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- Lipson, H. 1935 *Proc. Roy. Soc. A*, **151**, 347.
Lipson, H. & Beevers, C. A. 1935 *Proc. Roy. Soc. A*, **148**, 664.
Pryce, M. H. L. & Stevens, K. W. H. 1950 *Proc. Phys. Soc. A*, **63**, 36.
Spedding, F. H. & Nutting, G. C. 1934 *J. Chem. Phys.* **2**, 421.
Starr, C. 1941 *Phys. Rev.* **60**, 241.
Van Vleck, J. H. 1939 *J. Chem. Phys.* **7**, 61.
Van Vleck, J. H. 1940 *Phys. Rev.* **57**, 426.
Van Vleck, J. H. 1948 *Phys. Rev.* **74**, 1168.
Weiss, P. A., Whitmer, C. A., Torrey, H. C. & Hsiang, J. S. 1947 *Phys. Rev.* **72**, 975.
Whitmer, C. A., Weidner, R. T., Hsiang, J. S. & Weiss, P. A. 1948 *Phys. Rev.* **74**, 1478.

Thermal properties of potassium chromic alum between 0.05 and 1°K

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The entropy, specific heat and magnetic temperature (reciprocal of the susceptibility) of potassium chromic alum are measured as functions of the absolute temperature between 0.05 and 1° K. Their interpretation in the light of paramagnetic resonance measurements (preceding paper) is discussed.

1. INTRODUCTION

In 1938–9 the author carried out a series of measurements on the thermal properties of potassium chromic alum below 1° K, no detailed account of which has been published, though the results have been quoted on a number of occasions (Van Vleck 1940; Cooke 1949). The method of paramagnetic resonance gives an independent determination of the splitting parameters involved in the interpretation of the low temperature measurements, and it seemed of interest to discuss the latter in the light of the results reported in the preceding paper (Bleaney 1950). Moreover, de Klerk, Steenland & Gorter (1949) have recently published a far-reaching investigation of the thermal and magnetic properties of this substance in the region below 0.05° K, to which the author's results are complementary. The latter are presented below, without further excuse for their publication.

2. THE EXPERIMENTS

A very full account of the experimental technique used in these measurements has already been published by Hull (1947), so that only a brief outline is required here.

The sample consisted of an ellipsoid of powdered alum compressed to within 3 or 4 % of the crystalline density, suspended in a chamber surrounded by liquid helium at 1° K. The mode of suspension is shown in figure 1 of Hull (1947). The ratio, length to diameter, of the ellipsoid was 4:1 and its weight was 4.06 g.

The magnetic temperature was measured by a mutual inductance method, the reversal of a known current in the primary coil producing a ballistic throw in a galvanometer connected to a secondary coil. The magnetic temperature was reduced to that appropriate to a sphere, T^* , the correction constant being 0.022°K . The magnetic thermometer was calibrated against the helium vapour pressure curve of Schmidt & Keesom (1937). Below 1.6°K deviations were observed owing to the error in this curve, which led to the recalculation and measurement of the vapour pressure curve (Bleaney & Simon 1939; Bleaney & Hull 1941). This region was therefore not used in calibrating the magnetic thermometer.

Briefly, the method consists of three parts:

(a) the establishment of an entropy $-T^*$ curve by a series of demagnetizations from known fields and temperatures of about 1°K , the entropy being calculated from the theory for a free spin of $\frac{3}{2}$;

(b) the establishment of a 'magnetic specific heat' or C^*-T^* curve, using gamma-ray heating. Typical details have been given by Hull (1947);

(c) the absolute temperature for a given T^* is calculated from the relation

$$T = \left(\frac{\partial Q}{\partial T^*} \right)_{H=0} / \left(\frac{\partial S}{\partial T^*} \right)_{H=0} = C^* / \left(\frac{\partial S}{\partial T^*} \right)_{H=0}.$$

Since with gamma-ray heating the value of C^* is known only in arbitrary units, the same is true also of T . The appropriate reduction factor is obtained by setting the limit of T/T^* , which tends to a constant value at temperatures approaching 1°K , equal to unity.

