along an axis normal to the boundary through its center. The magnetic field along this axis due to the surface poles of density ω^* is

$$H_z=-\int\frac{\omega^* dS}{z^2[1+(r'/2)^2]^{\frac{3}{2}}}=-2\pi\omega^*\left\{1-\frac{z}{(z^2+L'^2/4)^{\frac{1}{2}}}\right\},$$

where r' is the distance from the foot of the axis to the element of area dS. The surface energy density then becomes

$$\sigma_0=\pi\omega^{*2}LG;\quad G=\{1+(L'/2L)-[1+(L'/2L)^2]^{\frac{1}{2}}\}.$$

If $L'=L$, $G=\frac{1}{3}$. If only those grain boundaries which are nearly perpendicular to the applied field are considered, θ_1 and θ_2 are each less than 45°, and the μ^* correction to σ_0 will be small. It is therefore neglected in this approximation.

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Magnetic and Thermal Properties of Chromic Methylamine Alum Below 1°K*

R. P. Hudson and C. K. McLane†
National Bureau of Standards, Washington, D. C.

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The earlier measurements of de Klerk and Hudson on a spherical mass of small crystals of chromic methylamine alum have been repeated, and extended, using a one-inch sphere ground from a large single crystal. The variation of susceptibility with entropy follows closely—down to 0.1°K—the predictions of the theory of Hebb and Purcell when a suitable choice is made for the value of δ, the splitting between the two spin-doublets in the ground level of the Cr^{+++} ion. It is found that $\delta/k=0.269\pm0.003$ degree.

Measurements have been made of the ballistic susceptibility χ, remanent magnetic moment Σ, and the in-phase and out-of-phase components of the ac susceptibility, χ' and χ'', respectively (these latter being measured at both 150 cps and 210 cps). The variation of χ' with entropy S is found to agree closely with that reported for the powder specimen, except in the region of the susceptibility maximum where the behavior appears to depend upon the rate of precooling the specimen. At approximately the same entropy as that corresponding to maximum χ', χ'' shows an extremely sharp maximum. The ballistic susceptibility depends upon the measuring field in the region of the maximum; remanence appears here and goes through a maximum as the entropy is reduced. The remanence maximum is found at a lower entropy the larger is the measuring field. Associated with this hysteresis are very marked "time-effects" in the adjustment of the magnetization to a change in measuring field, as encountered in tracing out hysteresis loops.

Measurements of the susceptibility in superimposed steady magnetic fields of 0–500 oersted show unusual behavior below the Curie point and suggest the existence of anisotropy. For application of the field along a cubic axis, a magnetization of about one-half the saturation value appears to have special significance; this value is attained in fields as small as 150 oersted, but increasing the field up to about 500 oersted produces little further change in the magnetization.

I. INTRODUCTION

THE magnetic and thermal properties of chromic methylamine alum, $Cr(CH_3NH_3)\cdot(SO_4)_2\cdot 12H_2O$, below 1°K were first described in an article by de Klerk and Hudson[1] (hereinafter referred to as A) dealing with adiabatic demagnetization experiments upon a powder specimen. The reasons for the interest in the properties of this particular salt are given in A. The present work concerns similar experiments made upon single-crystal specimens, wherein the magnetic properties might reasonably be supposed to be somewhat simple and more readily yielding to theoretical treatment. Independent measurements on this same salt have also been reported recently by Gardner and Kurti,[2] and by Steenland.[3]

II. APPARATUS

The salt specimen comprised a one-inch diameter sphere ground from a large single crystal.[4] This was mounted on a soft glass pedestal within a soft glass vacuum case as shown in Fig. 1. The crystal A rests on three raised points and is securely tied to the platform B by means of a nylon thread passing through holes in a polystyrene ring C and underneath B. The support D is a thin-walled glass tube with a rough ground joint at each end. Four flats were ground off the male part of each joint in order to diminish the area of thermal contact without impairing the rigidity or axial alignment of the assembly.

The vacuum case E is closed at the lower end by a plug F which constitutes another ground joint, and this is sealed by means of a glycerine-n-propanol mixture.[5] It is essential, of course, that this joint be tight to liquid helium II. The case E may be evacuated through

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* A brief summary of this work was presented at the Third International Conference on Low Temperature Physics and Chemistry at the Rice Institute, Houston, Texas, December 17–22, 1953 (unpublished).

† On a one-year leave of absence from the University of Wisconsin. Present address: Linde Air Products Company, Tonawanda, New York.

[1] D. De Klerk and R. P. Hudson, Phys. Rev. **91**, 278 (1953), hereinafter referred to as A.

[2] W. E. Gardner and N. Kurti (private communication).

[3] M. J. Steenland, in Rice Institute, Third International Conference on Low Temperature Physics and Chemistry; Abstracts of Papers, Houston, Rice Institute, 1953.

[4] We are greatly indebted to Mr. Walter Kuper for the preparation of the crystals used in this work.

[5] R. P. Hudson and C. K. McLane, Rev. Sci. Instr. **25**, 190 (1954).

the 6-mm o.d. tube *G*, which is spiralled just above *E* to provide a radiation trap. [Using this apparatus, it was possible to reduce the heat leak to the crystal to 20–50 ergs per minute at 0.1°K. The leak increased considerably at higher temperatures.]

