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Heat Capacity of $Mn(HCOO)_2\cdot 2H_2O$ between 1.4 and 20°K[†]

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The heat capacity of $Mn(HCOO)_2\cdot 2H_2O$ has been measured between 1.4 and 20°K. Sharp peaks associated with long-range spin ordering are found at 3.72 and 1.72°K. These anomalies can be correlated with corresponding effects in the magnetic and resonance properties of the salt. The present thermal data account for less than half the expected R ln6 of magnetic entropy, with little contribution expected above 20°K, suggesting that half the manganese moments remain highly disordered at 1.4°K. The response of the heat capacity to external magnetic fields supports this conclusion. A unit cell of $Mn(HCOO)_2\cdot 2H_2O$ contains two each of two inequivalent Mn^{++} sites, types A and B. Formate groups constitute AA and AB bridges and appear to mediate the dominant superexchange couplings. Analysis of the thermal and susceptibility data yields an antiferromagnetic AA exchange parameter $J/k=0.65$°K and a ferromagnetic AB coupling $J'/k=-0.10$°K. A simplified molecular-field treatment of $Mn(HCOO)_2\cdot 2H_2O$ using these parameters provides interpretations of several striking effects. In particular, it shows that below a common transition temperature, B spins order much more slowly than A spins and are nearly "free" at 1°K as seen in both magnetic and thermal data. The model also predicts anomalous behavior below 1°K as a consequence of a sharp temperature dependence of the B-spin order parameter at very low temperatures.

INTRODUCTION

Within the past few years, a number of studies of the isostructural dihydrates of manganous, ferrous, and nickelous formate have been published. The phenomena reported are both interesting and somewhat puzzling. While one might reasonably expect these salts to have quite similar behavior, a variety of magnetic properties has been observed. $Mn(HCOO)_2\cdot 2H_2O$, $Fe(HCOO)_2\cdot 2H_2O$, and $Ni(HCOO)_2\cdot 2H_2O$ all appear to undergo magnetic ordering transitions below 20°K. Below its critical temperature, ferrous formate dihydrate seems to behave quite simply. The manganese and nickel salts, however, exhibit more complex—but not identical—behavior in their ordered states. While the differences observed might, of course, be only superficial, additional information was clearly desirable in understanding the properties of these salts. We therefore undertook measurements of their low-temperature heat capacities. The results of the experiments on manganous formate dihydrate apre presented here. The data obtained for the iron and nickel salts will appear in a subsequent paper.

The results of a recent determination[1] of the structure of $Mn(HCOO)_2\cdot 2H_2O$ are shown in Fig. 1. The structure is monoclinic and is characterized by the space group $P2_1/c$. The unit cell contains four manganese ions occupying two each of two crystallographically inequivalent sites, denoted A and B, located alternately on successive sheets parallel to (100). Each manganese ion is coordinated with six ligands forming a distorted octahedron. Oxygen atoms from six distinct formate groups surround each A ion, while two oxygen atoms from formate groups and four water molecules surround each B ion. The formate groups act as bridges connecting various manganese ions. Each A ion is connected in this manner to four neighboring A ions and to two neighboring B ions, and each B ion to two A ions, as illustrated in Fig. 2. There are no formate linkages between B ions.

Several authors[2–4] have recognized that an extended but intimately coupled group of atoms such as the formate group may act as an effective intermediary in the superexchange interaction. Were this the principal mechanism responsible for the magnetic interactions in $Mn(HCOO)_2\cdot 2H_2O$, we should expect this fact to manifest itself in some physical property of the material. As we shall see in the following sections, many of the properties of manganese formate dihydrate are quite reasonably explained by such a model of its magnetic interactions.

The magnetic susceptibilities of both powder and single crystal specimens of $Mn(HCOO)_2\cdot 2H_2O$ have been reported in a number of papers.[3,5–9] Between 14 and 20°K, Flippen and Friedberg's powder data are adequately described by either of the Curie-Weiss expressions $\chi_m=4.10/(T+3.2)$ cgs/mole[3] or $\chi_m=3.82/(T+1.8)$ cgs/mole.[5] (The difference between the two expressions is slight in the 14–20°K interval, and is within the few percent experimental uncertainty.[5])

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At lower temperatures, the powder susceptibility deviates from Curie-Weiss behavior and at 3.68 and 1.72°K rather sharp peaks are seen in both the powder and the single-crystal data,[6] suggesting that $Mn(HCOO)_2 \cdot 2H_1O$ experiences magnetic phase transitions at these temperatures. Further evidence supporting this conclusion has been seen in the ESR[7,9] and proton resonance[7,10] experiments of Abe and coworkers. They have also obtained some evidence that the ordered state is weakly ferromagnetic, and that the anomalous behavior at 1.7°K is accompanied by a spontaneous reorientation of the sublattice magnetization.[11]

Below 3.7°K, the powder susceptibility of $Mn(HCOO)_2 \cdot 2H_2O$ does not decrease with decreasing temperature as does that of a simple antiferromagnet. Instead, between 0.56 and 2°K (excepting the immediate vicinity of 1.7°K), the powder susceptibility is observed to follow a second Curie-Weiss law, $\chi = 2.44/(T+0.1)$ cgs/mole,[5] with a Curie constant of roughly half the 4.37 expected for the Mn^{++} ion. This has led to the suggestion[6] that only half the manganese ions participate fully in the 3.7 and 1.7°K transitions. To temperatures well below 3.7°K, the state of the system appears to be one in which both highly ordered and essentially paramagnetic moments coexist. This view is supported by the proton-resonance data[7,10] and the results of adiabatic demagnetization experiments.[9]

