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Low-Temperature Magnetic Susceptibilities of the Hydrated Acetates of Ni^{++}, Co^{++}, and Mn^{++}†

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The magnetic susceptibilities of powdered $Ni(C_2H_3O_2)_2 \cdot 4H_2O$, $Co(C_2H_3O_2)_2 \cdot 4H_2O$, and $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ have been measured in the liquid hydrogen and helium ranges by an ac mutual inductance method. Measurements on the cobalt salt were extended to 0.4°K revealing a sharp maximum at 0.6°K. A similar, more pronounced susceptibility peak is observed in the manganous acetate at 3.2°K. Single crystal measurements have been made on the latter salt along the monoclinic *b* axis as well as in the ac plane. $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ appears to be a weak ferromagnet of the kind discussed recently by Dzyaloshinsky and Moriya.

INTRODUCTION

We shall be concerned in this paper with the experimental determination of the magnetic susceptibilities of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$, $Co(C_2H_3O_2)_2 \cdot 4(H_2O)$, and $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ at liquid hydrogen and helium temperatures. In addition to measurements on powdered specimens of all three salts, a study of the single crystal behavior of manganous acetate has been made which reveals it to be a substance of unusual magnetic properties.

Of the several common hydrated acetates of transition metals, $Cu(C_2H_3O_2)_2 \cdot H_2O$ has aroused most interest because of its novel magnetic characteristics.[1,2] These, as shown by Bleaney and Bowers,[3] are due to the fact that Cu^{++} ions in this substance occur in relatively isolated pairs.[4] In an effort to detect similar clustering of magnetic ions in other acetates, van Niekerk and Schoening[5] several years ago determined by x ray methods the structures of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$. No evidence for cluster formation was found in these monoclinic isostructural salts. Thus their magnetic properties would hardly be expected to resemble those of the cupric acetate. Until recently the most extensive magnetic data available on $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$ were the room temperature observations of Mookerji.[6] These revealed very pronounced anisotropy of the magnetic moments of the Ni^{++} and Co^{++} ions but, at the same time, gave no indication of the anomalously low moments which clustering might produce.

Guha[7] has recently pointed out that the unusually large magnetic anisotropy of the hydrated nickel and cobalt acetates may be attributable to a structural peculiarity evident from the x-ray studies. Each metal ion in these substances is situated within an octahedron composed of four water molecules and two oxygen ions. The latter are at opposite vertices of the octahedron and belong to different acetate groups. Guha notes that this arrangement could contribute to the crystalline electric field at each magnetic ion a sufficiently strong rhombic component to account for the room temperature anisotropy. In addition, he presents new data on the temperature variation of the anisotropy of $Co(C_2H_3O_2)_2 \cdot 4H_2O$ down to 80°K which are consistent with the suggested crystalline field distortion.

Our interest in the low-temperature magnetic behavior of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$ was stimulated by the knowledge that the local environment of their magnetic ions is not homogeneous. The environment, in fact, resembles that found to exist in the salts $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$.[8] Each metallic ion in these substances forms an octahedral complex with four water molecules and two chloride ions rather than with six water molecules as might be expected *a priori*. Exchange interaction among metallic ions is found to be comparatively strong, antiferromagnetism occurring below 2.3°K and 5.3°K for the cobalt[9,10] and nickel[10,11] chlorides, respectively. It appears quite possible that this coupling is indirect and is facilitated, if not largely effected, by the chloride ions. A likely path for indirect exchange coupling is apparently offered by the M^{++}—Cl^{-}—Cl^{-}—M^{++} linkages which connect neighboring metal ions (M^{++}).

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We wished initially to explore the possibility that the moments of metallic ions in $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$ might experience similar indirect exchange coupling via paths involving the specially situated O^{--} ions. Low-temperature magnetic susceptibility measurements were carried out for this purpose on powdered specimens of both substances. As we shall describe in detail below, strong evidence for the existence of cooperative interaction was found only in $Co(C_2H_3O_2)_2 \cdot 4H_2O$ and then only after the salt had been cooled to 0.6°K by adiabatic demagnetization. Thus, while spin coupling apparently occurs in the hydrated acetate of cobalt, and possibly that of nickel, it is much weaker and consequently more difficult to study by direct methods than that in the corresponding hydrated chlorides.

As will be shown later, the evidence for cooperative interaction in $Co(C_2H_3O_2)_2 \cdot 4H_2O$ is atypical, making it all the more regrettable that single crystal studies below 1°K have not proved practical with the present experimental arrangement. We have felt it desirable, therefore, to examine the susceptibility of one of the few other tetrahydrated acetates of a transition metal, namely, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ on the chance that analogous and possibly stronger cooperative interaction might be revealed. The magnetic properties of this salt at low temperatures, in fact, prove most unusual. Their description constitutes a major portion of this paper. We wish to emphasize, however, that there is as yet no reason to believe that any simple relation exists between the properties of the manganous acetate on the one hand and the nickel and cobalt acetates on the other. Manganous acetate, while monoclinic, is not isomorphous with the other two and its structure is still unknown.

