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Isotropic Magnetic Exchange in Manganese(II) Chloride Dihydrate, $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, a Chemical Linear Chain

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Magnetic susceptibility measurements on a single crystal of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, which consists of infinite linear chains of edge-sharing $\text{trans}[\text{MnCl}_4(\text{OH}_2)_2]$ octahedra, have been made from 1.5 to 20°K. The data show the presence of observable anisotropy in the paramagnetic state below about 12 or 14°K. In addition the material undergoes an antiferromagnetic-paramagnetic transition at $T_N = 6.90 \pm 0.03^\circ\text{K}$. The results, which have been analyzed using Fisher's classical Heisenberg model along with a molecular field correction, indicate that interchain and intrachain exchange are almost equal, in agreement with previous hypotheses. The value of intrachain exchange obtained, $J/k = -0.45 \pm 0.03^\circ\text{K}$, may be typical of dichloride-bridged Mn^{2+} ions.

Introduction

Chemically chained compounds have come under intensive study in recent years since they quite often behave as one-dimensional magnetic systems which are amenable to theoretical interpretation. Although the series $\text{MX}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu}$; $\text{X} = \text{Cl, Br}$) is one of the largest series containing like chemical chains, little work has been reported on the $\text{M} = \text{Mn}$, $\text{X} = \text{Cl}$ member of that series. The work done to date includes specific heat measurements¹ which indicated a magnetic phase transition at 6.68°K and showed the lack of magnetic linear chain characteristics, thus suggesting interchain and intrachain exchange to be of comparable magnitude. Nmr measurements,² which indicated the ordering to take place at 6.8°K, determined the magnetic space group of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. In addition, a short note on nuclear spin lattice relaxation in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ has appeared.³ Some susceptibility measurements which indicated the b axis to be the easy axis have also been made in the ordered state below about 4°K.⁴ As many of the theories applicable to linear chain magnetism are only valid for the paramagnetic region, measurements in that region are highly desirable. Thus, the magnetic susceptibility of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ has now been measured from 1.5 to 20°K and is reported here. Values for the intrachain and interchain exchange parameters have been obtained from an analysis of the data.

Crystals of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ are monoclinic, of space group $C2/m$, with $a = 7.409 \text{ \AA}$, $b = 8.800 \text{ \AA}$, $c = 3.691 \text{ \AA}$, and $\beta = 98.67^\circ$.⁵ The compound consists of chains of edge-sharing $\text{trans}[\text{MnCl}_4(\text{OH}_2)_2]$ octahedra which parallel the c axis. Nearest neighbor chains (chains adjacent along $\langle 110 \rangle$) are separated by about 5.7 Å and are linked together by an extensive amount of hydrogen bonding. Intrachain Mn^{2+} nearest neighbors are separated by 3.7 Å and are connected by two chloride ions, each of which forms an approximate 90° exchange pathway between the Mn^{2+} ions. The two Mn-Cl distances are slightly different (2.59 and 2.51 Å). The crystal structure, along with some of the hydrogen bonds, is shown in Figure 1. The corresponding spin structure of the ordered state obtained from the nmr work is shown in Figure 2.

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Experimental Section

Single crystals of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ may be grown by evaporation of an aqueous solution of MnCl_2 above 58°.⁶ However, large crystals grown in this manner quite often have pockets of occluded solution which produce the common tetrahydrate species when the crystals are cooled below their growth temperature. This problem was noted in both the nmr and preliminary heat capacity studies. Later heat capacity studies on a single crystal of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ grown from an aqueous solution of LiCl and MnCl_2 gave no indication of the presence of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in that crystal.⁷ A similar solution was used to obtain crystals for the present study. The solution was evaporated in a constant-temperature bath which was held stable to $\pm 0.01^\circ$. The actual temperature of the bath was $50.0 \pm 0.1^\circ$. The crystals thus obtained, which are relatively stable at room temperature, had the habit described by Neuhaus:⁸ the crystals were elongated along $\{001\}$, bounded by $\{110\}$ and $\{010\}$, and terminated by $\{001\}$. An additional aid in identifying crystal orientation is the presence of a cleavage plane parallel to (010) . As has been previously noted,⁵ attempts to cut $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ perpendicular to $\{001\}$ generally result in loose bundles of fibers; these result from the splintering of the "cleavage platelets" which initially appear in such a process. A solvent saw has been successfully used previously to avoid this problem.⁹ However, slow careful cutting and scraping can also be used to cut a crystal without inducing any strain or splintering into the crystal. The latter method was used to obtain a cuboid crystal weighing 0.076 g for the present studies. Careful examination of the crystal portion used, made with a polarizing microscope, revealed no occlusions or induced strain. After also being examined for lack of occluded material, several single crystals, harvested at the same time as the one used in the measurements, were chemically analyzed by Galbraith Laboratories, Inc. *Anal.* Calcd for $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$: Mn, 43.7; Cl, 56.3; H_2O , 22.2. Found: Mn, 42.4; Cl, 57.6; H_2O , 24.3. The lithium content was found to be negligible. (The Mn and Cl values are based upon the dried material.) Although not perfect, these results do agree within the usual accuracy of this commercial laboratory.

