

Multiple Ordering and the Low-Temperature Phase Transition in Fe_3O_4 [†]

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(Received 8 November 1971)

The multiple-ordering theory of the low-temperature transition in Fe_3O_4 is established by observation of two peaks in the heat capacity and by changes in the shapes of the Mössbauer lines, both occurring between 113 and 123 K. The two transitions are believed to arise from different mechanisms and the shapes of the heat-capacity peaks respond differently to impurities. Concern about the predictions of the theory regarding the low-temperature phase is occasioned by the paucity of structural data.

Recent theoretical calculations of the electronic band structure of Fe_3O_4 suggest that the low-temperature transition is characterized by multiple ordering.¹ That is, there are three order parameters in the low-temperature phase corresponding, possibly, to the fractional occupations of the four octahedral sublattices by the electrons itinerant above T_V , the Verwey transition temperature. A further consequence of this theory is the possibility of *multiple transitions*. First of all, the different order parameters can have different temperature dependences, and as each order parameter approaches some critical value, instabilities may occur in either the ionic or electron ordering or in both. NMR, Mössbauer, and neutron diffraction data below T_V have been cited in support of the existence of multiple ordering.² While the present authors have some reservations concerning the relevance of the Mössbauer data below T_V to the multiple-ordering theory, we present here data that support the existence of multiple ordering insofar as the transition itself is concerned.

Detailed heat-capacity measurements on well-characterized samples of Fe_3O_4 of widely differing origins reveal two closely spaced peaks in the heat-capacity-versus-temperature curve in the vicinity of T_V (actually at 118.9 and 113.3 K) as shown in Fig. 1. These results offer convincing evidence for the multiple-ordering theory of Cullen and Callen.¹

We also interpret the result of recent Mössbauer studies⁴ as providing additional evidence for multiple closely spaced transitions. These data (slightly recast for clarity) for Fe_3O_4 between 298 and 85 K are shown in Fig. 2. Only those peaks in the velocity region between -6 and -2 mm/sec are shown. There are two distinct phases of change in the shapes of these peaks; the first occurs at approximately 120 K, at which tempera-

ture the peak labeled 2c first becomes apparent. From approximately 120 to 115 K there is a redistribution of intensity between lines 2a, 2b, and 2c, although the positions of each of these lines are essentially constant. At approximately 115 K, however, the position of line 2b begins to change; this change signifies the second phase in the changes of the line shapes near T_V . Below 115 K, line 2b gradually coalesces with 2a but no further qualitative changes are observed in the spectrum in this velocity region. We note that this apparently synthetic specimen was stated

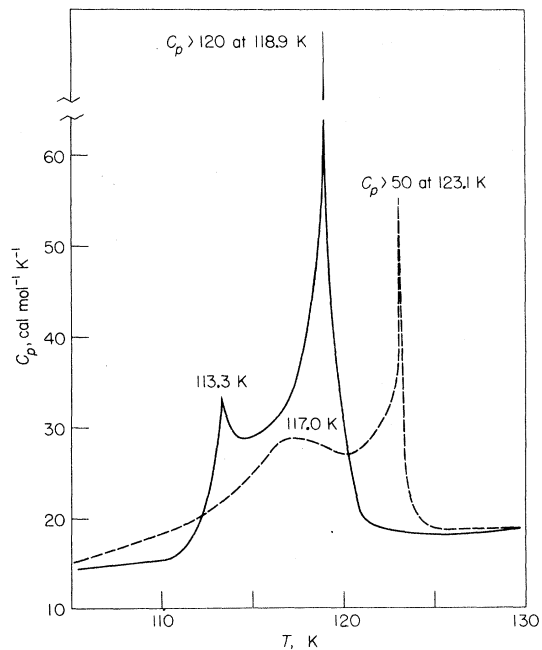


FIG. 1. Heat capacity of synthetic Fe_3O_4 is represented by solid line (see Ref. 2) and of hydrothermal Fe_3O_4 containing manganese by dashed line (see Ref. 3).