EXPERIMENTAL

The specimen materials used in this investigation were obtained from the Fisher Scientific Supply Company in their "Certified Reagent" grade. The lot analyses of these salts show the impurity content of foreign magnetic ions to be less than 0.09% by weight. All samples were taken from recrystallized material to ensure the proper degree of hydration. Powder samples were prepared by pulverizing the recrystallized salt and tightly packing thin-walled spherical soft glass containers 12 mm in diameter with the powder. Densities of samples thus prepared ranged from 0.65 to 0.85 of the corresponding crystal densities. The sample weights averaged about 1 g.

Single crystals of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ were grown from aqueous solution at room temperature. These had the form of thin six-sided plates 10 to 20 mm on a side. Crystal orientations were determined from the cleavage plane and the angles between well-developed faces using the goniometric data of Groth.[12] Because of the crystal morphology and easy cleavage it was necessary to prepare samples by stacking several crystals together to form short cylinders or rectangular rods. Detailed measurements were made with the measuring field in the crystallographic (a) and (b) directions and in a third direction (c') normal to these two. (c') lies in the ac plane and deviates from the crystallographic (c) direction by about 5°. Supplementary data were also taken along other directions in the ac plane. The crystal specimens were aligned with the aid of a goniometer; the accuracy of alignment is estimated to be $\pm 2°$.

Susceptibilities were determined by an ac inductance technique. The method consists essentially of observing the change in the mutual inductance of a pair of coaxial coils produced by insertion of the sample. This change is proportional to the susceptibility of the sample and is measured by means of an ac electronic mutual inductance bridge similar to that described by Pillinger, Jastram, and Daunt.[13] Details of the circuit are to be found in their report. It is possible with this bridge to measure both the real (χ') and the imaginary (χ'') components of the ac susceptibility $\chi = \chi' + i\chi''$. Unless otherwise specified, χ'' is negligible in the work to be described, indicating that relaxation effects are unimportant at the frequencies and applied fields employed. The present bridge is calibrated during each run against a sample of manganous ammonium sulfate which may be substituted directly for the unknown. The susceptibility of this salt closely follows a well-established Curie-Weiss law[14] between liquid nitrogen and liquid helium temperatures. Its comparative stability makes manganous ammonium sulfate a convenient reference material.

The bridge has a frequency range of 100 cps to 5000 cps with the parameters presently in use. Most measurements were made at a frequency of 500 cps. Only in the case of the manganous acetate was any frequency dependence of the susceptibility noted. The bridge sensitivity was 1×10^{-6} emu and the accuracy of measurement $\pm 6 \times 10^{-6}$ emu.

Measurements were taken in the temperature intervals 1.3°K to 4.2°K and 14.1°K to 20.2°K achieved by reducing the pressure over baths of liquid helium and liquid hydrogen. The cryostat is so designed that magnetic cooling can be employed to extend certain measurements to the range below 1°K. For this purpose, the substance of interest in the form of a powder is compressed about one end of a bundle of fine copper wires, the other end of which is imbedded in a compressed pill of cerium magnesium nitrate.[15,16] The

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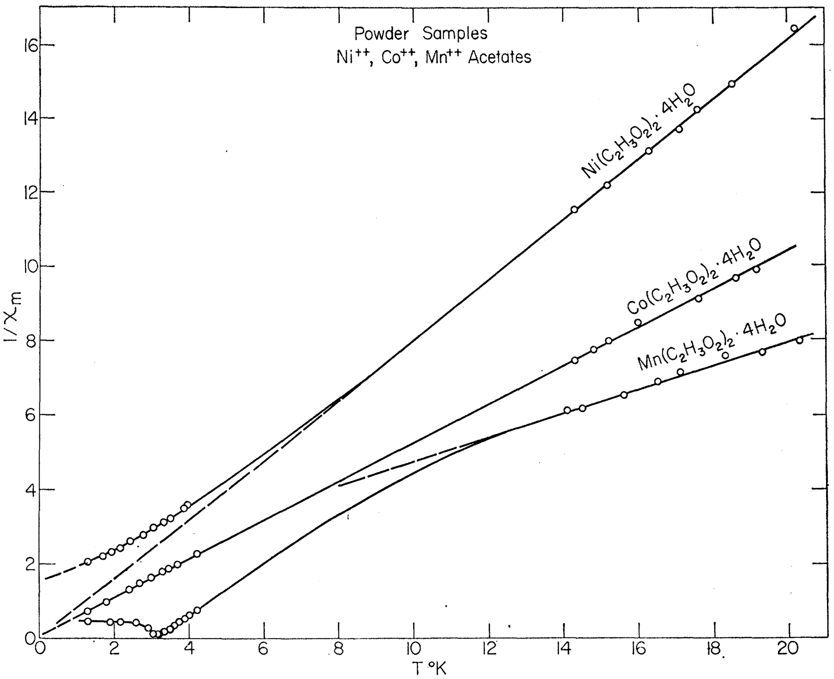