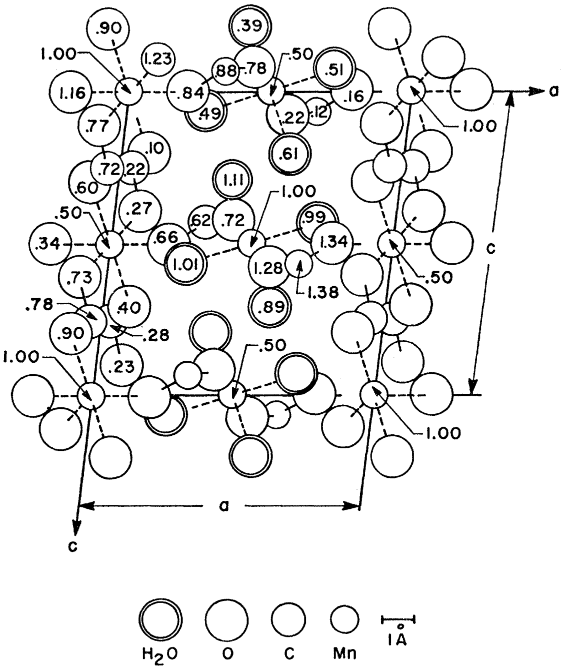

FIG. 1. Crystal structure of $Mn(HCOO)_2 \cdot 2H_2O$. The numerical values of the fractional coordinates y/b are indicated.

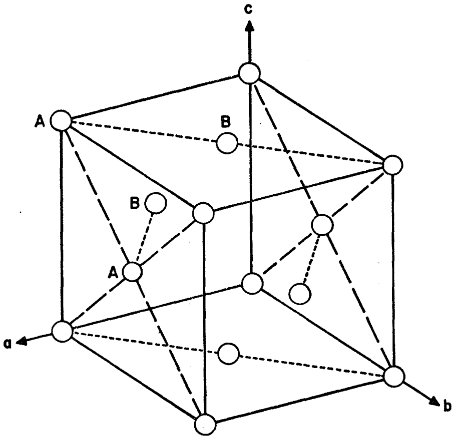

FIG. 2. Schematic three-dimensional representation of the $Mn(HCOO)_2 \cdot 2H_2O$ structure. The circles indicate the manganese ions and the dashed and dotted lines indicate the approximate positions of formate groups linking, respectively, *AA* and *AB* pairs. These formate ions are assumed to provide the principal superexchange paths in the salt.

At about 0.5°K, the susceptibilities pass through weak maxima, and below 0.4°K they show little variation with temperature.[9] An anomaly in the heat capacity also occurs near 0.5°K.[9] These effects presumably involve the degrees of freedom of the half of the spin system which did not order at 3.7°K.

EXPERIMENTAL

The heat-capacity measurements were performed in a vacuum calorimeter of conventional design. A $\frac{1}{10}$-W Allen-Bradley carbon radio resistor with a nominal resistance of 68 Ω served as the thermometer. During each series of measurements, the resistance of the thermometer was calibrated by bringing it into isothermal contact with the liquid-coolant bath, whose vapor pressure was measured and converted to a temperature by means of the liquid-hydrogen or liquid-helium temperature scale.[12,13] Usually seven or eight calibration points were taken between 14 and 20°K, and seven to ten between 1.35 and 4°K. A least-squares analysis of the calibration data was used to determine the coefficients in an empirical resistance versus temperature relation

$$[(\ln R)/T]^{1/2} = A + B \ln R + C(\ln R)^2 + D(\ln R)^3. \quad (1)$$

This relation was subsequently used to convert thermometer resistances to temperatures in the heat-capacity determinations. With properly chosen coefficients, Eq. (1) could be made to fit the calibration data to within one or two tenths of a percent. A discontinuous heating procedure was used to obtain most of the heat-capacity data. The over-all accuracy of the heat capacities is estimated to be a few percent.

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TABLE I. Heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ in calories per mole degree. Temperature in °K.

T	C_p	T	C_p	T	C_p
1.386	0.477	3.673	1.707	7.410	0.571
1.507	0.515	3.698	1.759	7.700	0.543
1.577	0.531	3.725	1.801	8.024	0.515
1.673	0.567	3.741	1.663	8.401	0.495
1.689	0.629	3.751	1.568	8.835	0.478
1.704	0.836	3.776	1.543	9.330	0.473
1.719	1.640	3.804	1.516	9.944	0.480
1.747	0.757	3.891	1.510	10.167	0.486
1.794	0.539	4.023	1.469	10.378	0.494
1.909	0.567	4.095	1.454	10.591	0.504
1.990	0.607	4.212	1.430	10.817	0.514
2.113	0.663	4.307	1.401	11.178	0.541
2.204	0.695	4.407	1.367	11.462	0.554
2.315	0.739	4.517	1.327	11.764	0.580
2.388	0.765	4.622	1.288	12.062	0.602
2.470	0.795	4.742	1.240	12.362	0.635
2.570	0.835	4.875	1.189	12.700	0.675
2.691	0.878	5.024	1.134	13.042	0.717
2.837	0.939	5.182	1.074	13.467	0.767
3.000	1.068	5.359	1.012	13.909	0.827
3.111	1.117	5.552	0.947	14.371	0.884
3.212	1.163	5.765	0.884	14.860	0.959
3.304	1.229	6.033	0.812	15.327	1.030
3.397	1.270	6.182	0.774	16.009	1.155
3.515	1.386	6.345	0.736	16.771	1.300
3.557	1.441	6.518	0.702	17.575	1.469
3.601	1.523	6.713	0.667	18.458	1.672
3.625	1.579	6.918	0.634	19.464	1.946
3.648	1.653	7.155	0.602	20.580	2.262

