An Antiferromagnetic Transition in Zinc Ferrite*

J. M. Hastings and L. M. Corliss

Department of Chemistry, Brookhaven National Laboratory, Upton, New York

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Neutron powder diffraction patterns have been obtained for zinc ferrite over the temperature range 2.7°K–300°K. The data strongly suggest that the compound undergoes a transition from a paramagnetic state to an antiferromagnetic state in the neighborhood of 9°K. Superlattice lines observed below this temperature can be indexed on a cubic unit cell whose edge is twice that of the chemical cell. A model consisting of an antiferromagnetic alternation of ferromagnetic "bands" is tentatively proposed and discussed in relation to the observed line intensities.

INTRODUCTION

RECENT neutron diffraction measurements[1] have confirmed the earlier x-ray result[2,3] that zinc ferrite has the normal spinel structure, in which the diamagnetic zinc ions occupy the tetrahedral or A sites. According to the Néel theory[4] of ferrimagnetism there are, in addition to the dominant antiferromagnetic coupling between magnetic ions on A sites and those on B sites, weaker A-A and B-B interactions. Since the A-B coupling is absent in zinc ferrite, this compound is ideally suited for observing a subsidiary B-B interaction, and might well be expected to exhibit antiferromagnetism at sufficiently low temperatures. Kittel[5] has estimated the Néel temperature to be $150\pm50°K$ by extrapolating the experimental measurements[6] of the Curie temperatures of Ni-Zn and Mn-Zn mixed ferrites. This extrapolation is difficult since the experimental data extend only to 10% Ni and 20% Mn. Nevertheless, the data suggest, as Kittel points out, a Néel point well below room temperature.

EXPERIMENTAL

The neutron diffraction apparatus used in this investigation has been previously described.[7] The neutron wavelength used throughout the work was 1.064 A. An all-metal cryostat similar in design to the one described by Erickson[8] was used in obtaining the low-temperature diffraction patterns. The capacity of the inner or helium reservoir of the cryostat was about 2.5 liters, while the outer or nitrogen reservoir had a capacity of 6 liters. At helium temperatures the heat leak was approximately 20 calories per hour and thus a filling of helium lasted about 80 hours. For the runs made at pumped helium temperatures the sample was in direct contact with the liquid, while for the higher temperatures thermal contact was established by an aluminum conductor. The sample temperature was determined by use of an Au-Co, Au-Ag thermocouple kindly supplied by Dr. J. F. Youngblood of the Gereral Electric Company.

The zinc ferrite powder was prepared by Dr. V. C. Wilson of the General Electric Company and analysis by Dr. R. W. Stoenner of Brookhaven National Laboratory gave 45.98% iron and 28.33% zinc compared with theoretical values of 46.33% iron and 27.12% zinc.

RESULTS

Figure 1 is a neutron diffraction pattern of zinc ferrite taken at 77°K. This pattern is essentially identical with the room temperature pattern and shows only the expected spinel lines. The sloping background (except for the rapidly rising region below about 5 degrees, coming from the direct beam) is produced by paramagnetic diffuse scattering. This aspect of the scattering has been extensively studied[9] using a modified experimental arrangement and indicates that zinc ferrite behaves at room temperature as a nearly ideal paramagnetic with a localized moment of 5 Bohr magnetons per iron atom. The paramagnetic scattering is, however, somewhat anomalous at liquid nitrogen temperature. This point will be further discussed below.

In the neighborhood of 9°K (Fig. 2) a broad maximum is present in the diffraction pattern at a counter angle of about 8 degrees. The growth of this diffuse maximum, which begins at somewhat higher temperatures, is accompanied by a simultaneous decrease in the paramagnetic scattering. A rapid sharpening of the diffuse peak takes place as the temperature is further decreased and a well-developed superlattice pattern can be seen in representative traces obtained at 6°K and 2.7K° (Figs. 3 and 4).[10] The dotted line in Fig. 3 represents the

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[8] R. A. Erickson, Phys. Rev. 90, 779 (1953).