FIG. 1. $1/\chi_m$ versus T for powdered Ni^{++}, Co^{++}, and Mn^{++} acetates.

cerium salt and copper wires have very small heat capacity and are in good thermal contact with the unknown salt at least above ~0.2°K. Upon adiabatic demagnetization of this salt, the whole assembly quickly reaches a common lower temperature which may be determined by measuring the susceptibility of the cerium salt. This susceptibility has been shown[16] to follow a Curie law down to 0.01°K. The susceptibility of the unknown salt may thus be determined as a function of temperature by making alternate measurements on the unknown and on the cerium magnesium nitrate during the warmup period.

DISCUSSION OF RESULTS

A. Nickelous Acetate Tetrahydrate—$Ni(C_2H_3O_2)_2\cdot 4H_2O$

A plot of $1/\chi_{\text{powder}}$ for nickelous acetate tetrahydrate as a function of temperature is shown in Fig. 1. The observed values of the powder susceptibility are given (in cgs units per mole) in the second column of Table I. It will be noted that to the lowest temperature reached in these measurements (1.3°K), there is no evidence of a cooperative transition. χ_{powder} in the range 14°K to 20°K follows a Curie-Weiss law, $\chi_p = 1.25/(T+0.1)$ (emu/mole), as will be seen in Table I by comparing the computed values of the third column with the observed values of the second column. The Curie constant in this region, $C = 1.25$ per mole, yields a splitting factor $g = 2.24$, assuming an effective spin of one for the Ni^{++} ion. This value of g is in the range commonly obtained for nickelous salts in paramagnetic resonance experiments.[17] The principal susceptibilities of single crystal $Ni(C_2H_3O_2)_2\cdot 4H_2O$ have been measured by Mookherji[6] at 303°K. These yield an average splitting factor, $g = 2.34$, slightly higher than the low-temperature powder value reported here.

In the helium temperature range the $1/\chi_{\text{powder}}$ plot deviates from linearity. It is not obvious to what extent, if any, this deviation is associated with interaction among Ni^{++} ions. The ground state of the Ni^{++} ion has an effect spin $S = 1$. If the three components of this triplet state were separated by energies comparable with kT in this region, one would expect the suscepti-

TABLE I. The molar susceptibility of powdered $Ni(C_2H_3O_2)_2\cdot 4H_2O$.

T°K	χ_m(observed)	$\chi_m = 1.25/(T+0.1)$	χ_m(calculated[a])
20.2	6.08×10^{-2}	6.16×10^{-2}	6.25×10^{-2}
19.2	6.59	6.48	6.58
18.0	6.95	6.91	7.02
17.2	7.28	7.23	7.34
16.3	7.60	7.62	7.75
15.2	8.18	8.17	8.32
14.3	8.67	8.68	8.83
4.18	26.5		25.7
3.85	28.5		27.5
3.31	32.0		30.7
3.03	33.7		32.7
2.76	35.8		34.7
2.15	41.0		40.5
1.91	43.0		43.3
1.68	45.4		47.0
1.28	48.6		55.8

[a] These values are obtained using Eq. (1) of the text with $D = -5.6$ cm^{-1} and $E = -0.83$ cm^{-1}.

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[17] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

bility to tend toward a constant value at $T \rightarrow 0$ in much the way seen here. Since the Ni^{++} ion contains an even number (8) of d electrons, this could presumably be accomplished just by the action of a crystalline field of appropriate symmetry and strength. If we assume that this occurs, it is possible to obtain an expression for the powder susceptibility of the salt which contains parameters characterizing the crystalline field. It is instructive to see if such an expression can be fitted to the data and, if so, whether the required crystalline field parameters are of reasonable magnitude.

In the presence of a crystalline field consisting of a cubic part and a noncubic part containing a contribution of rhombic symmetry, as well as an applied magnetic field, the lowest spin triplet of the Ni^{++} ion is approximately described by the spin Hamiltonian[17,18]

$$H = DS_z^2 + E(S_x^2 - S_y^2) + g\beta \mathbf{H}\cdot\mathbf{S}.$$

Here D and E are constants describing, respectively, axially symmetric and rhombic parts of the crystalline field, g is the spectroscopic splitting factor which is assumed isotropic, and β is the Bohr magneton. The inclusion of the rhombic term would appear to be consistent with the known structure of the octahedral complex in nickel acetate. The assumption that g is isotropic is supported only by observations on many other salts of Ni^{++} and is of uncertain validity in this case. The eigenvalues W of this Hamiltonian are given by the equation[18]