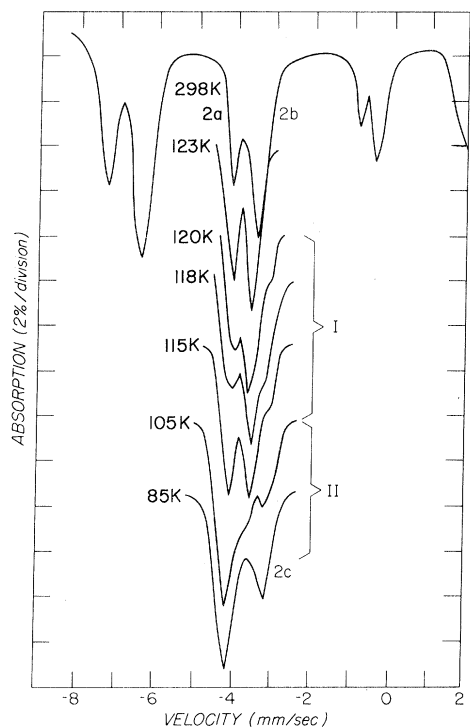


FIG. 2. Mössbauer peaks between -2 and -6 mm/sec for Fe_3O_4 in the region near T_V (see Ref. 3).

to be stoichiometric and therefore comparable to the synthetic sample used in the heat-capacity measurements. Consequently, it is of considerable importance that the temperatures at which changes begin to take place in the Mössbauer spectra are very close to those at which the peaks occur in the heat-capacity-versus-temperature curve. In fact, the temperature increment between the heat-capacity peaks is equal to that between the onset of changes in the Mössbauer peaks. Hence we consider that the phases of change of the Mössbauer peaks have a common origin with the peaks in the heat capacity.

At present, the physical phenomena that give rise to the two observed transitions can only be surmised. It is clear from the difference in the two distinct phases of changes in the Mössbauer spectra and also from the difference in the temperature dependence of the heat capacity that the two transitions are occasioned by different mechanisms. Studies are currently underway which should lead to an identification of the mechanisms for the two transitions. Some clues are provided by the heat-capacity measurements on the hydrothermal specimen (prepared by John L. Haas, Jr., of the U. S. Geological Survey). This sample which contained 0.2-mole% manganese had a lattice constant of $8.399 \pm 0.001 \text{ \AA}$ which is slightly

greater than that ($8.396 \pm 0.001 \text{ \AA}$) observed by us for the synthetic sample. This result indicates that the manganese in the hydrothermal sample is Mn^{2+} and occupies tetrahedral sites. As shown in Fig. 1, both peaks are displaced upwards 4 K from those of the purer specimen. The higher-temperature peak is reasonably sharp in both specimens; the lower-temperature peak in the hydrothermal specimen is considerably broadened. However, the areas under the peaks are not appreciably different from those of the purer specimen. It is tempting to attribute the second peak to ionic ordering on the basis of this comparison. Earlier thermal studies provided no indications of such a bifurcated peak, but double peaks were obtained on some samples in which the vacancy content of magnetite was varied.⁵ It is not certain that the width of the peaks in the heat-capacity-versus-temperature curves are minimal; strains resulting from the grinding of the powders or the presence of a distribution of the particle sizes in the specimens may cause a broadening of the transitions. Thermophysical measurements are presently being made on large single-crystal specimens of magnetite to obtain intrinsic widths for peaks in the heat-capacity-versus-temperature curve. Thereafter, consideration of the peak shapes in impure and polycrystalline magnetites may be undertaken.

