

(10.0) and (00.2) faces of the Brillouin zone, the latter being analogous to the existence of contact between the Fermi surface and the $\{111\}_\alpha$ faces within the stability range of the α phases. In the presently suggested model the observed maximum in the density of states in the ζ phase is identified with the approach and contact of the Fermi surface and the $\{10.1\}$ faces of the zone, and the general high level of the density of states is identified with the existence of the (10.0) overlap and perhaps also additional contributions due to the incompleteness of the zone. In the free-electron model, contact between the spherical Fermi surface and the $\{10.1\}$ zone faces occurs at 1.68 electrons/atom. Present results indicate this contact at ~ 1.53 electrons/atom, thus suggesting a relatively small distortion of the Fermi surface consistent with relatively small band gaps in the Brillouin zone. The above qualitative interpretation neglects the possibility of additional contributions discussed in the literature and summarized in our previous paper,⁴ namely, from the d band, or from the increased scattering by impurity atoms (virtual contribution) or from the existence of exceptionally large band gaps in the Brillouin zone.

An alternative interpretation of the density-of-states trends on alloying is gaining ground which makes use of the concept of bound states¹⁵ and a related displacement of a semirigid band while the Fermi level is virtually unchanged.¹⁶ For example, keeping the initial Fermi level as in Fig. 4, it is possible to obtain qualitatively the observed trend in the γ values by translating the whole density-of-states curve for the hcp structure towards lower values of energy. Hence, qualitatively, the two interpretations are not incompatible. A more detailed speculation about the band structure of the ζ phases seems unwarranted until more data on these phases are accumulated.

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¹⁵ J. Friedel, *Advan. Phys.* **3**, 461 (1954).

¹⁶ A. H. Lettington, *Phil. Mag.* **11**, 863 (1965).

Low-Temperature Magnetic Susceptibility of Ferrous Oxalate Dihydrate*

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The magnetic susceptibility χ_p of powdered $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ has been measured between 1.3 and 300°K. Above $\sim 80^\circ\text{K}$, $\chi_p = 3.40/(T+25.4)$ (cgs/mole). χ_p exhibits a broad, rounded maximum near 30°K and a sharp peak at 20°K. X-ray structural evidence indicates that Fe^{++} ions in this material are linked in chains by oxalate groups. Assuming an antiferromagnetic intrachain exchange constant $J = -4.9k$, it is possible to obtain a reasonable fit of the data above 25°K with the susceptibility computed for Ising interactions and $S=2$. If the upper maximum is due to chain ordering, the lower maximum then appears to be associated with the cooperative onset of long-range spin order in three dimensions induced by interchain coupling.

INTRODUCTION

RECENT Mössbauer studies¹ of powdered ferrous oxalate dihydrate reveal appreciable broadening of the two-line resonant absorption spectrum as the temperature is lowered from 77 to about 20°K. At temperatures close to the liquid-helium region these lines are split into a seven-line pattern indicative of the existence of long-range order among the electronic moments of the Fe^{++} ions. The temperature at which the cooperative onset of long-range order begins was not determined in these measurements nor was any detailed information obtained about the ordering process.

These observations are quite consistent with the results of magnetic susceptibility measurements performed by Welo² many years ago on powdered $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Between 200 and 300°K, Welo found $\chi_p = 3.33/(T+26)$ (cgs/mole). The magnitude of the Weiss constant, $\theta = -26^\circ\text{K}$, appears significant while its negative sign suggests that the interaction among Fe^{++} ions is antiferromagnetic. The Curie constant, $C = 3.33$, corresponds to an average splitting factor $g = 2.10$, if we assume the angular momentum of the Fe^{++} ion to be its spin only value, $S = 2$.

In an effort to learn more about the magnetic ordering process whose existence is inferred from the earlier work, we have measured the powder susceptibility of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ down to 1.3°K. This system acquires particular

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¹ F. de S. Barros, P. Zory, and L. E. Campbell, *Phys. Letters* **7**, 135 (1963).

² L. Welo, *Phil. Mag.* **6**, 481 (1928).