$$-W^3 + 2DW^2 + W(E^2 - D^2 + g^2\beta^2 H^2) - g^2\beta^2 H^2[D(l^2 + m^2) - E(l^2 - m^2)] = 0,$$

where l,m,n are the direction cosines of the angles between the magnetic field $\mathbf{H}$ and axes of the rhombic field (x,y,z). It will be noted that when $H = 0$, this equation still has three distinct solutions, i.e., the triplet is fully split. Adjacent levels in the triplet are separated by $|2E|$ and $|D| - |E|$. Haseda and Date[19] have solved the secular equation for the three energies as functions of an arbitrarily oriented weak field. They then form the partition function, calculate the susceptibility, and average over-all directions to obtain the following expression for the susceptibility of a powdered specimen containing N magnetic ions,

$$\chi_p = \frac{2Ng^2\beta^2}{3(D^2 - E^2)} \frac{2D - \{(3E^2 - D^2)/E \sinh E/kT + 2D \cosh E/kT\}\, e^{-D/kT}}{1 + 2\, e^{-D/kT} \cosh E/kT}. \tag{1}$$

As $T \rightarrow 0$, it will be seen that this formula approaches a constant value. It should be further noted that the N magnetic ions of the specimen need not all lie on equivalent lattice sites. It is assumed only that each sees the same crystalline field regardless of the orientation of the rhombic axis of that field. Thus, as Haseda and Date have shown, Eq. (1) describes quite accurately the low-temperature powder susceptibility of $Ni(NH_4)(SO_4)_2 \cdot 6H_2O$ which contains two inequivalent Ni^{++} ions per unit cell. The appropriate D, E, and g values in this case were just those obtained by magnetic resonance experiments at room temperature,[20] namely, $D = -2.24$ cm^{-1}, $E = -0.39$ cm^{-1}, and $g = 2.25$.

We have attempted to fit the observed powder susceptibility of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ with Eq. (1). Values of χ_{powder} calculated assuming $D = -5.6$ cm^{-1} and $E = -0.83$ cm^{-1} are shown in the fourth column of Table I. These values of D and E appear to give the best fit of the data in the helium range and correspond to splittings of adjacent levels in the lowest triplet of 1.7 cm^{-1} and 4.4 cm^{-1}. The agreement of the calculated and observed values of χ_{powder} is rather satisfactory although small systematic differences do persist. The crystalline field parameters deduced in this way are somewhat larger than those found in resonance experiments on other nickel salts, both concentrated and dilute,[17] an example of which was cited above. It is conceivable that interactions among Ni^{++} ions, not accounted for in Eq. (1), might affect both the quality of the fit and the magnitudes of the chosen parameters. The D and E values given above, however, are not unreasonably large nor is the fit of the data poor enough to suggest that interionic interaction is very important above 1°K.

Attempts were made to cool $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ below 1°K by adiabatic demagnetization from a field of 5000 gauss. These proved unsuccessful as might be expected if the specific heat of the salt were rather large near 1°K. On the basis of the ground-state splitting mentioned above, this is not unreasonable.

B. Cobaltous Acetate Tetrahydrate—$Co(C_2H_3O_2)_2 \cdot 4H_2O$

A plot of $1/\chi_{\text{powder}}$ versus T for cobaltous acetate tetrahydrate in the temperature range 1.3° to 20°K is shown in Fig. 1. These data are also summarized in the second column of Table II. In this interval, χ_{powder} is very well represented by a Curie-Weiss law, $\chi_m = 1.86/(T + 0.08)$, which gives values shown in the third column of Table II. The Curie constant, $C = 1.86$ per mole, yields a splitting factor $g = 4.46$ assuming an effective spin of $\frac{1}{2}$ for the Co^{++} ion. This high value is not unexpected on the basis of findings for other Co^{++}

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[18] K. W. H. Stevens, Proc. Roy. Soc. (London) **A214**, 237 (1952).

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[19] T. Haseda and M. Date, J. Phys. Soc. Japan **13**, 175 (1958).

TABLE II. The molar susceptibility of powdered $Co(C_2H_3O_2)_2 \cdot 4H_2O$.

