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Specific Heat of an Ising Linear-Chain Crystal*

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The specific heat of a single crystal of ludlamite [$Fe_3(PO_4)_2 \cdot 4\,H_2O$] has been measured in the temperature range 2.4–68°K, indicating a λ peak at (15.0±0.4)°K, thus suggesting the existence of a magnetically ordered state below that temperature. By subtracting the lattice contribution, which was obtained by measuring the specific heat of the isomorphic crystal hopeite [$Zn_3(PO_4)_2 \cdot 4\,H_2O$], a broad peak was observed above 15.0°K, suggesting linear-chain coupling. A calculation was made, based on a linear-chain Ising model, and the most satisfactory fit yielded $J/k = 10.0$°K for the intrachain exchange coupling. A sublattice-magnetization calculation has also been made and compared with the molecular-field approximation.

I. INTRODUCTION

PREVIOUS studies, including magnetic susceptibility,[1] nuclear magnetic resonance,[2–4] Mössbauer effect,[5] preliminary specific-heat measurements,[6] and neutron diffraction[7] have indicated that ludlamite [$Fe(PO_4)_2 \cdot 4\,H_2O$] undergoes a magnetic transition to an ordered state below ≈15°K. The neutron diffraction data indicated that the magnetic Fe atoms form ferromagnetically coupled triads which are linearly antiferromagnetically coupled. Such a linear coupling arrangement suggests the possibility of an analysis by means of a linear-chain Ising model, and if this is the case it might be possible to observe this chain effect in a specific-heat measurement. A preliminary study[6] has already been made and the present paper describes these experiments more fully.

II. EXPERIMENTAL

A single natural grown crystal of ludlamite, weighing 1.28 g, was used in the experiment. X-ray data by Ito and Mori[8] and Abrahams and Bernstein[9] indicated that ludlamite is a monoclinic crystal with space group $P2_1/a - C_{2h}{}^5$, two molecules per unit cell and crystal axes: $a = 10.54$ Å, $b = 4.65$ Å, $c = 9.32$ Å, and $\beta = 100°30'$. The Fe-Fe distance within the ferromagnetic triad is given as 3.27 Å and the triad separation is 4.03 Å for nearest neighbors.

The specific-heat experiments were performed in a triple-can calorimeter which has been described elsewhere.[10] Carbon thermometry was used, calibrating against the vapor pressure of liquid helium for measurements below 4°K, and a calibrated germanium resistor above 4°K. Four separate runs were made on the ludlamite single crystal. All of the calibrations and data were programmed for the MSU 3600 computer.

A separate experiment was also performed to determine the lattice contribution to the specific heat. To do this, a crystal of hopeite [$Zn_3(PO_4)_2 \cdot 4\,H_2O$], isomorphic to ludlamite, was used. A specific-heat measurement from 4.2–54°K, using a calibrated germanium resistor, was made. Again, computer methods were used to obtain the results.

The errors in the specific-heat results were approximately 0.5% for temperatures below 4.2°K, and 3% above 4.2°K.

III. RESULT AND DISCUSSION

The specific-heat curves are shown in Fig. 1, where both the ludlamite and hopeite results are plotted. A λ transition occurs at (15.0±0.4)°K suggesting the onset of magnetic ordering. Figure 2 shows the resultant curve after the hopeite results have been subtracted from the ludlamite results. Besides showing the λ peak, there is a broad rounded peak above 15°K which centers at approximately 38°K. This type of behavior suggested a linear-chain coupling between magnetic ions.

An entropy calculation, obtained graphically from a plot of C_{Mag}/T versus T gave $\Delta S = 9.58$ cal/mole deg which agrees very well with a possible expected value of $\Delta S = 3R \ln(2S+1) = 3R \ln 5$, where $S = 2$ for the Fe^{++} ion. Approximately 55% of this entropy is recovered above 15°K, again suggesting the possibility of a linear chain to explain this high degree of short-range ordering. Figure 3 shows a plot of the entropy change as a function of temperature.

