

Rev. Letters **19**, 356 (1967).

<sup>4</sup>Very stable light intensity at constant current was obtained with a GE Quartzline iodide cycle bulb specified as No. 6.6A/T2-1/2Q/CL-452 and available from GE Lamp Division, Nela Park, Cleveland, Ohio.

<sup>5</sup>Model No. RDE-1 radiation thermocouple, Charles Reeder and Co., Detroit, Mich.

<sup>6</sup>Type No. 2111A frequency standard, American Time Products, Inc., New York, N. Y.

<sup>7</sup>Material supplied by the High-Purity Metals Division, United Mineral and Chemical Co., New York, N. Y.

<sup>8</sup>Electro-glo Co., Chicago, Ill.

<sup>9</sup>R. E. Pawel and E. E. Stansbury, *J. Phys. Chem. Solids* **26**, 607 (1965).

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<sup>12</sup>R. E. Pawel and E. E. Stansbury, *J. Phys. Chem. Solids* **26**, 757 (1965).

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<sup>16</sup>Hereafter, the unsubscripted symbol  $C(t)$  is used to denote the analytic function defined in (1), to differentiate it from the experimentally derived magnetic specific heat  $C_m^*$ . It is desirable to observe this distinction since it will be shown that a satisfactory fit to  $C_m^*$  near  $T_C$  cannot be obtained by adjusting the constants in (1).

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<sup>32</sup>The need for such a shift indicates a discrepancy between the temperature scales used in the two investigations. This is mildly surprising since we both used the same model of commercially available calibrated platinum resistance thermometer for standardization. Although the absolute value of  $T_C$  is of secondary importance in these measurements, this discrepancy illustrates the considerable experimental difficulty of obtaining reliable absolute temperature values in this range.

## Heat Capacities of $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ between 1.4 and 20 °K<sup>†</sup>

R. D. Pierce\* and S. A. Friedberg

*Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213*

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The heat capacities of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  have been measured between 1.4 and 20 °K. Peaks associated with long-range spin ordering are found at 3.74 °K for  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  and at 14.5 °K for  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ . An additional Schottky-like maximum occurs at 3 °K in the heat capacity of the nickel salt. These anomalies can be correlated with corresponding features of the observed magnetic susceptibilities. A unit cell of these salts contains two each of two inequivalent metal ions, types *A* and *B*. Formate groups form *AA* and *AB* bridges and are thought to mediate the dominant superexchange interactions. The thermal data show that the *AB* interaction is much weaker than the *AA* interaction in  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ ; for  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  their relative strengths could not be determined.

### INTRODUCTION

In a previous paper<sup>1</sup> we described measurements of the low-temperature heat capacity of manganous formate dihydrate,  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ . In this paper

we report the heat capacities of the related salts  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ .

Ferrous formate dihydrate<sup>2</sup> and nickelous formate dihydrate<sup>3</sup> have both been shown to be isostructural with  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ .<sup>4</sup> The structure of

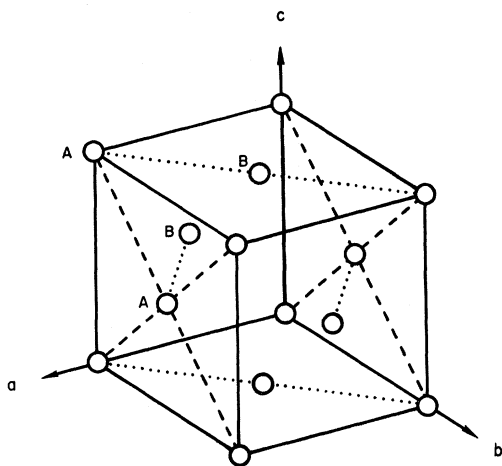


FIG. 1. Schematic representation of the crystal structure of the salts  $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , showing the positions of the inequivalent *A* and *B* metal-ion sites. Dashed and dotted lines indicate the approximate positions of formate groups linking, respectively, *AA* and *AB* pairs. These formate groups are assumed to provide the principal superexchange paths in the salts.

these salts is shown schematically in Fig. 1. The monoclinic unit cell (space group  $P2_1/c$ ) contains two each of two inequivalent metal-ion sites *A* and *B* lying alternately in successive sheets parallel to (100). Formate groups link each *A* ion to four neighboring *A* ions in the same sheet, and to a *B* ion in each of the two adjacent sheets. Each *B* ion is linked by formate groups to two *A* ions in different sheets, but to no other *B* ions. These formate bridges are indicated in Fig. 1 by dashed lines for *AA* pairs and dotted lines for *AB* pairs.

The thermal and magnetic properties of  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  are consistent with a model<sup>1,5</sup> in which only *AA* and *AB* interactions are significant. Presumably, the exchange part of these interactions is mediated by the formate group and the lack of significant *BB* interaction is associated with the absence of *B-B* formate links. In consequence of the fact that the *AB* interaction is much smaller in magnitude than the *AA* coupling, the *B* spins in  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  achieve only weak ordering and thus appear nearly free at temperatures in the vicinity of 1°K where a high degree of order exists among *A* spins. There is evidence<sup>6</sup> that the small *AB* interaction is predominantly dipolar in nature, although in the simplified molecular-field approximation in which the model has been treated, no distinction is made between exchange and dipolar couplings. Thus, while exchange interaction in this lattice appears to occur only via formate bridges, the effectiveness of the two types of formate links can be very different. A reason for this difference has been suggested<sup>7</sup> in terms of the electron distribution in the

ground state of the transition-metal ion.

