BNL-22802

CONF-770450--1

THE VERWEY TRANSITION IN MAGNETITE*

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We will first review the characteristics of the Verwey transition in magnetite at 123 K. An ordering takes place among Fe^{2+} and Fe^{3+} ions on the octahedral sites of the inverse spinel structure, accompanied by a sudden change of electrical resistivity. We shall discuss in some detail recent neutron scattering measurements at Brookhaven in collaboration with Chikazumi's group at the University of Tokyo.

I. INTRODUCTION

The Verwey transition in magnetite is one of the oldest problems in magnetism as well as in phase transitions.[1] We shall review a part of this complex problem from the viewpoint of electron-phonon interactions, the topic of this conference. In the first lecture, we shall survey the historical background up to 1973. The second lecture concerns recent neutron scattering experiments carried out at Brookhaven in collaboration with Professor Chikazumi's group at the University of Tokyo.

Let us start by discussing the major characteristics of this phase transition at 123 K. At higher temperatures, magnetite has the inverse spinel structure, a structure which many technically important magnetic materials possess. The unit cell contains 8 Fe_3O_4 units, 8 Fe^{3+} on the tetrahedral sites and the random distribution of 8 Fe^{2+} and 8 Fe^{3+} ions on the octahedral sites. A

* Work performed under the auspices of the U. S. Energy Research and Development Administration.

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very pronounced phase transition has been observed around T_V=123 K. The most dramatic anomaly is in resistivity, as shown in the most recent data (Fig. 1) in Chikazumi's review article.[2] It has a high conductivity for $T>T_V$, but it becomes a reasonably good insulator below T_V.

Verwey[1] proposed a model, thirty years ago, that this phase transition is caused by an electronic charge ordering among the Fe^{2+} and Fe^{3+} ions on the octahedral sites. This ordering scheme is shown in Fig. 2 together with the concomitant orthorhombic symmetry. This is a very simple and attractive model which implies that alternate layers (or strings) of Fe^{2+} and Fe^{3+} are stacked along the c axis. Subsequent magnetic[3], dilatometric, and x-ray[4] measurements all appeared to support the orthorhombic symmetry required by the Verwey model. Then in 1958, Hamilton[5] presented the most convincing evidence in his celebrated neutron scattering paper. A magnetic cross section was observed at (002) below T_V

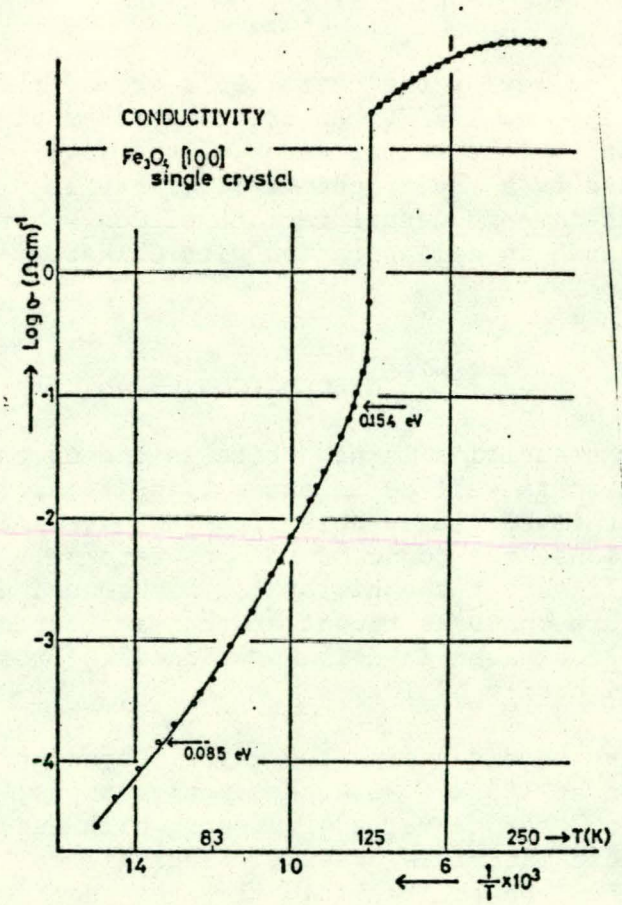

Fig. 1. Temperature dependence of conductivity for Fe_3O_4 along the cubic [100]. (Ref. 2).

