

Specific Heat of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}^*$

H. FORSTAT, N. D. LOVE, AND J. MCELEARNEY

Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan

(Received 10 March 1965)

Specific-heat measurements have been made on a single crystal of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ in the temperature range 1.8–25°K. Two λ -type anomalies were observed at 9.60° and 12.40°K and are associated with paramagnetic-antiferromagnetic transitions. The six iron ions per unit cell are not equivalent, giving rise to a two-step antiferromagnetic transition as observed in the two anomalies, and indicating a ratio of 2 for the entropy changes associated with the two sets of nonequivalent ions. The total entropy change associated with these transitions is 9.58 cal/mole deg, which differs by 1% from $3R \ln(2S+1)$, where $S=2$ for Fe^{++} , with approximately 27% of this entropy gained above 12.40°K. By using the simple molecular-field theory, an estimate of the magnitude of the exchange integral was obtained as well as the temperature dependence of the sublattice magnetization.

I. INTRODUCTION

NUCLEAR-MAGNETIC-RESONANCE (nmr) studies of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (vivianite) have been made by both Van der Lugt and Poulis¹ and Spence and Murty,² and they had shown that this compound exhibited antiferromagnetic properties in the liquid-helium temperature region. Sixteen lines were observed in the antiferromagnetic state, which from symmetry arguments could be classified into four groups of four lines each such that all of the lines within a single group had the same splitting. For any one group, the internal fields at the proton sites (measured in zero external field) decreased with increasing temperature for two of the lines, while for the other two lines, the internal fields remained constant with temperature. This would imply that the sublattice magnetization is not the same for all of the Fe^{++} ions and consequently that not all of the Fe^{++} ions in the unit cell are magnetically equivalent. It was suggested that there are two distinct types of Fe^{++} ions in order to account for the nmr data.

The crystallography of vivianite has been done by

Mori and Ito³ and the structure of the unit cell is shown in Fig. 1. Vivianite is monoclinic with a space group $C_{2/M}$ and has lattice constants $a=10.08 \text{ \AA}$, $b=13.43 \text{ \AA}$, and $c=4.70 \text{ \AA}$ with $\beta=104^\circ 30'$. The two types of Fe^{++} ions (as suggested by Poulis) have their positions as follows:

type I : (000) and $(\frac{1}{2}\frac{1}{2}0)$,

type II : $\pm(0.0390)$ and $(\frac{1}{2}\frac{1}{2}0) \pm (0.0390)$.

The type-II ions occur in pairs along the b axis and are separated by 2.96 \AA .

From the crystallographic data and the nmr results, it would appear that in the antiferromagnetic state, type-I ions are antiferromagnetically coupled and type-II ion pairs are antiferromagnetically coupled (with the possibility that the ions in the pairs of type II are ferromagnetically coupled). Furthermore, each of these antiferromagnetic couplings occur at different temperatures, so that one might refer to the final antiferromagnetic state as having been reached in two distinct steps. Specific-heat measurements on a single crystal of vivianite have been made in the temperature region 1.8–25°K in order to examine this possible two-step transition.

II. EXPERIMENTAL

A single crystal of vivianite, 1.3×0.7 cm, weighing 1.22 g, was used.⁴ A manganin wire heater and a $\frac{1}{10}$ -W Allen-Bradley resistor as thermometer were attached to the crystal, and the crystal was mounted in a triple-can calorimeter, described elsewhere.⁵ The thermometer calibration was fitted to the two-parameter equation of Clement⁶:

$$(\ln R/T)^{1/2} = a + b \ln R.$$

The liquid-nitrogen calibration point (77.3°K) was also

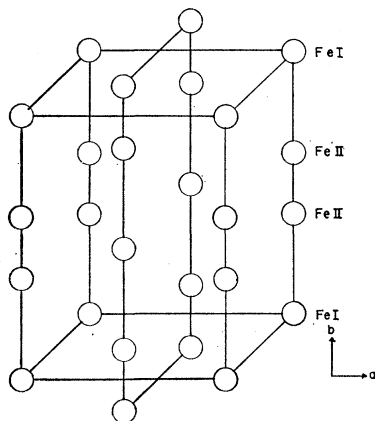


FIG. 1. The unit cell of vivianite. Only the iron positions are shown.

* Work supported by the U. S. Air Force Office of Scientific Research.

¹ W. Van der Lugt and N. J. Poulis, *Physica* **27**, 733 (1961).

² R. D. Spence and C. R. K. Murty (private communication).

³ H. Mori and T. Ito, *Acta Cryst.* **3**, 1 (1950).

⁴ Purchased from the Scott Williams Mineral Company, Scottsdale, Arizona. The origin of the crystal was the Patino mine, Llalagua, Bolivia.

⁵ W. R. Eisenberg, M. S. thesis, Michigan State University, East Lansing, Michigan, 1963 (unpublished).

