Lorentz term. Of this same magnitude also are the terms involving the square of the Lorentz term.[19]

As a caution, it should be pointed out that the present treatment may be applicable in a quantitative way only to certain molecular crystals in which the refracting electrons are relatively well confined to particular molecules, and thus do not have strong mutual overlapping of their wave functions. Just this condition may be satisfied, however, in crystals of some large organic dye molecules which are of great practical interest.

Finally, mention should be made of an important physical restriction not hitherto discussed. This is the fact that lattice vibrations have been left out of account. While these have only a very secondary effect on refractive phenomena, it would be necessary to discuss such effects should a treatment be attempted in analogy to that of Peierls,[13] dealing with the absorption of light. Even in discussing refractive effects, the lattice vibrations may need to be brought in when treating the optical properties of thin films, if the film thickness is much less than a wavelength; under these circumstances the energy spectrum of the single exciton levels, of primary importance in the present calculation, will be changed because of the long range of dipole-dipole forces, and the incoherence of the wave function, introduced by the collisions of excitons with the lattice vibrations, will be an essential factor.

This work was begun while the writers were members of the Physics Department of the University of Illinois. We welcome the opportunity to express our appreciation to members of the department, and particularly to F. Seitz, for the cooperation and hospitality extended to us at that time.

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[19] In view of the statements in reference 16, it is possible that the corrections to the Lorentz term are in fact larger than estimated here, for the alkali halides.

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Adiabatic Demagnetization of Chromium Methylamine Alum*

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Adiabatic demagnetization experiments have been performed on a specimen of methylamine chromic alum, $CH_3NH_3 \cdot Cr(SO_4)_2 \cdot 12H_2O$, comprising a spherical mass of small crystals. Using fields up to 23 000 oersteds and starting temperatures of the order of 1.15°K, the "free-spin" entropy of $R \log_e 4$ could be reduced to $0.26R$, and the magnetic susceptibility *versus* entropy relation has been obtained over this range of entropy. The susceptibility was measured at 210 cps with an ac mutual inductance bridge. For temperatures above 0.1°K very good agreement is obtained between these results and the Hebb-Purcell theoretical curve with a value of 0.275° (0.19 cm^{-1}) for the crystalline field splitting of the ground level of the Cr^{+++} ion. In the neighborhood of entropy $R \log_e 2$ the susceptibility begins to increase rapidly and goes through a maximum at $S=0.53R$. As in the case of other paramagnetic alums previously investigated, ac losses occur in the region of maximum susceptibility (the loss component also showing a maximum), and ballistic measurements show hysteresis effects occurring on the low entropy side of the susceptibility maximum.

SINCE the beginning of adiabatic demagnetization experiments many investigations have been made with chromium potassium alum.[1–6] This salt proved to have several properties especially suitable for measurements in the region of temperature below 1°K. It is chemically more stable than iron ammonium alum. In the region between 1°K and 0.1°K its magnetic behavior is in rather good agreement with theoretical predictions.[1,5] The temperatures obtained with initial fields of the order of 20 kilo-oersteds are very low (a few thousandths of a degree Kelvin) and these temperatures can easily be determined with some precision by means of caloric measurements with the help of ac heating.[3]

Recently, however, some disadvantages of the salt were noticed. The Stark splitting of the fourfold-degenerate ground level of the Cr^{+++} ion caused by the crystalline electric field varied considerably for different samples [values between 0.24° and 0.27° were found for the parameter, δ/k, where δ is the energy separation of the two spin doublets[6]]. Small but systematic deviations from the theoretical formulas occur in the neighborhood of 0.2°K. The flat part of the entropy *versus* temperature curve, which is expected to occur at $S=R \log_e 2$, was found at a much lower entropy value, namely, $S=0.4R$. And, finally, the measurements of the lowest temperatures made at Leiden gave results widely different from those found at Oxford.

An explanation for the deviations from the theoretical predictions in the neighborhood of 0.2°K was given by Bleaney.[5] From his microwave experiments it followed

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

[2] A. H. Cooke, Proc. Phys. Soc. (London) **A62**, 269 (1949).

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

[4] Steenland, de Klerk, and Gorter, Physica **15**, 711 (1949)

[5] B. Bleaney, Proc. Roy. Soc. (London) **A204**, 216 (1950).