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[10] A second preparation of zinc ferrite has been very kindly supplied by Dr. E. F. Westrum, Jr., and Dr. D. M. Grimes of the University of Michigan. The superlattice lines obtained with this sample are somewhat narrower than those shown in Figs. 3 and 4, but the line positions and indexing are identical for the two specimens. While the general level of magnetic intensity is higher, compared to the nuclear intensity, in the case of the second sample, the relative intensities of the superlattice lines are in sufficiently close agreement for the two preparations as to leave unaltered the conclusions reached in this paper.
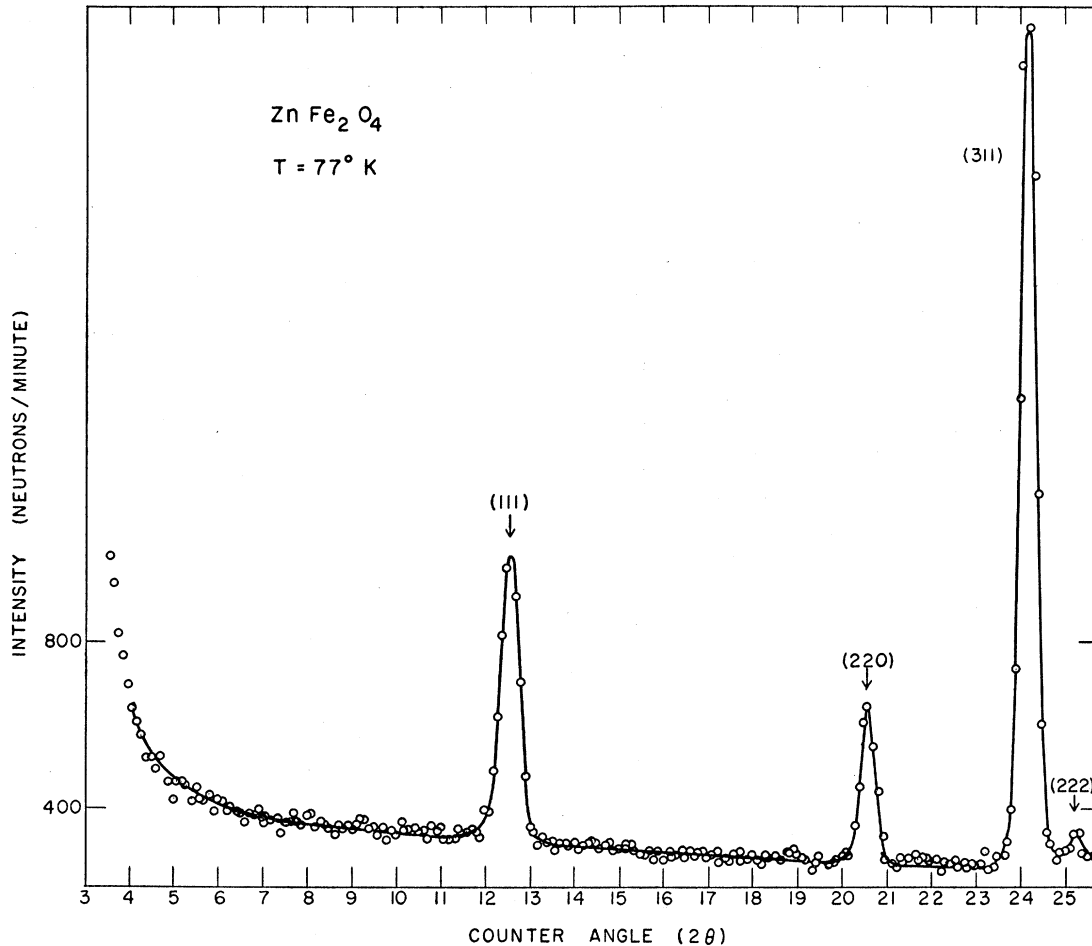
FIG. 1. Neutron diffraction pattern of polycrystalline zinc ferrite taken at 77°K. The sloping background is characteristic of paramagnetic scattering.

paramagnetic scattering level present at higher temperatures. In Table I the integrated intensities of the first few diffraction lines obtained at room temperature and liquid helium temperature are compared and found to be identical. In addition, inspection of the diffraction patterns reveals that to within the resolution of the instrument, no shift in peak positions has taken place.

The interpretation placed upon these observations is that zinc ferrite undergoes a transition to an antiferromagnetic state in the neighborhood of 9°K. The fact that the fundamental line intensities remain unchanged rules out the possibility of a crystal structure change or of either a ferromagnetic or ferrimagnetic transition. On the other hand, the appearance of superlattice lines

showing a general form factor dependence on angle, and the simultaneous disappearance of the paramagnetic scattering strongly suggest that the transition is anti-

FIG. 2. Neutron diffraction pattern of zinc ferrite taken at 9°K.