The whole apparatus was silvered on the outside and coated with several layers of well-thinned varnish (General Electric GE7031). A coil of No. 43 B. & S. "Formex" was wound astatically in three sections of 400, 800, and 400 turns, respectively, on the outside of *E* so that the center 800-turn section surrounded the crystal *A*. This winding formed the secondary of a mutual inductance of which *A* is the core and the primary was wound on to the outside of the liquid-helium Dewar. The coefficient of mutual inductance, which is proportional to the "experimental susceptibility" of the salt (the ratio of intensity of magnetization to measuring field), was measured by means of a Hartshorn-type mutual inductance bridge,[6] modelled on that used in the Kamerlingh Onnes Laboratory. Absolute values of the susceptibility were determined by calibrating against absolute temperature in the liquid helium range —always below the lambda point, since in the HeI region the points would scatter somewhat from the expected straight line owing to temperature inhomogeneities in the bath.

III. PROCEDURE

The salt was cooled by adiabatic demagnetization from fields up to 23 000 oersteds starting with temperatures of 1.1° to 1.2°K. The entropy was calculated from the starting conditions for a given demagnetization 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 a magnetic field.[7]

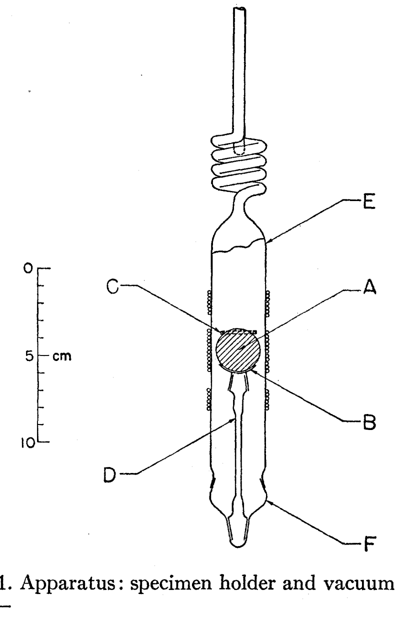

FIG. 1. Apparatus: specimen holder and vacuum case.

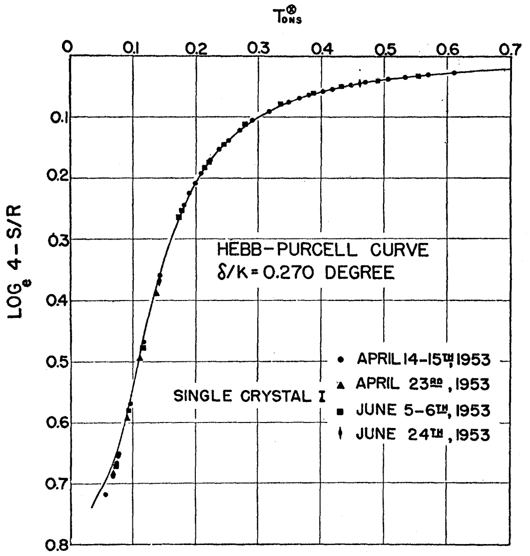

FIG. 2. "Magnetic temperature" $T_{\mathrm{Ons}}{}^*$ as a function of entropy. Measurements on Single Crystal I, April–June 1953.

The cryostat was swung out of the electromagnet and susceptibility measurements made at intervals of a few seconds, commencing within 30 seconds of the instant of demagnetization. Curves of bridge reading *versus* time were plotted and extrapolated to time zero. At the lowest entropies, where field-dependent effects are encountered, the influence of the earth's field was neutralized at the position of the crystal by a surrounding system of three mutually-perpendicular sets of Helmholtz coils. Either ac or ballistic measurements could be made as desired.

IV. RESULTS

(i) Susceptibility above 0.1°K

The "magnetic temperature" T^* is defined[8] by the Curie-law relation $T^*=CH_e/M$, where C is the Curie constant per cm^3, M is the magnetic moment per cm^3, and H_e, the external field. Above 1°K, T^* is equal to the absolute temperature T.

Assuming that the equivalence of T^* and T might persist to lower temperatures if one substituted for H_e in the foregoing expression the local field H_{loc}, i.e., the field actually acting on the ions, one may so define other "magnetic temperatures" (no longer simply experimental quantities) according as one uses the Lorentz, Onsager, or Van Vleck methods for calculating H_{loc}. Following the Leiden convention[9] we shall use the symbol T^* with a suffix to denote a magnetic temperature derived in terms of H_{loc}—thus $T_{\mathrm{Ons}}{}^*$, $T_{\mathrm{Lor}}{}^*$, etc.

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[6] L. Hartshorn, J. Sci. Instr. **2**, 145 (1925).

[7] R. P. Hudson, Phys. Rev. **88**, 570 (1952); R. P. Hudson and C. K. McLane, J. Research Natl. Bur. Standards **52**, 33 (1954).

[8] N. Kurti and F. Simon, Phil. Mag. **26**, 840 (1938).

[9] D. De Klerk, thesis, Leiden (unpublished), p. 15.