⁶ J. R. Clement, *Temperature* (Reinhold Publishing Corporation, New York, 1955), Vol. II, p. 382.

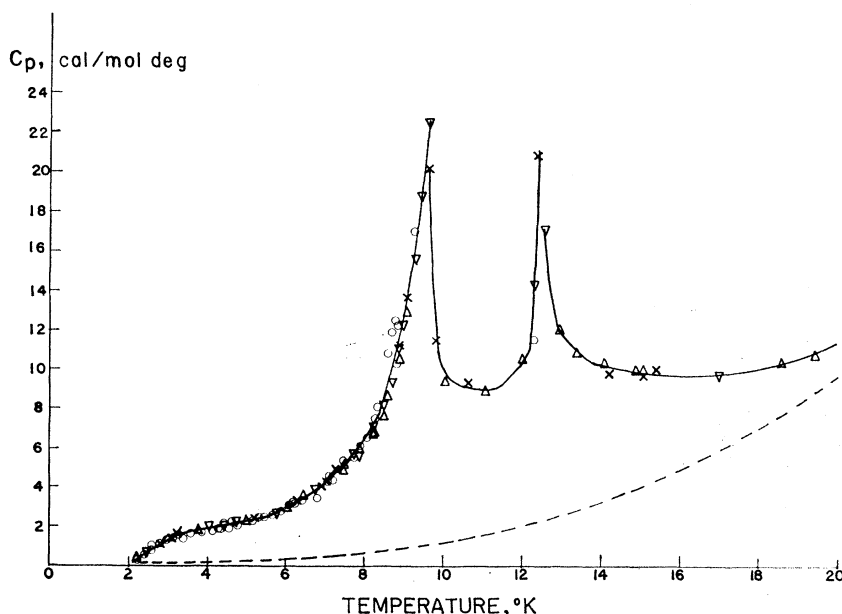


FIG. 2. The specific-heat-versus-temperature curve for vivianite. O, 10/29/64; X, 10/30/64; ∇ , 11/10/64; Δ , 11/11/64.

used in the above curve fitting. Between 4 and 10°K, the temperatures were read as extrapolations from the above curve. The estimated error in this temperature determination was 5%. Above 10°K, the carbon thermometer was calibrated against a Leeds and Northrup platinum resistance thermometer (National Bureau of Standards calibrated). The error in this region was less than 1%. This calibration, as well as all the specific-heat data, was programmed for the MSU 3600 computer. The deviations from a straight-line fit for the above equation, calculated as fractional errors, amounted to approximately 0.1% for each calibration made. An attempt was also made to fit the calibration data to a three-parameter equation but this seemed to give a poorer fit. Four separate experimental runs were made and the data from these runs are shown in the specific-heat-versus-temperature curve in Fig. 2. Approximately 300 experimental points were taken in the temperature region 1.8–25°K.

Two sharp transitions may be seen at 9.60 and 12.40°K. These peaks correspond to the paramagnetic-antiferromagnetic transitions associated with the two different types of Fe^{++} ions. There is also a small rounded peak at about 3°K which seems to correspond to a sudden increase in the intensity of two of the proton lines in the nuclear-magnetic-resonance experiments.

III. DISCUSSION OF RESULTS

Since the specific-heat curve contains both a magnetic and a lattice contribution, it was necessary first to subtract out the lattice part so that the magnetic specific heat (C_M) could more easily be discussed. The lattice specific heat which is shown as the dashed curve in Fig. 2 was estimated by extrapolation from the points

above 21°K. Figure 3 shows the specific-heat curve with lattice contribution subtracted out. From the simple molecular field theory,⁷ the magnetic energy E (per mole of Fe^{++} ions) may be written as $E/3R = S^2 |J|Z/k$ for magnetic ions with spin- S and spin- Z neighbors. The double peak in the specific heat slightly complicates the interpretation of the phenomenon by the simple theory, but nevertheless it appears worthwhile to make this calculation. By determining the area under the curve of Fig. 3, and using $S=2$ for the 5D ground state of Fe^{++} , it was possible to obtain a value for $|J|Z/k = 4.2^\circ\text{K}$.

The magnetic entropy associated with these transitions was also determined. To do this C_M/T versus T was plotted, as shown in Fig. 4. The area under this curve was calculated and amounted to 9.58 cal/mole

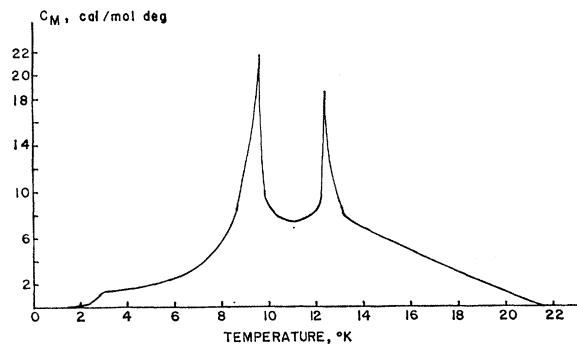


FIG. 3. The magnetic-specific-heat-versus-temperature curve for vivianite. The lattice contribution has been subtracted from Fig. 2.