When the relation between T^* and T has been obtained, the entropy and specific heat curves may be reduced to functions of the thermodynamic temperature T . The lowest value of T^* reached was 0.0616°K , by demagnetization from a field of 13.0 kG at 1°K . The method of Kurti, Lainé, Rollin & Simon (1936) was used to test for ferromagnetic remanence, no trace of which was found. De Klerk *et al.* (1949) have since found that remanence appears only below $T^* = 0.03^\circ (0.004^\circ \text{K})$.

3. THE ENTROPY

The results of a number of demagnetizations are shown in table 1. Here H_e is the external field, H_o the combined Lorentz and demagnetizing field, and $H_e - H_o = H_i$ the actual field acting on the paramagnetic ions. All fields are expressed in kilogauss. Here T_i is the temperature at magnetization,† and T^* the temperature reached after demagnetization, corrected for any thermal drift.

To construct a smoothed curve of entropy against T^* , use is made of the fact that the quantity $\alpha = H_i T^* / T_i$ remains fairly constant over a wide range of values of H_i / T_i for this substance. The values of α shown in the last column of table 1 have been plotted against T^* and from the best curve through these points an entropy $-T^*$ curve has been constructed. Values of $(\log_e 4 - S/R)$ are given in table 2, that for 1°K in zero field being taken as $\log_e 4 - 0.008$, where the correction 0.008 represents

† T_i is measured by the magnetic thermometer, and strictly should be written T_i^* . The deviation from the absolute temperature is small (*ca.* 0.003°K) and is neglected.

the decrease in S/R due to the crystalline splitting, calculated from the inverse square law for the specific heat (see §5 below). The contribution of the lattice vibrations at 1°K to S/R is about 10^{-4} , and has been neglected.

In the first column of table 2 is given the value of $y = H_i/T_i$; that is, the field required to reach the temperature T^* by demagnetization from 1°K exactly.

TABLE 1

T_i ($^\circ\text{K}$)	T^* ($^\circ\text{K}$)	H_o (kG)	H_o (kG)	H_i (kG)	α (kG)
0.983	0.591	1.211	0.013	1.198	0.72
0.977	0.461	1.694	0.019	1.675	0.79
0.970	0.340	2.38	0.026	2.35	0.82
0.972	0.264	3.18	0.035	3.14	0.85
0.973	0.214	3.80	0.040	3.76	0.83
0.975	0.147	5.59	0.055	5.53	0.84
0.976	0.129	6.45	0.062	6.39	0.84
0.966	0.112	7.29	0.066	7.22	0.84
0.961	0.1038	8.04	0.070	7.97	0.86
0.963	0.0845	9.39	0.08	9.31	0.82
0.970	0.0815	9.70	0.08	9.62	0.81
0.977	0.0762	10.45	0.08	10.37	0.81
0.984	0.0725	11.30	0.08	11.22	0.83
1.064	0.0754	11.77	0.08	11.69	0.83

TABLE 2

$y = H_i/T_i$	T^*	$\log_e 4 - S/R$	$y = H_i/T_i$	T^*	$\log_e 4 - S/R$
0	1.000	0.008	7.0	0.119	0.410
2.5	0.341	0.075	7.5	0.112	0.452
3.0	0.279	0.104	8.0	0.105	0.493
3.5	0.239	0.134	8.5	0.0984	0.533
4.0	0.209	0.166	9.0	0.0920	0.573
4.5	0.186	0.203	9.5	0.0871	0.611
5.0	0.167	0.242	10.0	0.0828	0.647
5.5	0.152	0.284	10.5	0.0782	0.685
6.0	0.139	0.326	11.0	0.0746	0.720
6.5	0.129	0.370			