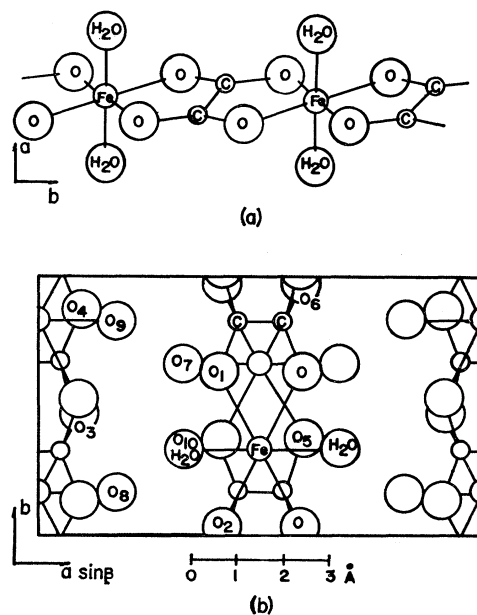


FIG. 1. (a) Projection of a single chain of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ units on the a - b plane (after Mazzi and Garavelli, Ref. 3). (b) Projection of the structure perpendicular to the $[001]$ or c direction (after Mazzi and Garavelli, Ref. 3).

interest in the light of information about its structure which came to our attention after the measurements were begun. Two independent x-ray determinations of this structure have been reported³ recently. $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ forms monoclinic crystals which are found to belong to the space group $C_{2/c}$. The unit cell dimensions are $a = 12.04 \text{ \AA}$, $b = 5.58 \text{ \AA}$, and $c = 9.89 \text{ \AA}$ with the angle $\beta = 127^\circ 34'$. Details of the structure are shown in Figs. 1(a) and 1(b). Each Fe^{++} is located at the center of a distorted octahedron whose vertices are occupied by the O atoms of two water molecules and four coplanar O atoms belonging to two different oxalate groups. Each Fe^{++} ion is linked by oxalate bridges to two neighboring Fe^{++} ions, 5.60 \AA to either side of it along the $[010]$ direction. As a result, the structure consists of chains of Fe^{++} ions extended along the $[010]$ direction. The two carboxyl groups comprising a single oxalate bridge are strongly reminiscent of the carboxyl groups which provide superexchange spin coupling in various formates and acetates of the transition metals.⁴ It appears likely that delocalized π electrons in the oxalate group can serve as an effective medium for significant intrachain superexchange coupling in $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

It is difficult to predict the relative magnitudes of the intrachain and interchain spin couplings. We note in Fig. 1(b) that Fe^{++} ions in neighboring chains are

also separated by about 6 \AA without, however, being linked by any obvious bridging groups. The most direct paths between Fe^{++} ions in neighboring chains involve the steps $\text{O}_1\text{-O}_7$ and $\text{O}_2\text{-O}_8$ whose separations are, respectively, 2.76 and 2.86 \AA . In each of these steps one passes from an O atom in a water molecule on one chain to an O atom in an oxalate group on a neighboring chain. Hydrogen bonding probably occurs across such steps, which are found to join each chain with four neighboring chains. It is quite likely that superexchange via these paths is weaker than that occurring within the chains. Thus we may be dealing with a system of Fe^{++} ions coupled in linear chains which are, in first approximation, at least, independent of one another. Such a physical system if of interest because it may approximate one of the several models of linear chain behavior whose properties are understood. Those systems in which linear-chain magnetism has already been identified have contained ions with $S = \frac{1}{2}$, e.g., Cu^{++} . A linear-chain system of Fe^{++} ions possessing relatively large spins ($S = 2$) and significant anisotropy offers additional possibilities for comparison of observation and theory.

EXPERIMENTAL

Measurements of the magnetic susceptibility have been carried out, of necessity, on powdered specimens only. Artificial single crystals of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ have not yet been prepared. Extremely small single crystals of this material occur in nature, and it is with these crystals that the x-ray structural studies³ were performed. We were unable, however, to obtain any natural crystals of sufficient size or purity to be of use in the present investigation. All of our specimens were prepared from purified powder obtained from Matheson, Coleman, and Bell Co., Norwood, Ohio.

