although it is much larger than those previously reported. We have observed similar large shifts in other divalent iron compounds, which has led to the suggestion by Blumberg and Jaccarino[14] that the exchange polarization of inner s electrons by the d shell causes a charge rearrangement of the s-electron wave functions at the nucleus. This effect is apparently considerably larger than the bonding effects (chemical shift) on the outer valence s electrons, and may account for the large shifts observed.

The linewidth of the absorption in the paramagnetic state, Fig. 3, allows an upper limit to be put on the spin correlation time, τ. This quantity is related to the linewidth, $\Delta\nu$ ($\frac{1}{2}$ width at $\frac{1}{2}$ amplitude), through the equation

$$\tau \leqslant 2\pi\Delta\nu(\hbar/IA)^2, \qquad (6)$$

where A is the hyperfine coupling of the Fe^{57} nucleus. The measured linewidth for the stainless steel source and the FeF_2 absorber is 0.023 cm/sec, while that obtained when the absorber is replaced by a piece of stainless steel identical to the source is 0.026 cm/sec. From these a linewidth of 0.010 cm/sec is deduced for the FeF_2 alone. This is about twice the natural width of the gamma ray, and yields a correlation time of less than 3×10^{-11} second for FeF_2 at room temperature, on the assumption that linewidths are additive. It should be recognized, however, that the difficulty of combining linewidths arising from various mechanisms is such that the uncertainty in the spin correlation contribution may be as large as a factor of two or three. In view of this, no correction has been made for the broadening due to the finite absorber thickness, which would amount to 30% for a line of natural width in the absorber used.

ACKNOWLEDGMENTS

The author is indebted to V. Jaccarino for suggesting this study of FeF_2 as well as for providing the oriented slabs of the material used. He has also benefited from discussions with many members of this laboratory and from the assistance of Miss C. Alff in carrying out the experiments.

[14] W. E. Blumberg and V. Jaccarino (private communication).

PHYSICAL REVIEW VOLUME 121, NUMBER 1 JANUARY 1, 1961

Magnetic Studies on Single-Crystal Chrome Potassium Alum Below 1° Kelvin*

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(Received August 29, 1960)

The magnetic susceptibility of a spherically shaped single crystal of chrome potassium alum has been measured as a function of entropy and applied external field along the [100], [110], and [111] directions in the crystal at temperatures below 0.1°K. Zero-field measurements of the static susceptibility were made with a moving coil apparatus and longitudinal field measurements were made using the conventional ballistic bridge method. A ballistic galvanometer with period 4.6 seconds was used in both circuits. Drop coil measurements indicate no long-time effects in the magnetization and show no appreciable difference from the susceptibility measured by the ballistic method. The isentropic susceptibility measured in fields up to 300 gauss indicates definite anisotropy below the Néel point in fields from 50 to 300 gauss.

INTRODUCTION

CHROME potassium alum has been one of the most widely investigated of the alums used in the production of temperatures below 1° Kelvin. In order to understand the mechanisms leading to the ordered state which occurs in these crystals well below 1°K, it is important to obtain a great deal of accurate quantitative and reproducible data. In recent years a large amount of information about the low-temperature properties of this salt has been obtained at the Leiden University, Oxford University, and National Bureau of Standards laboratories.[1–4] Magnetic susceptibiltiy measurements have indicated rather unusual behavior below the Néel point where magnetic ordering sets in. The susceptibility was found to depend on both the measuring field employed in the measurements and the time constants of the measuring circuit. Further, a secondary maximum in the susceptibility was observed at one laboratory.[4] These measurements indicate similarities between the properties of this salt and chrome methylamine alum. Using a moving coil apparatus it was found[5] that a long relaxation time is associated with the magnetization in the methylamine alum and a very pro-

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* Supported by the Robert A. Welch Foundation.

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[1] J. A. Beun, A. R. Miedema, and M. J. Steenland, Physica **23**, 1 (1957).

[2] J. A. Beun, M. J. Steenland, D. De Klerk, and C. J. Gorter, Physica **21**, 651 (1955).

[3] J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London) **A221**, 243 (1954).

[4] E. Ambler and R. P. Hudson, Phys. Rev. **95**, 1143 (1954).

