PHYSICAL REVIEW VOLUME 176, NUMBER 2 10 DECEMBER 1968

Linear Chain Antiferromagnetism in $CsMnCl_3\cdot 2H_2O$[†]

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(Received 22 July 1968)

The magnetic susceptibilities of orthorhombic single crystals of $CsMnCl_3\cdot 2H_2O$ have been measured along the a, b, and c axes between 0.35 and 77°K. Above ~9°K, the susceptibility is essentially that of a system of extended weakly interacting chains of spins ($S=\frac{5}{2}$, $g=2.00$) antiferromagnetically coupled by nearest-neighbor Heisenberg exchange interaction. The magnitude of the intrachain interaction has been deduced by comparison with Fisher's classical limiting form of the theory of the Heisenberg chain, with and without corrections for the finite spin of the Mn^{++} ion. With such corrections one finds $J=-3.00k$. A small uniaxial anisotropy evident at hydrogen temperatures is attributed primarily to single-ion effects. Below ~5°K, interchain interaction apparently causes long-range antiferromagnetic ordering, with the a axis the preferred direction of spin orientation. At 0.35°K an anomalous temperature dependence of uncertain origin is seen.

I. INTRODUCTION

THE thermal and magnetic properties of a system of paramagnetic ions coupled in infinite linear chains by nearest-neighbor exchange interaction have been studied theoretically in several approximations. When the interaction is assumed to have the highly anisotropic Ising form, the theory[1] yields simple exact expressions for some of these quantities. Recent intensive investigation[2] of the case of isotropic Heisenberg interaction of ions with moments corresponding to $S=\frac{1}{2}$ has produced a quite detailed picture, which matches nicely the observed behavior of several copper salts.

Several years ago, Fisher[3] pointed out that the Heisenberg chain problem became exactly soluble in the classical limit, i.e., for $S\rightarrow\infty$. He obtained compact closed expressions for the magnetic susceptibility of such a system as well as its specific heat, the latter, of course, becoming clearly nonphysical as $T\rightarrow 0$°K. Struck by the simplicity of these results, we have considered it to be a matter of some interest to see whether an actual physical system could be found meeting even approximately the requirements of this model. A suitable substance would contain paramagnetic ions of large spin, isotropic moment and charge distribution, and large separation to minimize dipolar interaction, as well as likely paths for dominant super-exchange linkage in one-dimensional chains.

A salt which appears to have many of these characteristics is $CsMnCl_3\cdot 2H_2O$, whose structure has been determined by Jensen *et al.*[4] This material forms orthorhombic crystals characterized by the space group *Pcca*. The unit cell contains four formula units and has the dimensions $a=9.060$ Å, $b=7.285$ Å, and $c=11.455$ Å. A projection of the structure on the (001) plane is shown in Fig. 1. Each Mn^{++} ion is surrounded by a highly distorted octahedron of ligands including four Cl^- ions, two of which are shared by two neighboring Mn^{++} ions. Chains of the form -Cl^--Mn^{++}-Cl^--Mn^{++}-Cl^-- thus extend indefinitely along the a axis in relative isolation from one another. Mn^{++} ions on neighboring chains are linked only by rather indirect paths involving several intermediate atoms or H_2O groups. The ground state of the free Mn^{++} ion is ^6S, and in all but strong crystal fields it exhibits a moment corresponding to $S=\frac{5}{2}$ with an isotropic splitting factor $g=2.00$.

In this paper we present the results of measurements of the magnetic susceptibility performed on single crystals of $CsMnCl_3\cdot 2H_2O$ between 0.35 and 77°K. As we shall see, these results indicate that intrachain interaction among Mn^{++} moments is much larger than interchain coupling and that Fisher's antiferromagnetic Heisenberg chain model describes the observed susceptibility over a wide range of temperature rather well. Corrections to this model to account for finite spin and small anisotropy effects will be described.

II. EXPERIMENTAL METHODS

The magnetic-susceptibility measurements to be reported below were performed by an audio-frequency mutual-inductance technique with a mutual-inductance bridge and cryostat built previously in this laboratory and described elsewhere.[5] It will suffice to mention here some modifications of this equipment which materially aided the taking of reliable data.