Below 77°K , the susceptibility was measured by an ac mutual-inductance technique,⁵ usually at a frequency of 275 cps. The mutual-inductance bridge was calibrated during the course of the measurements by substitution of the sample of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ for the $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ specimen. The susceptibility of the calibrating sample was taken to be⁶ $\chi = 11.19 \times 10^{-3}/T$ (cgs/g). Between 1.3 and 4.2°K , 14 and 20°K , and from 65 to 77°K , samples and mutual-inductance coils were immersed directly in the appropriate liquid refrigerant, and the temperature determined from the liquid vapor pressure. Intermediate temperatures were achieved by means of a device, previously described,⁷ which permits the specimen and calibrating material to be removed from good thermal contact with the refrigerant. In this arrangement, specimen temperatures were determined

³ C. Mazzi and F. Garavelli, *Periodico Mineral. (Rome)* **26**, No. 2-3 (1957); S. Cavid, *Bull. Soc. Franc. Mineral. Crist.* **82**, 50 (1959).

⁴ R. L. Martin and H. Waterman, *J. Chem. Soc.* **1959**, 1359; R. B. Flippen and S. A. Friedberg, *J. Chem. Phys.* **38**, 2652 (1963); N. Uryu and S. A. Friedberg, *Phys. Rev.* **140**, A1803 (1965).

⁵ R. B. Flippen and S. A. Friedberg, *Phys. Rev.* **121**, 1591 (1961).

⁶ A. H. Cooke, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), p. 238.

⁷ L. Berger and S. A. Friedberg, *Phys. Rev.* **136**, A160 (1964).

by using the calibrating sample as a magnetic thermometer. Susceptibilities measured by the audio-frequency method were found to be reproducible to within $\pm 3\%$.

Supplementary susceptibility data were obtained at several fixed points between 77°K and room temperature by means of a simple Gouy balance.⁸ These values were found to be reproducible to within $\pm 2\%$.

RESULTS AND DISCUSSION

From room temperature down to about 80°K our values for the magnetic susceptibility of powdered $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are well represented by the Curie-Weiss law $\chi_p = 3.40/(T + 25.4)$ (cgs/mole), in quite good agreement with the results of Welo² mentioned above. The slightly larger Curie constant corresponds to an average splitting factor $g = 2.12$, if we assume $S = 2$ for Fe^{++} . This g value is comparable with that found in other ferrous compounds,⁹ e.g. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, at temperatures such that kT is large in comparison with the spin splitting of the Fe^{++} ground state. As might be expected from the structure, the crystalline electric field at an Fe^{++} ion is evidently of sufficiently low symmetry to remove any orbital degeneracy of that ground state.

A plot of measured χ_p versus T below 100°K is shown in Fig. 2. After passing through a smooth maximum near 30°K , χ_p exhibits a second, apparently sharp peak near 20°K and then falls rapidly with temperature to a constant value of ~ 0.0142 cgs/mole in the liquid-helium region. While the interval between 20 and 30°K is a rather awkward one in which to work and data obtained there show significant scatter, the abrupt minimum and steep maximum seen in Fig. 2 have been found to be reproducible in several independent sets of measurements.

Two possible interpretations of the sequence of two maxima in χ_p suggest themselves. They differ primarily in the interpretation given the upper rounded maximum, namely, whether or not it is associated with the establishment of long-range spin order. It is now generally recognized¹⁰ that the susceptibility maximum of a simple antiferromagnet need not be particularly sharp and that the Néel point T_N will occur at a slightly lower temperature than that of the maximum. If, in the present case, the maximum at 30°K were identified with the onset of long-range antiferromagnetic spin order, the Néel point would occur probably between 30 and 25°K . The lower peak at 20°K would appear then to be associated with a transition from one state characterized by long-range order to another.