[6] D. de Klerk, thesis, Leiden, 1948, page 54 (unpublished).

TABLE I. Corresponding values of entropy and temperature. For the method of deriving absolute temperature from entropy and susceptibility data, see appendix and reference 10.

H oersteds	T_i °K	S/R	$\chi'/R\times10^8$ degrees/oersted^2	$T_{\text{Lor}}{}^*$	T_{Lor} °K	T_{Ons} °K	$T_{\text{V.Vl}}$ °K	T_{theor} °K
1363	1.166	1.3644	3.34	0.674	0.670	0.669	0.670	0.663
1451	1.164	1.3623	3.57	0.629	0.625	0.624	0.624	0.632
1451	1.158	1.3621	3.47	0.650	0.646	0.645	0.646	0.630
1717	1.165	1.3555	4.10	0.549	0.544	0.543	0.543	0.555
2005	1.164	1.3470	4.46	0.505	0.500	0.499	0.499	0.493
2293	1.157	1.3366	5.13	0.439	0.433	0.431	0.432	0.437
2597	1.160	1.3252	5.65	0.398	0.392	0.390	0.391	0.391
2866	1.164	1.3142	6.13	0.367	0.360	0.358	0.359	0.356
3533	1.161	1.2823	7.45	0.302	0.294	0.292	0.293	0.291
4367	1.165	1.2374	9.18	0.245	0.235	0.232	0.234	0.237
4936	1.163	1.2019	10.09	0.223	0.212	0.209	0.211	0.209
5794	1.187	1.1532	11.66	0.193	0.181	0.178	0.179	0.179
6730	1.196	1.0934	13.47	0.167	0.153	0.149	0.151	0.152
7610	1.163	1.0175	15.10	0.149	0.134	0.130	0.132	0.127
8805	1.175	0.9386	17.58	0.128	0.112	0.107	0.109	0.106
10265	1.210	0.8587	19.91	0.113	0.0960	0.0906	0.0928	0.0870
11705	1.189	0.7548	24.04	0.0936	0.0757	0.0692	0.0718	0.0636
11705	1.156	0.7345	25.03	0.0899	0.0720	0.0652	0.0678	0.0579
13075	1.214	0.6895	28.77	0.0782	0.0603	0.0532	0.0559	0.0426
13075	1.164	0.6581	33.99	0.0662	0.0491	0.0416	0.0442	0.0307
13610	1.199	0.6505	35.27	0.0638	0.0469	0.0394	0.0419	0.0280
14140	1.195	0.6197	42.37					
14140	1.190	0.6165	42.90					
14410	1.177	0.5948	46.9					
13345	1.090	0.5948	45.82					
15930	1.165	0.5138	48.9					
16490	1.155	0.4827	47.2					
17285	1.182	0.4658	45.45					
18920	1.144	0.3816	38.07					
20220	1.142	0.3376	35.94					
20985	1.147	0.3175	34.14					
21685	1.142	0.2952	32.80					
22320	1.143	0.2788	31.82					
22920	1.143	0.2637	30.61					
22940	1.142	0.2627	30.78					

that the Stark splitting of the ground level of the Cr^{+++} ion is different for different ions in the lattice. Two level splittings were found, the δ/k parameters being 0.21° and 0.38°. It is obvious that in these circumstances the specific heat resulting from the Stark effect cannot be represented by a Schottky curve but, approximately, by a superposition of two Schottky curves —hence broader and with a lower maximum. Although the results were qualitatively in accordance with this picture, no good numerical agreement could be obtained with the experiments below 1°K. (Bleaney pointed out that the spectrum intensities suggest equal numbers of ions with the different splittings, whereas the shape of the "tail" of the specific heat curve would require a proportion of 85 percent with the smaller δ to 15 percent with the larger.)

Bleaney performed microwave experiments with four more chromium alums:[7] the ammonium, rubidium, caesium, and methylamine alums. It was found that the ammonium salt showed results similar to those obtained with the potassium alum, but in the rubidium, caesium and methylamine alums only one Stark splitting occurred.