T°K	χ_m(observed)	$\chi_m = 1.86/(T+0.08)$
20.1	9.21×10^{-2}	9.22×10^{-2}
18.6	9.92	9.97
17.6	10.4	10.5
17.0	10.9	10.9
16.0	11.2	11.6
15.2	11.9	12.2
14.3	12.5	12.9
4.18	44.3	43.8
3.67	50.5	49.7
3.25	55.9	55.9
2.97	61.2	61.0
2.37	77.0	75.9
2.13	85.9	84.2
1.77	102.0	101.0
1.28	140.0	137.0

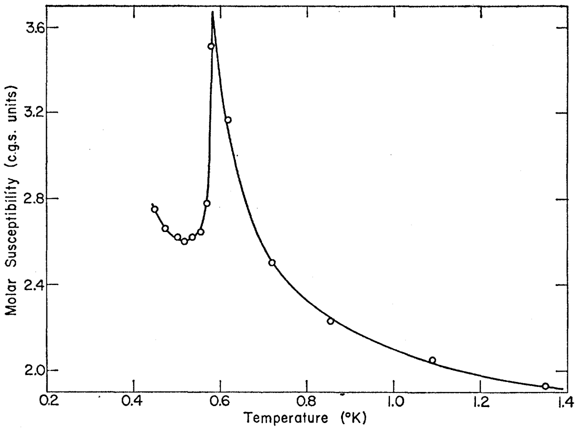

FIG. 2. χ_m versus T for powdered $Co(C_2H_3O_2)_2 \cdot 4H_2O$ below 1°K.

salts.[17] It results from the close proximity of excited states to the ground-state doublet of the Co^{++} ion in crystalline fields of low symmetry.

The single crystal susceptibilities of this salt were measured at 300°K by Mookherji,[6] who observed that the anisotropies were unusually large. In work referred to earlier, Guha[7] has determined single crystal susceptibilities of $Co(C_2H_3O_2)_2 \cdot 4H_2O$ between 80°K and 300°K. He finds an interesting temperature variation of the effective moments parallel and perpendicular to the crystalline field axis, the parallel moment falling and the perpendicular moment rising with decreasing temperature in this region. The average moment decreases with temperature, giving a value of $g = 4.6$ at 80°, consistent with that obtained in the present powder measurements at 20°K, $g = 4.5$.

It was found possible to cool $Co(C_2H_3O_2)_2 \cdot 4H_2O$ by adiabatic demagnetization, a temperature of 0.4°K being reached with an initial field of 5000 gauss from a starting temperature of 1.3°K. χ_{powder} versus T between 0.4°K and 1.0°K for this salt is shown in Fig. 2. The striking susceptibility "spike" near 0.6°K was studied by repeated demagnetizations. This spike and the rise of χ_{powder} near 0.4°K hardly represent the susceptibility behavior expected of a simple antiferromagnet although the occurrence of a cooperative transition is strongly indicated. Single crystal measurements would obviously be very helpful in any attempt to explain this effect. The technique employed below 1°K, however, does not lend itself readily to single crystal observations so that such measurements have not been undertaken.

One conclusion, possibly significant, can be drawn from the powder susceptibility data on $Co(C_2H_3O_2)_2 \cdot 4H_2O$. If an estimate is made of the strength of magnetic dipole-dipole coupling between neighboring Co^{++} ions in this salt, it is found that the interaction energy $\mu^2/r^3 \simeq 0.016\ k$. Equating this energy to kT, one concludes that the dipolar interaction is roughly an order of magnitude too small to account for a cooperative transition at 0.6°K. Thus it appears likely that exchange coupling of some kind occurs between Co^{++} ions in $Co(C_2H_3O_2)_2 \cdot 4H_2O$.

C. Manganous Acetate Tetrahydrate—$Mn(C_2H_3O_2)_2 \cdot 4H_2O$

A plot of $1/\chi_{\text{powder}}$ versus T for the manganous acetate tetrahydrate powder susceptibility data is shown in the lower part of Fig. 1. The hydrogen temperature powder values are summarized in the second column of Table III while those for the helium range are included on an expanded scale in Fig. 3. A very large, rather sharp susceptibility maximum is found to occur at ~3.2°K. This peak resembles the one observed at a lower temperature in $Co(C_2H_3O_2)_2 \cdot 4H_2O$ (see preceding section) and is strongly suggestive of the occurrence here of a magnetic ordering transition. This supposition is supported by the single crystal measurements described below as well as by preliminary specific heat determinations performed in this laboratory by Schelleng which reveal a lambda-type anomaly at the same temperature.

The single crystal susceptibilities of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ in the helium temperature range are shown in Fig. 3. It is seen that quite distinct behavior takes place in each of the three directions (a), (b), and (c'). χ_a passes through a very sharp, possibly singular, peak at 3.18°K. χ_b shows a less pronounced maximum at the same temperature and decreases to about half of the peak value at 1.3°K. The results of two separate runs are shown for $\chi_{c'}$. These coincide except in the vicinity of the transition point where slightly different weak peaks are seen. It seems likely that these peaks could result from slight misorientation of the specimens toward either the (a) or the (b) direction and that $\chi_{c'}$ remains nearly temperature-independent throughout this region. The behavior of χ_a alone indicates that the transition taking place at 3.18°K is not of the usual paramagnetic-antiferromagnetic type encountered in other hydrated salts at low temperatures, including those of manganese.