The original bridge and coil assembly were patterned after those of Pillinger, Jastram, and Daunt.[6] The primary of the mutual inductance had previously contained unequal numbers of oppositely wound layers in order to reduce interaction with external paramagnetic materials. It was found, however, that less noise as well as higher sensitivity were actually obtained when the resistance of the primary was minimized by

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[†] Work supported by the National Science Foundation and U.S. Office of Naval Research. Much of this material is contained in a thesis submitted by T. Smith to the Carnegie-Mellon University in partial fulfillment of the requirements for the Ph.D. degree. A brief report of this work was presented before the American Physical Society [Bull. Am. Phys. Soc. **13**, 461 (1968)].

[*] Now at Airborne Instruments Laboratory, Melville, N.Y.

[1] See, for example, C. Domb, Phil. Mag. Suppl. **9**, 149 (1960).

[2] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964), and numerous other references cited there.

[3] M. E. Fisher, Am. J. Phys. **32**, 343 (1964).

[4] S. J. Jensen, P. Andersen, and S. E. Rasmussen, Acta Chem. Scand. **16**, 1890 (1962).

[5] J. T. Schriempf and S. A. Friedberg, J. Chem. Phys. **40**, 296 (1964).

[6] W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. **29**, 159 (1958).

using fewer layers all wound in the same direction. The mutual inductance employed in the present work consists of a secondary similar to that described by Pillinger *et al.*, and a primary of 10 layers of No. 37 AWG copper wire wound on a form having the same dimensions specified by these authors. This set of coils, together with improved wiring layout and additional shielding of the bridge, yielded a system sensitive to changes in susceptibility of about 2×10^{-7} emu. The data reported below were taken at a frequency of 275 cps.

We have used for these measurements the cryostat built by Schriempf and Friedberg[5] which has provision for cooling with liquid He^3. The principal modification of this apparatus was the replacement of the sample control-tube assembly (see Ref. 5, Fig. 1) by a new specimen-manipulating device. This consists of three externally operated winches made of standard glass-tapered fittings. One reference and two unknown samples can be independently inserted in the mutual inductance with this arrangement.

The bridge-calibration constant was established in the He^4, H_2, and N_2 ranges by measuring the susceptibility of a powdered specimen of $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ in a spherical Lucite container. This salt was assumed to obey the Curie law[7] $\chi=(0.01119/T)$ emu/g. The bridge constants deduced by fitting data taken between 1.5 and 4.2°K, at the hydrogen triple point, and at the N_2 triple point differed by less than $\frac{1}{2}\%$. Using the calibration constant thus established we have measured the susceptibility of single-crystal cerium magnesium nitrate perpendicular to the c axis. In the interval 1.50 to 4.2°K, in which temperatures were given by the 1958 He^4 vapor-pressure scale,[8] we found values of the Curie constant and temperature-independent term in excellent agreement with those reported by Leask *et al.*[9] We estimate the accuracy of the calibration constant to be $\pm1\%$ or better.

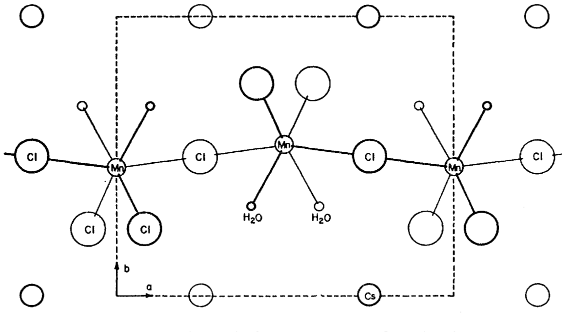

FIG. 1. Projection of the structure of orthorhombic $CsMnCl_3\cdot 2H_2O$ on the (001) plane (after Jensen *et al.*).