TABLE I. A comparison of integrated intensities at 300°K and 4.2°K.

| (hkl) | Integrated intensity (arbitrary units) | |
	300°K	4.2°K
(111)	467	453
(220)	153	154
(311)+(222)	1110	1122

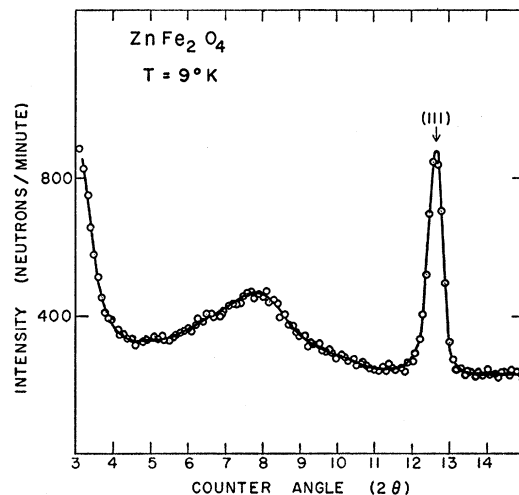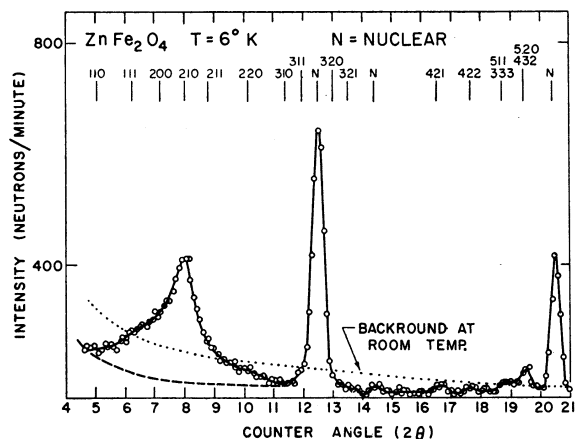FIG. 3. Neutron diffraction pattern of zinc ferrite taken at 6°K. Indexing of the superlattice peaks with respect to a double unit cell is shown by the short vertical bars at the top of the figure. The fundamental lines are designated by the letter N.
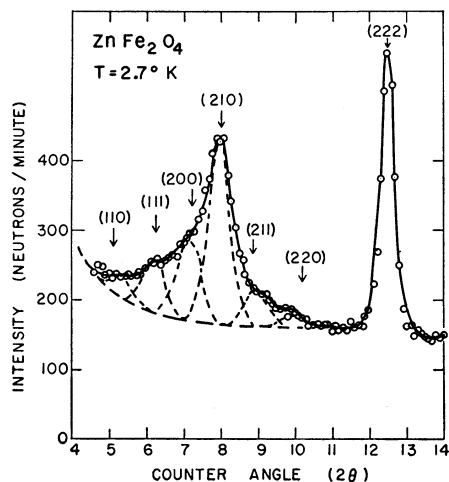

FIG. 4. Neutron diffraction pattern of zinc ferrite taken at 2.7°K. The indexing refers to the double unit cell. Decomposition of the first group of superlattice lines is shown by the dashed lines.

ferromagnetic. In Fig. 3 about ten incompletely resolved superlattice lines can be seen. These lines can be indexed on a cubic unit cell whose edge is twice that of the original spinel unit cell. The indexing is shown by the short vertical lines at the top of the figure.

DISCUSSION

The complexity of the diffraction pattern and the large size of the unit cell make it unlikely that an unambiguous model of the antiferromagnetism can be established on the basis of powder data alone. Nevertheless it is of interest to see if one can account even qualitatively for the general features of the extra scattering in terms of an antiferromagnetic model. It is indeed possible to construct a model which gives qualitative agreement between calculated and observed intensities. Figure 5 is a schematic representation of a projection

TABLE II. A comparison of observed intensities with those calculated from the model shown in Fig. 5.

(hkl)	Calculated	Observed
(100)	0	0
(110)	8.5	6
(111)	11.2	14
(200)	10.2	20
(210)	40.2	50
(211)	5.7	9
(220)	3.4	4
(300)	0 ⎫	2
(310)	2.4 ⎭	
(311)	3.5 ⎫	⎰obscured by
(222)	0 ⎭	⎱nuclear (111) peak
(320)	2.3 ⎫	3
(321)	2.0 ⎭	
(400)	0	0
(410), (322)	0	0
(411), (330)	0.7	0
(331)	0.9	0
(420)	1.5	0
(421)	7.6	4
(332)	0.4	0
(422)	2.6	3
(430), (500)	0.2	0
(431), (510) ⎫	3.8	4
(511), (333) ⎭		
(520), (432)	7.5	8

of the model on a (100) face, showing only the iron or B sites. Each algebraic symbol denotes two atoms superimposed by the projection, one from the upper and one from the lower half of the unit cell. In the case of the unshaded symbols the spin of the upper atom is the same as that of the atom in the lower half of the unit cell, whereas in the case of the shaded symbol the two are opposite. Qualitatively, the structure is seen to consist of parallel bands 2–3 atoms wide, of alternating spin, with occasional "mistakes" along the boundaries. The spin orientation is taken to be parallel to (010).