Manganous formate was prepared by reacting $MnCO_3$ ("Baker Analyzed" reagent grade) with formic acid (Matheson, Coleman, and Bell, reagent grade). The samples, composed of small crystals of $\frac{1}{2}$- to 2-mm size, were obtained by crystallization from the aqueous solution. The sample masses ranged from 7.637 to 8.400 g. Calorimetry was performed with the sample sealed copper capsule to which the heater and thermometer were attached. A small quantity of helium gas was sealed in the capsule along with the sample to aid in heat transfer. The heat capacity of the capsule and addenda was determined in an auxiliary experiment.

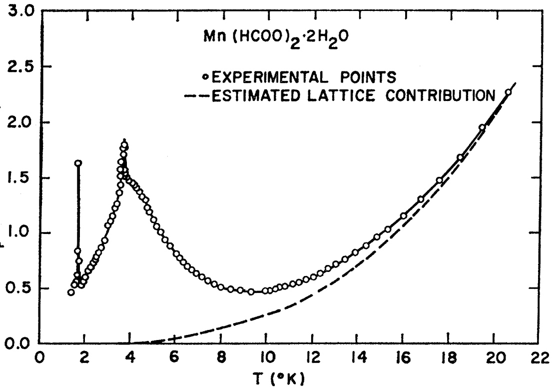

FIG. 3. Heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ in zero external field. The dashed line indicates the estimated lattice heat capacity aT^3.

RESULTS

The heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ in zero magnetic field is shown in Fig. 3. Table I summarizes these data. Three prominent features are evident. Between 2 and 6°K, the heat capacity exhibits a broad maximum. At 3.72°K a sharp peak, about 0.1°K in width, rises abruptly from the gentler variation. At 1.72°K, a second sharp peak occurs. It is narrower and much stronger than that at 3.7°K, with a width of about 0.05°K. The anomaly at 1.7°K may be seen in more detail in Fig. 4. The two anomalous peaks in C_p suggest, as do the magnetic susceptibility and resonance experiments,[3,5–11] that magnetic phase transitions occur at these temperatures.

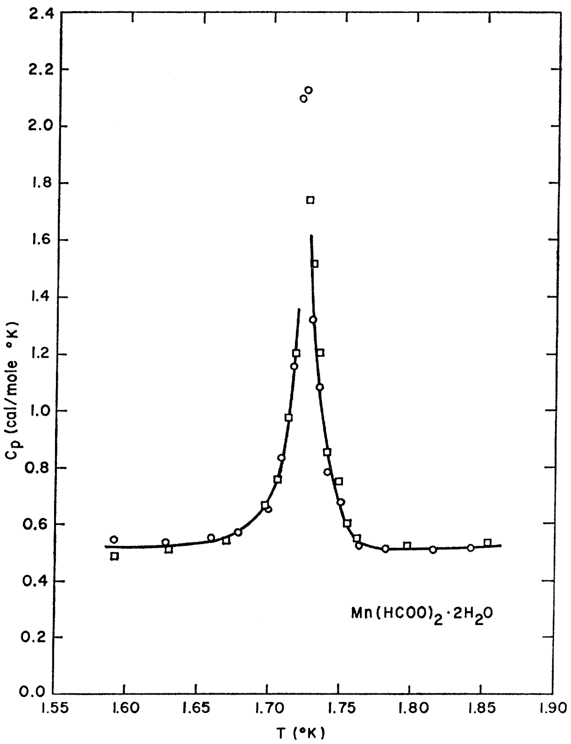

FIG. 4. Detailed plot of the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ near 1.7°K. The circles and squares indicate data obtained on two different days. The data were obtained by a continuous heating technique.

The magnetic susceptibility of $Fe(HCOO)_2 \cdot 2H_2O$ has a very strong peak at 3.7°K,[14] a fact which has caused some concern that the anomalies seen in $Mn(HCOO)_2 \cdot 2H_2O$ at 3.7°K may not be intrinsic properties of the manganese salt, but rather effects of iron impurities. Microanalysis of material from one of our samples showed, however, an iron contamination

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of only 31 ppm. That such a minute fraction of iron could be responsible for the effects seen is difficult to conceive.

At low temperatures, the lattice heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ will vary as T^3. At temperatures large compared to the ordering temperature, the magnetic contribution to the heat capacity will have a T^{-2} variation. If the magnetic ordering temperature is sufficiently small, a range of temperature may exist in which heat capacity is given by

$$C = aT^3 + b/T^2. \qquad (2)$$

That such an interval does exist in the case of $Mn(HCOO)_2 \cdot 2H_2O$ is illustrated in Fig. 5, where CT^2 is seen to vary linearly with T^5 above 10°K. With $a = 2.59 \times 10^{-4}$ cal/mole °K^4 and $b = 22.2$ cal °K/mole, Eq. (2) fits the experimental data above 10°K to within an rms deviation of 1%.