It seems reasonable to suppose that exchange interaction in other paramagnetic salts isostructural with  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  will also occur via formate bridges. It is a matter of some interest to see whether this is so, i. e., whether the *BB* interaction is negligible. Equally interesting is the variation from one compound to another of the relative magnitudes of the *AA* and *AB* interactions. There is some evidence from powder susceptibility measurements<sup>8</sup> that in  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , as in the  $\text{Mn}^{++}$  salt, the *B* spins are independent of one another and only weakly coupled to the *A* spins at temperatures below which long-range ordering is initiated.  $\chi_p$  exhibits a peak at 15.6°K, but resumes its rise with falling temperatures below ~14°K. Temperature independence is achieved only below ~2°K, the constant value being that expected if one-half the  $\text{Ni}^{++}$  ions were independent and their  $S=1$  ground states were split in zero field by amounts similar to those found in other  $\text{Ni}^{++}$  salts.

In contrast, the powder susceptibility<sup>8</sup> of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  exhibits a single sharp peak at 3.7°K and falls steadily with temperatures below that point. In this case, *A* and *B* spins appear to be ordering at comparable rates suggesting that the *AB* interaction may be much larger than in either the  $\text{Mn}^{++}$  or the  $\text{Ni}^{++}$  salt. The heat-capacity measurements to be reported were undertaken to confirm the magnetic observations and, if possible, to test the inferences drawn from them.

#### EXPERIMENTAL

The ferrous formate used in these experiments was prepared by reacting 99.9% pure iron sponge (Johnson, Matthey, and Co. Ltd.) with reagent grade formic acid (Matheson, Coleman, and Bell). Since the aqueous solution of  $\text{Fe}(\text{HCOO})_2$  is quite unstable in air, the preparation was carried out in a helium atmosphere. Crystallization of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  from the filtered reaction products was performed at about 35°C under aspirator vacuum. When crystallization was almost complete, ethyl alcohol was admitted to the crystallization vessel, the liquid was quickly decanted, and the crystals were rinsed again in ethyl alcohol and allowed to dry in air. The material obtained by this procedure was pale green in color and consisted of aggregates of microcrystals. The material was verified to be the desired  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  by its x-ray powder pattern. Although the aqueous solution was unstable in air, the crystals of ferrous formate dihydrate seemed to be quite stable and could be stored for long periods of time without apparent deterioration.

The nickelous formate dihydrate sample consisted of material recrystallized from technical grade  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  obtained from Fisher Scientific Co. Although the purity of this material is not known,

magnetic-susceptibility measurements performed on the technical grade material gave results in good agreement with those obtained using reagent grade material.<sup>9</sup>

A brief description of the procedures used in the heat-capacity measurements has been given previously.<sup>1</sup>

## RESULTS AND DISCUSSION

### A. $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$

The measured heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  between 1.4 and 20 °K is shown in Fig. 2. Table I summarizes the data. The most striking feature is the single strong peak which occurs at 3.74 °K. This is essentially the temperature at which the magnetic susceptibility<sup>8</sup> also exhibits a pronounced peak. It appears likely that long-range magnetic order is established in  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  below a transition temperature of 3.74 °K.

Several features of Fig. 2 are noteworthy. Above the peak,  $C_p$  passes through a broad, almost flat minimum before beginning to increase with  $T$  above ~10 °K. Near 5 °K there is evidence of a "shoulder" or unresolved rounded subsidiary maximum. Such a feature could be associated either with the presence of low-lying excited components of the single  $\text{Fe}^{2+}$  ion ground state, as in  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,<sup>10,11</sup> or with the persistence above  $T_C$  of pronounced short-range order in the two-dimensional sheets comprising the lattice.<sup>1</sup> A combination of both of these effects is quite likely.

It is often possible in such a system to resolve the measured  $C_p$  well above  $T_C$  into a  $T^3$  lattice contribution and a  $T^{-2}$  high-temperature "tail" representing the magnetic contribution. Figure 3 is a plot of  $C_p T^2$  vs  $T^5$ . The considerable curvature of this plot makes any separation difficult. However, using only data near 20 °K, one can define an approximate straight line of the form  $C_p \approx aT^3 + bT^{-2}$

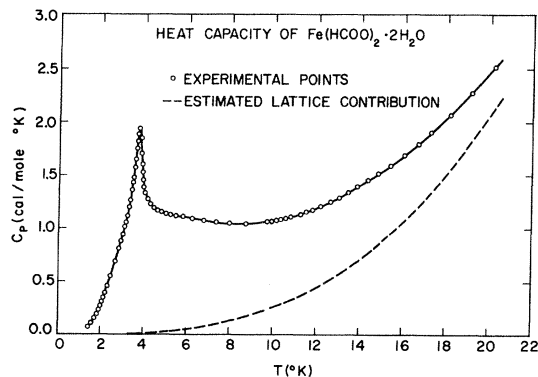


FIG. 2. Heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  in zero external field. The dashed line indicates the estimated lattice heat capacity  $aT^3$ .

TABLE I. Heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  without applied field.  $C_p$  in cal/mole deg. Temperature in °K.