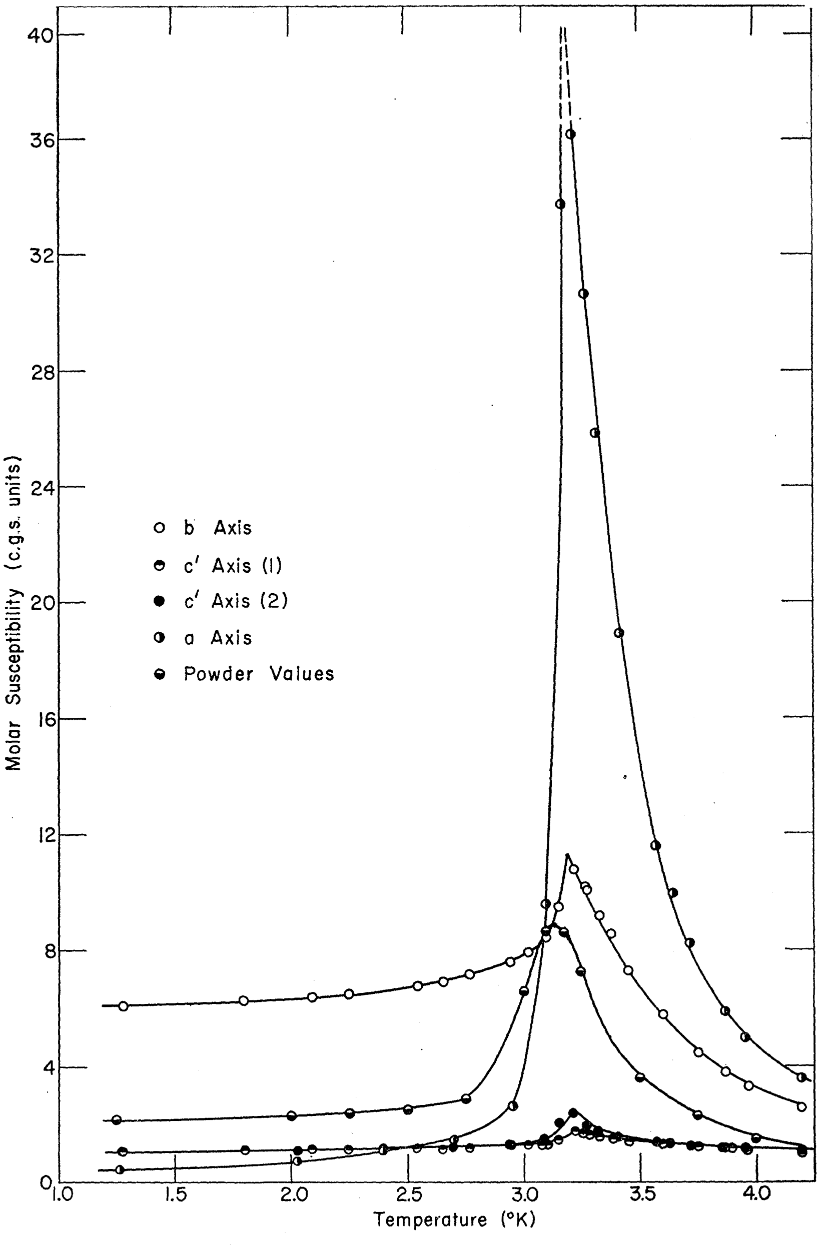

FIG. 3. Powder and single crystal susceptibilities of $Mn(C_2H_3O_2)_2\cdot 4H_2O$.

The largest measured value of χ_a, ~40 cgs units per mole, is very large compared with the susceptibilities of even the strongest normal paramagnets in this temperature region. Manganous ammonium sulfate, for example, has a powder susceptibility of 1.46 cgs units/mole at 3°K. Thus even in the small magnetic field of the measuring coils, the demagnetizing field of the specimen may become significant. In the case of $Mn(C_2H_3O_2)_2\cdot 4H_2O$, a correction of the susceptibility data for the effects of demagnetization is negligible except for those values of χ_a near the peak. While the rather irregular shape of the specimens precludes the accurate calculation of this correction, a reasonable estimate suggests that it would increase the indicated susceptibilities by no more than 10%. Thus, no attempt has been made to correct the χ_a values given in Fig. 3 for demagnetization.

Two other effects were noted near the peak. First of all, χ_a showed a small but detectable frequency dependence in this region. Secondly, the imaginary component χ_a'' differed slightly from zero and was seen to pass through a maximum value as the temperature was lowered through the transition point. Both effects were barely detectable and so were not studied in detail. They were not seen during the measurement of either χ_b or $\chi_{c'}$.

In the paramagnetic region, the magnetic susceptibility is expected to be a symmetric second rank tensor.

TABLE III. The molar susceptibility of powdered $Mn(C_2H_3O_2)_2\cdot 4H_2O$.