Susceptibility measurements were made in several temperature ranges. Below about 1.2°K the specimen was immersed directly in liquid He^3 and its temperature determined by measurements of the vapor pressure of the bath. Direct use of the 1962 He^3 vapor-pressure scale[10] yielded estimates of the specimen temperature that were significantly improved by application of corrections deduced from measurements on a cerium magnesium nitrate sample. Between 1.2 and 4.2°K the specimen was placed in contact with a liquid He^4 bath by means of He^3 exchange gas. The 1958 He^4 scale[8] was used to obtain bath temperatures from the measured vapor pressure. Near the lowest temperatures reached with He^3 and He^4, $\sim$0.35 and $\sim$1.2°K, respectively, the maximum absolute errors in temperature amount to $\pm$0.02°K. From 9.3 to 13.813°K the refrigerant was solid H_2 and temperatures were measured by means of a $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ thermometer with an estimated accuracy of $\pm$0.05°K. A liquid-hydrogen bath was employed between 13.81 and 20.2°K. The 1951 equilibrium liquid-hydrogen vapor-pressure scale[11] yielded temperatures in this region accurate to about $\pm$0.02°K. Temperatures between 63.2 and 78°K were achieved with liquid N_2 and measured with an accuracy of about $\pm$0.1°K with a magnetic thermometer of $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$.

III. SAMPLES

Crystals of $CsMnCl_3\cdot 2H_2O$ were grown by slow evaporation of saturated aqueous solutions of equal molar amounts of reagent grade CsCl and $MnCl_2\cdot 4H_2O$. When carried out at about 30°C, this procedure gave only the desired pink orthorhombic crystals. At lower temperatures a pale pink, triclinic phase, $Cs_2MnCl_4\cdot 2H_2O$, could also be obtained. With care it was possible to grow crystals of $CsMnCl_3\cdot 2H_2O$ ranging in size up to about $10\times6\times2$ mm.

To facilitate orientation of the specimens, the Miller indices of the crystal faces were determined. This was accomplished by comparing the measured interfacial angles with the computed angles between the atomic planes whose *hkl* values are known from the x-ray structural studies.[4]

IV. RESULTS AND DISCUSSION

The magnetic susceptibilities of single-crystal $CsMnCl_3\cdot 2H_2O$ determined with the measuring field along the a, b, and c axes are shown at temperatures between 0.35 and 77.3°K in Fig. 2. No anisotropy was detectable in the nitrogen range. A small roughly uniaxial anisotropy becomes noticeable in the hydrogen region and grows with decreasing temperature. Below 4.2°K the susceptibility was observed to be highly anisotropic, χ_a falling rapidly and χ_b and χ_c increasing as the tempera-

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[7] A. H. Cooke, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1955), Vol. I, p. 238.

[8] J. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).

[9] M. J. M. Leask, R. Orbach, M. J. D. Powell, and W. P. Wolf, Proc. Roy. Soc. (London) **A272**, 371 (1963).

[10] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. **68A**, 579 (1964).

[11] H. J. Hoge and R. D. Arnold, J. Res. Natl. Bur. Std. **47**, 63 (1951).