For this reason we decided to carry out some experiments with chromium methylamine alum, expecting that for this salt the results should be in agreement with theory down to a lower temperature than in the case of the potassium alum. The material was obtained commercially from Johnson Matthey and consisted of small crystals. A glass sphere 24 mm in diameter and mounted on a thin-walled glass pedestal was filled with these crystals, the filling factor being $\frac{2}{3}$. The assembly was enclosed in a glass envelope connected to a vacuum system. Demagnetizations from fields up to 23 kilo-oersteds were performed, using the new adiabatic demagnetization equipment of the National Bureau of Standards. The susceptibility of the salt after a demagnetization was measured by means of a Hartshorn mutual inductance bridge very similar to the one used in the Kamerlingh Onnes Laboratory. The ac frequency was 210 cps.

Some results are collected in Table I. The entropies of column 3 were calculated from the initial fields and temperatures using a Brillouin function with $J=\frac{3}{2}$. A correction was applied for the influence of the crystalline electric field upon the pattern of the energy level separation in the magnetic field.[8]

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[7] B. Bleaney, Proc. Roy. Soc. (London) **A204**, 203 (1950).

[8] R. P. Hudson, Phys. Rev. **88**, 570 (1952).

The susceptibility χ' is the real part of the ac susceptibility. It is defined as the quotient of the part of the magnetic moment that is in phase with the ac field and the magnetic field produced by the measuring coil, the so-called "external field." In the case of the Lorentz approximation[9] and a spherical sample this is equal to the field really acting on the magnetic ions, the "local field," hence T_{Lor}^* of column 5 obeys the relation $T_{\mathrm{Lor}}^* = c/\chi'$, where c is the Curie constant.

From T_{Lor}^* we could calculate the T^* values in the Onsager and Van Vleck approximations (they are not given in Table I), and from these T^* data we derived absolute temperatures with the help of the susceptibility formula for chromium alums given by Hebb and Purcell.[10] The T_{theor} of the last column was calculated from the entropy of column three, using Hebb and Purcell's formulas for the specific heat caused by the Stark splitting and magnetic interaction.

It was found, that in the region between 0.7 and 0.3°K, where the difference between T_{Lor}, T_{Ons}, and $T_{\mathrm{V.Vl}}$ is negligible, the best agreement with T_{theor} was obtained with a Stark splitting parameter of 0.275°K. From Table I and Fig. 1 it can be seen that with this splitting parameter good agreement is obtained between the theoretical and experimental values of T down to 0.1°K. No systematic discrepancies occur in the region between 0.1 and 0.2°K as in the case of chromium potassium alum. The T_{Ons} and $T_{\mathrm{V.Vl}}$ are in slightly better agreement with T_{theor} than T_{Lor}, but the accuracy of the measurements is insufficient to decide between T_{Ons} and $T_{\mathrm{V.Vl}}$. Our splitting parameter is much higher than the one derived from Bleaney's microwave measurements, his value being 0.245°K. Below 0.1°K the experimental temperature values are higher than the theoretical ones, but here also the deviations are much smaller than in the case of chromium potassium alum. The range of agreement between experiment and theory, that is, between the absolute "Onsager temperature" and the absolute temperature derived from the entropy (column 7 *vs* column 9, Table I) may be seen most readily from Fig. 2. (The scatter at the highest temperatures is a consequence of the smallness of the specific heat in this region: the high rate of warm-up after demagnetization causes an uncertainty in extrapolating the susceptibility measurements to time zero, while the value of T_{theor} is very sensitive to small variations in the entropy.) Hence for the temperature range down to about 0.09°K one may use the Hebb-Purcell relation between T^* and T with confidence and derive the absolute temperature directly from a measurement of the susceptibility, i.e., from T_{Ons}^*.

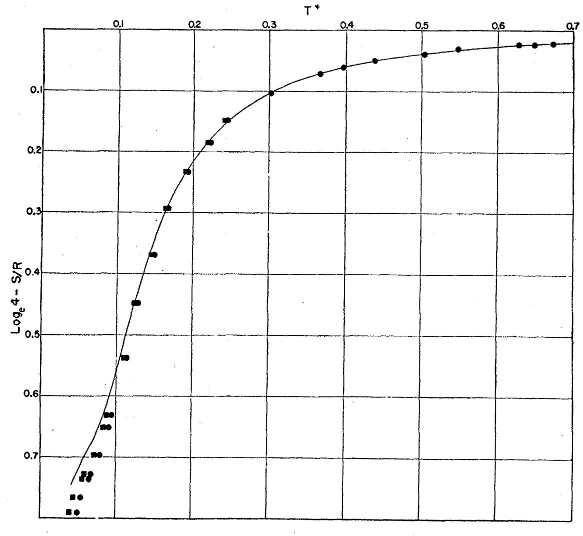

FIG. 1. Entropy of chromium methylamine alum as a function of "magnetic temperature." ● Lorentz approximation, ■ Onsager approximation. The "Van Vleck points" are intermediate and have been omitted for the sake of clarity. The curve represents the Hebb and Purcell formula with $\delta = 0.275$°K.