That Eq. (2) is a good representation of the data between 10 and 20°K implies that aT^3 is a reasonable approximation of the lattice heat capacity below 20°K. We are therefore enabled to isolate the magnetic heat capacity C_m, from which we may obtain quantititive information concerning the manganese spin system.

A calculation of the magnetic entropy differences between fully ordered and disordered states,

$$\Delta S_m = \int_0^\infty \frac{C_m}{T} dT, \qquad (3)$$

is particularly illuminating. The Mn^{++} ion has a $(3d)^5$ configuration. The lowest spectral term of the free ion is $^6S_{5/2}$. In a crystalline field of moderate strength, the free-ion ground state will suffer only small splittings of the order of 0.1 cm^{-1}, which we may neglect. The effective spin will therefore be $\frac{5}{2}$, and we expect $\Delta S_m = R \ln 6 = 1.79R$, assuming only the single-ion ground state to be occupied during the ordering process. Numerical integration of our data between 1.39 and 20.6°K yields an entropy difference of 0.86 R. Using the asymptotic formula $C_m = b/T^2$ to extend the integration to $T = \infty$ adds an almost negligible 0.01 R, giving an entropy increase above 1.39°K of 0.87 R. Rather remarkably, a large fraction of the expected 1.79 R remains in the spin system at temperatures below which it has undergone what appear to be two marked changes in state.

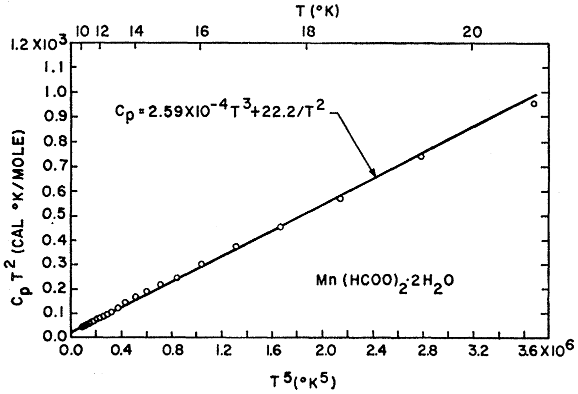

FIG. 5. CT^2 versus T^5 plot of the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$, indicating the separation of the lattice and magnetic contributions.

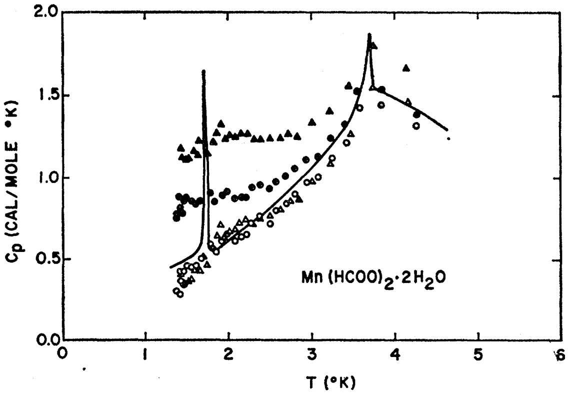

FIG. 6. Heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ in nonzero external fields. The solid circles are the data at 5000 Oe, the solid triangles at 9000 Oe. The open circles and open triangles indicate the same data from which has been subtracted the heat capacity of $\frac{1}{2}$ mole of free Mn^{++} ions. The solid line represents the zero-field data.

As we have previously noted, a number of experimental results concerning $Mn(HCOO)_2 \cdot 2H_2O$ are readily interpreted by assuming that only half its spins become highly ordered at 3.7°K. Were this the case, we should expect an entropy change of only $\frac{1}{2}R \ln 6 = 0.90R$ to appear in the present experiments. The experimental $0.87R$ is close to this figure, providing added evidence of a coexistance of equal numbers of highly ordered and essentially paramagnetic moments in $Mn(HCOO)_2 \cdot 2H_2O$ below 3.7°K.

Some heat-capacity measurements were performed in an applied magnetic field. The 3.7°K peak was unaffected by a 530-Oe field, indicating that the ordering is to a basically antiferromagnetic state. This is consistent with the observation of only rather weak anomalies in the magnetic susceptibility at 3.7°K, and with the proton-resonance studies.

The response of the heat capacity to applied fields was more interesting in the region below 3.7°K, where measurements were performed in fields of 5 and 9 kOe. The results are shown in Fig. 6. Because of field fluctuations, the data are not very precise[15]; this lack of precision precludes any statement concerning the behavior of the 3.7°K anomaly in these fields. The 1.7°K peak, while very prominent in zero field, was not detected at 5 or 9 kOe. Below 3.7°K, the magnetic

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[15] The fact that $Mn(HCOO)_2 \cdot 2H_2O$ is a fairly effective magnetocaloric salt makes magnetic-field fluctuations particularly troublesome, since they produce appreciable temperature fluctuations. The efficiency of the salt as a magnetic coolant is probably traceable to the presence of the $\frac{1}{2}$ mole of essentially free manganese moments.

field causes a general increase in the heat capacity. The effect is more pronounced at the lower temperatures, and is greater for the higher field.