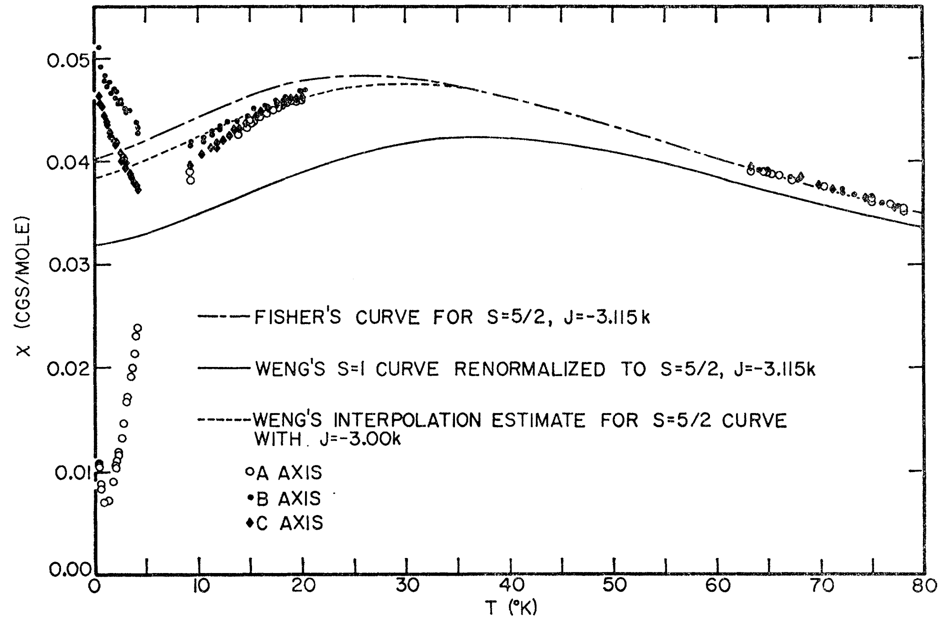

FIG. 2. Measured magnetic susceptibilities of $CsMnCl_3 \cdot 2H_2O$ along the a, b, and c axes below 77°K. The indicated theoretical curves are discussed in the text.

ture is lowered. Below 1°K χ_a begins to rise rapidly and at 0.35°K all three are rising with falling temperature.

The presence of significant antiferromagnetic interaction among Mn^{++} ions in this substance is suggested immediately by the fact that the susceptibilities measured at nitrogen temperatures are much smaller than predicted by Curie's law for $S=\frac{5}{2}$ and $g=2.00$. At the same time, neither the magnitude nor the temperature variation of the susceptibility in this region seems to indicate that strong crystal field or covalency effects are reducing the size of the Mn^{++} ionic moment. Comparing hydrogen- and nitrogen-temperature data, we infer the existence of a broad maximum in the susceptibility near 30°K. Such a maximum is, of course, expected for an antiferromagnetic linear chain system. Broad susceptibility maxima could occur also in systems of isolated clusters or two-dimensional sheets of exchange coupled spins. The structural evidence on $CsMnCl_3 \cdot 2H_2O$ cited above, however, suggests that a linear chain interpretation is apt to prove the more fruitful. In attempting to apply such a model to this system we shall also exploit the fact that the rounded maximum to which both the hydrogen- and nitrogen-temperature data evidently belong is well removed from the helium region in which long-range ordering effects appear. Such ordering presumably results from interchain spin coupling much smaller in magnitude than the intrachain interaction. The fact that the broad susceptibility maximum is "resolved" is thus taken as justification for ignoring interchain interaction and treating the system approximately as one of independent antiferromagnetic chains.

Because we are dealing with chains of super-exchange-linked Mn^{++} ions, it seems plausible, at least initially, to apply Fisher's classical Heisenberg result.[3] In passing to the classical limit, Fisher replaces the quantum-mechanical spin operators with classical vectors. Inserting appropriate scaling factors we may write the resulting classical Hamiltonian for a chain of $N+1$ spins in a magnetic field H as

$$\mathcal{H}_0=-2JS(S+1)\sum_{i=1}^{N}\mathbf{s}_i\cdot\mathbf{s}_{i-1}-g\mu_B[S(S+1)]^{1/2}\sum_{i=0}^{N}\mathbf{H}\cdot\mathbf{s}_i, \quad (1)$$

where the unit vector $\mathbf{s}_i$ is associated with the ith spin, whose magnetic moment is $g\mu_B[S(S+1)]^{1/2}$. Assuming N to be very large and scaling the spin magnitudes as in Eq. (1), Fisher's expression for the magnetic susceptibility of the chain becomes

$$\chi_0=\frac{Ng^2S(S+1)\mu_B{}^2}{3kT}\frac{(1+u)}{(1-u)}, \quad (2)$$

where

$$u=\coth[2JS(S+1)/kT]-1/[2JS(S+1)]. \quad (3)$$

The leading terms in the high-temperature expansion of Eq. (2) agree with those of the exact series expansion of the Heisenberg linear-chain susceptibility given by Rushbrooke and Wood.[12] If the interaction is ferromagnetic, i.e., $J>0$, χ_0 diverges as $1/T^2$ as $T\to 0$ according to Eq. (2). For antiferromagnetic interaction, i.e., $J<0$, χ_0 exhibits a rounded maximum and approaches $Ng^2\mu_B{}^2/-12J$ as $T\to 0$.