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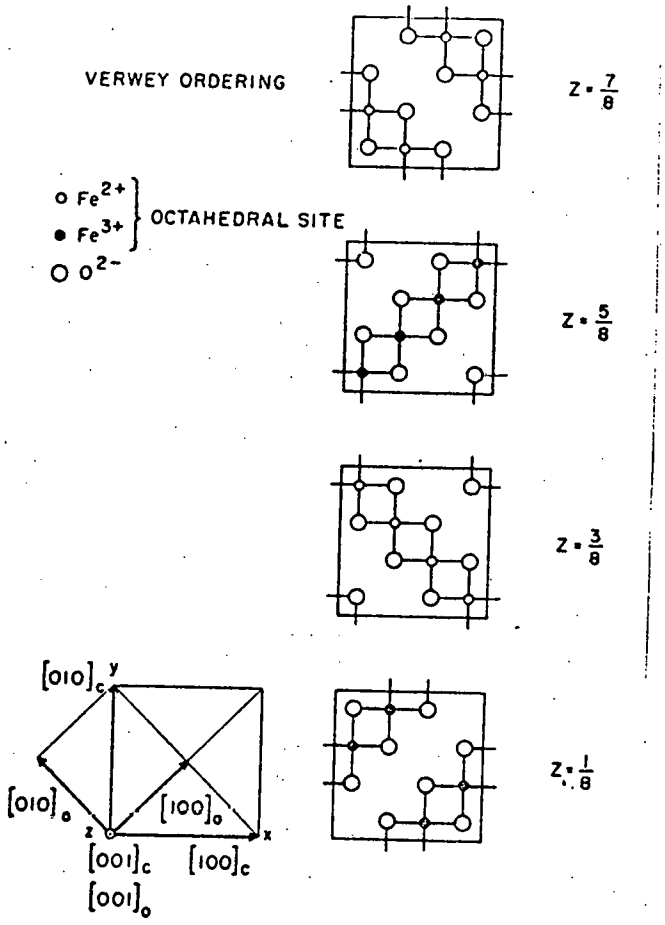

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Fig. 2. The Verwey ordering scheme together with the resulting orthorhombic symmetry.

where none is allowed above T_V. At that point, the problem appeared to be completely solved.

Since then, many new experimental results have been reported which indicate that some basic modification is needed to the original Verwey model. The most important discovery was reported by Samuelsen et al[6] in 1968. In their neutron diffraction experiment below T_V, they observed satellites at reciprocal-lattice points with half integer such as (4 0 ½). This study, as well as independent electron diffraction work by Yamada et al[7] both reported that such satellites appear only along the orthorhombic c axis. In particular, Samuelsen et al noted that the satellite intensities are proportional to Q^2, where $\vec{Q}$ is a reciprocal lattice

vector. Based on this fact they concluded that the satellites result mainly from atomic displacements and they are not directly due to the magnetic ordering of Fe^{2+} and Fe^{3+}. Other experiments such as NMR and Mössbauer measurements showed the existence of more than two nonequivalent octahedral sites below T_V. There was other experimental evidence to indicate that the low temperature symmetry is lower than orthorhombic.

II. CRYSTAL AND SYMMETRY

Let us now examine more closely the crystallographic aspect of this problem. Figs. 3 and 4 are taken from Chikazumi's review article[2] and demonstrate the crystallographic notation used in this talk. The unit cell below T_V has a nearly rhombohedral shape as shown in Fig. 4, though the true symmetry is monoclinic or lower. We may use two types of cell description: (A) Pseudo-rhombohedral cell with [001] axis as the unique magnetic c axis and [110] axis as the monoclinic b axis. In this, $\alpha = 90° - 0.16°$. (B) Pseudomonoclinic cell with the common c axis with the rhombohedral cell.