[5] C. W. Dempesy and R. C. Sapp, Phys. Rev. **110**, 332 (1958).

nounced double maximum occurs in the susceptibility versus entropy curve.

The crystal structure of the paramagnetic salt, $KCr(SO_4)_2 \cdot 12H_2O$ is well known. It will be recalled that the chromium ion which gives rise to the paramagnetic properties is situated on a face-centered cubic lattice and is surrounded by an octahedron of water molecules. The effect of the surrounding atoms is to quench the ^4F state of the free Cr ion into a ^4S state, and further split the fourfold-degenerate spin state into two doublets separated by an energy δ. In cooling a sample of this substance from room temperature to liquid helium temperatures a number of solid state transitions occur. Evidence for a transition below 160°K was detected first by Bleaney[6] from microwave evidence and recently by Norwood[7] by ultrasonic attenuation measurements. Further a transition has been observed by Ancenot and Couture[8] at 60°K where optical birefringence properties are observed. It is possible that the rate of cooling through these transitions could influence the low-temperature properties of this salt since similar effects have been observed in chrome methylamine alum.

Measurements made in transverse external magnetic fields have revealed the presence of magnetic anisotropy in chrome potassium alum.[1] In the case of magnetization in longitudinal fields, results from Leiden University have shown the equivalence of the cubic axes. No measurements of the longitudinal magnetization have as yet been reported for other directions in the crystal.

In the present work we report measurements of the magnetic susceptibility along the [100], [110], and [111] directions of a single crystal of chrome potassium alum using the moving coil apparatus. Ballistic measurements have also been made along these three directions in external longitudinal fields up to 300 gauss.

APPARATUS

The single-crystal specimen used for the present work was grown in this laboratory by slow evaporation of an aqueous solution of commercial Baker's C.P. salt. The crystal was then ground into a spherically shaped sample having a diameter of 1.27 cm. Mounting of the sample was accomplished by two different methods. For the drop coil measurements the sample was held in place by four thin nylon threads. Details of this mounting arrangement are described in a previous publication from our laboratory.[5] For the longitudinal field measurements the sample rested on a four-inch long, thin-walled Pyrex tube which was flared at the top to accommodate the sample. The sample and tube are held in place by inserting the lower portion of the Pyrex stem in a cylinder of compressed chrome potassium alum. The cylinder of salt, which acted as a thermal dam, was machined to fit snugly in a glass tube which could easily be inserted into the sample chamber.

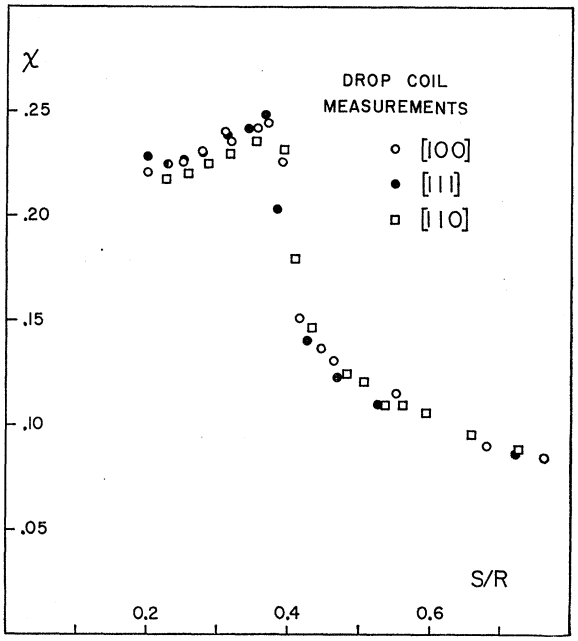

FIG. 1. Magnetic susceptibility per unit volume of a single crystal of chrome potassium alum as a function of entropy (divided by R).

The moving coil apparatus for making susceptibility measurements is almost identical to that described earlier[5] where a schematic figure is given. The moving coil, or secondary coil, is connected directly to a ballistic galvanometer of period 4.6 seconds. The primary coil, mounted on the helium Dewar is 39.1 cm long and provides a field of 120.4 gauss per ampere. This coil is located symmetrically with respect to the drop coil motion.