The response of the heat capacity to applied fields is rather direct evidence of a coexistance of ordered and disordered halves of the manganese spin system. Below 3.7°K, half of the spins in the salt, probably the *A* spins, are antiferromagnetically ordered. The forces holding these spins in alignment are strong compared to those produced by the highest field applied in this experiment. Consequently, the thermal properties of the spins in the *A*-ion sheets are not greatly influenced by the applied field. The field indeed eliminates the 1.7°K peak, but that it does so merely demonstrates the weakness of the effective anisotropies responsible for the spin reorientation. The *B* spins, on the other hand, are essentially free, and the field produces a Zeeman splitting of the ground state of each ion. The result is a Schottky-like heat capacity for the *B* spins. Therefore, if we subtract from the experimental molar heat capacity the contribution due to $\frac{1}{2}$ mole of free Mn^{++} spins in an applied magnetic field H, we should obtain a field-independent result agreeing, except near 1.7°K, with the heat capacity in zero field. Figure 6 shows this decomposition of the heat capacity; the results seem to confirm our assumptions.

In our subsequent analysis, we shall assume that the formate ions, acting as intermediaries in the superexchange mechanism, are responsible for the dominant magnetic interactions in manganous formate dihydrate. This interaction would couple the *A* ions to one another in (100) sheets, and the *B* ions to neighboring *A* ions in each of two adjacent sheets, as in Fig. 2. We take the coupling between *A* ions to be $J\mathbf{S}_i\cdot\mathbf{S}_j$, and that of *A* ions to *B* ions to be $J'\mathbf{S}_i\cdot\mathbf{S}_j$. The possible existence of anisotropic exchange or of a Moriya-Dzyaloshinski type of interaction will not be considered. Since Mn^{++} is an *S*-state ion, its spin should not experience appreciable single-ion anisotropy forces, and its g tensor should be nearly isotropic with a value near $g=2$. The problem will be further simplified by also ignoring magnetic dipole interactions. The spin Hamiltonian thus becomes

$$\mathcal{H}=\sum_{\langle AA\rangle} J\mathbf{S}_i\cdot\mathbf{S}_j+\sum_{\langle AB\rangle} J'\mathbf{S}_i\cdot\mathbf{S}_j+g\mu_B\mathbf{H}\cdot\sum_i \mathbf{S}_i. \qquad (4)$$

Here $\mathbf{S}_i$ is the spin of the i-th manganese ion, $\mathbf{H}$ is the applied magnetic field, and the notations $\langle AA\rangle$ and $\langle AB\rangle$ indicate summations over all formate-coupled *A*-*A* and *A*-*B* pairs, respectively.

Much evidence has been presented here and elsewhere indicating that $Mn(HCOO)_2\cdot 2H_2O$ contains equal numbers of Mn^{++} ions, some of which interact only rather weakly and others more strongly. Equation (4) can represent such a situation only when J' is small compared to J, because every Mn^{++} ion participates in two *A*-*B* interactions. In the limit $J'=0$, the *A*-ion moments are coupled in sheets, while the *B*-ion moments are free. Henceforth we assume $|J'|\ll|J|$.

In order to estimate the interaction parameters J and J', it is desirable to separate, if possible, their contributions to the thermal properties of the salt. We have been partially successful in doing so. We write

$$C_m(T)=C_A(T)+C_B(T), \qquad (5)$$

where $C_A(T)$ is the contribution to the heat capacity which arises from the *A*-*A* interactions, and $C_B(T)$ is that arising from the *A*-*B* interactions. While in principle such as decomposition is quite proper, it is not true that C_A depends only on J and C_B only on J'. It seems reasonable, however, that C_A should not be strongly dependent on J' provided that J' is small compared to J and to kT. On this basis we expect C_A not to differ greatly from the heat capacity of a simple two-dimensional antiferromagnet with very small anisotropy. At sufficiently low temperatures, spin-wave calculations should then give $C_A=\alpha T^2$. Anticipating that C_B may be adequately represented by some T^{-2} "tail", $C_B=\beta/T^2$, we plot our lowest temperature data in the form CT^2 versus T^4, as in Fig. 7. The linearity of the plot shows that between 1.4 and 1.7°K the data are adequately represented by $C_m=\alpha T^2+\beta/T^2$, which allows one to determine α and β. (The limited data available, however, are equally well represented by $C_m=\alpha T^3+\beta/T^2$, so that the linearity seen in Fig. 7 does not entirely justify the expressions used for C_A and C_B. The range of temperature is too small and the data not sufficiently precise to permit such distinctions.)