There are two types of twins: i) c axis zig-zag (c* common) as shown in Fig. 3 and ii) monoclinic a and b axes rotated. One can view these domains as 4 different <111> directions of the rhombohedral cell. These twinnings have caused considerable difficulty and confusion in the interpretation of experimental results. A truly untwinned crystal has been obtained recently by Chikazumi's group by a combined field cooling and a squeezing operation.[2,8] It has been known for some time that the magnetic

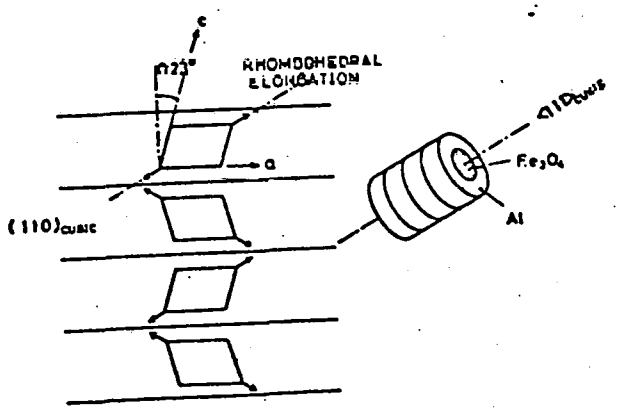

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Fig. 3. Twinning of Fe_3O_4 and the squeezing technique to create an untwinned crystal. (Refs. 2 and 8).

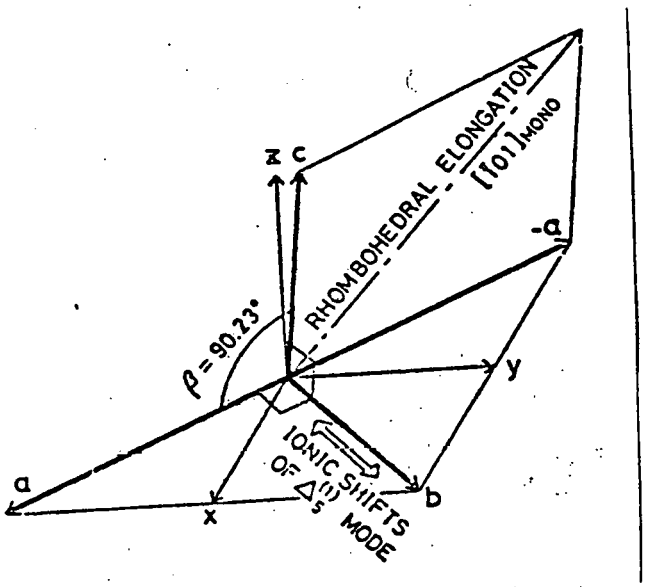

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Fig. 4. Low temperature unit cell of magnetite. abc refers to the monoclinic axes. (Ref. 2).

c axis can be aligned by an <100> magnetic field through T_V. If one puts tight aluminum rings aroung the <111> axis, then this particular rhombohedral elongation will be established. For neutron scattering purposes, a cylindrical crystal (3mm in diameter and 6mm in length) was successfully made into a 99% untwinned crystal.

There is an additional advantage to these squeezed crystals. In order to separate out magnetic components from nuclear scattering,one has to apply a magnetic field below T_V. In a field cooled crystal (without squeezing) the c axis tends to follow the field direction. The desired experimental condition is to reorient the spin direction without changing the c axis. This is realized in the squeezed monocrystal and thus we can experimentally separate out small magnetic components.

The rhombohedral cell shape was properly identified by early x-ray studies[9] but was disregarded in favor of the orthorhombic assignment by the single crystal studies.[4] More recent x-ray[10] as well as neutron diffraction studies[11,12] have now clearly established the rhombohedral cell shape.

A series of neutron scattering experiments have been carried

out as a joint project between the University of Tokyo and Brookhaven. In the following we shall discuss in some detail the results of these measurements.

III. CRITICAL SCATTERING

When our neutron scattering work was initiated, the c-axis doubling was already established. We, however, assumed that the basic magnetic ordering was already firmly established by Hamilton's neutron experiment. It appeared that the transition is accompanied by atomic displacements as clearly established by Samuelsen et al.[6] The key experiment was to look for critical scattering at both reflections, the (40½) type due to atomic displacements and the magnetic (002) reflection. This could give us a clue to the true order parameter of this complex phase transition. As we will see later, the (002) reflection has been absent at all temperatures! But this is the story after.

One crystallographic piece of information. The space group above T_V is Fd3m; reflections such as (200), (600), and (420) are missing because of space group requirements. The Verwey ordering scheme requires (002) type magnetic reflections appear as one can easily see in Fig. 2.