$T$	$C_p$	$T$	$C_p$	$T$	$C_p$
1.462	0.070	3.539	1.571	5.787	1.101
1.499	0.078	3.549	1.592	6.211	1.086
1.521	0.084	3.562	1.595	6.747	1.068
1.538	0.086	3.584	1.644	7.332	1.054
1.578	0.098	3.606	1.684	7.943	1.043
1.582	0.102	3.627	1.751	8.695	1.040
1.652	0.124	3.650	1.781	9.703	1.059
1.727	0.151	3.661	1.817	9.929	1.065
1.825	0.190	3.673	1.835	10.140	1.074
1.909	0.227	3.696	1.886	10.352	1.082
1.981	0.263	3.721	1.942	10.565	1.096
2.050	0.300	3.747	1.946	10.779	1.104
2.124	0.340	3.773	1.934	10.926	1.114
2.208	0.387	3.794	1.671	11.007	1.112
2.320	0.453	3.800	1.848	11.249	1.132
2.470	0.550	3.828	1.710	11.271	1.137
2.669	0.685	3.856	1.602	11.500	1.155
2.835	0.804	3.884	1.525	11.570	1.158
2.934	0.875	3.918	1.450	11.806	1.173
3.017	0.941	3.946	1.339	11.872	1.180
3.077	1.009	3.951	1.386	12.184	1.206
3.079	0.991	3.984	1.351	12.321	1.211
3.123	1.053	4.018	1.323	12.635	1.243
3.144	1.059	4.053	1.307	13.033	1.291
3.176	1.098	4.090	1.292	13.447	1.338
3.210	1.112	4.127	1.245	13.884	1.395
3.225	1.138	4.127	1.275	14.360	1.457
3.277	1.196	4.165	1.263	14.823	1.513
3.278	1.186	4.203	1.258	15.392	1.590
3.339	1.266	4.275	1.225	16.010	1.684
3.358	1.287	4.437	1.188	16.683	1.794
3.386	1.323	4.602	1.171	17.251	1.904
3.422	1.361	4.788	1.155	18.139	2.067
3.446	1.412	5.003	1.140	19.112	2.278
3.460	1.427	5.204	1.127	20.177	2.540
3.500	1.479	5.461	1.116		

with  $a = 2.60 \times 10^{-4}$  cal/mole °K<sup>4</sup> and  $b = 168$  cal °K mole. The lattice term  $aT^3$  so obtained very closely matches that previously found<sup>1</sup> for  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ .

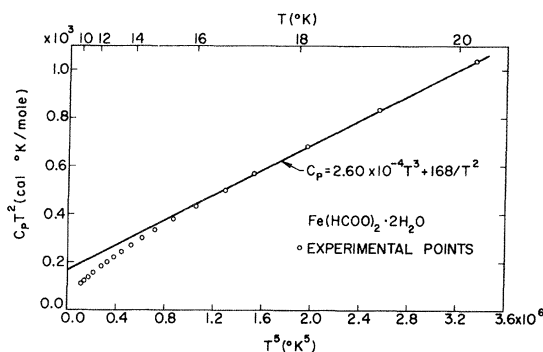


FIG. 3.  $CT^2$ - vs  $-T^5$  plot of the heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , indicating the separation of the lattice and magnetic contributions.

The near identity of the structures and atomic masses in these compounds suggests that this may be a reasonable estimate of the lattice heat capacity in both cases. This estimate is plotted as a dashed line in Fig. 2 and is used to extract the magnetic contribution,  $C_{\text{mag}}$ , to  $C_p$ . We note the large magnetic heat capacity in excess of the lattice part above  $T_C$ , even up to 20 °K. Short-range ordering and single-ion excitation may well both be quite important over the whole range.

We note that the peak in  $C_p$  at  $T_C$ , while quite pronounced, is distinctly rounded in comparison with other  $\lambda$  anomalies in  $\text{Fe}^{2+}$  salts.<sup>12</sup> We have performed various auxiliary experiments to demonstrate that this is not an instrumental effect. While intrinsic rounding of such peaks is common in  $\lambda$  transitions in finite imperfect crystals, previous experience<sup>13</sup> with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  suggests that the temperature interval over which such rounding occurs is usually smaller by at least an order of magnitude. While we cannot exclude rounding due to imperfection or strains, in this case we are more inclined to attribute most of the effect to the sensitivity of this system to externally applied magnetic fields and the fact that these measurements were performed near a large electromagnet whose residual field at the sample amounted to  $\sim 2$  Oe.

This sensitivity is shown explicitly in Fig. 4, where we plot the heat capacity  $C_p$  vs  $T$  in fields of

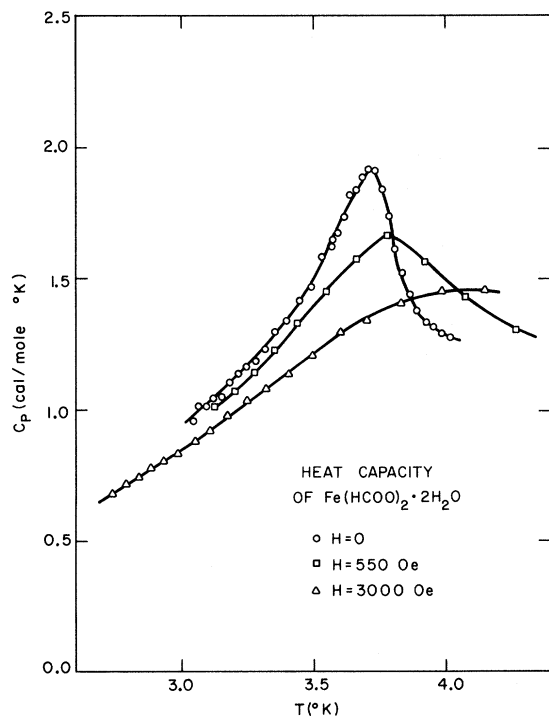


FIG. 4. Magnetic field dependence of the heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  near 3.7 °K.