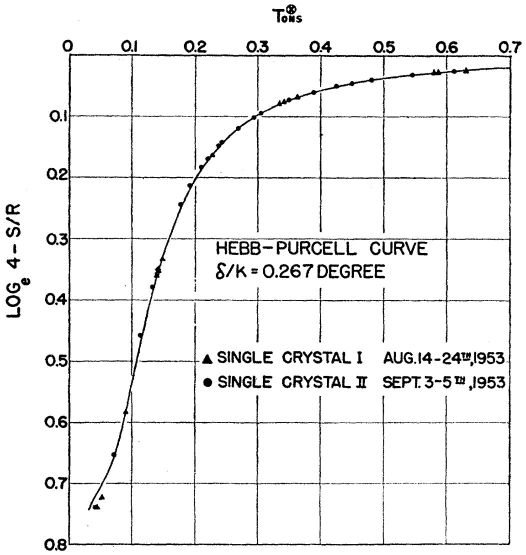

FIG. 3. "Magnetic temperature" T_{Ons}^* as a function of entropy. Measurements on Single Crystal I, August 1953, and on Single Crystal II, September 1953.

Hence $T_{Ons}^* = C[H_{loc}]_{Ons}/M$, etc.

The method of calculation is given fully in A. The density of this alum is 1.645 g cm^{-3},[10] and so 1.69 is a reasonable estimate for the density at liquid helium temperatures.

The best agreement between theory and experiment was obtained when the Onsager method of calculating H_{loc} was used. A graph of entropy *versus* T_{Ons}^* is shown in Fig. 2. The curve is calculated from the Hebb-Purcell theory[11] using a value for the level splitting δ/k of 0.270 degree; this was chosen to fit the experimental points at the highest temperatures. It may be seen that the points lie very close to this curve down to about 0.08°. In actual fact, small systematic differences are detectable between the results of different runs—for example, in the region of 0.3° the points for June 5–6 fall a little above the curve.

After this series of experiments the protective coat of varnish on the crystal (for minimizing possible damage by dehydration), which was badly cracked and peeling, was removed and then the crystal was recoated. During this process a few small grains of material were lost from points where the surface of the sphere had deteriorated (there was, however, no evidence of dehydration). The material removed was of the order of a few milligrams; the mass of the sphere was about 13 grams. (A more satisfactory coating, used in later work, was a dilute solution of Apiezon grease in benzene.)

Further experiments were then made with this crystal and the susceptibility now showed slightly larger values than those of the earlier measurements. Following these, a new series of measurements was carried out on a second specimen and the results are shown in Fig. 3. In order to fit a theoretical curve to the points it was necessary to choose $\delta/k = 0.267$ degree. It may be seen, however, that the points obtained for Crystal I only begin to deviate markedly from the curve at 0.08° whereas those for Crystal II show a small displacement towards lower temperature in the range 0.1° to 0.25°.

The difference in the two values of δ/k, although small, is none the less definite and is most probably a rate-of-precooling effect (see the following). Single Crystal I was grown from a solution of the alum prepared at NBS, while Crystal II was grown from material supplied by Johnson-Matthey (and used in powder form in A). The experimental results may be fairly summarized by $\delta/k = 0.269 \pm 0.003$ degree.

[The value of δ/k obtained for a powder specimen, as reported in A, was 0.275 degree, which is in fairly satisfactory agreement with the present results. The interpretation of results for a loosely-packed powder, however, presents considerable difficulty. The situation has been examined by de Klerk[9] who derives four different formulas, resulting from combinations of the Lorentz and Onsager viewpoints. The Onsager (magnetostatic) approach may be used throughout—dealing first with the macroscopic and then the microscopic situations—as was done in A. It can be argued, however, that a Lorentz-Onsager combination is *no less* valid in dealing with the complicated situation for a powder. Using the latter approach, T_{Ons}^* values derived from the results reported in A would give best agreement with theory for $\delta/k = 0.272$ degree.]

In Table I a list of corresponding values is given of T^* (for a sphere) and T, the absolute temperature calculated from the Hebb-Purcell theory using $\delta/k = 0.269$ degree. For the listed values of H_i/T_i, initial field

TABLE I. Corresponding values of H/T, entropy (actually calculated for $T = 1.15$°K), magnetic temperature and absolute temperature.

H/T	$\log_e 4 - S/R$	T_{Lor}^*	T_{Ons}^*	T
1000	0.0180	0.724	0.722	0.719
1250	0.0242	0.624	0.622	0.618
1500	0.0317	0.544	0.542	0.538
1750	0.0404	0.482	0.479	0.474
2000	0.0505	0.431	0.427	0.422
2500	0.0739	0.355	0.351	0.344
3000	0.1013	0.302	0.297	0.289
3500	0.1325	0.262	0.257	0.248
4000	0.1668	0.232	0.226	0.216
4500	0.2034	0.208	0.202	0.191
5000	0.2422	0.189	0.183	0.170
6000	0.3234	0.160	0.152	0.138
7000	0.4064	0.138	0.129	0.114
8000	0.4885	0.120	0.111	0.0938
9000	0.5677	0.105	0.0936	0.0763

Values of T are calculated from the Hebb-Purcell entropy-temperature relation with $\delta/k = 0.269$ degree. From these are derived values of T_{Ons}^* (using the Hebb-Purcell susceptibility formula) and T_{Lor}^* follows simply from the latter.

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[10] We are indebted to C. T. Collett for this determination. The value of the Curie constant C used in A was based upon an incorrect estimate of the density. In consequence, the value of $4\pi C/3$ (for a powder) quoted therein, *viz.*, 0.0191, should be amended to 0.0180 but this has no significant effect on the results.