Assuming $S=\frac{5}{2}$ and $g=2.00$ we have fitted Eq. (2) to our data in the nitrogen range by adjusting J. The best fit is obtained with $J=-3.115k$. The resulting curve of χ versus T is shown together with the data in

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[12] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).

Fig. 2. The fit of the nitrogen-temperature data is a quantitative one. In the hydrogen region, the theoretical curve follows the general trend of the data rather well, but is systematically high. Since the model, as described by Eq. (1), is isotropic it cannot account for the small anisotropy that appears in the hydrogen range. The evident failure of the model below 4.2°K is expected since it ignores interchain interaction.

There is good reason to believe that the discrepancy between the data and theory in the hydrogen range is the result of the fact that a spin of $S=\frac{5}{2}$, while large, is still finite and thus not strictly classical. Recently Weng and Griffiths[13] have calculated the susceptibility of the infinite Heisenberg chain for $S=1$ as a function of temperature by extrapolation of exact results for finite chains. In Fig. 2 we have plotted their result (solid curve) suitably renormalized so that at high temperature it joins Fisher's curve for $S=\frac{5}{2}$ and $J=-3.115k$. We see that the curve for finite spin lies below the classical-limiting curve, the two actually bracketing the data in the hydrogen region. The corresponding curve obtained by renormalizing the known solution for $S=\frac{1}{2}$ would lie still lower.

Using the accurate results now available for the Heisenberg chain with $S=\frac{1}{2}$, 1, and ∞, Weng[14] has developed an interpolation scheme applicable to large but finite spins. The dashed curve in Fig. 2 has been computed by this method with $S=\frac{5}{2}$ and $J=-3.00k$. We note, that above ~35°K, this result is indistinguishable from the classical one and thus well represents the nitrogen-range observations. At hydrogen temperatures, the finite-spin calculation differs appreciably from the classical theory in just the way needed to fit the data, which it does rather well. We conclude, therefore, that to a reasonable degree of approximation, $CsMnCl_3\cdot 2H_2O$ behaves above ~9°K as a system of weakly interacting linear Heisenberg chains with $S=\frac{5}{2}$, $g=2.00$, and $J=-3.00k$.

Let us consider now the small, essentially axial anisotropy that appears in the susceptibility in the hydrogen range. As in the matters of magnitude and temperature variation of the susceptibility itself, one might hope that at least a semiquantitative description of this anisotropy might be built upon Fisher's classical Heisenberg model. Griffiths[15] has suggested a perturbation procedure by which this may be done. It yields results which are expected to be valid only where the anisotropy is not large compared to the average susceptibility. The data and symmetry requirements suggest that a suitable perturbing Hamiltonian consist of a sum of axially symmetric single-ion terms of the form $D(S_i^z)^2$. Going to the same classical limit employed in Eq. (1), we write it as

$$\mathbf{H}_a=DS(S+1)\sum_{i=0}^{N}(s_i^z)^2, \tag{4}$$

where D is the same constant for each of the $N+1$ atoms in the chain. Using the total Hamiltonian $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_a$, Fisher's expression for the susceptibility in terms of spin-correlation functions becomes, to first order in D,

$$\chi_{\parallel}=\frac{g^2S(S+1)\mu_B^2}{kT}\times\left\{\sum_{i=0}^{N}\sum_{j=0}^{N}\langle s_i^z s_j^z\rangle-\frac{DS(S+1)}{kT}\sum_{i=0}^{N}\sum_{j=0}^{N}\sum_{k=0}^{N}\times[\langle s_i^z s_j^z(s_k^z)^2\rangle-\langle s_i^z s_j^z\rangle\langle(s_k^z)^2\rangle]+\cdots\right\}. \tag{5}$$

The analogous expression for $\chi_\perp$ differs only in the substitution of $(s_k^x)^2$ for $(s_k^z)^2$. Angular brackets in Eq. (5) refer to averages with respect to $\mathcal{H}_0$. Note that the first term containing only the pair-correlation function $\langle s_i^z s_j^z\rangle$ leads to the unperturbed susceptibility χ_0 of Eq. (2).