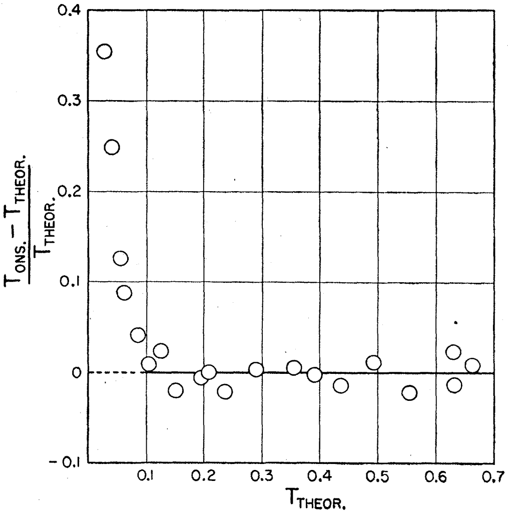

FIG. 2. Fractional deviation of absolute temperature as derived from the susceptibility from absolute temperature as derived from the entropy as a function of the latter.

In Fig. 3 we have plotted the susceptibility as a function of the entropy. As in the case of the other paramagnetic salts used for adiabatic demagnetization experiments, the susceptibility increases sharply to a maximum.[3, 11–15] In chromium potassium alum the horizontal part of the curve was found at a value of the entropy which was much too low ($S = 0.4R$ instead of $S = R\ln 2$). The present measurements with the methylamine alum show that here the sudden increase occurs at the correct entropy value.

In the region of lowest entropy (below the susceptibility maximum) experiments were performed with two different ac measuring fields (about 0.4 and 2 oersteds),

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[9] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

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

[11] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **149**, 152 (1935).

[12] Kurti, Lainé, and Simon, Compt. rend. **204**, 675 (1937).

[13] Steenland, van der Marel, de Klerk, and Gorter, Physica **15**, 906 (1949).

[14] Steenland, de Klerk, Beun, and Gorter, Physica **17**, 161 (1951).

[15] Steenland, de Klerk, Potters, and Gorter, Physica **17**, 149 (1951).

and a small systematic difference was found (see Fig. 3), but since the earth's magnetic field was only compensated during the measurements in the field of 2 oersteds these investigations must be repeated.

Preliminary experiments showed that an imaginary part of the ac susceptibility, χ'', occurs at the lower temperatures and that this also shows a maximum similar to the case of the potassium alum.[3] Remanent magnetism was found at the lowest temperatures.

Summarizing, we can say that qualitatively the behavior of the chromium methylamine alum is the same as that of the chromium potassium alum, but quantitatively it is in some respects slightly more favorable. No systematic deviations from the Hebb and Purcell formulas occur down to 0.1°K, and the flat part of the entropy curve is found at the correct value of S/R. On the other hand, our value of the Stark-splitting parameter is appreciably different from that found by Bleaney. (Measurements upon a single crystal specimen in progress at present appear to confirm our value of 0.275°.) The energy absorption from an alternating magnetic field at the lowest temperatures, however, appears to be much smaller than in the potassium alum, hence it is possible that the determination of temperatures by the caloric method will be more difficult with the present salt than with the potassium alum.

APPENDIX

The several formulas used in the derivation of the temperatures in the above are well-known[9,10] but are listed here for the sake of clarity.