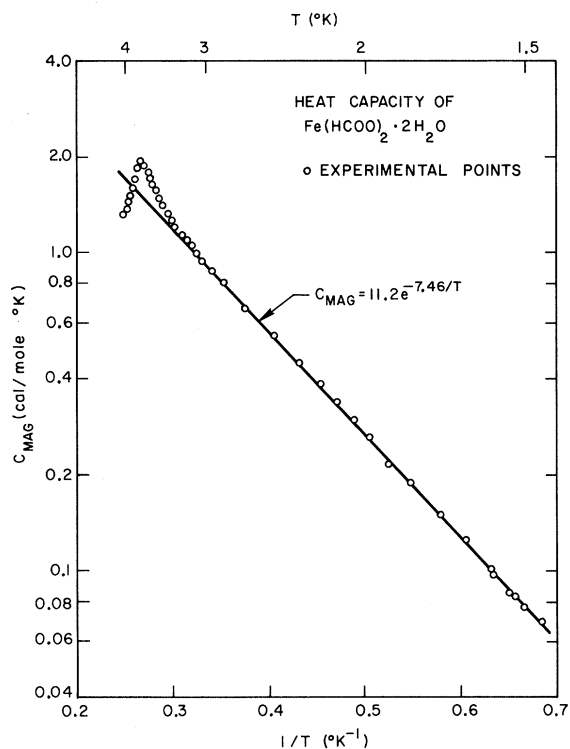


FIG. 5. Exponential temperature dependence of the heat capacity of  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  below 3 °K.

550 and 3000 Oe applied perpendicularly to the axis of the cylindrical polycrystalline specimen. It is not possible in this case to correct for the uncertain effects of demagnetization or field inhomogeneity. However, it is noteworthy that the rather modest field of 550 Oe broadens the anomaly, shifts it to slightly higher temperatures and reduces its maximum value. These changes are even more pronounced in a field of 3 kOe, the maximum being shifted upward in temperature to the extent that it is no longer resolved in the interval covered by our measurements. We consider it quite likely that the broadening and rounding evident in the peak in our "zero-field" data are due in large measure to the analogous effect of a small stray field.

The fact that increasing applied fields shift the heat-capacity maximum in  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  to higher temperatures is evidence that the ordered state below 3.74 °K is in some sense ferro- or ferrimagnetic,<sup>14</sup> i. e., has a spontaneous magnetic moment. At liquid-hydrogen temperatures, the powder susceptibility of this salt obeys the Curie-Weiss law<sup>8</sup>  $\chi_p \approx 2.78/(T + 1.3)$  cgs/mole. The sign of the Weiss constant indicates that the dominant interaction is antiferromagnetic. At 3.7 °K,  $\chi_p$  is strongly peaked, while above that temperature  $1/\chi_p$  exhibits the hyperbolic temperature dependence which one associates with ferrimagnetism<sup>15</sup> or the

weak ferromagnetism of a canted antiferromagnet.<sup>16,17</sup>

Either of these situations is compatible with the structure of this substance which contains equal numbers of Fe<sup>2+</sup> ions at two crystallographically inequivalent sites *A* and *B*. The moments on *A* and *B* sites need not be the same. Were antiferromagnetic ordering to develop without independent compensation among the *A* sites and among the *B* sites, ferrimagnetism could result. It could also arise under these circumstances even with equal moments on *A* and *B* sites if the sublattices order at different rates below 3.7 °K. Crystal symmetry in Fe(HCOO)<sub>2</sub> · 2H<sub>2</sub>O also permits the occurrence of canted antiferromagnetism<sup>17</sup> caused either by single-ion anisotropy or by anisotropic superexchange or a combination of these mechanisms. The present data, while suggestive, do not definitely establish the existence of a spontaneous moment in this material, much less its origin. Single-crystal magnetization data and neutron-diffraction studies would help to clarify the situation.

We note in Fig. 2 the very rapid fall of *C<sub>p</sub>* with temperature below 3.7 °K. The semilogarithmic plot of *C<sub>mag</sub>* vs 1/*T* in Fig. 5 yields a straight line below 3 °K. Thus we may write in this region *C<sub>mag</sub>* = *Ae*<sup>-*B/T*</sup> where *A* = 11.2 cal/mole °K and *B* = 7.46 °K. The root-mean-square deviation of this expression from the data below 3 °K is 1.1%, a value consistent with the estimated precision of the data.

The exponential temperature dependence of *C<sub>mag</sub>* implies the existence of a gap (5 or 6 cm<sup>-1</sup>) in the energy spectrum of the spin system associated with substantial magnetic anisotropy. In this case, the gap energy is comparable with or larger than the exchange energy. A similar situation exists in FeCl<sub>2</sub> · 4H<sub>2</sub>O.<sup>11,12</sup> In order to learn more about the spin excitations in Fe(HCOO)<sub>2</sub> · 2H<sub>2</sub>O, one might wish to fit the data with a theoretical expression for *C<sub>mag</sub>* appropriate to some tractable model. In this case, the choice of such a model is not obvious since the character of the ordered state, including its dimensionality, is unknown. In addition, it is not clear that the spin interactions may be suitably approximated either in the Heisenberg or Ising limits, although the size of the anisotropy gap perhaps favors the latter. It should be noted that most of the likely models yield a magnetic heat capacity well below *T<sub>C</sub>* of the form *C<sub>mag</sub>* = *A'T<sup>n</sup>e*<sup>-*B/T*</sup>. We have attempted to fit our data with an expression of this form for various positive and negative fractional and integral values of *n*. The exponential factor is so dominant, however, that we find no significant improvement in the fit of the data over that cited above for *n* = 0.