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

divided by initial (magnetization) temperature, corresponding values of the entropy have been calculated with the tacit assumption that T_i is not very different from 1.15°K. (The entropy correction to be applied to the "Brillouin value" is a function of T_i.) The Hebb-Purcell entropy-temperature relation then leads to the values of T in Column V, for each of which one may calculate a "magnetic temperature" by using the Hebb-Purcell susceptibility-temperature formula. This has been identified with $T_{\text{Ons}}{}^*$—as supported by the experimental observations—and T^* (which is identical with $T_{\text{Lor}}{}^*$ in the case of a sphere) is readily derived from the $T_{\text{Ons}}{}^*$ as described in A.

(ii) Susceptibility in the Region of the Maximum

The variation of susceptibility with entropy throughout the entire range of the experiment is shown in Fig. 4. In the region of the maximum it was found that the values of χ' could vary considerably from run to run, dependent upon the rate at which the specimen was precooled to liquid nitrogen temperature. The more rapid the precooling the smaller were the values of χ' and the extent to which reproducibility could be obtained by careful, slow precooling (several hours) is illustrated in Fig. 5.[12] The latter is an enlargement of the region around χ'_{max} in Fig. 4.

In Fig. 5 the June measurements are sufficiently numerous to show up a fine detail of the curve at the maximum, where it is not smoothly rounded but shows what might be construed as two maxima separated slightly in entropy. These occur at entropies of 0.54_1R and 0.52_6R, respectively.

The ballistic susceptibility χ was also investigated and remanence was detected by using small measuring fields in the sequence: on, off, on-reversed, and off again. By using an appropriate value of bridge mutual inductance in opposition to that of the measuring coils, the remaining uncompensated part of the latter could be measured at the maximum galvanometer sensitivity, thus greatly increasing the accuracy of measurement.

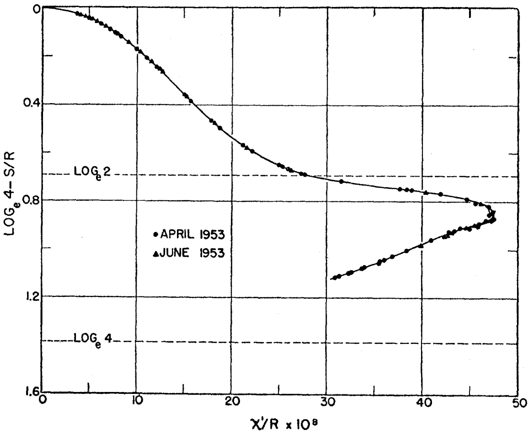

Fig. 4. Ac susceptibility, measured at 210 cps, as a function of entropy, for Single Crystal I.

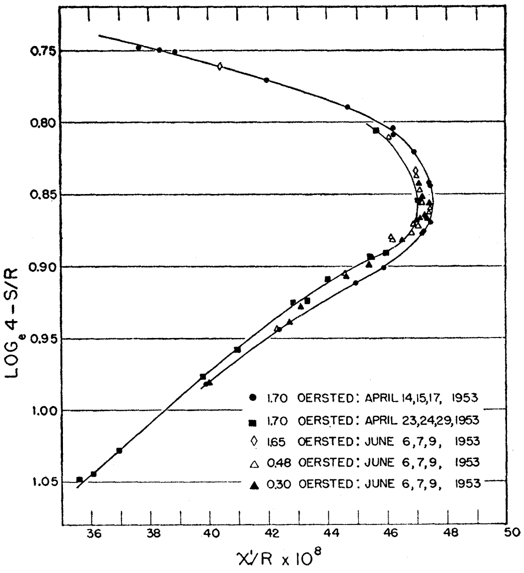

Fig. 5. Ac susceptibility as a function of entropy in the region of the maximum (enlarged from Fig. 4). Measurements at 210 cps and with various values of measuring field.

For small measuring fields, χ also showed the "double-peak" feature but as the measuring field was increased the susceptibility values at the lower-entropy peak decreased progressively until the latter had effectively disappeared. This field-dependence effect may be seen in Fig. 6. The higher-entropy peak occurs at an entropy of 0.53_6R, almost coincident with the first peak of the ac (χ') curve.

It should be emphasized that the curves of χ are less well defined than those of χ' because of the relatively small number of experimental points per curve and because the ballistic method of measurement was less accurate than the ac method. From the available evidence, however, one would conclude that χ shows a field dependence only in the region of the maximum.

Susceptibility measurements on Single Crystal II, both ac and ballistic, yielded curves very similar to those of Fig. 6 with the exception that the values of χ' and χ were about five percent greater in the region of the maximum. They are shown in Fig. 7.

(iii) Frequency Dependence of χ'

Measurements of χ' were made at frequencies of 210 cps and 150 cps. Both sets of points lie on a single curve (dashed curve of Fig. 6) within the accuracy of measurement. (Note, however, that the χ' values at the maximum are about four percent higher than those obtained for the same crystal two months earlier.)

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[12] In this paper, the experimental points in the diagrams are plotted with open symbols and solid symbols for poor and good reliability, respectively. The reliability depends upon the degree of certainty with which one may extrapolate measurements back in time to the instant of demagnetization, and upon the stability of the magnetic field and bath temperature prior to demagnetization.