4. THE THERMODYNAMIC TEMPERATURES

The fact that α remains practically constant from 0.3° down to $0.09^\circ (T^*)$ is of great convenience in calculating the absolute temperature. In the equation

$$T = C^* / \left(\frac{\partial S}{\partial T^*} \right)_{H=0}, \tag{1}$$

the determination of dS/dT^* from the $S-T^*$ curve by a graphical method does not permit of great accuracy. From the relation

$$y = H_i/T_i = \alpha/T^*, \tag{2}$$

we have

$$\begin{aligned} \frac{\partial S}{\partial T^*} &= \frac{\partial S}{\partial y} \frac{\partial y}{\partial T^*} \\ &= \frac{\partial S}{\partial y} \left[\frac{1}{T^*} \frac{d\alpha}{dT^*} - \frac{\alpha}{T^{*2}} \right]. \end{aligned}$$

Hence

$$\frac{T}{T^*} = \frac{C^*}{\frac{\partial S}{\partial y} \left[\frac{d\alpha}{dT^*} - \frac{\alpha}{T^*} \right]} \quad (3)$$

When α is constant

$$\frac{T}{T^*} = -\frac{C^*}{\frac{\alpha}{T^*} \frac{dS}{dy}} = -\frac{C^*}{y \frac{\partial S}{\partial y}} \quad (4)$$

The formula (4) is very convenient to work with; for a given value of y , the corresponding T^* is obtained from table 2; the value of C^* is given by the gamma-ray heating experiment and dS/dy is calculated from the theoretical magnetization curve. Below 0.1°K $d\alpha/dT^*$ is not negligible and formula (3) is used, the value of $d\alpha/dT^*$ being taken from the $\alpha-T^*$ curve. Above 0.3°K α begins to vary rapidly, for equation (2) shows that it must fall to zero for $H_i = 0$ and $T^* = T_i$; $d\alpha/dT$ thus becomes of the same order as α/T . A $Q-S$ curve has therefore been constructed in this region, from which the absolute temperature is obtained by differentiating; the values so obtained are in good agreement with those obtained by using formula (3). The values of T^* for values of T throughout the range of experiments are shown in column (2) of table 3.

TABLE 3

T	T^*	C/R (exp.)	$\log_e 4-S/R$	T	T^*	C/R (exp.)	$\log_e 4-S/R$
1.000	1.000	0.0160	0.008	0.180	0.195	0.296	0.187
0.600	0.604	0.042	0.022	0.160	0.174	0.325	0.226
0.480	0.485	0.064	0.034	0.140	0.156	0.350	0.271
0.400	0.406	0.089	0.047	0.120	0.138	0.374	0.329
0.360	0.368	0.108	0.057	0.100	0.121	0.391	0.404
0.320	0.330	0.130	0.072	0.080	0.103	0.40	0.503
0.280	0.291	0.163	0.091	0.060	0.086	0.39	0.616
0.240	0.252	0.206	0.120	0.050	0.079	0.36	0.682
0.200	0.215	0.266	0.158	0.045	0.075	0.33	0.720

A discussion of these results and their comparison with theory of Hebb & Purcell (1937) has already been published by Cooke (1949). Figure 5 of Cooke's paper shows the fractional deviation of T^* from T , together with the theoretical curves based on three different methods of allowing for the magnetic interaction between the ions. This figure shows that either the Onsager method or the Gaussian method of Van Vleck gives a reasonable interpretation of the experimental results down to 0.05°K , while the Lorentz method is decidedly worse. It may be pointed out in this connexion that the calculation assumes a value 0.24°K for the crystalline splitting δ (see below) which is not supported by paramagnetic resonance experiments. Nevertheless, a very large change in δ would be required to bring the Lorentz curve into agreement with experiment, and the maximum ratio of T^* to T allowed by it is 1.67. De Klerk, Steenland & Gorter (1949) find that T^*/T approaches 10 at lower temperatures. The Onsager formula predicts a minimum value for T^* of 0.063° ; the Leiden measurements give a minimum value of 0.037° .

5. THE ABSOLUTE SPECIFIC HEAT

To convert the C^*-T^* curve into a $C-T$ curve, the values of both T^* and dT^*/dT for various values of T were obtained from the T^*-T relation. In figure 1 C/R is shown as a function of T below 0.25°K (curve A); the author's measurements extend down to 0.045°K and are joined by the broken line to meet the measured values of de Klerk *et al.* below 0.03°K (curve B).