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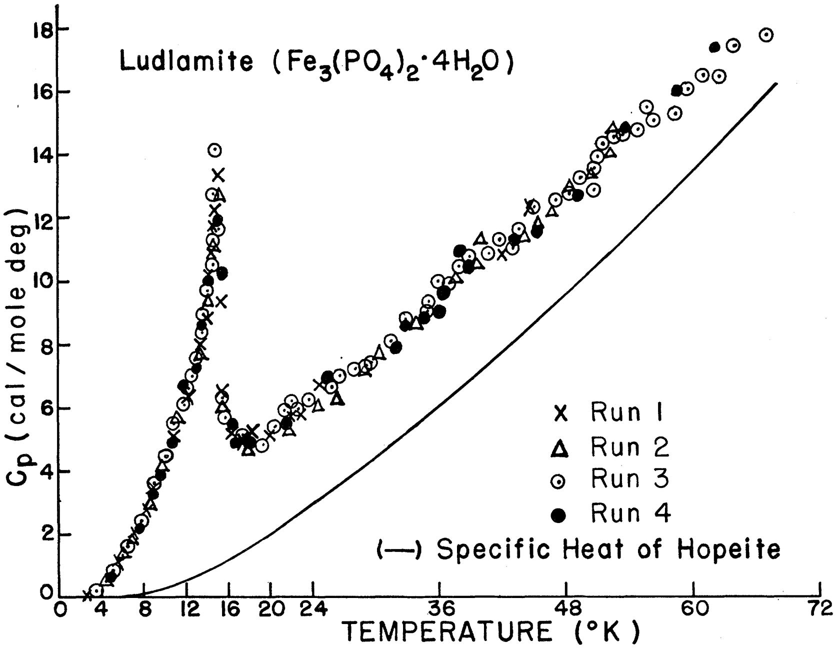

FIG. 1. Specific heats of ludlamite and hopeite. The datum points correspond to the ludlamite results and comprise four separate experimental runs. The solid curve refers to the results on hopeite.

Additional evidence for the possibility of chains is given by the neutron diffraction data and Fig. 4 shows the suggested magnetic spin structure as given by Abrahams.[7]

Therefore, it would appear that a linear-chain model is strongly suggested as an explanation for the large amount of short-range ordering. In an attempt to calculate this, we have used an Ising model similar to that used in the method by Newell and Montroll[11] and Stout and Chisholm.[12] In the Ising model, one replaces the interaction energy $2J\mathbf{S}_i \cdot \mathbf{S}_j$ between two magnetic ions i, j by $2J\mathbf{S}_{z,i} \cdot \mathbf{S}_{z,j}$, where S_z is the projection of $\mathbf{S}$ along the axis of easy magnetization and J is the exchange interaction constant. Therefore the energy may be

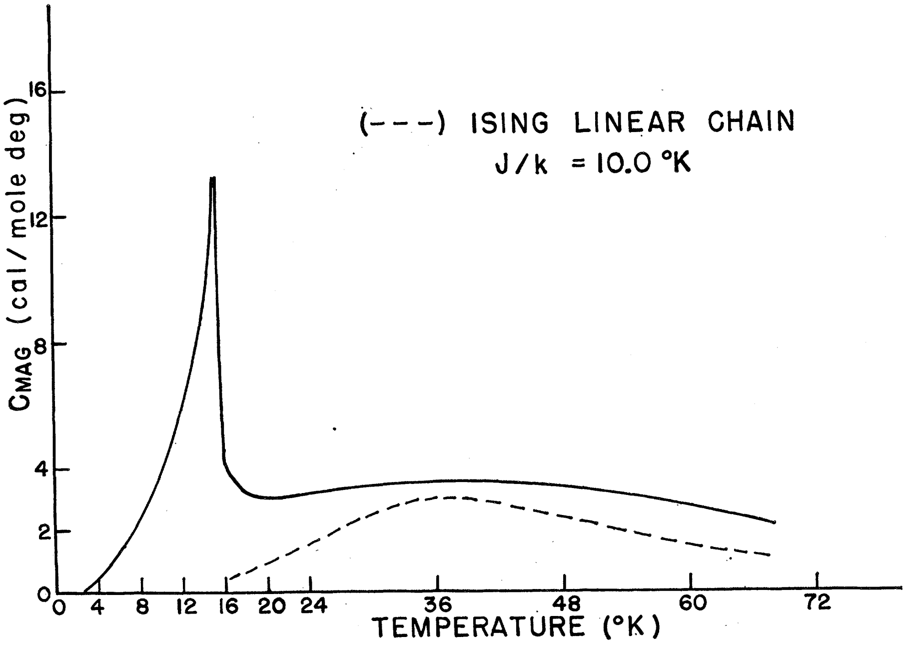

FIG. 2. Magnetic specific heat of ludlamite. This solid curve was obtained by subtracting the two curves of Fig. 1. The dashed curve represents the calculated specific heat for a linear Ising chain with $J/k = 10$°K.