In a ferrous compound, magnetic anisotropy of the magnitude implied by the limiting behavior of the heat capacity just described may well be a single-ion effect. The free Fe<sup>2+</sup> ion has the (3*d*)<sup>6</sup> electronic

configuration whose ground state is <sup>5</sup>*D*<sub>4</sub>. In a moderate crystalline field of sufficiently low, e.g., rhombic, symmetry the orbital angular momentum is quenched leaving a ground state which retains only the fivefold spin degeneracy. Spin-orbit interaction, however, prevents quenching from being quite complete and also splits the five spin components of the ground state even in the absence of applied or exchange fields. The energetic differences among these states account for the single-ion anisotropy found<sup>18</sup> in a number of ferrous compounds in which the Fe<sup>2+</sup> ion is coordinated with a distorted octahedron of ligands. If the splitting of the spin quintet is not too large relative to the exchange energy, we expect all five components to be occupied as one goes from the fully ordered state to one of complete disorder. The corresponding entropy increase in this process should be Δ*S<sub>m</sub>* = *R* ln 5 = 1.61*R*.

The magnetic entropy increase in Fe(HCOO)<sub>2</sub> · 2H<sub>2</sub>O has been calculated by numerical integration of

$$\Delta S_{\text{mag}} = \int_0^\infty (C_{\text{mag}}/T) dT \quad , \quad (1)$$

where *C<sub>mag</sub>* is the magnetic contribution to *C<sub>p</sub>*. The entropy change between 1.46 and 20.2 °K is 1.04*R*. Plausible extrapolations to *T* = 0 and to *T* = ∞ were made using *C<sub>mag</sub>* = *Ae*<sup>-*B/T*</sup> and *C<sub>mag</sub>* = *b/T*<sup>2</sup>, respectively. The contribution to Δ*S<sub>mag</sub>* below 1.46 °K is 0.01*R* and that above 20.2 °K is 0.10*R*. The total entropy increase is 1.15*R*. This is about 30% smaller than the value *R* ln 5 expected if the system contained ions all having access to five states, i. e., with an effective spin *S* = 2, equal, in this case, to the real spin.

The discrepancy between these entropy changes is large enough that it must be considered real. Several explanations suggest themselves. For example, it is conceivable that an additional anomaly in *C<sub>p</sub>* might occur below 1.46 °K, making simple extrapolation of *C<sub>mag</sub>* to *T* = 0 °K impossible. The extremely rapid fall of *C<sub>mag</sub>* with *T* at 1.46 °K, however, makes this possibility appear remote. A more attractive interpretation is suggested by the observation that Δ*S<sub>mag</sub>* = 1.15*R* is just  $\frac{1}{2}R(\ln 5 + \ln 2)$  =  $\frac{1}{2}R(1.61 + 0.69)$ . This would be the expected behavior if, below ~20 °K, one-half the Fe<sup>2+</sup> ions had access to two energy levels while the rest were distributed over five levels, that is, the system contained equal number of ions with effective spins *S* =  $\frac{1}{2}$  and *S* = 2.

Such a division of the Fe<sup>2+</sup> system is plausible, since there is no *a priori* reason why ions at *A* and *B* sites should have the same level schemes. In order to explain the temperature dependence and relative magnitudes of the quadrupole splittings of the Mössbauer lines originating at the two kinds of sites in Fe(HCOO)<sub>2</sub> · 2H<sub>2</sub>O, Hoy and Barros<sup>19</sup> found it necessary to allow the dominant parts of the crys-

talline fields at these sites to have different symmetries. They assume the  $A$  site to have nearly cubic symmetry ( $O_h$ ) with a small axial distortion splitting the  $T_2$  orbital triplet into a doublet ground state and an upper singlet separated by  $\Delta_A = 175 \text{ cm}^{-1}$ .  $B$  sites are taken to have tetragonal symmetry ( $D_{4h}$ ) with a  $B_2$  orbital singlet ground state and an excited  $E$  orbital doublet at  $\Delta_B = 590 \text{ cm}^{-1}$ . While adequate to explain the quadrupole splittings, the model of Hoy and Barros does not include spin-orbit coupling and thus cannot give the level structure of importance in the present problem. We have extended these calculations to include spin-orbit interaction. The results are promising in that one can justify qualitatively the assignment of effective spins of  $\frac{1}{2}$  and 2 to  $A$  and  $B$  ions, respectively. However, a proper test of this picture would require the fitting of the available thermal and magnetic data. Even above  $T_N$ , this is possible only if the model takes into account the interactions among  $\text{Fe}^{2+}$  ions. We prefer not to attempt this until single-crystal data are obtained with which we might hope to determine the many parameters entering the problem.

Another possible interpretation of the entropy difference  $\Delta S_{\text{mag}}$  is compatible with the uncertainty in our estimates of this quantity. If the effective spin of ions on both  $A$  and  $B$  sites were  $S=1$  then  $\Delta S_{\text{mag}}$  would be just  $R \ln 3 = 1.10R$ , which is within 5% of the empirical estimate  $1.15R$ . Inomata and Oguchi<sup>20</sup> have shown how the tetragonally symmetrical crystalline field at an  $\text{Fe}^{2+}$  ion in  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  can produce a group of three low-lying levels describable by an effective spin  $S=1$ . While both  $A$  and  $B$  sites in  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  appear to have tetragonal character to different degrees of approximation, it is not obvious that  $S=1$  would be suitable for both of them. Again, a rather full calculation, including interactions, would be required before a critical comparison with the data could be attempted.