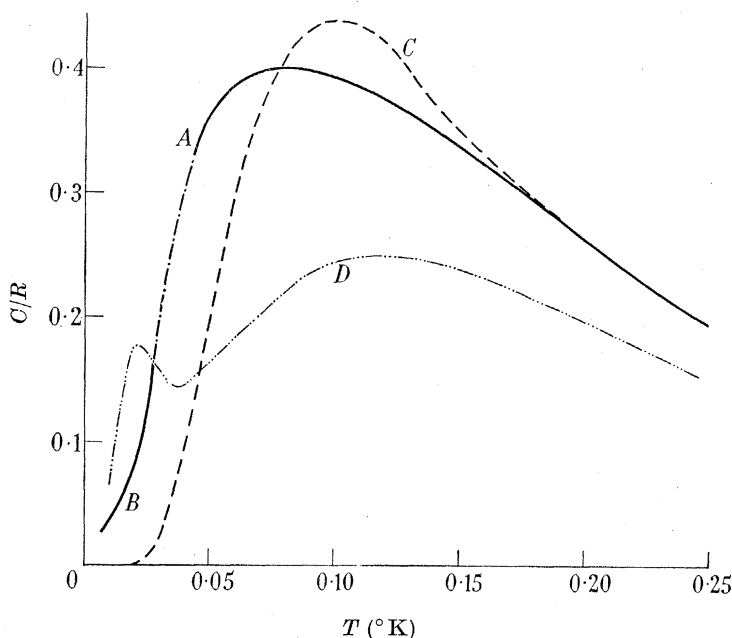


FIGURE 1. The absolute specific heat of potassium chrome alum. A , experimental curve (this paper). B , experimental curve (de Klerk *et al.*). C , calculated curve for splitting $\delta = 0.245^\circ$. D , calculated curve for mixture of splittings (see text).

Above 0.6°K the specific heat obeys the law $CT^2/R = \text{constant} = 0.0160$. From this one can obtain the splitting δ , making the usual assumption that all ions have the same splitting. From Hebb & Purcell (1937)

$$CT^2/R = 2.40\tau^2 + \frac{1}{4}\delta^2,$$

where the first term arises from the spin-spin interaction, and the second from the crystalline splitting. Taking the theoretical value of 0.0204°K for τ , one finds $\delta = 0.245 \pm 0.004^\circ\text{K} = 0.170 \pm 0.003\text{cm.}^{-1}$. This is in reasonable agreement with de Klerk *et al.*, who find 0.25°K , by correcting their $S-T^*$ curve to an $S-T$ curve using the formulae of Hebb & Purcell. (de Klerk *et al.* refer several times to the theoretical relation of Hebb & Purcell without stating which of the three methods of allowing for the magnetic interaction is applied; from figure 3 of their paper it appears that they intend always the Lorentz method.) In a previous set of measurements Casimir, de Klerk & Polder (1940) found $\delta = 0.26_3^\circ\text{K}$, and it has been suggested that the difference between this and the later Leiden measurements is real, and that the value of δ may vary with the origin of the salt.

The value of CT^2/R has been determined by a number of workers using the method of paramagnetic relaxation. The values deduced for the splitting using the same assumption as above are given in table 4. In this table the first section contains the paramagnetic relaxation measurements, the second the adiabatic demagnetization measurements, and the last the splittings determined directly from the paramagnetic resonance spectrum.