Fig. 5 depicts a typical example of critical scattering reported by Fujii et al.[13] The sharp increase of the (40½) type reflection is limited to a narrow temperature range above T_V. It shows the typical divergence toward T_c, which is a few degrees below T_V (see Fig. 10). The critical scattering was measured at several Brillouin zones and shown, in general, to be quite similar to those of the satellite below T_V.

Yamada[14] proposed a model to explain this critical scattering based upon an electron phonon coupling. This model involves the Δ_5 phonon mode as shown in Fig. 6. Ionic shifts of oxygen and Fe ions are such that they give a larger space for Fe^{2+} ions and a smaller space for Fe^{3+}. The most important result of the Yamada model is the charge ordering scheme which differs from that predicted by the Verwey model. The Fe^{3+} ions are not forming chains in c planes but both Fe^{2+} and Fe^{3+} form alternate chains as shown in Fig. 6. Since the Yamada model modulates a charge density wave along the c axis, it creates grey (disordered) layers as well.

There is a unique and simple prediction of the Yamada model for the magnetic cross section due to the spin ordering below T_V. The (002) type should be missing and the (20½) type reflection should show the main magnetic scattering. This prediction, however, is only partially fulfilled. Before discussing the low

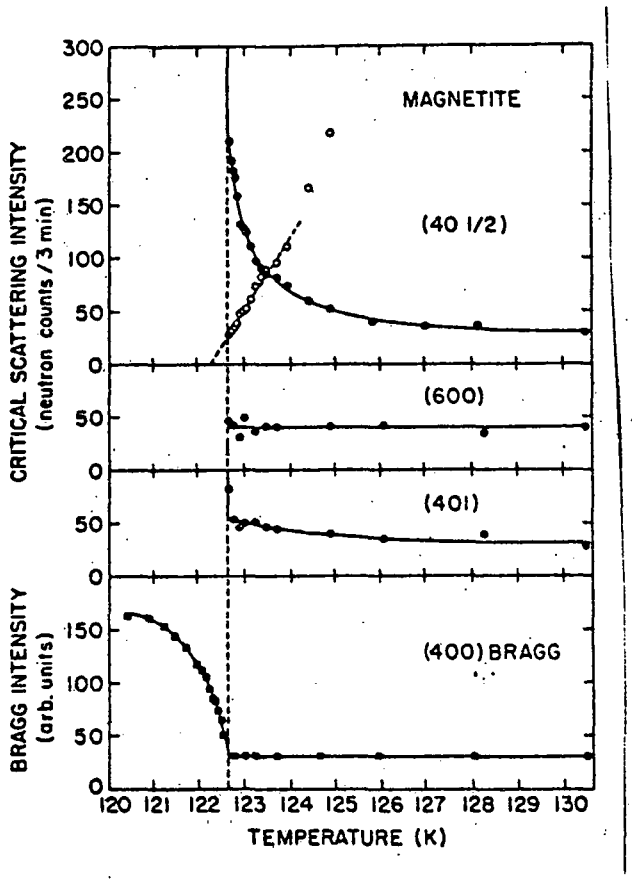

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Fig. 5. Critical scattering just above T_V. Open circles for (40½) is T/I. (Ref. 13).

temperature study, we describe an additional type of diffuse scattering which is widely distributed in q space over a large temperature range, as shown in Fig. 7 and 8. This type of diffuse streak was first recognized by Chiba et al[15] in their electron diffraction study. A detailed study was carried out by Shapiro et al[16] on a large magnetite crystal. Somewhat surprisingly, this scattering showed one-dimensional nature along the <001> direction. It shows a gradual temperature dependence (Fig. 9) with extrapolated divergence at 106 K.