⁷ J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).

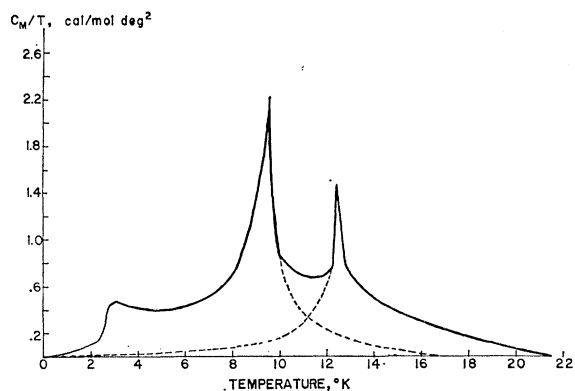


FIG. 4. C_M/T versus T for vivianite. The area under this curve represents the total magnetic-entropy change occurring in these paramagnetic-antiferromagnetic transitions.

deg. The expected value for this entropy change is 9.66 cal/mole deg as calculated from $3R \ln(2S+1)$. This difference amounts to less than 1%. Figure 5 shows this magnetic change in entropy as a function of temperature, and it should be noted that approximately 24% of this entropy is gained above 12.40°K due primarily to the short-range ordering. In order to estimate the separate contributions of each of the two transitions observed, both the high-temperature side of the 9.60°K peak and the low-temperature side of the 12.40°K were extrapolated, as the dashed curves indicate in Fig. 4. The ratio, $\Delta S(9.60^\circ\text{K})/\Delta S(12.40^\circ\text{K})$ yielded the value 1.87. Earlier, Van den Handel,⁸ had suggested that this ratio should be 2.

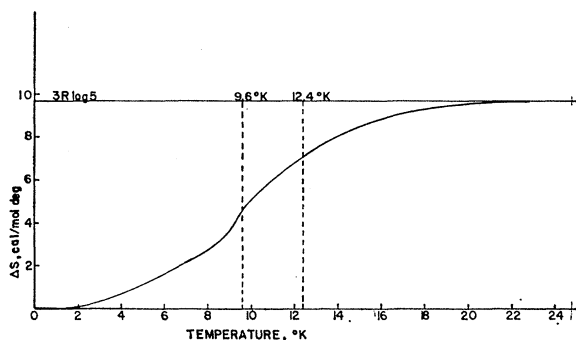


FIG. 5. Magnetic-entropy change as a function of temperature. The vertical dashed lines correspond to the positions of the two Néel temperatures. The expected entropy change is given as $3R \ln(2S+1)$.

⁸ J. Van den Handel, Proceedings of International Conference on the Ninth Low Temperature Physics, Ohio State University, 1964 (to be published).

A further calculation was made to compare the temperature dependence of the magnetization, as determined from the specific-heat data with that obtained from the nuclear-magnetic-resonance data for the 15.21-Mc/sec proton line. From the molecular field theory, C_M is proportional to the product of the sublattice magnetization and the slope of the sublattice-magnetization curve, below the transition. In the present case the temperature dependence of the specific heat below the 9.60°K transition was determined and yielded $C_M \sim T^{4.7}$. Consequently, the sublattice magnetization will be proportional to $T^{2.85}$. Figure 6 shows the com-

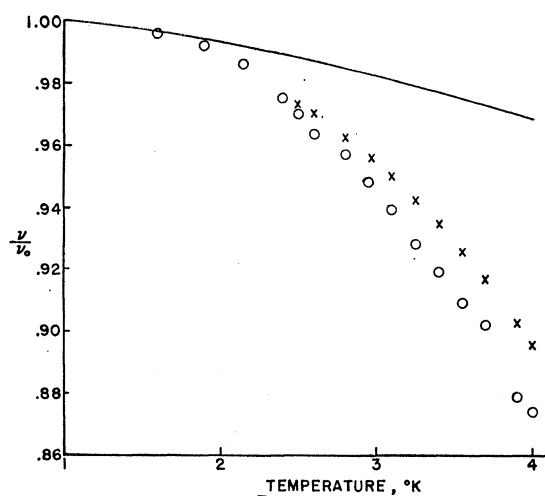


FIG. 6. Sublattice magnetization as a function of temperature. The solid line is the T^2 dependence from spin-wave theory. Specific-heat calculation, X; nmr data, O. The data are drawn in terms of the proton resonance frequencies in order to compare them directly with the nmr data.

parison obtained for the sublattice-magnetization curves. The nmr data gave the sublattice magnetization as proportional to T^3 . This result is considerably different from the T^2 sublattice-magnetization dependence and T^3 specific-heat dependence expected from spin-wave theory.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor R. D. Spence for many helpful discussions.