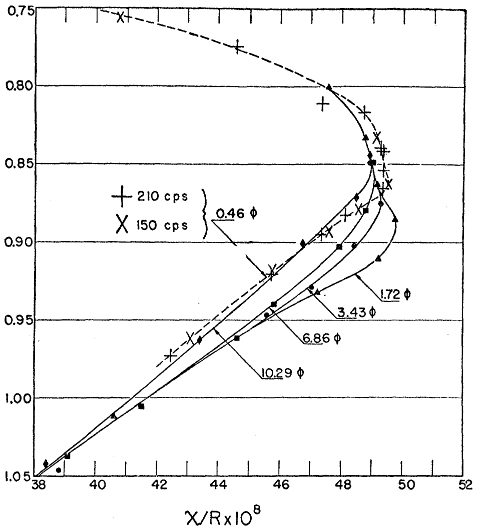

FIG. 6. Susceptibility as a function of entropy, for Single Crystal I, in the region of the maximum. Ac susceptibility measured at 150 cps and 210 cps, August 21–24, 1953 (broken line); dc susceptibility for various values of measuring field, August 14–15, 1953 (full lines)

(iv) Hysteresis and Remanence

By using the well-known cyclical procedure referred to above in the ballistic measurements, the occurrence of hysteresis was detected for all values of the entropy below $0.53R$ (corresponding to $H_i/T_i = 14.9$ kilogauss/1.11°K). This is also the position of the low-entropy peak in χ'. The variation of the remanence with entropy and with measuring field was investigated and some results are given in Fig. 8. It is seen that curves of remanence *versus* entropy for constant measuring field display a maximum which occurs at a lower entropy the larger the measuring field. These results were closely reproduced in similar measurements on Single Crystal II.

Before commencement of a series of ballistic determinations the galvanometer (period 5.6 seconds) was made slightly underdamped and the circuit calibrated. With the onset of remanence it was found that the apparent damping increased and at the lowest entropies the "time-effects" became enormous. These varied, moreover, from an "on" throw to an "off" throw; for example at "on" the mirror would swing to its maximum deflection and then creep slowly back to zero in a time of the order of 15 seconds, whereas equilibrium would be restored after an "off" throw in about 5 seconds.

The difference in the two cases is that "on" involves a reversal of the magnetic moment, from an initial state of remanence under forces within the crystal to a final state maintained by the presence of an external field, whereas "off" involves the opposite case of initial and final states with, too, a decrease but not reversal of the magnetic moment. For "on," the external field is present during the realignment of the ionic moments but not in the case of "off." The time-delay cannot, however, be simply a function of external field since no time effects could be observed for double throws, i.e., for successive complete reversals of the current. [This had the corollary that a double throw was always greater than the sum of successive "on" and "off" throws.]

For an "on-off" sequence involving *no* reversal of field, however—that is, remaining in one quadrant of a hysteresis cycle—reproducible throws were obtained but with the "on" values now greater than the "off."

Thus the time-effects were most marked for "on" throws in a hysteresis cycle, less so for "off," still less for "off" in a no-reversal on-off sequence, unnoticeable for the corresponding "on" throw, and also negligible for a simple complete-reversal sequence.

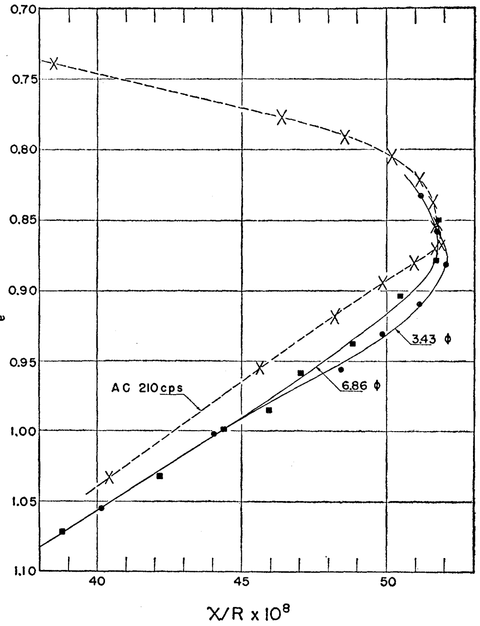

FIG. 7. Ac and dc susceptibilities as functions of entropy in the region of the maximum. Data for Single Crystal II, corresponding to that for Single Crystal I shown in Fig. 6.

The existence of such time-effects and consequent damping of the galvanometer swing must result in the observed values of the remanence (and to a smaller extent the susceptibility) depending upon the period of the galvanometer used. In these experiments the galvanometer had a period of 5.6 seconds.

(v) Ac Loss Component, χ''

As reported in A, an out-of-phase component of the ac susceptibility χ'' occurs in a relatively small range of entropy in the neighborhood of that corresponding to the χ' maximum. More precise determinations of this quantity made on Single Crystal I are summarized in Fig. 9, a plot of entropy *versus* χ''. These data were essentially duplicated in corresponding measurements on Single Crystal II.

The values of χ''/R are small compared with those found in potassium chrome alum[13] and the curve is seen to rise to a very sharp peak at an entropy of $0.52R$. The apparent field dependence of χ''/R in Fig. 9—curves A and B being drawn through points obtained with measuring fields of 0.30 oersted and 0.45 oersted, respectively—may or may not be real. These fields are very small and not very different. It was practically impossible to measure χ'' with the field normally used at higher temperatures, *viz.*, 1.7 oersted, since the heat developed in the salt was sufficient to warm the salt through the entropy range of measurable χ'' values in such a short time that extrapolation to time zero would have been meaningless. The few such measurements that were attempted, however, and particularly in cases where the measuring current was changed during warm-up, suggested that up to this point at least, χ'' decreased with increased measuring field. [The possibility that the χ'' peak is double, as appears to be the case for χ', is dealt with in Sec. V.]