At present, we can offer only a qualitative picture for this diffuse scattering and its relation to the sharp critical peak described above. A major feature of the profile can be explained by an elongated correlation range based upon the Yamada model. The shape of the elliptical cross section is determined by the shape of the 1-D "clusters." This correlation grows with little change of shape for wide temperature range (see Fig. 10). Only at

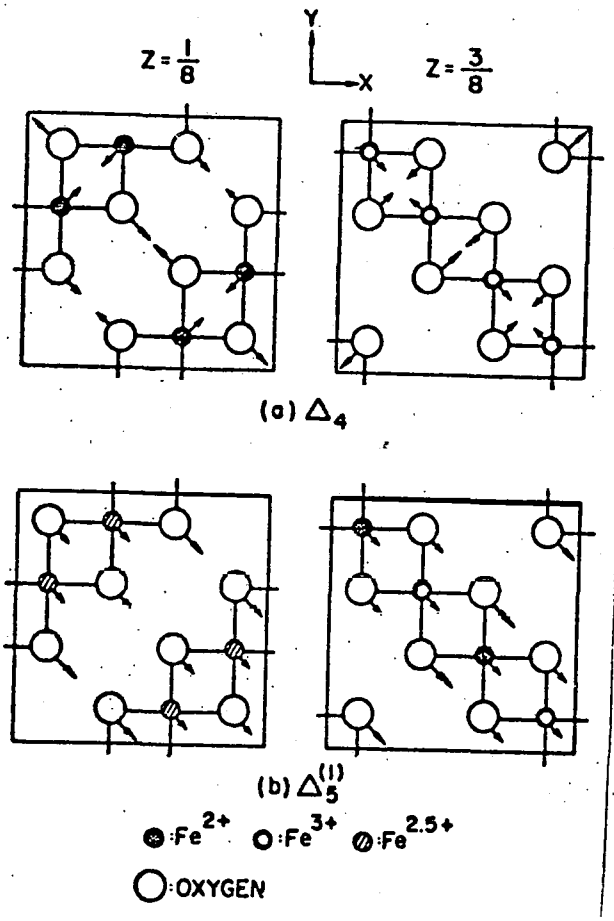

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Fig. 6. The Yamada model based upon the Δ_5 phonon mode. Δ_4 corresponds to the Verwey model. (Ref. 14).

a few degrees above T_V, the 3-D critical scattering sets in, peaking at positions corresponding to low temperature satellites. The latter behavior is shown for (40½) by the steep broken line in Fig. 10.

IV. STRUCTURE BELOW T_V

It is essential to have a reliable knowledge of the low temperature structure to establish the charge ordering scheme in magnetite. As it turned out, this is a difficult and complex problem. Moreover, there is one important aspect of the analysis we did not fully appreciate at the outset.[12] In ordinary magnetic structure determination, one uses the magnetic structure factor