While the salient aspects of the multiple-ordering theory for the low-temperature phase transition in Fe_3O_4 are definitely verified by our interpretations of the heat-capacity and Mössbauer measurements, some caution should be exercised insofar as the details are concerned. For example, the Mössbauer parameters for the four B -site Fe ions below T_V are anomalous relative to those of distinct Fe^{2+} and Fe^{3+} ions in other spinel ferrites,^{6,7} and this fact would tend to support the conclusion that one does not have distinct Fe^{2+} and Fe^{3+} on the B sites in Fe_3O_4 below T_V . Nonetheless, these Mössbauer data do not offer any real support for the existence of four crystallographically inequivalent Fe sites. Under the influence of the combined electric quadrupole and magnetic dipole interactions, a single-crystal Fe_3O_4 absorber will give rise to two B -site Mössbauer patterns even though the Fe sites are all equivalent. In addition, if the conduction electrons can be localized to give a random distribution of distinct Fe^{2+} and Fe^{3+} ions over the B sites, then four B -site Mössbauer patterns will be observable, in principle, even though all of the Fe sites are crystallographically equivalent. Furthermore, there is definitely a change in the crystal structure of Fe_3O_4 at T_V .⁸ The apparent splitting of the B -site Mössbauer patterns into two or more sets could result in this case from a lowering in

space-group symmetry. The order parameters devised for the spinel space group would then have little significance for the low-temperature phase. More important, though, is the fact that in none

of the published spectra have four *B*-site Mössbauer patterns been resolved below T_V ; only three patterns for the entire spectrum have been definitely resolved.^{8,9}

[†]Work supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society and by the Division of Research of the U. S. Atomic Energy Commission.

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²E. F. Westrum, Jr. and F. Grønvd, *J. Chem. Thermo.* **1**, 543 (1969). The synthetic Fe_3O_4 sample of this study has been further characterized by Mössbauer measurements. The unusually narrow linewidths confirm the stoichiometry and the lack of crystallographic or chemical disorder. [cf. B. J. Evans, in "National Conference on Magnetism and Magnetic Materials," November 1971 (unpublished)]. It is worthy of note that our observed lattice constant on this sample is identical to the value reported by H. E. Swanson, H. F. McMurdie, M. C. Morris, and E. H. Evans, in *Standard X-Ray Diffraction Powder Patterns* (Nat'l. Bur. Std. Monograph No. 25,

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Comment on the Behavior of the Lorenz Number of Chromium at the Néel Temperature

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(Received 5 October 1971)

The high-precision data of Laubitz and Matsumura showing the behavior of the Lorenz number of chromium in the vicinity of the Néel temperature have been analyzed by a two-electron-group model in which a BCS-like gap is allowed to open in the antiferromagnetic group. The agreement of the data with this model indicates that spin-fluctuation effects in well-annealed pure chromium have a negligible effect on the conductivities.

There has been a recent controversy about the exact behavior of the electrical (σ) and thermal (k) conductivities of chromium at its Néel temperature T_N .¹⁻⁴ These measurements are all claimed to be quite precise; where stated the absolute error is about $\pm 1\%$ or better and the relative error is as small as $\pm 0.1\%$. However, the resulting Lorenz numbers $L = k/\sigma T$, which are derived from these data, differ markedly, and the ensuing controversy is essentially whether spin-fluctuation phenomena are seen^{1,4} in the vicinity of T_N or not.^{2,3} The purpose of this comment is to point out that the most accurate measurements, which were made by Laubitz and Matsumura (LM),³ agree well with a model that has been proposed by Goff⁵⁻⁷ to explain the anomalous values of L (Cr) that are observed in the temperature range from 100 to 1000 K.⁸⁻¹⁰ Since this model explains the anomalous change

of L below T_N in terms of the BCS long-range-order parameter $\Delta(T)$, it will be seen that spin fluctuation phenomena have a negligible effect on the transport properties of well-annealed pure chromium.

A comparison of these various measurements is best seen in Fig. 2 of LM,³ where they are expressed as the ratio L/L_0 ; $L_0 = 2.4453 \times 10^{-8}$ (V/K)² is the theoretical value of L .¹¹ One should also refer to the subsequent paper of Meaden, Rao, and Tee,⁴ which shows the effect of further annealing of their sample. Here the data of LM are shown in Fig. 1 without comparison with the other measurements. LM obtained L by simultaneously measuring k and σ with three different temperature gradients. The solid black points, which were taken with a temperature difference of 1 K, were the most precise; they had a relative precision of