In neither of the above proposals for assigning effective spins, other than  $S=2$ , to one or both of the sets of  $\text{Fe}^{2+}$  ions in this salt are there any obvious implied restrictions on the relative magnitudes of the  $AA$ ,  $AB$ , and, for that matter,  $BB$  interactions. Thus, entropy considerations do not provide, as they did for  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , a compelling argument for believing that  $B$  spins in the  $\text{Fe}^{2+}$  salt interact only weakly with  $A$  spins and with one another. At the same time, obvious clues of such behavior are absent from the susceptibility data.

It would, however, be unwarranted at this point to conclude that  $AA$  and  $AB$  interactions are necessarily of comparable magnitude in this compound. There is some suggestion from the Mössbauer work that  $AB$  coupling may, in fact, be the weaker of the two. Indirect hints of this may also be inferred

from the magnetic and thermal observations. We have noted earlier that the enhancement of  $C_p$  above the transition point may be attributable, at least in part, to significant short-range order. This would seem most likely to occur if sheets of  $A$  spins were rather independent of one another, i. e., if  $AA$  interaction were much larger than  $AB$  coupling. The persistence of such short-range order in  $A$  sheets may also be needed to explain the anomalously low splitting factor ( $g \approx 1.95$  for  $S=2$ ) deduced from the powder-susceptibility data in the hydrogen range by requiring them to fit a Curie-Weiss law. This anomaly, incidentally, is not removed by invoking effective spins less than  $S=2$  for some or all the  $\text{Fe}^{2+}$  ions in this temperature region.

To the extent that we are presently able to interpret them, our heat-capacity data on  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  provide no firm indication of the relative magnitudes of the spin-spin interactions in this material.

#### B. $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$

The heat capacity  $C_p$  of  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  is shown at various temperatures between 1.4 and 20 °K in Fig. 6. These data are representative of the results of several runs. It must be noted, however, that this material proved less stable than the corresponding manganous and ferrous salts. As a result, some systematic nonreproducibility was detected from run to run with a given specimen. The experimental points displayed in Fig. 6 are smaller by several percent than those of an earlier less complete run on the same sample, probably as a result of partial specimen decomposition. We report them because they exhibit the general features found in all of our experiments on  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ . However, we do not represent them as definitive data and, therefore, refrain from presenting them in tabular form.

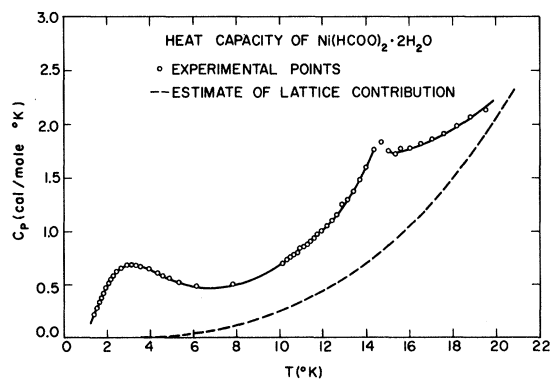


FIG. 6. Heat capacity of  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  in zero external field. The dashed line is the  $T^3$  lattice heat capacity of  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  used to approximate the lattice contribution to the heat capacity of the nickel salt.

Two anomalous maxima are evident in Fig. 6, a rounded one of the Schottky type near 3 °K and an angular peak near 14.5 °K. While the data points are too widely spaced to determine the precise shape of the latter anomaly, it does appear to be of the sharp  $\lambda$  type which would accompany the cooperative onset of long-range order in the Ni<sup>2+</sup> spin system. A corresponding maximum in the powder susceptibility has been detected<sup>8</sup> at 15.6 °K. If, as appears likely, the ordered state is basically antiferromagnetic, the difference in temperature between the susceptibility and heat-capacity maxima may not be unreasonable. The critical temperature would be that of the heat-capacity anomaly,<sup>21</sup> i. e.,  $T_N = 14.5$  °K.

The appearance below the cooperative peak at  $T_N$  of a second maximum of the Schottky type seems to provide strong support for the notion that some of the Ni<sup>2+</sup> spins are nearly independent at temperatures where the rest are substantially ordered. As noted above, the powder susceptibility has been found to resume its rise with falling  $T$  below  $\sim 14$  °K and achieve temperature independence below  $\sim 2$  °K. Hoy *et al.*<sup>8</sup> found it possible to fit the observed limiting value of  $\chi_p$  assuming only one-half the Ni<sup>2+</sup> ions in the system to be effective and that these could be described by the single-ion spin Hamiltonian

$$\mathcal{H} = D[S_x^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + g\mu_B \vec{S} \cdot \vec{H} \quad (2)$$

A satisfactory fit was obtained for  $D/k = -8.00$  °K,  $E/k = -2.85$  °K,  $S = 1$ , and  $g = 2.25$ , values quite comparable with those found for other salts<sup>22</sup> containing Ni<sup>2+</sup> ions in distorted octahedral environments. In Fig. 7, we show the observed heat capacity of Ni(HCOO)<sub>2</sub> · 2H<sub>2</sub>O below 6 °K together with a theoretical Schottky curve calculated with the same Hamiltonian (for  $H = 0$ ) and the same set of constants indicated above. Again we assume only one-half the Ni<sup>2+</sup> ions to contribute. The agreement with the data is quite reasonable and could probably be improved by small changes in  $D$  and  $E$ . Because of