In making both ballistic and drop coil measurements the same coils and galvanometer were used. In the drop coil measurements a field is applied by the primary and deflections are observed when the secondary coil is moved. For the ballistic measurements the secondary coil is fixed in position and ballistic deflections are observed upon application of a primary field.

The large magnetic fields used for the magnetization of the sample were produced by the Rice University 25-kilogauss solenoid. The lowest entropies studied were obtained by applying the maximum field with the helium bath at approximately 1.080°K or a lesser field with the bath temperature at 0.926°K.

Fields of 6 to 300 gauss could be applied to the sample by a 15.2-cm long auxiliary solenoid that was slipped on the Dewar tail following a demagnetization. This solenoid provided a field of 265 gauss per ampere. The external field, primary field, and large magnetizing field are consequently all in the same direction and along a particular axis of the crystal under study.

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

[7] M. H. Norwood and A. C. Thorsen, Proceedings of the Seventh Annual International Conference on Low-Temperature Physics, Toronto, Canada, 1960 (unpublished).

[8] C. Ancenot and L. Couture, J. phys. radium **21**, 47 (1960).

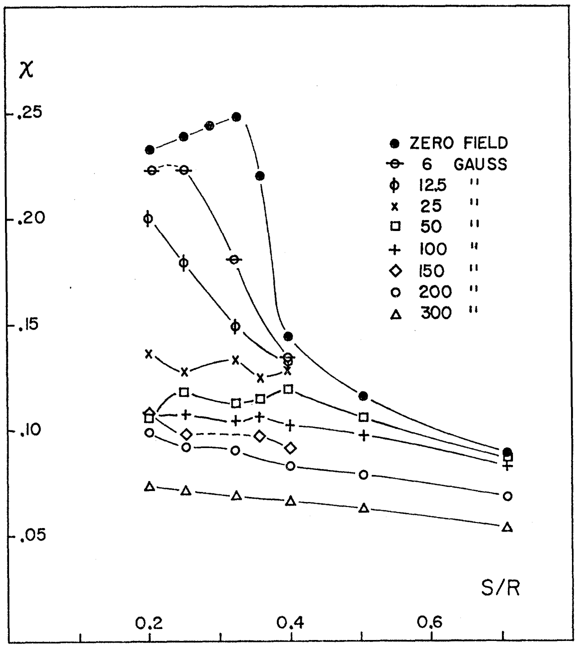

FIG. 2. Magnetic susceptibility per unit volume of CrK-alum as a function of S/R for a series of steady fields applied along the [100] crystal direction.

Surrounding the Dewar system are three mutually perpendicular Helmholtz coils used to cancel the earth's magnetic field and any stray magnetic fields caused by the surrounding apparatus and building. Using a Rawson rotating coil gaussmeter (Type 726), these residual fields could be reduced to less than 0.02 gauss in each of the three mutually perpendicular directions.

PROCEDURE

The galvanometer deflections were calibrated against the known susceptibility of the salt in the liquid helium temperature range. For a spherical sample the salt obeys a Curie law $M = CH_p/T$, where M is the magnetization (magnetic moment per unit volume), C the Curie constant per unit volume (=0.00674°K for chrome potassium alum), and T the absolute temperature. Galvanometer deflections were thus plotted versus $1/T$ and the resulting line used to determine the constants A and B in the calibration formula $\delta - B = A/T$, where δ is the galvanometer deflection. This procedure was followed for both the drop coil and ballistic measurements; the only difference being the value of the constants. The primary field H_p used for the calibration was from 11.4 to 12.1 gauss for the drop coil runs and 10 gauss for the ballistic runs.

Data were started 12 to 15 seconds after demagnetization. When an external solenoid was placed around the Dewar tail for longitudinal field measurements, readings were delayed until 22 to 27 seconds after turning off the magnetizing field. In all cases two deflections were taken corresponding to the application of the primary field in the vertical direction followed by two deflections for the primary field in the opposite direction. Measurements in these alternate directions were continued for three to four minutes. These deflections were extrapolated back to the time of demagnetization to calculate the susceptibility at the known entropy. A primary field of 0.61 gauss was used for the drop coil measurements and a field of 0.90 gauss for the ballistic data.