Griffiths has evaluated the higher-order spin-correlation functions of Eq. (5), permitting us to write

$$\chi_{\parallel}=\chi_0-\frac{4Ng^2\mu_B^2[S(S+1)]^2D}{45(kT)^2}\times\left[\frac{(1+u)(1+v)}{(1-u)(1-v)}+\frac{2u}{(1-u)^2}\right]$$
$$=\chi_0-(4/15)\chi_c[DS(S+1)/kT]F \tag{6}$$

and

$$\chi_\perp=\chi_0+(2/15)\chi_c[DS(S+1)/kT]F, \tag{7}$$

where

$$v=1-[3ukT/2JS(S+1)];$$
$$F=\frac{(1+u)(1+v)}{(1-u)(1-v)}+\frac{2u}{1-u};$$
$$\chi_c=Ng^2\mu_B^2S(S+1)/3kT;$$

and χ_0 and u are as defined in Eqs. (1) and (2). It will be seen that the average susceptibility $\frac{1}{3}(\chi_{\parallel}+2\chi_\perp)$ is just χ_0, and that the anisotropy is simply

$$\chi_{\parallel}-\chi_\perp=-\tfrac{2}{5}\chi_c[DS(S+1)/kT]F. \tag{8}$$

For negative values of J, $F\to-\frac{1}{6}$ as $T\to 0$. F is zero at a temperature of $(-J/k)S(S+1)$ and approaches unity at high temperatures.

We see from Fig. 2 that the b axis of the crystal must correspond to the $\parallel$ or z direction of our anisotropy calculation. This is quite reasonable since each Mn^{++} ion lies on one of the twofold axes parallel to the b axis. There is no reason, of course, to expect that the anisotropy should have a higher symmetry than the orthorhombic symmetry of the *Pcca* space group. We see that it clearly does not in the helium range.

The anisotropy in the hydrogen range is reasonably well represented by Eq. (8) if we choose D to be about $+0.08$ cm^{-1} and J to have the value $-3.12k$ as determined above in the fitting of the susceptibility. The

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[13] C. Y. Weng and R. B. Griffiths (to be published).

[14] C. Y. Weng (private communication).

[15] R. B. Griffiths (private communication).

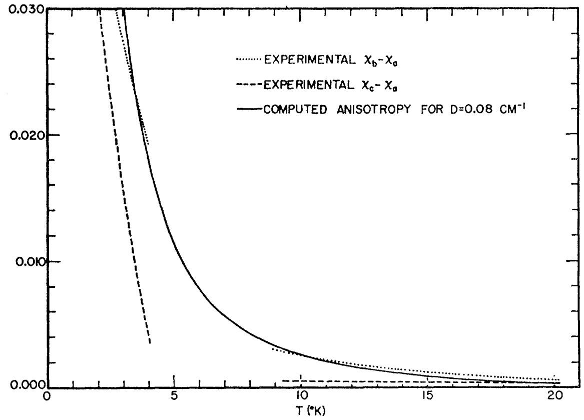

FIG. 3. Measured and calculated magnetic anisotropy of $CsMnCl_3 \cdot 2H_2O$ below 20°K. The theoretical curve is computed with Eq. (8) of the text.

curve computed with Eq. (8) is plotted in Fig. 2 together with the measured anisotropy. Equation (8) predicts an anisotropy at nitrogen temperatures below the limits of experimental resolution in agreement with our observations.

The quantity $D=+0.08$ cm^{-1} needed to fit the anisotropy measures formally the splitting in zero field of the Mn^{++} ion ground state into three Kramers doublets. This splitting is observed in paramagnetic resonance experiments on single Mn^{++} ions in diamagnetic host crystals. The largest value reported in the literature[16] was found for Mn^{++} in $Zn(HCOO)_2 \cdot 2H_2O$ and amounts to 0.0485 cm^{-1}. The somewhat greater value inferred from our results is not unreasonably large particularly when we note that it applies to a concentrated salt and may contain contributions from interactions other than that of an ion with its immediate environment. An important source of anisotropy in noncubic spin arrays is the magnetic dipolar interaction. Because of its long range, a proper treatment of this interaction requires summation over all neighbors in a large volume around each ion. A crude estimate of the magnitude of the effect can be obtained, however, by considering only the nearest neighbors within an isolated chain. If d is the nearest-neighbor separation, then the dipolar energy is of the order of $g^2\mu_B{}^2/d^3 \approx 0.01$ cm^{-1} which is not negligible in comparison with $D=0.08$ cm^{-1}. It is thus possible that dipolar effects would account in part for the apparent enhancement of our fitted D coefficient over those found for isolated Mn^{++} ions in diluted salts.