TABLE 4

method	temperature (° K)	splitting		authors
		(° K)	(cm. ⁻¹)	
paramagnetic relaxation	77 and 90	0.243	0.169	Broer (1947)
	77 and 90	0.243	0.169	Gorter, Dijkstra & van Paemel (1942)
	77	0.231	0.161	Starr (1941)
	2	0.260	0.181	Casimir, Bijl & du Pré (1941)
adiabatic demagnetization	below 1°	0.270	0.188	Casimir, de Haas & de Klerk (1939)
	„	0.263	0.183	Casimir, de Klerk & Polder (1940)
	„	0.251	0.175	de Klerk, Steenland & Gorter (1949)
	„	0.245	0.170	Bleaney (this paper)
paramagnetic resonance	20°	{ 0.388	{ 0.270 }	Bleaney (1950)
		{ 0.22	{ 0.15 }	

In the figure the theoretical specific heat curve calculated from the theory of Hebb & Purcell for a splitting of 0.245° K is shown in figure 1, curve *C*. It will be seen that near and below the maximum the experimental curve departs markedly from the theoretical. This is not surprising in view of the presence of two splittings reported in the preceding paper. It was pointed out there that the assumption that different sets of ions have different splittings also leads to difficulties. The first assumption, that only 15 % of the ions have $\delta = 0.388^\circ \text{K}$ and the other 85 % $\delta = 0.22^\circ \text{K}$, leads to a specific heat curve hardly different from that in the figure for a single splitting of 0.245° K, as well as being at variance with the intensity ratios in the paramagnetic resonance spectrum. The other assumption, that 30 % have 0.388° K, 30 % have 0.22° K and the remainder a small splitting of 0.05° K gives curve *D* in figure 1. It is clear that any distribution of splittings between different percentages of ions which can be arranged to give the spread in the experimental specific heat anomaly will give too low a value near the maximum. This can be seen more clearly from a consideration of the entropy curve, where de Klerk *et al.* find a plateau, not at $S/R = \log 2$, but about half this value. This requires that some of the entropy corresponding to the Kramers' degeneracy is also removed in passing down through the anomaly. The suggestion of a hyperfine splitting in the 9 % abundant ^{53}Cr isotope has been considered in the preceding paper, where it was pointed out that the paramagnetic resonance spectrum could not be explained by such an effect. Here it may be pointed out that the hyperfine structure would have to be of the same order as the crystalline electronic splitting to cause a material shift in the position of the entropy plateau. Although the observed *hfs* in vanadium is of this order, it seems unlikely to be so large in chromium, for ^{51}V has a very large magnetic moment,† and

† Paramagnetic resonance measurements by Ingram, Scovil and the author show conclusively that the nuclear spin of ^{51}V , hitherto slightly doubtful, is $\frac{7}{2}$. The magnetic moment is therefore 5.15 nuclear magnetons, as calculated by Knight & Cohen (1949) on this assumption.

that of ^{53}Cr , which has an even atomic number, is probably much smaller. Moreover the nuclear spin of ^{53}Cr would have to be enormous, owing to its low abundance, in order to account for the shift in the entropy plateau of the salt as a whole. For these reasons it seems extremely improbable that the shift is due to a hyperfine structure.

6. CONCLUSION

Potassium chromic alum has long been regarded as one of the simpler and more desirable substances for use in experiments below 1°K . Exchange interaction between the paramagnetic ions was expected to be small, and the presumption of only a single crystalline splitting seemed to make the theoretical interpretation of the results relatively simple. In this paper the author has attempted to show that the information obtained from adiabatic demagnetization and paramagnetic resonance investigations is consistent with none of the simple explanations advanced, nor is it easy to reconcile one set of results with the other. It is a great pity that this alum and the chromic ammonium alum appear to be the only substances so far which cannot be investigated by paramagnetic resonance when highly diluted with the corresponding isomorphous diamagnetic substance (aluminium alum). Otherwise, one may confidently anticipate that a great deal more detailed information would have been obtained which might have afforded a clue to this problem.

For work below 1°K , the paramagnetic resonance measurements suggest that the chromic alums of rubidium, caesium and methylamine would offer the best comparison with the theoretical work of Hebb & Purcell, since they appear to have only one splitting. The methylamine alum which is inexpensive and easy to grow in the form of large crystals, seems to be the most suitable. Preliminary experiments have shown that very narrow lines may be obtained in the paramagnetic resonance spectrum of this salt, diluted with the corresponding aluminium alum, and it is hoped to make a thorough investigation and obtain an accurate value for the splitting. If satisfactory agreement can be obtained with adiabatic demagnetization experiments on this salt, it should replace the potassium chrome alum as a 'standard substance' for work below 1°K .