Susceptibility measurements were made along the a' , b , and c axes (a' is the direction perpendicular to the bc plane). The sample was visually oriented for measurements along the c axis by use of crystal edges which correspond with that direction. For measurements along the a' and b axes, the crystal was oriented by seating it on a well-developed (010) face and butting an edge of it which was parallel to c against the sample holder. Thus the uncertainties in the a' and b axis alignments are negligible and the c axis alignment should be off by no more than 5° . The measurements were made using a mutual-inductance technique in which the sample is placed in the center of the measuring secondary of a mutual-inductance coil so that a change in the sample's susceptibility will cause a corresponding change in the mutual inductance of the coil. That change, in turn, may be determined using a 17-Hz bridge. Bridge readings are converted to susceptibility units through use of $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a calibrant. Temperatures are measured at the sample site using a calibrated germanium resistance thermometer in a potentiometric circuit. A Janis variable-temperature dewar

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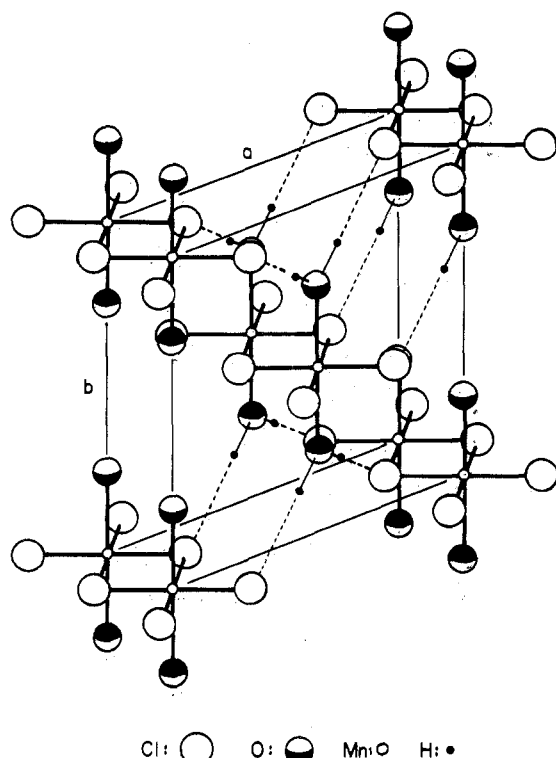


Figure 1. The structure of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Hydrogen bonds are shown as dashed lines. Not all of the hydrogens and hydrogen bonds are shown.

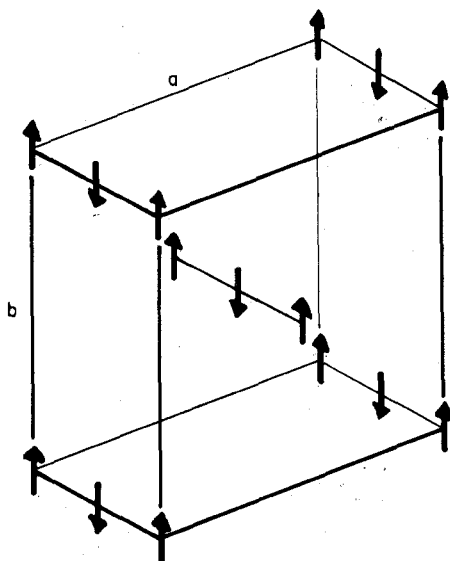


Figure 2. The ordered-state spin arrangement of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ as determined from the nmr work. The magnetic unit cell shown is twice the size of the chemical unit cell shown in Figure 1.