The fact that the coefficient D is positive indicates that it is energetically favorable for the spins of this system to lie in the a-c plane, at least at hydrogen temperatures. Below 4.2°K, however, the equivalence of a and c directions has clearly been lost. Instead, we see in Fig. 2 that χ_a has split away from χ_c as well as χ_b and is falling rapidly with decreasing temperature. The general relationship of the susceptibilities suggests the onset somewhere between 4.2 and 9°K of long-range antiferromagnetic order with the preferred direction of spin alignment along or near the a axis. This is consistent with the conclusion drawn from the nuclear resonance work of Spence *et al.*,[17] which indicates a cooperative antiferromagnetic transition with $T_N \sim 4.8$°K. Since a purely linear chain system cannot sustain long-range order, we infer the presence of interchain interactions which raise the dimensionality and allow long-range order to propagate below T_N. That the a axis is the preferred direction for spin alignment indicates the presence of anisotropy effects of lower symmetry than that given by Eq. (4). These could include rhombic contributions to the crystal-field splitting of the single-ion ground state as well as magnetic dipole interactions. Anisotropy of the exchange interaction would presumably be small in view of the closeness of the splitting factor g to its free-spin value.

It is perhaps worth noting that Eq. (8), with its parameters chosen as above to fit the anisotropy in the hydrogen region, may be extrapolated below 4.2°K where it is seen [Fig. (3)] to reproduce $\chi_b-\chi_a$ rather well. It is uncertain, however, how much weight this result should receive since below 4.2°K the anisotropy is no longer small in comparison with the susceptibilities themselves. Under these conditions the perturbation procedure used to obtain Eq. (8) should break down.

While generally consistent with the existence of long-range antiferromagnetic order, χ_a, χ_b, and χ_c all exhibit atypical temperature variations below 4.2°K. Instead of vanishing as $T \rightarrow 0$°K, as might be expected of $\chi_{\|}$, χ_a passes through a minimum near 1°K and rises with falling temperature below that point. χ_b and χ_c, instead of approaching constant values at low temperatures as would $\chi_{\perp}$ of a simple antiferromagnet, are both rising rapidly at 0.35°K. So far as we have been able to determine this behavior is intrinsic to the specimens and not the result of instrumental effects. The fact that all three susceptibilities are rising at the lowest temperature suggests that the specimen contains some paramagnetic ions whose moments are still essentially free in spite of the magnetic ordering processes which have taken place. The only paramagnetic ion present in sufficient quantity to produce so large an effect is probably Mn^{++}, itself. We find no evidence in our specimens of gross departures from stoichiometry or the inclusion of phases other than orthorhombic $CsMnCl_3 \cdot 2H_2O$. It is possible, of course, that Mn^{++} ions in interstitial positions or lattice sites normally occupied by Cs^+ ions could produce the observed effects in crystals having nearly the correct composition and general structure. This possibility would imply, however, a sensitivity to specimen preparation which we have not detected in the limited number of samples studied to date.

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[16] D. J. E. Ingram, Phys. Rev. **90**, 711 (1953).

[17] R. D. Spence, J. A. Casey, and V. Nagarajan, J. Appl. Phys. **39**, 1011 (1968).

Other mechanisms which might produce the observed low-temperature behavior of the susceptibilities suggest themselves. For example, the occurrence below 0.35°K of another cooperative phase transition, perhaps to a weakly ferromagnetic state, could introduce sharp susceptibility peaks of which we might be seeing only the high-temperature side. Unlike the impurity effects outlined above, there would probably be little preparation sensitivity in this case.