T°K	χ_m(observed)	$\chi_m=3.19/(T+5.2)$
20.3	12.5×10^{-2}	12.5×10^{-2}
19.0	13.0	13.2
18.1	13.5	13.7
17.1	14.0	14.3
16.5	14.5	14.7
15.6	15.3	15.3
14.5	16.1	16.2
14.1	16.7	16.5

It should, therefore, be possible to determine the three principal susceptibilities as well as the directions of the three orthogonal principal susceptibility axes of the crystal by a suitable combination of measurements. $Mn(C_2H_3O_2)_2\cdot 4H_2O$ is monoclinic so that one of its principal axes necessarily coincides with the crystallographic (*b*) diad axis.[17] The other two principal axes must lie in the ac plane and be orthogonal to one another. These may be located by determining the susceptibility with the measuring field along three arbitrary directions in the ac plane. Supplementary data for this purpose have been obtained and the diagonalization of the susceptibility tensor carried through. In this way the principal axes of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ are found to be very close to, if not coincident with, the (*a*) and (*c'*) directions in addition to the (*b*) direction. Thus, above about 3.18°K, χ_a, χ_b, and $\chi_{c'}$ may be regarded as the principal paramagnetic susceptibilities of manganous acetate. Below 3.18°K, i.e., in the ordered condition, it is not obvious that the (*a*), (*b*), and (*c'*) directions need be particularly significant.

The character of the peak found in χ_a is very suggestive of the occurrence of ferromagnetism. We have, therefore, examined the dependence of the susceptibilities of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ on external magnetic fields. Fields ranging up to 1000 gauss were applied to the specimen parallel to the small measuring field by means of an iron-free solenoid cooled with liquid nitrogen. Such fields produced little effect on $\chi_{c'}$ but even very weak fields dramatically changed both χ_a and χ_b. The peak values in the (*a*) and (*b*) directions were reduced in magnitude and shifted to lower temperatures. A field of 1000 gauss completely removed the peak in χ_a. At the lowest temperatures it was evident that even the weak field of the measuring coils (<2 gauss) was capable of influencing χ_a. Thus the low-temperature values of χ_a shown in Fig. 3 are probably significantly different from zero field values. In the presence of the external field, the imaginary components of the susceptibilities in the (*a*) and (*b*) directions, χ_a and χ_b, were different from zero. Upon cyclic reversal of the large static field parallel to the (*a*) direction, hysteresis is observed below 3.18°K. No hysteresis was found with the external fields in either the (*c*) or (*b*) directions.

The extremely large values of χ_a, its particular sensitivity to applied fields, and the occurrence of hysteresis strongly suggest that a ferromagnetic moment appears along or near the (*a*) direction when manganous acetate is cooled through 3.18°K. The behavior of χ_b and $\chi_{c'}$ is, in addition, consistent with this moment being restricted to the ab plane, $\chi_{c'}$ behaving essentially as an antiferromagnetic susceptibility. The unusual character of this transformation is evident when one looks at the graph of $1/\chi_{\text{powder}}$ vs T shown in Fig. 1. In the hydrogen region this plot is very nearly linear, i.e., χ_p obeys a Curie-Weiss law, the Weiss constant being negative as expected of an antiferromagnet. Between 4.2° and 3.18°K, however, χ_p rises to values much higher than extrapolation of the Curie-Weiss law would predict. This is not the behavior of a typical antiferromagnet above its Néel point. It should be noted that the Curie constant calculated from the hydrogen temperature data $C=3.19$ is significantly smaller than the value $C=4.37$ expected for Mn^{++} ions with spin $\frac{5}{2}$ and $g\sim 2$. This may mean that $1/\chi_{\text{powder}}$ vs T actually exhibits some curvature in the hydrogen region and that true Curie-Weiss behavior would only be realized at higher temperatures while the antiferromagnetic Weiss constant $\theta=5.2$°K might become even larger. Whatever its origin, this fact serves to accentuate the difference between the observed behavior and that of a simple antiferromagnet.

Several possible explanations of the magnetic properties of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ suggest themselves. In the absence of detailed structural information about this substance, it is not possible to exclude some of these possibilities *ab initio*. It is conceivable, for example, that the manganese ions might occupy two kinds of lattice sites on which they would have different moments. The crystal could then be treated as a conventional Néel ferrimagnet. By introduction of isotropic exchange interactions of the appropriate sign and magnitude such a model might well account for the observed temperature variation of $1/\chi_{\text{powder}}$ above T_N. This scheme looks less attractive, however, when one attempts to find a mechanism for the postulated difference in the moments of Mn^{++} ions on the two types of lattice site since the ground state of the free ion is ^6S.