The following procedure was followed in all of the longitudinal field measurements. For each demagnetization the susceptibility was found for two values of external field (except at the lowest entropy where only one field was applied). After cooling the sample, the external solenoid was mounted around the nitrogen Dewar and eight galvanometer deflections were observed for the first field setting (H_1). The external field was then changed to a new value (H_2) and four more deflections were observed. The first field (H_1) was again applied and further deflections were recorded. By extrapolation of the deflections corresponding to H_1 the susceptibility in the field H_1 could be calculated. In order to find the susceptibility in the field H_2 it was necessary to know the rate of decrease of the deflections corresponding to H_2. An approximate method was used to find this quantity which assumes only that the heat leak to the sample is a constant for any series of demagnetizations. The percentage decrease of the H_1 deflections after a given time are plotted as a function of applied external field. After a series of demagnetizations with different H_1 fields a smooth curve is usually obtained which will give the percent decrease in deflections for any applied field. A value from this curve is then

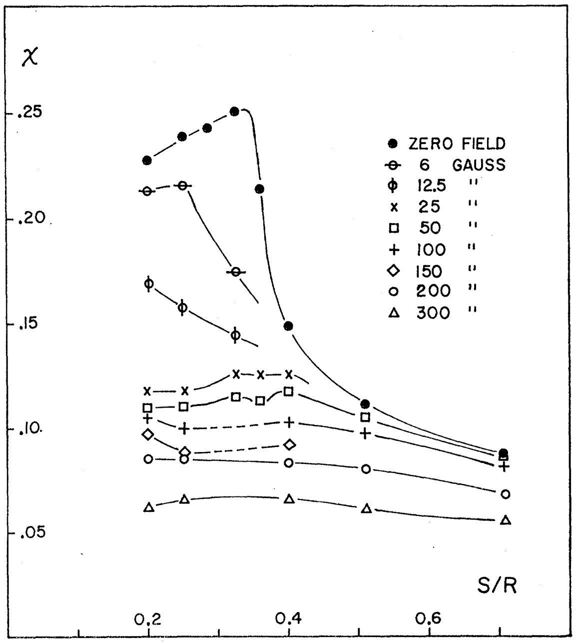

FIG. 3. Magnetic susceptibility per unit volume of CrK-alum as a function of S/R for a series of steady fields applied along the [100] crystal direction.

used to correct the H_2 deflections. In the region of low entropy where the susceptibility in small fields is rapidly changing, only one field is applied and these deflections are extrapolated in the usual manner. For most entropies, fields larger than 50 gauss always reduce the susceptibility to such a magnitude that the deflections are not decreasing rapidly enough to introduce any error and two fields can be applied for one demagnetization.

RESULTS

The results of the drop coil measurements of susceptibility are shown in Fig. 1. Within the limits of our experimental error the susceptibility in the [100] and [111] directions in the crystal is the same in the low-entropy region, $S/R<0.38$. The susceptibility values in the [110] direction appear to be slightly lower, the difference being a few percent. The wide variation in susceptibility around $S/R=0.40$ is probably, to a large extent, caused by the inaccuracy in extrapolating deflections in this region due to the rapid decrease in susceptibility. The maximum value in the χ versus S/R curve lies at $S/R=0.37$. No relaxation times associated with the magnetization were observed in this salt. It should be mentioned however, that the time constant associated with such a relaxation effect would have to be greater than 7 or 8 seconds to be observable with our apparatus.

The susceptibility measured by the ballistic method is shown plotted in Figs. 2, 3, and 4. The zero-field curves are very similar for the three orientations. All show a maximum in the susceptibility at an entropy of about $0.34R$, slightly lower than the drop coil measurements.