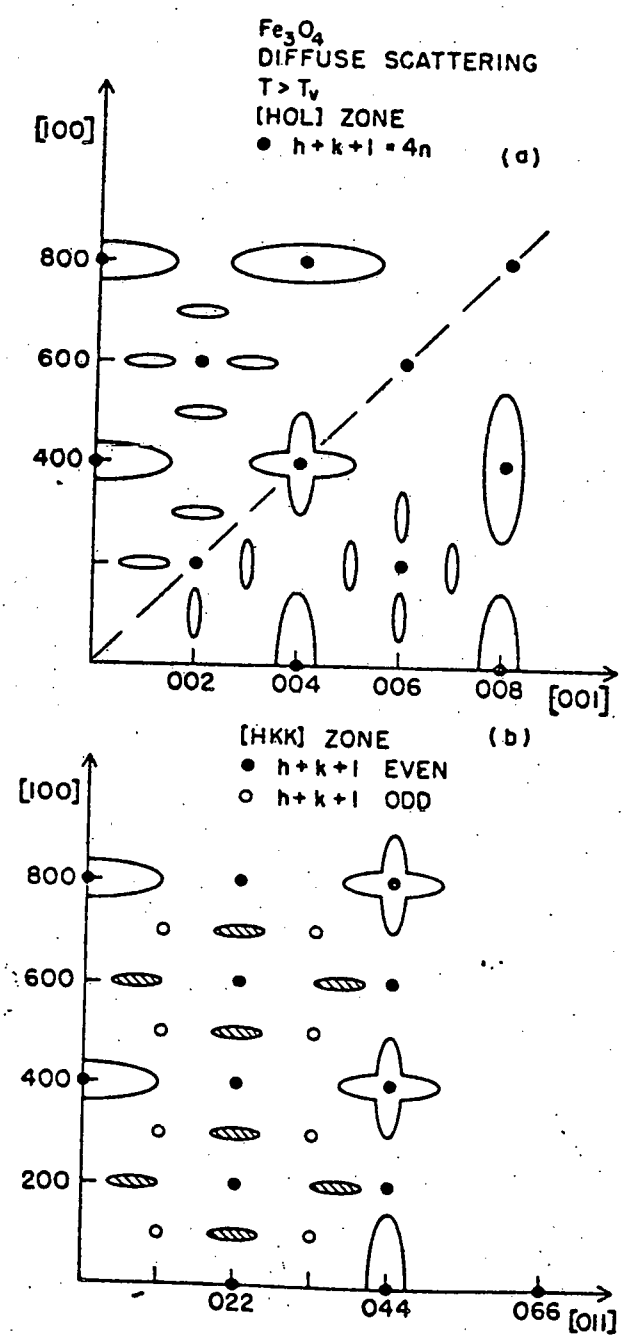

Fig. 7. Intensity distribution of diffuse scattering in two different zones. (Ref. 16).

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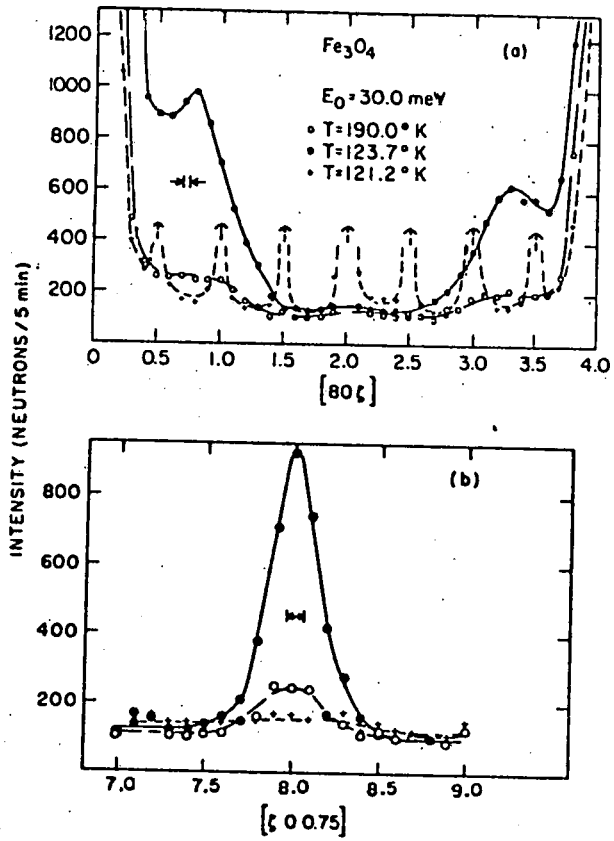

Fig. 8. Cross sections of diffuse streak shown in Fig. 7. (Ref. 16). Broad peaks around ζ=0.75 and 3.25 result from 1-D correlation.

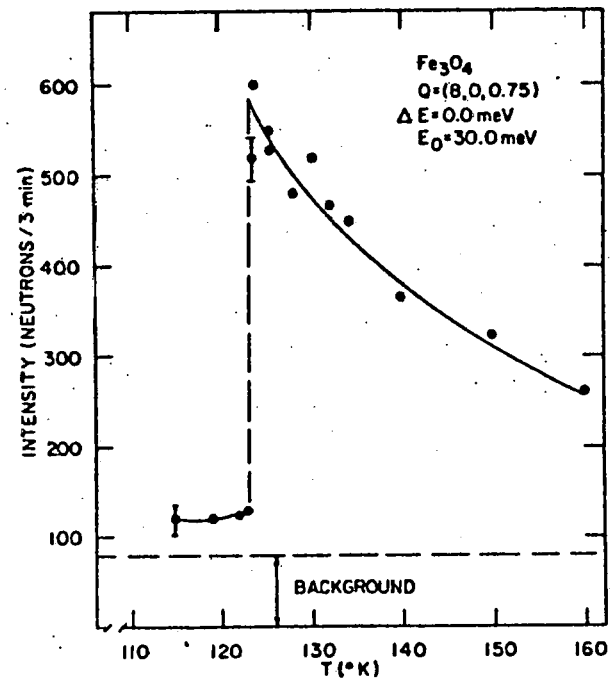

Fig. 9. Temperature dependence of diffuse scattering in Fe_3O_4. (Ref. 16).