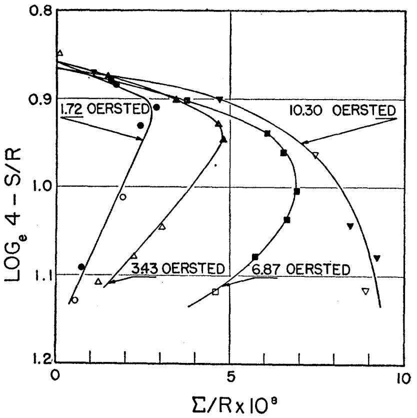

FIG. 8. Remanent magnetic moment as a function of entropy for various values of measuring field. Data for Single Crystal I, August 14–15, 1953.

(vi) Frequency Dependence of χ''

Measurements of χ'' were made at 210 cps and 150 cps and the values obtained are plotted in Fig. 10. It will be noted that no frequency dependence is detectable within the accuracy of the measurements. This is at first sight surprising but the explanation doubtless lies in the extreme narrowness of the χ'' peak. The mechanism of this low-frequency loss phenomenon has yet to be explained but, discussing it in terms of some characteristic relaxation time τ, it is evident that τ changes from a value very small compared with the period of the alternating field to a value very much greater than that period in an extremely narrow range of temperature. In comparison, the change from 1/210 sec to 1/150 sec is relatively insignificant and the effect must be obscured by the limited accuracy of measurement.

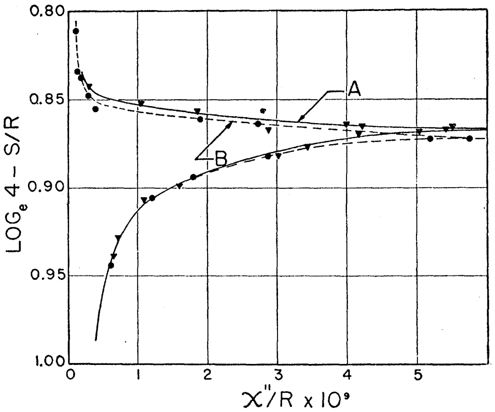

FIG. 9. Ac "loss component" (out-of-phase component of susceptibility) χ'', as a function of entropy for Single Crystal I, June 5–9, 1953. Measuring field 0.30 oersted (Curve A) and 0.45 oersted (Curve B).

(vii) Magnetic Field Dependence of χ'

When a magnetic field H is applied to a paramagnetic substance, a certain moment M will be established. If now a susceptibility determination be carried out by applying a small field h perpendicular to H and measuring the corresponding moment m, then it may be readily shown that—for $h \ll H$ and with an isotropic substance—$m/h=M/H$. Thus the saturation curve (M *vs* H) may be obtained directly. [Alternatively, h may be applied parallel to H, when the differential susceptibility ($\partial M/\partial H$) is measured and the $M-H$ curve must be obtained by integration.]

The measurements were carried out using a polarizing field of up to 540 oersteds and an ac measuring field of 0.45 oersted at 210 cps. After demagnetization, the field H was increased in 8 steps to the aforementioned maximum value, an m/h determination being carried out for each value of H. The sequence was retraced several times and curves plotted for extrapolation to zero time; the corresponding entropy was, of course, determined by the initial demagnetization conditions.

The behavior above the Curie point was that for normal paramagnetic saturation but below this point (where the zero-field susceptibility reaches its maximum and thereafter decreases for further decrease in entropy) the behavior underwent a radical change. For small polarizing fields (about 20 oersteds) the value of m/h still decreased with increasing H, but for larger fields the susceptibility suddenly rose very steeply and with $H=180$ oersted for example, became much larger over a part of the entropy range than the maximum value on the $H=0$ curve. For the highest fields the susceptibility decreased again to relatively small values at all entropies.

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[13] De Klerk, Steenland, and Gorter, Physica 15, 649 (1949).

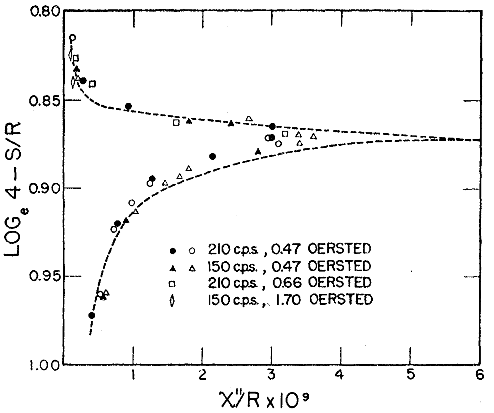

FIG. 10. χ'' as a function of entropy. Measurements on Single Crystal I at frequencies of 150 cps and 210 cps, August 21–24, 1953. The broken curve is identical with B of Fig. 9 and is given here for comparison, and to indicate the degree of reproducibility of the data.

The course of m/h *versus* entropy for various fixed values of H is shown in Fig. 11. Thus once again the methylamine salt was found to behave in a manner markedly different from that of potassium chromic alum, for which m/h was found to decrease with H for all values of the entropy.[14]

The variation of m/h with H for various fixed values of the entropy is shown in Fig. 12. The susceptibility is seen to go through a preliminary minimum and then a pronounced maximum for entropies slightly less than that of the Curie point. At still lower entropies (that is, less than about $0.48R$) the preliminary minimum is not observed, while the maximum becomes progressively more accentuated.