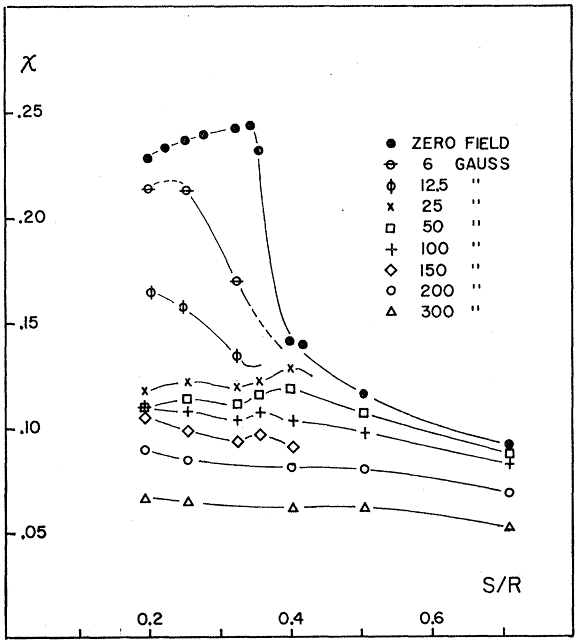

Fig. 4. Magnetic susceptibility per unit volume of CrK-alum as a function of S/R for a series of steady fields applied along the [111] crystal direction.

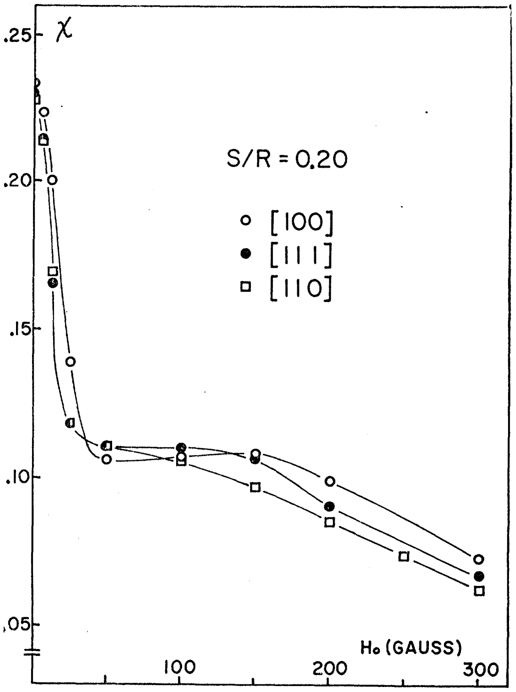

Fig. 5. Magnetic susceptibility per unit volume of CrK-alum as a function of applied external field at constant entropy. The different curves correspond to a field applied along a specific axis of the single crystal.

For all orientations the susceptibility at constant entropy shows a rapid decrease when measured in external fields, at entropies less than $0.40R$. At the lowest entropies obtained the susceptibility in a relatively small field of 25 gauss is almost half of its value in zero field. The secondary maxima observed at Leiden along the cubic axes, is apparent for all orientations in fields from 25 to 100 gauss. The location and magnitude of these maxima vary with orientation and are more pronounced along the [100] direction.

The susceptibility at the lowest entropy obtained ($S=0.20R$) is plotted versus external field in Fig. 5. Anisotropy is quite apparent in this graph, being about 11% between the [110] and [100] directions in a field of 150 gauss. (The anisotropy is defined by the formula $\chi_{\max}-\chi_{\min}/\bar{\chi}$.) The interesting feature of this curve is the increase in susceptibility with increasing field for the [100] direction. The [110] direction does not exhibit this behavior and shows a steady decrease in all fields. The susceptibility in the [111] direction becomes flat out to approximately 125 gauss but begins a rapid decrease in larger fields. At an entropy of $0.25R$ all curves show this steady decrease in χ with increasing field, and at this entropy also, the susceptibility measured in the [110] direction is consistently below that of the other two orientations.

By numerical integration of the curves of susceptibility versus applied field, the magnetization as a function of field is obtained. The results of these integrations