The Hebb and Purcell formula for the susceptibility,

$$\chi_0=\gamma c/T, \tag{1}$$

modifies the Curie law by the factor γ to take into account the effects of the crystalline electric field. This factor is given by

$$\gamma=(5Z_c/2)^{-1}\{(3+4kT/\delta)+(3-4kT/\delta)e^{-\delta/kT}\}, \tag{2}$$

where Z_c is the partition function per ion in the crystalline field,

$$Z_c=2(1+e^{-\delta/kT}). \tag{3}$$

Since χ_0 is the ratio of the intensity of magnetization in the sample to the local field acting upon the ions, the measured susceptibility must be corrected for shape-dependent demagnetization effects and magnetic interaction. In the Lorentz treatment, these two effects cancel for the case of a sphere and χ_0 is identical with the experimental susceptibility χ_e. The magnetic temperature T^* is defined by

$$T^*=c/\chi_e, \tag{4}$$

and thus

$$T^*=T/\gamma. \tag{5}$$

If we define a third susceptibility χ_i as the ratio of the intensity of magnetization to the field in the sample (i.e., the external field corrected for demagnetizing effects) one has

$$\chi_i=\chi_0/(1-4\pi\chi_0/3), \quad \text{(Lorentz)} \tag{6}$$

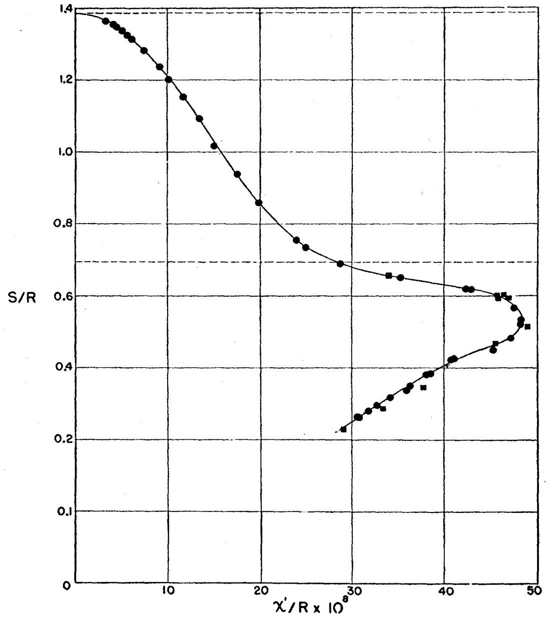

FIG. 3. Susceptibility χ' of chromium methylamine alum as a function of the entropy. ● measuring field 2ϕ. Measuring field 0.4ϕ.

and

$$\chi_i=\chi_0[1+4\pi\chi_i/(3+8\pi\chi_i)], \quad \text{(Onsager)} \tag{7}$$

From these equations one may derive the relation

$$T_{\text{Ons}}^*=(T_{\text{Lor}}^*-4\pi c/3)(T_{\text{Lor}}^*+8\pi c/3)(T_{\text{Lor}}^*+4\pi c/3)^{-1}. \tag{8}$$

The Curie constant c may be calculated from

$$c=Ng^2\beta^2J(J+1)/3k, \tag{9}$$

where N is the number of magnetic ions per cc. For the quantity $4\pi c/3$ we used the value 0.0191, making allowance for the $\frac{2}{3}$ filling factor of our powder specimen.

The relation between T_{Lor}^* and $T_{\text{V.VI}}^*$ is given by

$$T_{\text{Lor}}^*=T_{\text{V.VI}}^*[1+15.84(c/T_{\text{V.VI}}^*)^2]. \tag{10}$$

The T_{theor} values are calculated from the Hebb and Purcell S *vs* T relation, wherein the S is computed in two parts:—the free-ion value of $R\log_e 4$ is diminished by (a) the effect of the crystalline electric field, such that

$$S/R=\partial(T\log_e Z)/\partial T, \tag{11}$$

and Z is given in Eq. (3); and (b) the effect of the magnetic interaction, giving an additive contribution

$$S_s/R=\tau^2(d/dT)(\Omega/T), \tag{12}$$

where τ is three times the Curie constant and Ω is given by

$$\Omega=4.80\times Z_c^{-2}\left\{\left(\frac{3}{50}+\frac{223}{150}\frac{kT}{\delta}\right)+\left(\frac{88}{75}+\frac{8}{15}\frac{kT}{\delta}\right)e^{-\delta/kT}+\left(\frac{49}{150}-\frac{142}{150}\frac{kT}{\delta}\right)e^{-2\delta/kT}\right\}. \tag{13}$$