Having determined α and β, we may extract C_A from the experimental data and, using extrapolation formulas for C_A below 1.4 and above 20°K, may com-

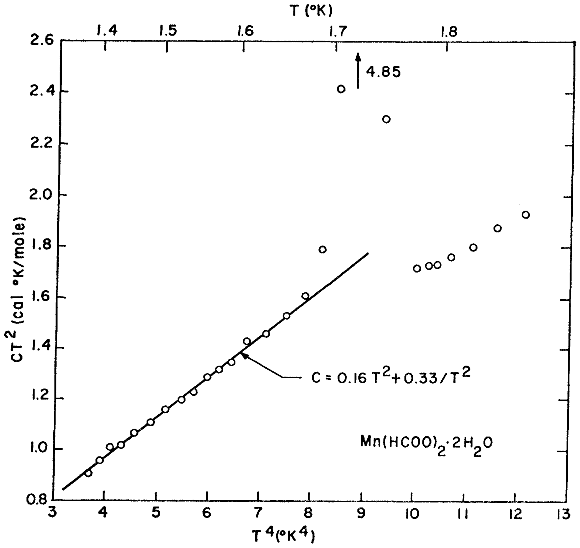

FIG. 7. CT^2 versus T^4 plot of the heat capacuty of $Mn(HCOO)_2\cdot 2H_2O$ below 2°K.

pute the total entropy change ΔS_A of the A-ion system. The computation yields $\Delta S_A = 0.90R$, a value within 1% of the expected $\frac{1}{2}R \ln 6$. (Writing $C_A = \alpha T^3$ gives $\Delta S_A = 0.84R$, which is 7% too small.)

The energy

$$\Delta U_A = \int_0^\infty C_A dT$$

may also be calculated. The result is $\Delta U_A = 8.52$ cal/mole. But ΔU_A is just the negative of the ground-state energy E_g of the antiferromagnetic A-ion sheets, and, according to Anderson,[16] must lie between the limits

$$-\tfrac{1}{3}N_A JzS^2 \geq E_g \geq -\tfrac{1}{3}N_A JzS^2(1/1/zS), \qquad (6)$$

where N_A is the number of A ions and $z(=4)$ is the coordination number. Since these limits differ by only 10%, their mean

$$E_g \approx \tfrac{1}{3}N_A JzS^2(1+1/2zS) \qquad (7)$$

gives E_g to within 5%. Combining this relation with the experimental ΔU_A yields the value $J/k = 0.65$°K.

The exchange parameter J may also be determined, along with J', from the asymptotic form of the total magnetic heat capacity, $C_m = b/T^2$, and the Weiss constant of the powder susceptibility θ. These quantities are easily obtained from the Hamiltonian, Eq. (4), by expanding the canonical partition function in powers of $1/T$. For $Mn(HCOO)_2 \cdot 2H_2O$, the results are

$$C_m = (1225/48)Nk(J^2 + J'^2)/(kT)^2 \qquad (8)$$

and

$$\theta = (35/6)(J + J')/k. \qquad (9)$$

Using the value $b = 22.2$ cal °K/mole obtained in this work, $\theta = 3.2$°K as reported by Flippen and Friedberg,[3] and requiring $|J| \gg |J'|$, we find $J/k = 0.65$°K and $J'/k = -0.10$°K, the negative sign of J' indicating a ferromagnetic A-B coupling. The consistency of the value of J obtained in this analysis with that obtained from ΔU_A seems to indicate that the model from which we have deduced these results is correct in its basic features.

The value of J' deduced from Eqs. (8) and (9) is strongly dependent on the numerical value of θ. The corresponding value of J does not depend so critically on θ, provided that $|J| \gg |J'|$. In light of the apparent difficulty of obtaining precise experimental values of θ, therefore, the value $J'/k = -0.10$°K should be viewed as tentative. Additional data or analysis of existing data are needed to determine J' more precisely.

DISCUSSION

The experimental evidence seems to indicate that the cooperative effects seen in manganous formate dihydrate above 1°K involve chiefly the A-ion sheets. The B spins appear to remain quite independent at these temperatures. It seems reasonable to assume that the dominant interaction among the Mn^{++} ions is of the isotropic Heisenberg exchange form. However, that a two-dimensional system of spins coupled by Heisenberg interactions of ferromagnetic sign cannot exhibit a spontaneous moment at nonzero temperatures is well known and has generally been interpreted as proof that such a system does not undergo cooperative ordering.[17] While this conclusion has recently been challenged,[18] reasonable doubt still remains whether cooperative transitions occur in either these systems or their antiferromagnetically coupled counterparts.

The peculiar shape of the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ near 3.7°K is almost certainly a consequence of the essentially two-dimensional character of the magnetic system. The broad maximum which occurs is reasonably attributed to substantial short-range ordering within the A-ion sheets below 6°K. Upon this broad maximum the 3.7°K peak seems to be superposed almost incidentally. The conspicuous weakness of this peak and the relative importance of short-range order suggest that the dominant forces in the magnetic system are not able of themselves to support long-range order above absolute zero, but are enabled to do so because of qualitative modifications of the system by weaker interactions. An example of such a situation occurs in the two-dimensional Ising problem.[19] Consider a square Ising net for which the interactions between nearest neighbors in the two orthogonal directions are characterized by the parameters J_1 and J_2. When one of the interaction parameters is zero, say, $J_2 = 0$ but $J_1 \neq 0$, the system decomposes into a collection of independent Ising linear chains. These possess no cooperative ordering transition, although short-range ordering produces a rounded maximum in the heat capacity near $kT \sim J_1$. For any $J_2 \neq 0$, however, the system does possess a nonzero transition temperature, a fact which apparently is related to the change in dimensionality of the problem. For $|J_2| \ll |J_1|$, however, the transition temperature may be considerably smaller than the temperature at which the maximum in the linear chain heat capacity occurred. In this case, short-range order produces a heat capacity closely approximating that of the linear chains at the higher temperatures, but when the transition temperature is reached a singular anomaly rises abruptly from the gentler variation. Qualitatively, the heat capacity which results is quite similar to that observed for $Mn(HCOO)_2 \cdot 2H_2O$.