An explanation of a rather different kind is suggested by the chainlike characteristics of $CsMnCl_3 \cdot 2H_2O$. In our earlier discussion, it was assumed that the antiferromagnetic chains of Mn^{++} ions in this substance were essentially infinitely long. For finite Heisenberg chains in the classical limit Fisher[3] shows that Eq. (2) is replaced by the more general result

$$\chi_n = \frac{Ng^2\mu_B{}^2S(S+1)}{(n+1)3kT} \times \left((n+1)\frac{1+u}{1-u} - 2u\frac{1-u^{n+1}}{(-u)^2}\right), \quad (9)$$

where N is the total number of spins, $n+1$ the number of spins per chain, and u is as previously defined [Eq. (3)]. If $n+1$ is a large odd number and $J<0$, Eq. (9) yields a result quite similar to that given by Eq. (2) except that as T falls to sufficiently low values χ will begin again to rise. In Fig. 4 we have plotted as a solid line the curve given by Eq. (9) for $n=2000$, $S=\frac{5}{2}$, $g=2.00$, and $J=-3.12k$. Also shown (dashed curve) is the average of the three single-crystal susceptibilities. There is a close resemblance between these curves. Presumably, they would be brought more nearly into coincidence by the application of correctons for finite spin. It is not difficult to conceive of various types of crystalline imperfection which could limit the average effective chain length to the assumed magnitude.

While these considerations are quite attractive we must remember that no allowance has been made for long-range ordering through interchain coupling which sets in below ~5°K. In this picture the anomalous paramagnetism at very low temperatures is essentially that of the unpaired spins at the free ends of independent chains with an odd finite number of Mn^{++} ions. It is not obvious that these spins could remain free in the presence of significant interchain interaction and long-range ordering. In the light of such a serious objection, we must conclude that this mechanism is at least as speculative as the others. Further experiments are probably necessary in order to establish clearly the source of the anomalous susceptibility of $CsMnCl_3 \cdot 2H_2O$ near 1°K.

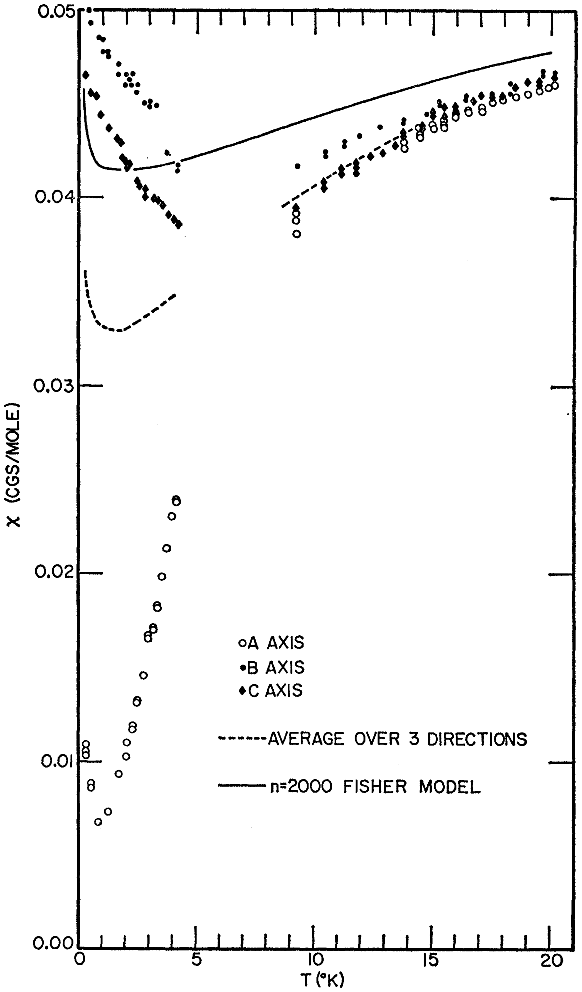

FIG. 4. Magnetic susceptibilities of $CsMnCl_3 \cdot 2H_2O$ below 20°K.

ACKNOWLEDGMENTS

We are most grateful to Professor R. B. Griffiths and C. Y. Weng for numerous discussions and for permission to use results of their work prior to publication.