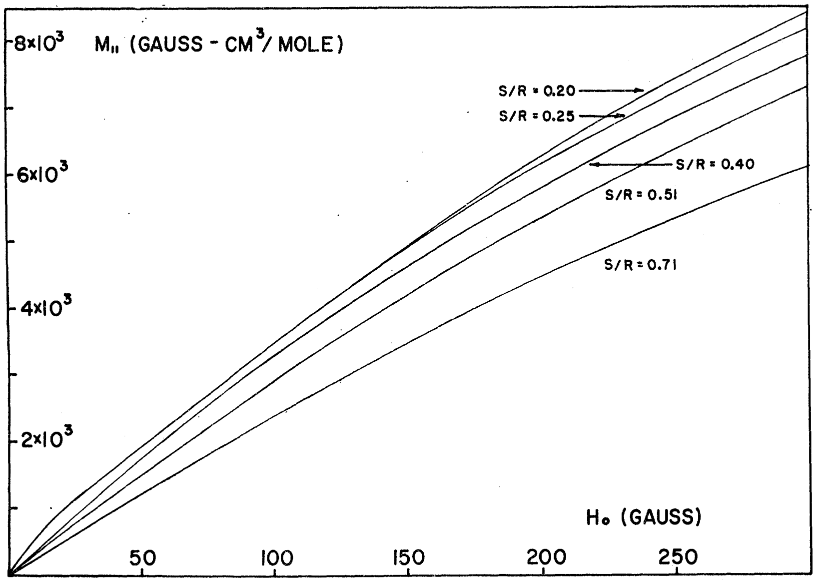

FIG. 6. Magnetization of CrK-alum as a function of an external magnetic field applied along the [100] crystal axis. The different curves correspond to different values of S/R.

are shown in Figs. 6, 7, and 8 where the parallel magnetization (M_{11}) is plotted versus applied external field (H_0) for five values of entropy. The magnetization curves for the higher entropies (greater than $0.40R$) are almost identical. At an entropy of $0.20R$, however, the magnetization reaches 53% of the saturation magnetizaton in a field of 300 gauss along the [100] direction, while having 51% and 48% of saturation value along the [111] and [110] directions, respectively. (The saturation magnetization is approximately 16 600 gauss-cm³/mole.)

For measurements of the ballistic susceptibility (along the [111] direction) at higher entropies (not shown in the figures) agreement with the theory of Hebb and Purcell[9] using the Onsager approximation for the local field is obtained for temperatures down to 0.2°K if the electric field splitting energy (δ) is taken to be $\delta = k(0.29°\text{K})$. This value is slightly higher than has been reported previously.[9]

DISCUSSION

Considering the measurements made with the moving coil apparatus, two important results should be pointed out. First, the lack of any long relaxation effects in the magnetization. If such an effect is due to irreversible domain wall displacements as suggested by Dempesy and Sapp,[5] it is apparent that the walls have a somewhat different character in the potassium and methylamine

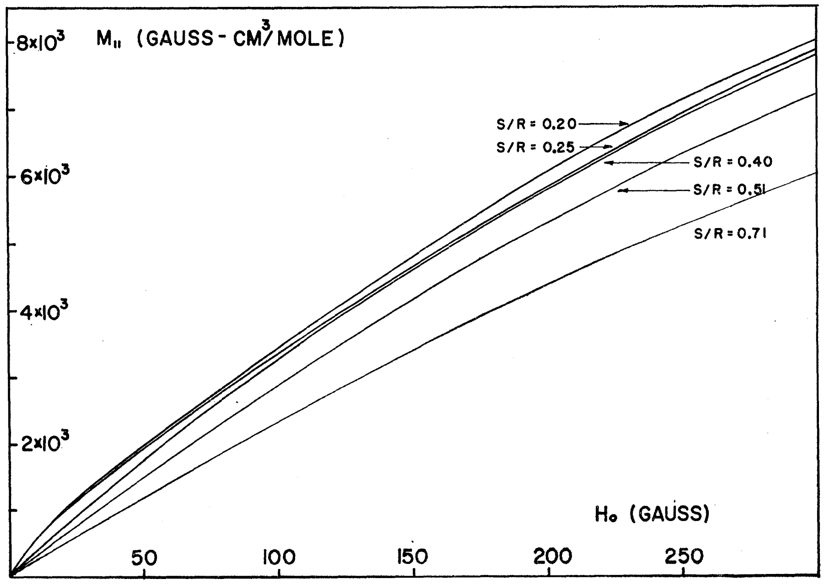

FIG. 7. Magnetization of CrK-alum as a function of an external magnetic field applied along the [110] direction.

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[9] D. de Klerk, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 15, pp. 84 and 91.