is used and the temperature at the sample site generally can be held stable to better than 0.01°K . Further details of the experimental setup have been given elsewhere.¹⁰

Results

The results of the measurements are shown in Figure 3. The uncertainty in the absolute values is estimated to be less than 3%. The antiferromagnetic ordering observed by previous investigators is clearly indicated by the behavior of the susceptibilities below about 7°K . The essentially constant behavior of χ_a' and χ_c , as well as the decrease of

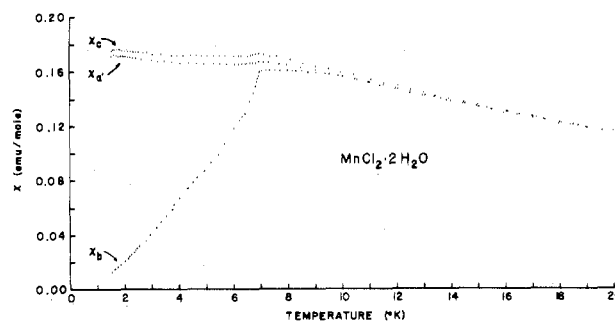


Figure 3. The magnetic susceptibility of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$.

χ_b , with decreasing temperature below 7°K shows that the ordering is antiferromagnetic with the preferred axis of alignment being the b axis, as previously noted.

Several minor features of the data must first be noted. As should be expected for Mn^{2+} , which is an S state ion, essentially no anisotropy is seen at high temperatures in the paramagnetic state. However, below 12 or 14°K , although χ_a' and χ_b are still essentially indistinguishable in that region, an observable anisotropy develops between them and χ_c , with χ_c being larger than either χ_a' or χ_b at lower temperatures. Further anisotropy between χ_a' and χ_b develops below about 9°K , with χ_a' being larger than χ_b . Below about 7°K , χ_b abruptly drops with decreasing temperature. Careful examination of the data indicates an inflection point in the χ_b data at $T_N = 6.90 \pm 0.03^\circ\text{K}$. This temperature, as indicated by theory,¹¹ should be the actual ordering temperature and is in reasonable agreement with the nmr observation. (Since the heat capacity sample had a very large $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ impurity, the transition temperature observed there quite likely was reduced by the presence of the impurity which orders at 1.62°K .¹²) It is interesting to note that near T_N both χ_a' and χ_c drop very slightly with decreasing temperature before becoming constant. Such behavior has been observed in other compounds.^{13,14} It also should be noted that below about 4°K , both χ_a' and χ_c begin to rise very slightly with decreasing temperature until about 1.6°K , when they then begin to drop. This behavior might have been attributable to a $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ impurity, since that material orders antiferromagnetically at 1.62°K , but since similar behavior was not noted in χ_b in that region, that explanation does not seem valid. Lower temperature measurements would be useful in clarifying the situation.

Although the features of the data noted above are interesting, the most notable feature of the measurements is the lack of a much more gradual rounding and dropping, with decreasing temperature, of the paramagnetic susceptibility measured along the preferred axis, as found with other Mn^{2+} linear chain compounds.^{15,16} In fact, the behavior is very similar to that of systems with isolated monomers in which there is little short-range magnetic order above T_N .^{12,13} This lack of short-range order in the paramagnetic state was noted in the heat capacity measurements¹ and cited as evidence for the approximate equality of intrachain and interchain exchange in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$.