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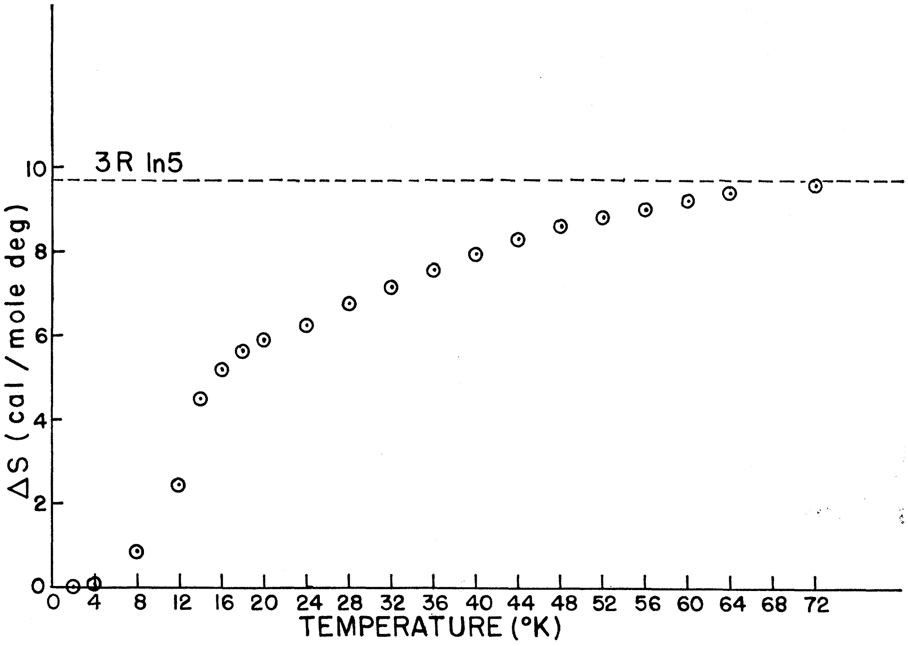

FIG. 3. Entropy change versus temperature. The expected entropy change is $3R$ ln5.

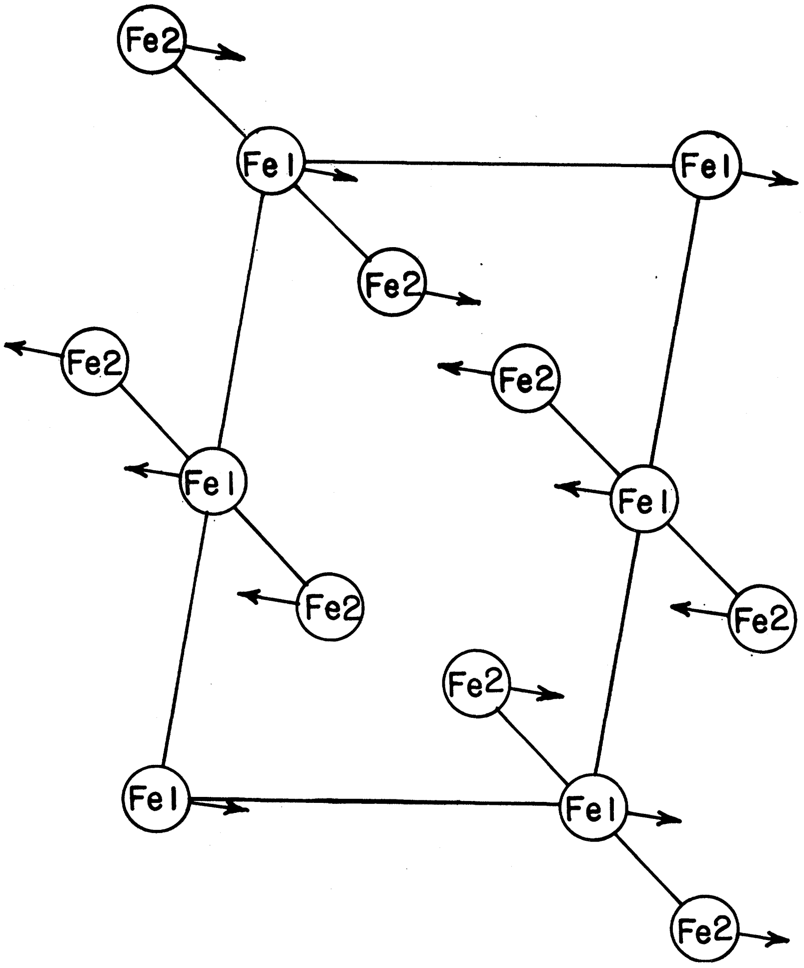

FIG. 4. Magnetic spin structure of ludlamite (after Abrahams, Ref. 7).