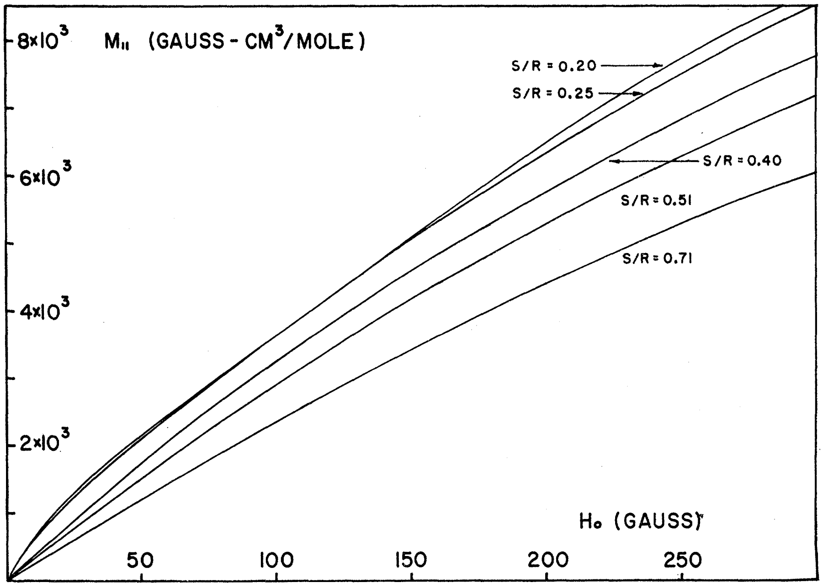

FIG. 8. Magnetization of CrK-alum as a function of an external magnetic field applied along the [111] direction.

alums. Secondly, a double maxima was not observed in the susceptibility of the present salt. Comparing again the two chrome alums, ballistic measurements by Hudson and McLane[10] and by Ambler and Hudson[4] indicated a double maximum in the susceptibility, in both alums. Drop coil measurements at this laboratory strikingly verified the existence of this second peak in the methylamine alum.

The results of measurements in longitudinal fields agree reasonably well with those made by Beun *et al.*[1] along a cubic axis. The susceptibility is found to fall rapidly in the presence of small external fields followed by an increase in susceptibility in fields from 50 to 150 gauss. Along the [110] and [111] directions, however, no such increase was observed. The explanation for such an increase of χ with field was proposed by Néel and discussed more recently by Beun *et al.*[11] Their model of antiferromagnetism is based on the existence of domains with an antiparallel ordering of spins. Under the influence of magnetic fields the reorientation of domains aligned approximately along the direction of an external field can cause an increase in χ with field. Domains preferentially aligned along the cubic axes might then possibly explain the behavior we observe.

In fields from zero to 25 gauss the rapid decrease in χ is possibly explained by the existence of domain walls. It has been suggested[11] that the wall magnetization is easily oriented in the direction of the external field. There results a large increase in the magnetization as shown in Fig. 6 and the sharp decrease in susceptibility. If one extrapolates the χ versus H_0 curves horizontally to zero field from a field of 50 gauss and assumes that the low-field peak is due entirely to domain walls, then the contribution of the walls to the total magnetization can be estimated. From Fig. 5 one finds that the walls contribute 4.2% of the saturation magnetization in the [100] direction, and 2.6% in the [111] and [110] directions.

In regard to our determination of the electric field splitting δ, it would be well to mention that in all cases the sample was cooled to liquid nitrogen temperatures in a period of from 8 to 12 hours and from liquid nitrogen to liquid helium temperature in about 6 to 8 minutes. The determination of δ requires a precise knowledge of the final entropy value. To obtain these high entropies we had to demagnetize from a starting bath temperature of 2.17°K; hence, the entropy of the lattice can no longer be neglected when calculating the final entropy of the system. In correcting for this lattice entropy we have used the recent specific heat work of Kapadnis,[12] giving $C_p=4.11\times10^{-3}T^3$.

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks and appreciation to Professor C. F. Squire for his continued interest and discussions during the course of this work. He would also like to express his gratitude to Mr. C. W. Belcher, Mr. Homer Utley, Mr. Truman Black, and the other members of the low-temperature staff who helped with much of the experimental work.

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[10] R. P. Hudson and C. K. McLane, Phys. Rev. **95**, 932 (1954).

[11] J. A. Beun, M. J. Steenland, D. de Klerk, and C. J. Gorter, Physica **21**, 767 (1955).

[12] D. G. Kapadnis, Physica **22**, 159 (1956).