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In order to obtain values for those exchange parameters, the present data have been fit using Fisher's classical Heisenberg results¹⁷ for infinite linear chains. A molecular field approximation has been used to account for interaction between chains. Fisher's equation for the magnetic susceptibility of a classical spin S chain is¹⁷

$$\chi_{LC} = \frac{Ng^2\beta^2 S(S+1)}{3kT} \frac{1-u}{1+u} \quad (1)$$

where

$$u = (T/T_0) - \coth(T_0/T) \quad (2)$$

and

$$T_0 = 2JS(S+1)/k \quad (3)$$

and where J is the intrachain exchange parameter. If there are interactions between chains, the actual observed susceptibility may then be obtained using the results of a molecular field calculation^{14,18}

$$\chi_{\text{obsd}} = \frac{\chi_{LC}}{1 - (2zJ'/Ng^2\beta^2)\chi_{LC}} \quad (4)$$

where J' is the interaction between chains and z is the number of nearest neighbor chains. Since the model upon which eq 1 is based is an isotropic one, the above equations will not be capable of reproducing the observed anisotropy. The χ_a' data set was arbitrarily chosen to be fit using eq 1 and 4. The parameters resulting from a fit of those data between 7 and 20°K are $J/k = -0.45 \pm 0.03^\circ\text{K}$ and $zJ'/k = -1.9 \pm 0.1^\circ\text{K}$. (An isotropic value for g of 2.00 was assumed, since that is the value usually observed for Mn^{2+} .) Susceptibilities calculated using these values agree with those experimentally observed to within about 1.5%. Such agreement, especially to within 0.1°K of T_N is truly gratifying. Since there are four nearest neighbor chains for any given chain in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, $z = 4$, and thus $J'/k = -0.48 \pm 0.03^\circ\text{K}$. So it is seen that, indeed, as previous experiments indicated, the intrachain and interchain exchange parameters are equal within experimental error. Furthermore, it must be noted that the negative sign of J is in agreement with the nmr results which showed antiferromagnetic intrachain exchange. The correctness of the negative sign of J' , indicating antiferromagnetic interchain coupling, is not obvious. The nmr results indicated that nearest interchain neighbor spins were aligned in such a manner as to suggest ferromagnetic coupling. However, the complex hydrogen bonding in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ makes it quite possible that the major coupling between spins in nearest-neighbor chains is between those which are next-nearest interchain neighbors, in which case antiferromagnetic coupling would produce the observed parallel alignment of nearest interchain neighbor spins. Further evidence that the magnitudes of J and J' are of the correct order of magnitude is obtained upon consideration of the molecular field (as well as spin wave) prediction¹⁹

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for the limiting low-temperature ordered state perpendicular susceptibility

$$\chi_{\perp}(0) = Ng^2\beta^2/4z|J| \quad (5)$$

The low-temperature experimental values for χ_a' and χ_c used in eq 5 result in a value of $z|J/k| = 2.19 \pm 0.06^\circ\text{K}$. For isotropic interaction between six nearest neighbors (two neighbors in a chain and four in adjacent chains), $|J/k| = 0.36 \pm 0.01^\circ\text{K}$. This value is in reasonable agreement with the values obtained above for the paramagnetic region. It is not unreasonable that the values differ by about 25%, since there is a clear indication from the observed low-temperature anisotropy that other mechanisms, perhaps single-ion anisotropy, are important at low temperatures and that therefore eq 5 may not be perfectly applicable without modification.

Discussion and Conclusions

The relatively large interchain exchange in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ emphasizes the importance of hydrogen-bonded pathways for exchange processes. It is interesting to consider what the magnetic behavior of chemical chains of edge-sharing $[\text{MnCl}_4(\text{OH}_2)_2]$ octahedra would be if they were more separated than those in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Were J' essentially zero, a broad maximum would then appear near 4°K for $J/k \approx -0.5^\circ\text{K}$. Although for such a small J' the transition temperature should be lower than that found in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, how much it would be lowered is not easily predicted. More than likely, in that case the specific heat would indicate far more short-range order in the paramagnetic state than is exhibited by $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Thus with the increased separation of the chains, characteristics associated with the magnetic linear chain behavior might be more easily studied. In particular, since the Mn-Cl-Mn bond distances and angles would likely vary in any set of real compounds containing the same chains as in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, some information regarding the relationship of these parameters to the intrachain exchange might be gained. Such a study which has already been completed on a set of similar Co^{2+} chains has indicated J might vary by about 30%.²⁰ A similar study for Mn^{2+} is desirable, as some data²¹ already indicate that even the sign of the exchange between two dichloride-bridged Mn^{2+} ions is very sensitive to the geometry. This study has been the first step in gathering such information. Similar information regarding the behavior of another Mn^{2+} compound containing the same chemical chains, but with greater isolation between chains, will be reported elsewhere.²²

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