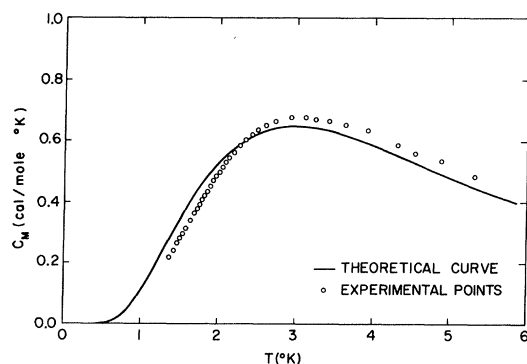


FIG. 7. Comparison of the magnetic heat capacity of one mole of Ni(HCOO)<sub>2</sub> · 2H<sub>2</sub>O with that of one-half mole of Ni<sup>2+</sup> ions with  $D/k = -8.00$  °K and  $E/k = -2.85$  °K.

other uncertainties, however, such as the contribution to  $C_p$  of the low-temperature portion of the cooperative peak, further adjustment of parameters was not deemed worthwhile.

As in the case of Mn(HCOO)<sub>2</sub> · 2H<sub>2</sub>O, it is reasonable to assume that those Ni<sup>2+</sup> ions which appear nearly independent below  $T_N$  occupy  $B$  sites linked by formate groups with  $A$  sites but not with one another. Ni<sup>2+</sup> ions on  $A$  sites, on the other hand, are linked by formate bridges with one another and presumably experience a strong  $AA$  interaction which is primarily responsible for the long-range ordering initiated among them at  $T_N$ . The splitting of the  $A$ -ion ground state in the exchange field produced largely by other  $A$  spins is great enough to make their contribution to  $C_p$  very small near 3 °K, as our calculation indicates.

In Mn(HCOO)<sub>2</sub> · 2H<sub>2</sub>O the presence of nonzero  $AB$  interaction inevitably means<sup>1,5</sup> that long-range ordering of  $B$  spins is initiated with that of  $A$  spins at  $T_N$  although at a much slower rate with respect to falling temperature. In Ni(HCOO)<sub>2</sub> · 2H<sub>2</sub>O the same tendency is presumably present. However, if the zero-field splitting of the ground state of a Ni<sup>2+</sup> ion on a  $B$  site is sufficiently large<sup>23</sup> in comparison with the  $AB$ -coupling energy it is possible that  $B$  spins may be effectively quenched before they can order significantly, if at all. It should also be noted that, as in Mn(HCOO)<sub>2</sub> · 2H<sub>2</sub>O, the  $A$  spins may become almost fully ordered at temperatures rather near  $\frac{1}{2}T_N$ , so that  $B$  spins will be exposed to a nearly constant effective field over a wide temperature range. The magnitude of this field depends on the size of the  $AB$  interaction. The Zeeman splitting of the ground state of the Ni<sup>2+</sup> ions on  $B$  sites which it produces is, perhaps, not negligible in comparison with the zero-field splitting due to the crystal field and spin-orbit interaction. To what extent the coefficients  $D$  and  $E$  obtained by fitting Eq. (2) to the data reflect this many-ion effect is difficult to estimate at present. It is quite possible that the zero-field splitting of the  $S = 1$  ground triplet of the Ni<sup>2+</sup> ion at a  $B$  site in a specimen diluted, for example, with Zn<sup>2+</sup> would be substantially smaller than that inferred here for the concentrated salt.

Lack of data in a range where magnetic and lattice contributions to  $C_p$  have simple asymptotic forms precludes a reliable separation of these terms for Ni(HCOO)<sub>2</sub> · 2H<sub>2</sub>O. If we assume that the lattice contribution is essentially that of the isomorphous Mn<sup>2+</sup> and Fe<sup>2+</sup> salts, however, a rough separation is possible. It is this estimate which is shown in Fig. 6 and which has been subtracted from the measured  $C_p$  values to give the  $C_{\text{mag}}$  points of Fig. 7. Subtracting this estimated lattice correction from all of our data, we can obtain  $C_{\text{mag}}$  and from it, by integration, the magnetic entropy increase on

warming from 1.37 to 19.5 °K. This is found to be 0.7*R*. Plausible extrapolation of the integral to 0 °K increases this total by no more than a few per cent.

The ground state of the free  $\text{Ni}^{2+}$  ion, having the  $(3d)^8$  configuration, is  $^3F_4$ . In a crystalline environment of cubic symmetry the orbital angular momentum is quenched leaving a ground state with the threefold degeneracy corresponding to the true  $S=1$ . Low-symmetry crystal-field components combine with spin-orbit interaction to produce the zero-field splittings of this triplet. Since all  $\text{Ni}^{2+}$  ions in  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  have distorted octahedral coordination we would expect them to exhibit the split triplet ground state. The separations of the component levels normally amount to a few  $\text{cm}^{-1}$ . Thus, we would expect the entropy increase, on going from the fully ordered to the disordered state, to be  $\Delta S_m = R \ln 3 = 1.10R$ . Up to 19.5 °K, we are able to account roughly for about two-thirds of this entropy change. Whether it is reasonable to expect the remainder to appear above 19.5 °K is unclear. The pronounced two-dimensional character of these structures certainly raises the possibility of strong short-range ordering even at temperatures of  $2T_N$  and above.<sup>5</sup> The fact that the cooperative anomaly at  $T_N$  is rather small may support the belief that such short-range effects are important outside the range of the present measurements and that these could account for the entropy "deficit."