The alternative view is one suggested by the structural evidence that $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ contains extended chains of Fe^{++} ions linked by oxalate groups as de-

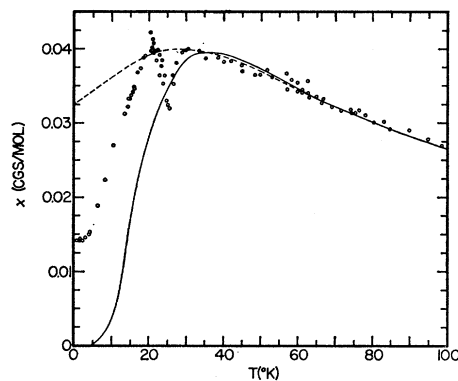


Fig. 2. Open circles represent values of the magnetic susceptibility of powdered ferrous oxalate dihydrate in units of cgs/mole. Dashed curve is the computed susceptibility of the Heisenberg linear chain in the classical limit for $S = 2$, $J = -4.9k$ and $g = 2.23$. Solid curve is the parallel susceptibility of the Ising linear chain calculated for $S = 2$, $J = -4.8k$, and $g = 2.20$.

scribed earlier. If the intrachain exchange coupling J is antiferromagnetic and the interchain coupling negligible it may be expected¹¹ that the susceptibility will exhibit a rounded maximum at a temperature of the order of $|J|/k$. As the temperature is lowered through this maximum, the spin system gradually orders but only in the short-range sense, the linear chain being incapable of sustaining long-range order. Thus there is no abrupt cooperative transition as would occur at a Néel point. If the rounded maximum in the χ_p of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is associated with short-range ordering in quasi-independent chains of Fe^{++} ions, then the lower peak ($\sim 25^\circ\text{K}$) would most probably be attributable to the abrupt onset of long-range order in three dimensions under the influence of interchain interaction.

We are inclined at present to prefer the second of these interpretations. Not only does it appear to be the one most readily reconciled with the chain-like structure of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, but also it seems to be most consistent with the available Mössbauer data. The fully split pattern seen near 4°K implies the existence of long-range order among Fe^{++} moments. Were long-range order established between 25 and 30°K , such splitting might be expected above 20°K . Instead, only broadening of the two line spectrum is seen at these temperatures, possibly the result of short-range ordering within the chain structure. Heat-capacity measurements on this solid, which we hope to perform in the near future, may provide more conclusive evidence for or against one of these pictures. Two sharp cooperative anomalies should appear in C_p if long-range ordering occurred near 30°K .

Tentatively, we shall assume that the rounded maximum in χ_p near 30°K is a linear-chain effect. Since the two maxima are resolved, it may be meaningful to try to fit the upper one using a model which ignores interchain coupling. We have done this for two tractable

⁸ See, for example, P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1956), 2nd ed., p. 3.

⁹ R. D. Pierce and S. A. Friedberg, *J. Appl. Phys.* **32**, 66S (1961).

¹⁰ See for, example, M. E. Fisher, *Phil. Mag.* **7**, 1731 (1962).

¹¹ See, for example, C. Domb, *Advan. Phys.* **9**, 166 (1960).

models of chain antiferromagnetism, each of which contains severe approximations but possibly also some useful physical features. Fisher¹² has shown that the problem of a linear chain of $n+1$ spins with isotropic Heisenberg interaction, $-2J \sum_{i=1}^n \mathbf{S}_i \cdot \mathbf{S}_{i-1}$ becomes exactly soluble in the classical limit, i.e., when $S \rightarrow \infty$. If we choose scaling factors to give agreement at high temperatures with the exact expansion of Rushbrooke and Wood¹³ for the susceptibility of the Heisenberg chain, Fisher's result may be written

$$\chi = [N_0 S(S+1)g^2 \mu_B^2 / 3kT] \times \{[1+u(K)]/[1-u(K)]\}, \quad (1)$$

where $u(K) = \coth(K-1/K)$ and $K = 2JS(S+1)/kT$. Retaining the two leading terms, this expression and the Rushbrooke and Wood result yield at high temperatures