The similarity between the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ and that of the Ising model just

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[16] P. W. Anderson, Phys. Rev. **83**, 1260 (1951).

[17] Y. Y. Li, Phys. Rev. **84**, 721 (1951); N. D. Mermin and H. Wagner, Phys. Rev. Letters **17**, 1133 (1966).

[18] H. E. Stanley and T. A. Kaplan, Phys. Rev. Letters **17**, 913 (1966).

[19] L. Onsager, Phys. Rev. **65**, 90 (1944).

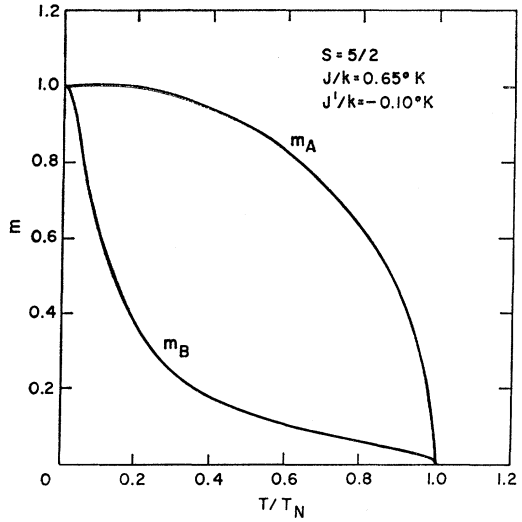

FIG. 8. Sublattice magnetizations m_A and m_B as obtained from the molecular-field calculation, Eq. (10).

described strongly suggests that cooperative behavior in $Mn(HCOO)_2 \cdot 2H_2O$ is brought about be interplay between a stronger coupling, presumably the isotropic A-A coupling, which of itself is not quite sufficient to produce a transition, and a weaker force which by some subtle modification of the system makes occurrence of long-range order possible. An attractive possibility is that the A-B interactions promote the transition by alternating the dimensionality of the system in much the manner discussed above for the quadratic Ising model. Alternatively, the weaker forces may be anisotropic in nature, promoting cooperative behavior in the A-ion sheets by making the effective intrasheet interactions somewhat Ising-like. Dipole-dipole interactions, anisotropic superexchange, and single-ion anisotropy forces could all contribute to this process. The present state of the theory does not, of course, exclude a third possibility, namely, that the observed form of the heat capacity near 3.7°K is due to pure Heisenberg interactions within the A-ion sheets.

If we assume that long-range order in $Mn(HCOO)_2 \cdot 2H_2O$ depends on the three-dimensional character which the A-B couplings impart to the interaction scheme, we are forced to reconcile with this point of view the experimental observation that the B ions remain essentially paramagnetic well below the Néel point. A simple molecular-field calculation[20] provides some qualitative understanding of the manner in which this might occur. Applying the molecular-field approximation to the Hamiltonian given by Eq. (4) leads to a set of transcendental equations which must be solved to obtain the sublattice magnetizations and other properties of the system. In general, the molecular-field solution of Eq. (4) requires four sublattices, two on A sites and two on B sites. In zero magnetic field, however, the spontaneous magnetizations of the two A sublattices differ at most in sign only, with the same relationship holding also between the two B sublattices. In this case the four vector equations of the molecular field approximation may be reduced to two scalar equations,

$$m_A = B_S(\alpha m_A + \alpha' m_B), \qquad (10a)$$

$$m_B = B_S(\alpha' m_A). \qquad (10b)$$

Here $\alpha = 4 | J | S^2/kT$ and $\alpha' = 2 | J' | S^2/kT$, the m's are the magnitudes of the reduced sublattice magnetizations $m = -\langle \mathbf{S} \rangle / S$ of the A and B sublattices, and $B_S(x)$ is the Brillouin function. Figure 8 shows the solution of these equations for $J/k = 0.65$°K, $J'/k = -0.10$°K, and $S = \frac{5}{2}$, values appropriate for $Mn(HCOO)_2 \cdot 2H_2O$. The solution indicates that the magnetizations of both the A and the B sublattices are nonzero at all temperatures below a common critical temperature T_N, at which both fall abruptly to zero. Below the critical temperature the A-site sublattice magnetization approaches its saturation value rather rapidly. The B-site magnetization, however, does not saturate until the temperature is well below T_N. Although m_B is not zero, over a considerable range of temperature it is small enough that the derivative of the Brillouin function is close to its value at zero argument. Thus the B ions respond to a magnetic field much as they would if they were paramagnetic. This is not true of the A ions, which experience large exchange fields and more quickly approach saturation. Thus the molecular-field model accounts for the apparent coexistance of highly ordered A spins and nearly paramagnetic B spins in $Mn(HCOO)_2 \cdot 2H_2O$ below 3.7°K, while still permitting active participation of the B spins in the ordering transition.

As the temperature decreases to values such that $kT \sim 2 | J' | S$, the B sublattice magnetization rapidly approaches saturation in the nearly constant exchange field produced by the A sublattice. Consequently, in addition to a discontinuity at the critical temperature, when $| J' | \ll | J |$ the heat capacity exhibits a Schottky-like maximum at a much lower temperature.[21] The resulting heat capacity is illustrated in Fig. 9.

