the aligning effect of the external magnetic field. Thus H (above) is to be taken as the field acting upon the ions and this may be derived from the external field by correcting for the interaction and for the demagnetizing effect of the shape of the specimen.

VI. DISCUSSION

In measurements of the magnetic saturation curve of potassium chromic alum at liquid helium temperatures Henry[3] finds deviations from the Brillouin curve (up to three percent) over a wide range of H/T values. The experimental points lie below the Brillouin curve between $H/T=3000$ and about 16,000 gauss/degree (corresponding to $\mu H/kT$ values between 0.2 and 1.1), and the deviation apparently becomes greater as the temperature of measurement increases. Henry suggests that the cause of the deviations is the interaction of the crystalline electric field with the paramagnetic ions, but the aforementioned treatment indicates that the deviations to be expected from this cause are much smaller than are found experimentally; in any case, they should be smaller at higher temperatures, for a given value of H/T.

In deriving Eqs. (6) and (7) we have made the simplifying assumption of a unique value of δ, the crystalline-field Stark splitting of the ground state of the Cr^{+++} ion. In the potassium alum, however, paramagnetic resonance spectra[7] indicate that below 160°K two splittings of 0.27 cm^{-1} and 0.15 cm^{-1} (0.38 and 0.21 degree) are found, but no simple division of the ions into two groups each having one or other of these two possible splittings can explain both the shape of the tail of the specific heat curve and the spectrum intensities. The former might be accounted for by ascribing the smaller splitting to 85 percent of the ions, but the latter require roughly equal proportions.[7] Until this problem is resolved one can only seek the best approximation in the calculation of the magnetic moment by making the assumption of a single splitting, the value of which is derived from the specific heat measurements. [The variation of the calculated magnetic moment with δ may be demonstrated by using the formula derived above to find what would be the effect of all the ions having the larger splitting (0.38 degree), and it is found that even then the deviations would be quite small. Thus for 1°K and $\mu H/k=0.1$ and 0.5 degree, the corresponding values of $M/N\mu$ are 0.4886_6 and 1.9731_0, or deviations of, respectively, 1.2 percent and 0.6 percent from the corresponding points on the Brillouin curve.]

A much more desirable situation obtains in the case of the chromic alums of caesium, rubidium, and methylamine inasmuch as these alums exhibit only one splitting at low temperatures.[8] For these substances, Eqs. (6) and (7) would apply more rigorously and permit one to examine the corresponding experimental results more critically. (The experiments should be made preferably upon a single crystal and with the magnetic field along a cubic axis. In this case the energy level pattern is the same for all ions, and it is this case which is treated above.) There remain to be discussed, of course, the deviations from the "ideal curves" to be expected as a result of other interaction effects such as magnetic dipole-dipole and exchange (or "super exchange") coupling between the ions, although these effects are presumably very much smaller than that due to the action of the crystalline electric field, at the temperatures considered.

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[6] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 338 (1937).

[7] B. Bleaney, Proc. Roy. Soc. (London) **204**, 213 (1950).

[8] B. Bleaney, Proc. Roy. Soc. (London) **204**, 222 (1950).