Table II gives a comparison of observed intensities with those calculated from the model. The former are necessarily only qualitative since the majority of the lines are incompletely resolved. Calculated and observed intensities agree to within about 25%. Crude agreement
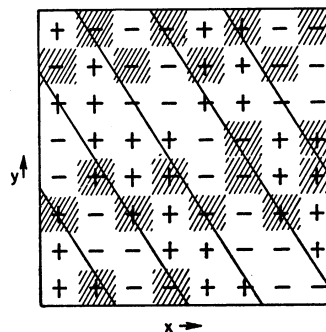

FIG. 5. A schematic representation of a proposed antiferromagnetic model for zinc ferrite in (100) projection. Each symbol represents two iron atoms superimposed by the projection. The spins of the upper and lower atoms are alike for unshaded symbols and opposite for shaded symbols. The spin orientation is parallel to the y axis of the figure.

of this kind clearly cannot be taken as detailed confirmation of the proposed model. It is felt, however, that the general features of the model are perhaps suggestive of the true state of affairs. Although the model is based upon trial and error calculations, it is not completely arbitrary. The "banding," which is seen to be roughly parallel to the (210) direction, is closely related to the presence in the diffraction pattern of a dominant (210) peak. Some improvement in the agreement can be achieved by slight modifications of the model and by adjustment of the form factor for magnetic scattering.

It was felt, however, that further refinement was unwarranted in view of the uncertainty in the experimental intensities. Furthermore, small undetected departures from the completely normal spinel structure may have some effect on the superlattice pattern.

It is worth noting that the anomaly in the paramagnetic diffuse scattering at liquid nitrogen temperatures referred to earlier may be interpreted[9] as arising from a short-range ferromagnetic interaction. This is not inconsistent with the picture suggested here of an antiferromagnetic alternation of ferromagnetic bands.

New Low-Temperature Ferromagnets

A. N. HOLDEN, B. T. MATTHIAS, P. W. ANDERSON, AND H. W. LEWIS
Bell Telephone Laboratories, Murray Hill, New Jersey
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Certain of the complex cyanides of elements of the $3d$ transition group appear to be ferromagnetic at very low temperatures.

WE have observed large positive susceptibilities and ferromagnetic remanence at liquid helium temperatures in a number of complex cyanides of iron transition group metals.

The apparatus is the same as that used in previous work on superconductivity.[1] It measures the change in mutual inductance of two coils surrounding a sample in powder form; for the measurement of remanence, the sample was pulled out and the current pulse from one coil observed. It is incapable of precision measurements on ferromagnetic substances, both because of the small fields available and of the difficulty of calibration. On the other hand, purely paramagnetic susceptibilities of the order of magnitude expected in these substances would be nearly unobservable with our sensitivity.

Our results are shown in Table I. The entries are the temperatures of maximum observed susceptibility. For each entry not zero, a remanence was also observed.

0's indicate that the substance was tested with negative results down to 1°K; some may be ferromagnetic at lower temperatures.

The field used in the measurement of susceptibility was about 10 oersteds. The maximum moment was about 0.2 to 2/cc. For all the substances in Table I, the observed remanence was about $B_r{\sim}5$ gauss but, of course, this must be understood as an extreme limit for the saturation remanence.

The materials were precipitated by slowly adding 25 cc of solution 0.2 molar in the potassium salts of the anions to 50 cc of solutions 0.2 molar in the cations, and isolating and washing the precipitates in the centrifuge. The existence, as chemical individuals, of some of the substances ostensibly produced in these reactions has been questioned. It is also well known that such precipitates often contain potassium, and that the valence states of the heavy metal ions are ambiguous. This is particularly so for Prussian and Turnbull's blues:

$(Fe^{+3})_4[(Fe(CN)_6)^{-4}]_3$ and $(Fe^{+2})_3[(Fe(CN)_6)^{-3}]_2$.
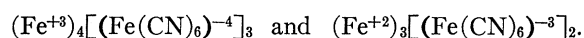
We can merely point to the use of excess cation and of comparable conditions of precipitation to justify the nominal formulas of Table I.[2]

Measurements of Curie points and magnetizations are to be published by R. M. Bozorth, H. J. Williams, and D. E. Walsh.

TABLE I. Absolute temperature of maximum susceptibility of cyanides.

	K+	Zn++	Cr+++	Mn++	Fe+++	Fe++	Co++	Ni++	Cu++
Ferricyanide (Fe(CN)₆)⁻³	0			2°	15°	3.5°	12°	19°	11°
Ferrocyanide (Fe(CN)₆)⁻⁴			2°		3.5°				
Cobalticyanide				0	0		0	0	0
Manganicyanide	0	0	0	35±5°		0	16°	17°	0
Chromicyanide		0		0	0	0	0	0	0

[1] B. T. Matthias and J. K. Hulm, Phys. Rev. 87, 799 (1952).

[2] Weiser, Milligan, and Bates, J. Phys. Chem. 46, 99 (1943).