The Schottky-like maximum obtained in the molecular-field calculation presumably corresponds to the anomalies observed in the susceptibility and heat capacity near 0.5°K.[9] Indeed, since only half the available $R \ln 6$ of magnetic entropy appears above 1.4°K, we should expect further anomalous behavior at lower temperatures. The molecular-field calculation does not, of course, give an accurate representation of the heat-capacity anomaly at T_N nor correctly predict T_N, for which it gives $T_N = 7.6$°K; it cannot reasonably be expected to do so. Finally, the anomaly at 1.7°K is

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[20] R. D. Pierce, thesis, Carnegie Institute of Technology, 1966 (unpublished). A similar calculation is carried out by N. Uryû, J. Chem. Phys. **43**, 2233 (1965).

[21] Similar behavior has been observed in ytterbium iron garnet by A. B. Harris and H. Meyer, Phys. Rev. **127**, 101 (1962).

not given by the calculation. Additional interaction must be includes to obtain such an effect.[22] Nagai[23] has attempted a calculation of the 1.7°K transition. His model assumes negligible *A*-*B* coupling but includes both isotropic and anisotropic intrasheet *A*-*A* interactions. Presumably the anisotropic contributions can insure the establishment of long-range order below 3.7°K. A nonzero J' is thus not essential in Nagai's model, while it is in the simple model described above. However, the results obtained for the simple model suggest that any nonzero J' may necessarily involve the simultaneous initiation of long-range ordering among both *A* and *B* spins even though they order at quite different rates. It may be possible to test this inference by neutron-diffraction experiments planned for the near future.

A detailed study of the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ below 1°K has been undertaken by C. A. Raquet of this laboratory. His preliminary data are consistent with a maximum heat capacity of about 0.8 cal/mole °K near 0.5°K. The molecular-field calculation yields a maximum $0.42R = 0.84$ cal/mole °K. The detailed shape of the anomaly, however, has not yet been established by the experiments.

CONCLUSIONS

The heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$ shows sharp peaks at 3.72 and 1.72°K. The anomaly at 3.72°K apparently results from a transition between paramagnetic and basically antiferromagnetic states of the magnetic system, while that at 1.72°K seems to be associated with a reorientation of the sublattice magnetization.[11] Analysis of the magnetic entropy suggests that half the manganese spins are highly disordered above 1°K. The peculiar shape of the 3.7°K anomaly in the heat capacity further suggests that the ordered state is strongly two dimensional in character. These observations may be correlated by observing the sheet-like nature of the crystal structure: sheets of *A* ions connected to one another by formate groups, with *B* ions lying between the *A* sheets and connected to them by the formate groups. Assuming the superexchange couplings to proceed via the formate groups and the *AB* interaction to be much weaker than the *AA* interaction yields an ordered state with strong two-dimensional character (the order in the *A* sheets) and a coexisting "nearly paramagnetic" component (the weakly coupled *B* ions). While the *B* ions remain "nearly paramagnetic", a small but nonzero *AB* coupling may nevertheless be required to permit the cooperative ordering of the *A* sheets by providing an effective sheet-to-sheet coupling.

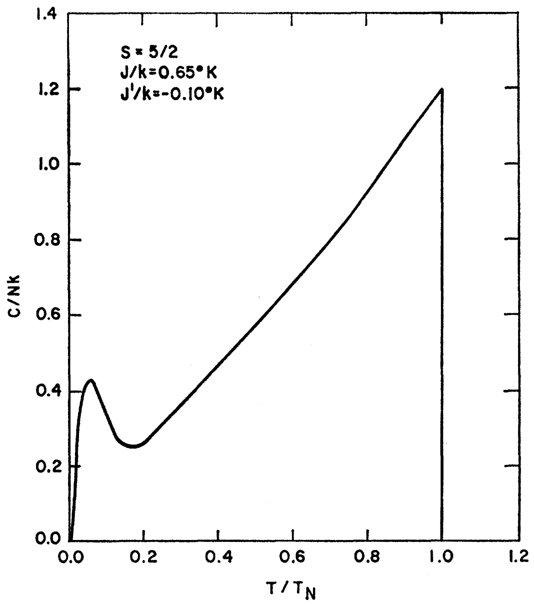

FIG. 9. Molecular-field approximation to the heat capacity of $Mn(HCOO)_2 \cdot 2H_2O$.

Analysis of the thermal and magnetic data permit estimates of the *AA* coupling, J, and the *AB* coupling, J', to be derived. It is indeed found possible to take $|J'| \ll |J|$ the values $J/k = 0.65$°K and $J'/k = -0.10$°K correctly describing the hydrogen temperature susceptibility, the magnetic heat capacity "tail," and the ground-state energy of the *A*-ion sheets. A simplified molecular-field calculation demonstrates that the *B* ions may be intimately involved in the ordering transition and still appear "nearly free" at quite low temperatures. The model also predicts that below 1°K anomalies arising from the *B* spins may be expected. Experiments below 1°K confirm the presence of these anomalies.[9]

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[22] See, e.g., J. O. Artman, J. C. Murphy, and S. Foner, Phys. Rev. **138**, A912 (1965).

[23] O. Nagai, J. Phys. Soc. Japan **22**, 947 (1967); K. Yamagata, *ibid.* **22**, 582 (1967).