If this is not the case, then a conceivable alternative would be to require the effective spin of half the  $\text{Ni}^{2+}$  ions, probably those on *A* sites, to be  $S = \frac{1}{2}$  rather than  $S=1$ . The expected entropy increase over the range where this assumption would be valid then becomes  $\Delta S_{\text{mag}} = \frac{1}{2}R(\ln 3 + \ln 2) = 0.90R$ , a value much closer to the empirical estimate when a small additional contribution above 19.5 °K is included. An effective spin  $S = \frac{1}{2}$  would imply a strong axial crystal-field component causing *D* to be very large and negative at *A* sites. This highly unusual situation would be accompanied by a very large Ising-like anisotropy in the magnetic susceptibility of  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ .

Presumably, such behavior would be easily detected in single-crystal susceptibility measurement well above  $T_N$ . Such experiments are clearly very desirable since they could also detect two-dimensional short-range ordering, if it were pronounced, and thus help us to judge the relative merits of these suggestions.

#### FINAL REMARKS

The heat-capacity data on  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  reported above bring out interest-

ing similarities and differences between them and the isostructural compound  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ . All three salts show cooperative ordering to basically antiferromagnetic states, the transition temperatures being 3.72 °K for  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , 3.74 °K for  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , and 14.5 °K for  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ . The  $\text{Mn}^{2+}$  salt is weakly ferromagnetic<sup>24</sup> below  $T_N$ . The presence of a spontaneous moment below  $T_N$  in  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  has been inferred from the response of the cooperative heat-capacity anomaly to applied magnetic fields and from the powder susceptibility. The origin of this moment remains to be unravelled. Whether  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  also exhibits a nonzero moment below  $T_N$  is not known.

At 1.72 °K, a spontaneous reorientation<sup>24</sup> of the sublattice magnetization occurs in  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  accompanied by magnetic and thermal anomalies. No such phenomenon has been observed in the  $\text{Fe}^{2+}$  or  $\text{Ni}^{2+}$  salts. However, such transitions, of which the Morin transition in  $\alpha\text{-Fe}_2\text{O}_3$  is the prototype, appear to be caused by a competition between single-ion and dipolar anisotropies,<sup>25</sup> and can be expected to occur only in systems with small single-ion anisotropy. Salts of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ , with their ground *S* states, satisfy this requirement. On the other hand, the zero-field ground-state splittings and thus the single-ion anisotropies of  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  in the dihydrated formates should far outweigh the dipolar anisotropies in these crystals, so that spontaneous sublattice reorientation is not to be expected. These splittings may be large enough in  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  to cause half or all of the  $\text{Fe}^{2+}$  ions to exhibit effective spins less than the free-spin value  $S=2$  in the ordering process. While a similar possibility exists for *A* ions in the  $\text{Ni}^{2+}$  salt, it is much more speculative.

In  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  it is well established that the *AA* interaction is larger than the *AB* interaction, while *BB* coupling is negligibly small. The present work lends support to a similar picture of the interactions in  $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  although no estimates of the magnitudes of the interactions have been attempted. The available evidence on  $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$  neither requires such a coupling scheme nor excludes the possibility that it may exist.

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\*National Science Foundation Graduate Fellow.



Present address: Bell Telephone Laboratories,  
Murray Hill, N. J. 07974.

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## Localized Correlations in Narrow Conduction Bands. II

Joel A. Appelbaum

*Bell Telephone Laboratories, Murray Hill, New Jersey 07974*

and

David R. Penn\*

*Brown University, Providence, Rhode Island 02912*

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The problem of a magnetic impurity in a narrow conduction band is studied using double-time Green's functions. We have used a Wolff model in which a repulsive Coulomb interaction of strength  $U$  is limited to the impurity site. The coupling of the impurity site to its neighbors because of the kinetic energy is reduced by a scale factor relative to the coupling of host atoms to their neighbors. The difference in the one-electron potential between host and impurity sites is also taken into account. We have solved the decoupled Green's-function equations in the infinite- $U$  limit in the presence of a finite magnetic field. From this solution, a conserving calculation of the zero-field magnetic susceptibility  $\chi$  is performed and numerical results obtained. We find that for a sufficiently weak coupling between the impurity atom and its neighbors, a Curie-law behavior of  $\chi$  can be obtained over the four decades of temperature studied. Evidence of Kondo saturation of  $\chi$  is found for more strongly coupled impurities. The susceptibility shows no evidence of singular behavior at zero temperature.

### I. INTRODUCTION

Recently the authors undertook a study of the problem of a magnetic impurity in a narrow energy band.<sup>1-3</sup> An equation-of-motion technique was used in which particular care was taken in the treatment of electron correlations at the impurity site. A similar decoupling scheme has also been used in the study of the Anderson model.<sup>4</sup>

The model studied by the authors was a modification of the Wolff<sup>5</sup> model; it was assumed that the

sole effect of the magnetic impurity was the introduction of a strong repulsive interaction between electrons of opposite spin on the impurity site. The coupling of the impurity to its neighbors via the hopping term in the kinetic energy was assumed to be the same as that for any other atom and its neighbors. The one-electron potential of the impurity was assumed to be the same as that of a host atom. Our purpose is to study this model, relaxing the above-mentioned restrictions (equal coupling and equal one-electron potentials), in the presence