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REFERENCES

- Bleaney, B. 1950 *Proc. Roy. Soc. A*, **204**, 203.
 Bleaney, B. & Hull, R. A. 1941 *Proc. Roy. Soc. A*, **178**, 74.
 Bleaney, B. & Simon, F. 1939 *Trans. Faraday Soc.* **35**, 1205.
 Broer, L. J. F. 1947 *Physica*, **13**, 352.
 Casimir, H. B. G., Bijl, D. & du Pré, F. K. 1941 *Physica*, **8**, 449.
 Casimir, H. B. G., de Haas, W. J. & de Klerk, D. 1939 *Physica*, **6**, 365.
 Casimir, H. B. G., de Klerk, D. & Polder, D. 1940 *Physica*, **7**, 737.
 Cooke, A. H. 1949 *Proc. Phys. Soc. A*, **62**, 269.
 Gorter, C. J., Dijkstra, L. J. & van Paemel, O. 1942 *Physica*, **9**, 673.

- Hebb, M. H. & Purcell, E. M. 1937 *J. Chem. Phys.* **5**, 338.
Hull, R. A. 1947 *Report of Cambridge Conference on Low Temperatures*, p. 72. London: Physical Society.
de Klerk, D., Steenland, M. J. & Gorter, C. J. 1949 *Physica*, **15**, 649.
Knight, W. D. & Cohen, V. W. 1949 *Phys. Rev.* **76**, 1421.
Kurti, N., Lainé, P., Rollin, B. V. & Simon, F. 1936 *C.R. Acad. Sci., Paris*, **202**, 1576.
Schmidt, G. & Keesom, W. H. 1937 *Physica*, **4**, 971.
Starr, C. 1941 *Phys. Rev.* **60**, 241.
Van Vleck, J. H. 1940 *Phys. Rev.* **57**, 426.
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The scattering of gamma-rays in extended media

I. Perpendicular incidence on a plane slab

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Ministry of Supply

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As the simplest problem involving the multiple scattering of gamma-rays, the case of perpendicular incidence on a plane slab has been studied by various simple theoretical methods. No exact solution is available as a test of these methods, but approximations of increasing accuracy, known to give too small a dose under the slab, have been combined with a theoretical upper limit for the dose, forming a zone in which the exact solution must lie. Most of the methods tested could be used even if pair-creation or the photoelectric effect gave an appreciable absorption, though for simplicity the computations have been carried out for pure Compton scattering and for quantum energies of a few MeV. Polarization by the Compton effect has been neglected. The best of the simple methods is a modification of the upper limit solution; in problems where this is too difficult to formulate, a good alternative is to calculate the dose from unscattered and once-scattered quanta, giving the latter the penetrating power of the incident quanta and the maximum possible energy-absorption cross-section.

I. INTRODUCTION

When the scattering coefficient of a slab of material for radiation, such as visible light or gamma-rays, is measured experimentally, it is arranged, if possible, that the scattered radiation shall not reach the detector at the far side of the slab. Such an arrangement is said to have 'good geometry'. Arrangements where scattered radiation has still an appreciable chance of reaching the detector are said to have 'poor geometry'. It is much more difficult to deduce the scattering coefficient from experiments of the second type, and, conversely, if we know the scattering coefficient it is difficult to estimate how much radiation reaches the detector in conditions of 'poor geometry'. In many fields, however, the attenuation of radiation occurs under such conditions; for example, in high-voltage radiography these problems occur frequently, and are there usually called 'wide-beam' conditions. It was the increasing use of gamma-rays in radiography and radiotherapy which led to the investigations reported here. The aim was to find simple mathematical methods for solving such problems and to obtain some idea of the accuracy inherent in the methods, and then to analyze some simple lay-outs which resemble those occurring in radiography.