On the assumption that the relation $m/h=M/H$ is valid, the M *vs* H curves at constant entropy may be derived and these are given in Fig. 13. On this type of plot the curves are difficult to separate near the origin and for this reason only four curves have been plotted. Below the Curie-point entropy one sees that the (apparent) magnetic moment increases very rapidly with increasing H before leveling off at a value which is roughly one-half of the saturation moment ($M/R = 2.015\times10^{-4}$ gauss cm^3 degree erg^{-1}). The fact that the plateaux are not flat but actually show a depression (negative differential susceptibility) must be taken, presumably, as evidence that the assumption made above is not strictly valid and that the substance is no longer magnetically isotropic.[15] [The relatively small number of experimental points in Figs. 12 and 13 introduces some uncertainty in the course of the curves, particularly in the region of highest susceptibility (or magnetic moment) for the curves of lowest entropy. The two figures were constructed, however, so as to be smooth and quite consistent with each other, and in such a construction it is a great help that the most curved portion of a particular curve in one figure corresponds with a fairly linear portion of the associated curve in the other. The portions of greatest uncertainty have been drawn with broken lines.]

An anisotropy below the Curie point is not surprising, however, since the appearance of a susceptibility maximum and hysteresis effects (above) must be associated with antiferromagnetic (or perhaps ferromagnetic) ordering[16] in which the crystal structure will play a dominant role. The chromic alums present a complicated case in that there are four ions in unit cell. The spins will most probably be aligned in four groups, with one of the four spins in each unit cell along one of the four trigonal axes. Since, however, h and H were each directed along a (different) cubic axis, and a cubic axis makes very closely equal angles with all the trigonal axes, the true course of M with H might still be fairly well represented by the curves of Fig. 13 to the extent of a very steep rise followed by a temporary levelling—but no depression.[17]

(viii) Absolute Temperature of the Curie Point

The "Leiden method" of measuring absolute temperatures,[18] supplying heat to the specimen by means of ac losses, proved to be impracticable with this salt, because of the smallness of χ'' and the narrowness of the entropy range wherein it appears. To maintain χ'' at a measurable level for a convenient time, the measuring field had to be kept small so as to reduce the heating rate. In consequence of this the "drift" heating became proportionally large and this reduced the accuracy. χ' is useless as a thermometric parameter since

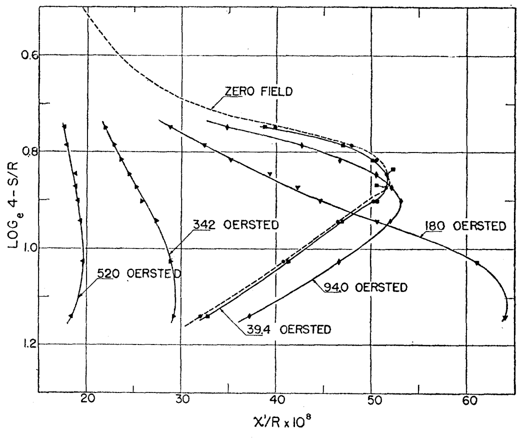

FIG. 11. Ac susceptibility as a function of entropy, in the region of the maximum, for various values of superimposed transverse steady field. Single Crystal II, measuring field 0.47 oersted at 210 cps.

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[14] M. J. Steenland, thesis, Leiden (unpublished), p. 44.

[15] Steenland (see reference 3) has recently reported observing marked anisotropy in ballistic measurements of susceptibility for various directions of the polarizing field.

[16] N. Kurti, J. phys. 12, 281 (1951).

[17] This appears to be confirmed by preliminary measurements of the differential susceptibility.

[18] Casimir, de Haas, and De Klerk, Physica 6, 255 (1939).

in the range of useful χ'' it is an insensitive function of entropy and it is here that the course of the susceptibility during warmup deviates most widely from the "ideal" χ *vs* S curve (Fig. 4). χ'' is also a bad thermometric parameter since it changes so very rapidly with time that $d\chi''/dt$ is very difficult to estimate accurately. (χ'' heating can only be usefully employed, in any case, on the high-entropy side of its maximum, otherwise its effect will be to aggravate temperature inhomogeneities and it is on this side where it falls most rapidly to inconveniently small values.) The remanence Σ is the best thermometric parameter, but the measurements take longer to perform, magnifying problems of temperature inhomogeneity. It would appear that a combination of γ-ray heating with use of Σ to trace the change of entropy would be the most reliable method of determining absolute temperatures and such experiments are in course of preparation. Many attempts were made to measure thermodynamic temperatures but the scatter in the results was extremely bad. The temperature of the Curie point most probably lies in the range 0.015–0.020°K.

V. SUMMARY AND DISCUSSION

The behavior of methylamine chromic alum below 1°K is very different in many respects from that of potassium chromic alum and the former salt appears to be more useful as a standard thermometric substance. Above 0.1°K the theory of Hebb and Purcell fits the behavior very well although the nonreproducibility is sufficient to introduce an uncertainty of several millidegrees in the value of the level splitting δ/k. This value is found to be 0.269±0.003 degree.