$$\chi = [N_0 S(S+1)g^2 \mu_B^2 / 3kT][1 + \frac{4}{3}S(S+1)|J|/kT]^{-1},$$

which is just the Curie-Weiss law with

$$\theta = \frac{4}{3}S(S+1)|J|/k.$$

The Weiss constant observed above 80°K, $\theta = -25.4^\circ\text{K}$ gives $J = -3.18k$ for $S=2$. As already noted, the high temperature Curie constant, $C = 3.40$, yields $g = 2.12$. The best fit of Eq. (1) to the data over the whole range was obtained with the help of the C.I.T. Bendix G20 computer and required slightly different parameters, namely, $g = 2.23$ and $J = -4.8k$. This result is shown as a dashed line on Fig. 2. While an independent chain model is not expected to yield useful results in the vicinity of the lower peak and below, it is perhaps significant that the classical Heisenberg chain theory, because of its nonzero susceptibility at 0°K, fails to reproduce the lower side of the rounded maximum.

The second model we have considered is the linear chain with Ising interactions of the form $-2J \sum_{(j,k)} S_j^z S_k^z$ where the summation is over neighboring pairs j, k . The parallel susceptibility is easily calculated¹¹ for this model, if $S = \frac{1}{2}$. The calculation may be carried through for arbitrary spin by means of the matrix method described in the literature.^{14,15} This has been done explicitly only for $S = \frac{1}{2}$ and $S = \frac{5}{2}$.¹⁶ We have found it useful, therefore, to perform the solution of the problem for $S=2$.

The partition function Z for a chain of N spins with nearest neighbor Ising interaction in an applied

field H is $\text{Tr}(P)^N$ where P is the symmetric matrix $P_{MM'} = \exp[4LMM' - B(M+M')]$. Here $L = J/2kT$, $B = g\mu_B H/2kT$ and, since $S=2$, M and M' take all values 2, 1, 0, -1, -2. The partition function is approximately $[\lambda(P)]^N$ where $\lambda(P)$ is the largest eigenvalue of the matrix P . The magnetic susceptibility is thus

$$\chi = \lim_{H \rightarrow 0} (kT/H) \partial(\ln Z) / \partial H = \lim_{H \rightarrow 0} (NkT/H) \partial \ln \lambda(P) / \partial H.$$

Diagonalization of the 5×5 matrix $P(M, M')$ has been performed with the Bendix G20 computer, as has the calculation of the parallel susceptibility. In the absence of any readily obtained values for the perpendicular susceptibility, we have fitted the powder data with this result. The solid curve in Fig. 2 is the Ising chain susceptibility for $S=2$ using $J = -4.9k$ and $g = 2.20$. The features of the data above 25°K are reasonably well reproduced, perhaps lending credence to the notion that the upper maximum in χ_p is essentially that of linear antiferromagnetic chains. Note that the agreement achieved in this fitting procedure implies that the perpendicular chain susceptibility would be small in this case.

Several authors have discussed the addition to the linear chain problem of interchain coupling.^{15,17} While we suggest that interchain coupling and the onset of long-range spin order can account for the susceptibility peak at 20°K in $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, we have not attempted to compare the low temperature data with any of these models. Such efforts should best await confirmation of the assumption of chain-like behavior and the availability of single-crystal data.

Dihydrated oxalates of other transition metals exist, although their structures have not yet been determined. It is natural to inquire, in the light of the present discussion, whether they give evidence of chain-like behavior. Preliminary powder susceptibility data have been obtained on $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. While suggesting that the magnetism of these materials is not simple, these data give no clear indication of linear-chain properties. They will be reported later.

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¹² M. E. Fisher, Am. J. Phys. **32**, 343 (1964).

¹³ G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).

¹⁴ See, for example, C. Domb, Advan. Phys. **9**, 149 (1960) or G. F. Newell and E. W. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

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¹⁶ G. Wagner and S. A. Friedberg, Phys. Letters **9**, 11 (1964).

¹⁷ T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955); Phys. Rev. **133**, A1098 (1964); W. Marshall, J. Phys. Chem. Solids **8**, 159 (1958).