Another model of the ferrimagnetic variety is one in which some manganese ions on one kind of lattice site are in a higher oxidation state, e.g., Mn^{+++}, than the rest. While it is not necessary in this case to endow different lattice sites with different properties, the ferromagnetic moment becomes an impurity effect and the characteristics of variously prepared specimens should not be the same. In fact, the properties of several different specimens of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ have been found to be quite reproducible, leading us to discount this possibility. It should also be noted that the highly anisotropic behavior of this substance evident in Fig. 3 would be very difficult to describe with any conventional ferrimagnetic model.

A third and rather different kind of explanation appears to be more acceptable. Dzyaloshinsky[21] has recently discussed the origin of the weak ferromagnetism observed in such substances as α-Fe_2O_3 and $MnCO_3$. He shows by group theoretical arguments that in crystals of appropriate, usually low, symmetry it is possible for the sublattice magnetization vectors of an essentially antiferromagnetic system to deviate slightly from antiparallelism producing a weak ferromagnetic moment in a particular crystalline direction. Moriya[22] has placed the theory on a microscopic basis by showing that two distinct mechanisms can lead to such tipping or canting of sublattice magnetizations. The first involves just the effect of the crystalline field on individual ions situated at nonequivalent lattice sites and antiferromagnetically coupled by exchange interaction of the usual form, $J\mathbf{S}_i\cdot\mathbf{S}_j$. He has successfully explained the properties of NiF_2 on the basis of this so-called single-spin anisotropy. The second mechanism, however, involves a new interaction between magnetic ions of the form suggested by Dzyaloshinsky on symmetry grounds, namely $\mathbf{D}\cdot\mathbf{S}_i\times\mathbf{S}_j$. Moriya calls this the anisotropic superexchange interaction and shows that the constant vector $\mathbf{D}$ is of magnitude $D\sim(\Delta g/g)J$ where Δg is the difference between the actual splitting factor and the free spin value and J is the ordinary or isotropic superexchange integral between ions i and j. Whether $\mathbf{D}$ is different from zero as well as the direction in which it points depend on the symmetry of the crystal, the new interaction occurring only when this symmetry is low. Moriya has shown that, qualitatively at least, anisotropic superexchange accounts for weak ferromagnetism in α-Fe_2O_3, $MnCO_3$, and CrF_3.

Moriya points out that one of the distinctive features of a weak ferromagnet of either type is the temperature variation of its paramagnetic susceptibility. He shows that, in the molecular field approximation at least, the susceptibility measured perpendicular to both the preferred direction of antiferromagnetic spin orientation and the direction of the ferromagnetic moment, referred to as χ_z, should obey a Curie-Weiss law above the transition temperature T_N, i.e., $\chi_z=C/(T+\theta)$ for $T>T_N$. On the other hand, the susceptibility measured along the direction in which the ferromagnetic moment will appear $\chi_\perp$ is found to rise rapidly above the Curie-Weiss value as T approaches T_N from above according to the relation $\chi_\perp=[C/(T+\theta)][(T-T_0)/(T-T_N)]$, where T_0 is a constant and $T_N-T_0>0$. The powder susceptibility will, of course, reflect the rapid increase in $\chi_\perp$ near T_N.

The temperature variation of the powder and single crystal susceptibilities of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ above 3.18°K strongly suggests that it is a weak ferromagnet of the kind described by Dzyaloshinsky and Moriya. χ_a behaves essentially as expected of $\chi_\perp$ although the data are too meager to permit evaluation of the constants appearing in the expression given above for this quantity. Lacking knowledge of the structure of this salt, it is not possible at present to decide whether the dominant mechanism might be one of anisotropic superexchange or single spin anisotropy. Moriya has noted that the latter mechanism is likely to be important in those substances with low Néel temperatures since it is independent of the exchange interaction. He also points out that the single spin anisotropy energy and the exchange energy may be comparable if the Néel temperature is low and as a result the weak ferromagnetic moment can be comparatively large. This may well be the case in manganous acetate.

An x-ray investigation of the crystal structure of $Mn(C_2H_3O_2)_2\cdot 4H_2O$ has been begun by Dr. W. H. Robinson of this Institute as a necessary preliminary to an attempt to interpret the magnetic properties of this salt on a microscopic basis.

It is perhaps appropriate to conclude this discussion by pointing out that weak ferromagnetic behavior may also occur in at least one of the other acetates dealt with earlier in this report. The powder susceptibility of $Co(C_2H_3O_2)_2\cdot 4H_2O$ (see Fig. 2) rises rapidly as $T\rightarrow 0.6$°K. Assuming that temperatures in this region have been determined to within about 0.05°K, χ_{powder} reaches values well above those expected from the Curie-Weiss law valid above 1.3°K. It was this fact that originally led us to regard the susceptibility maximum near 0.6°K as unusual. In the light of Moriya's conclusions outlined above, it may also suggest the onset of weak ferromagnetism. Clearly, single crystal observations on this salt below 1°K would be of interest.

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