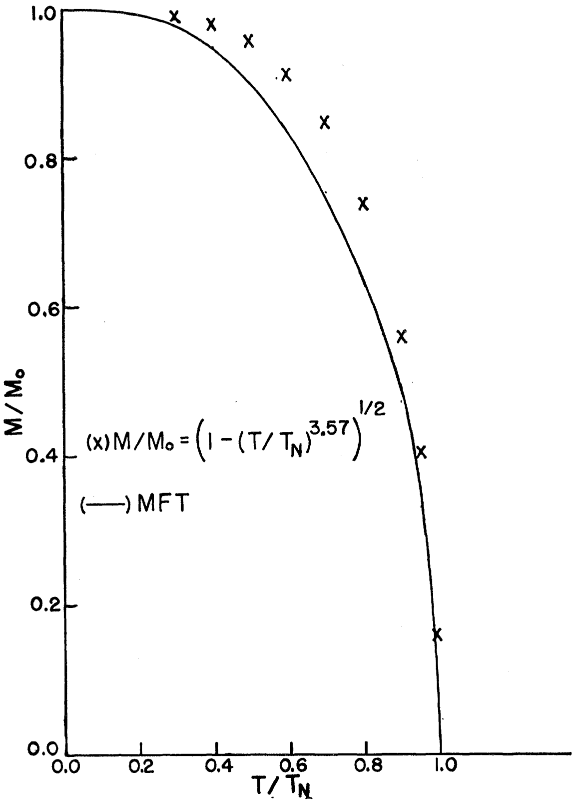

FIG. 5. Sublattice magnetization of ludlamite. The solid curve represents the molecular field approximation for $S=2$.

written as

$$W(M_1, \ldots, M_n) = \sum_{i=1}^{N} (2JM_iM_{i+1} + g\beta H_i^M M_i) \quad (1)$$

for the case of zero external magnetic field. Here M_i is the magnetic quantum number of the spin on the ith atom. It may assume $2S+1$ values ranging from $-S$ to S, where S is the spin quantum number; g and β are the usual magnetic factors. H_i^M is the molecular field on the ith atom which describes the interactions between atoms in different chains. The partition function is therefore

$$Z = \sum_{M_i} \cdots \sum_{M_n} \exp[-W(M_i, \ldots, M_n)/kT]. \quad (2)$$

By considering only the temperature region in which the short-range ordering is effective, viz., above the transition temperature, and thus neglecting terms in $W(M_i, \ldots, M_n)$ which have to do with interchain coupling, we may rewrite (2) as

$$Z = [\lambda(R)]^N, \quad (3)$$

where $\lambda(R)$ is the largest eigenvalue of the matrix R which is given as

$$R_{MM'} = e^{-4KMM'}. \quad (4)$$

M and M' correspond to the values of the magnetic quantum number and $K=J/2kT$. K is positive for the present ferromagnetic intrachain coupling in which $S=2$ for the Fe^{++} ion. This leads to a 5×5 matrix for Eq. (4). To calculate C_M, the following equation was used:

$$C_M = N_0kT\{2(\partial/\partial T)[\ln\lambda(R)] + (\partial^2/\partial T^2)[\ln\lambda(R)]\}. \quad (5)$$

This calculation is then for the case of a chain of three Fe atoms. It is possible to consider that the short-range ordering arises from the antiferromagnetic coupling between triads of Fe atoms. In this case one would expect to find that the entropy change $\Delta S = R\ln 13$, which does not agree with the experimentally determined value. Furthermore, it appears from the magnetic susceptibility, neutron diffraction, and Mössbauer data, that the Fe atoms occupy two nonequivalent positions in the unit cell, and that the triad consists of two Fe atoms of the first type and one Fe atom of the second type. It may, therefore, not be justified in considering the triad as a "single" atom of spin 6.

Figure 2 shows the plot of Eq. (5). It appears to give the approximate shape of the experimental curve, peaking at 38°K, but yielding smaller absolute values of C_{Mag} than the experimental data. To obtain the calculated curve, a value of the exchange constant $J/k = 10.0$°K was assumed. This corresponds to a Curie-Weiss constant, $\theta = 40$°K. It is possible therefore to calculate an effective magnetic moment per Fe^{++}. This turns out to be 4.90 Bohr magnetons. This compares rather favorably with the value of 4.56 Bohr magnetons obtained by Abrahams.[9]

An additional calculation has been made for the sublattice magnetization as a function of temperature, below the critical temperature. To do this, a molecular-field approximation has been assumed. The temperature dependence of the specific heat below the critical temperature has been calculated from the data. Since the specific heat is proportional to the product of the magnetization and the slope of the magnetization curve, it was possible to determine the temperature dependence of the magnetization curve. This was

$$M/M_0 = [(1-T/T_c)^{3.57}]^{1/2}. \quad (6)$$

Figure 5 shows a plot of Eq. (6), as well as the expected curve for the molecular-field approximation with $S=2$. The experimental data lies approximately 15% higher than the theoretical curve which is due primarily to anisotropic effects.

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