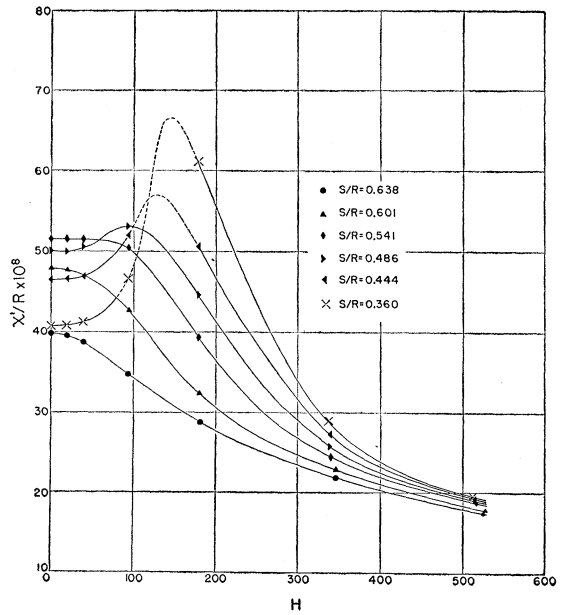

FIG. 12. Ac susceptibility in superimposed transverse field as a function of that field, along isentropes. Data correspond to that of Fig. 11.

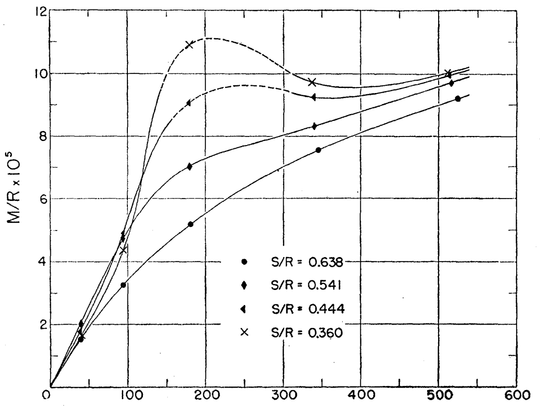

FIG. 13. Magnetic moment as a function of field, along isentropes. Values are derived from data of Fig. 12 on the assumption that $M/H=m/h$ (see text).

The nonreproducibility becomes most marked in the region of the susceptibility maximum and may be associated with the rate of precooling to liquid nitrogen temperature, since unusually small susceptibility values could be obtained for this region by precooling rapidly. No crystallographic transition takes place between 1° and 300°K which might account for this behavior—as there does in the potassium salt. There was some evidence with Crystal I that measurements on a not-previously-cooled specimen yielded higher susceptibility values than were found in subsequent runs. The initial experiments with I, however, were not very precise owing to high drift-heating rates (subsequently improved by redesign of apparatus) and only one cooling of Crystal II has been made so far. The latter gave the highest susceptibility values reported here. A further possibility, which cannot yet be excluded, is that once "low-susceptibility behavior" has been induced by a rapid precooling the crystal recovers to a "normal" state only after being kept for a number of weeks at room temperature.

The variation with entropy of both χ'' and the remanence is very different from that found with the potassium salt[13] and indicative of a long relaxation time within the spin system below the Curie point. The χ'' rises to a very sharp peak and falls again within a very small range of entropy centered on the entropy of the χ' maximum. (Within the accuracy of measurement, both χ' and χ'' appeared to be independent of frequency for the range 150–210 cps.) Remanence is detected at all entropies below a point slightly less than that of $\chi'_{\max}$, namely $0.53R$, and for a constant measuring field the remanence goes through a maximum as the entropy decreases. For a larger measuring field the remanence maximum is found at a lower entropy. The time effects observed in the ballistic measurements are so large as to greatly modify the swing of a 5.6 second galvanometer.

From a sequence of measurements made at fairly regular, small intervals of entropy some evidence was adduced that the χ'' peak is not single but perhaps consists of two very closely spaced peaks. This may be compared with the definite double-hump characteristic of the χ' curves. The existence of such an effect is by no means clearly established above the general scatter of points in the plots of Figs. 9 and 10 and hence the possibility must be regarded as somewhat speculative. (Note, however, the strong suggestion of two separate peaks in Fig. 9—already discussed as a possible but unlikely manifestation of measuring-field-dependence—and some slight evidence in Fig. 10, although here the crucial points are unfortunately somewhat uncertain as to their entropy values.)

Below the Curie point, the susceptibility at constant entropy changes markedly with applied field—first decreasing for small fields, then increasing to a high maximum before falling again. This behavior is suggestive of a rather abrupt change from antiparallel to parallel ordering as the external field exceeds a certain critical value. The latter is seen to be a function of entropy and presumably provides a measure of the antiferromagnetic interaction (compare Garrett[19]). The method of measuring the magnetic moment in an applied field by determining the susceptibility for a small measuring field applied perpendicularly to the polarizing field most probably breaks down below the Curie point, presumably owing to the development of anisotropic behavior. For application of the two fields along different cubic axes the magnetic moment *appears* to level off in the range of 100–500 oersted at a value approximately one-half the saturation moment. [See IV, (vii) and reference 17.]

The method of measuring thermodynamic temperatures by measuring the entropy change for a known heat input and supplying the latter by means of the ac losses in the salt could not be employed satisfactorily. This was due to the fact that (a) χ'' values are small even at their maximum, (b) χ'' decreases very rapidly to vanishingly small values in an extremely narrow range of entropy, and (c) the range of existence of a measurable χ'' is just that region where χ' is a very insensitive function of entropy.

ACKNOWLEDGMENT

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[19] C. G. B. Garrett, Proc. Roy. Soc. (London) **A206**, 242 (1951).