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$$F_M = \sum_j \Delta P_j \, e^{i(\vec{Q}\cdot\vec{r}_j)} \qquad (1)$$

where $Q = a^*h + b^*k + c^*\ell$, and $\vec{r}_j$ atomic position and ΔP_j is due to magnetic modulation, namely $\pm 0.5\mu_B$ for the difference between the Fe^{2+} and Fe^{3+} magnetic moments. Usually we can use the cubic parameter $\vec{r}_j$ and neglect the higher order effect of atomic shift Δ_j at T_V.

For magnetite we have to use a more complete formula. This originates from the unusual situation that the spin modulation ΔP_j is superposed on a much larger average component $\bar{P}$, corresponding to $4.5\mu_B$. Now (1) becomes

$$F_M = \sum_j (\bar{P} + \Delta P_j) \, e^{i\vec{Q}\cdot(\vec{r}_j+\vec{\Delta}_j)} \qquad (2)$$

Expanding in Δ_j we obtain

$$F(Q) \cong \sum_j \bar{P} \, e^{i\vec{Q}\cdot\vec{r}_j} + \sum_j \Delta P_j \, e^{i\vec{Q}\cdot\vec{r}_j} + i \sum_j \bar{P} \, (\vec{Q}\cdot\vec{\Delta}_j) \, e^{i\vec{Q}\cdot\vec{r}_j} \qquad (3)$$

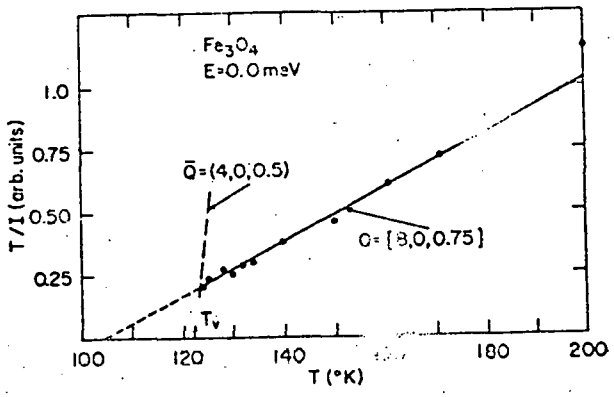

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Fig. 10. Comparison of temperature dependence of 1-D diffuse peak at (8,0,0.75) and 3-D critical scattering at (40½). (Ref. 16).

The last term cannot be ignored for magnetite because $\bar{P}$ is considerably larger than ΔP_j. Thus we can establish ΔP_j only if we know Δ_j accurately enough.

Three types of neutron scattering experiments have been carried out so far for this purpose: (1) High resolution data were obtained for selected reflections, in particular (002) and (20½) to establish magnetic scattering below T_V. Measurements were carried out on a "regular" field cooled[12] as well as "squeezed" field cooled crystals.[18] (2) A polarized beam study on selected reflections from squeezed monocrystal.[17] Structure analysis at 78 K utilizing 1400 reflections.[18] Only the part (1) has been published and the other two are now in the process of final data analysis.

Table I lists some examples of the high resolution scattering experiment. The attempt here is to establish reliably a weak scattering cross section in the presence of much stronger reflections. The most crucial part of the experiment was to eliminate simultaneous reflections (see Fig. 11). Table I includes two simple charge ordering schemes, the Verwey model and the AB model. The latter is calculated for the double c axis. The Yamada model is a more general AB type modulation based upon the specific phonon mode coupling.

We have not yet established a satisfactory charge ordering scheme below T_V. We can, however, rule out some models unambiguously because of very low limits established in this experiment. First of all, the original Verwey ordering scheme is ruled out because of extremely low limits set for the magnetic cross sections for (402) and (002). The Chikazumi-Chiba model[19] is also ruled out. Previous neutron data must have been severely distorted by simultaneous reflections.

In Table I, F_M^2(cal) for AB model (Fig. 12) involves only ΔP_j terms and not $i\bar{P}(\vec{Q}\cdot\vec{\Delta}_j)$ terms. Agreement with observed is less than satisfactory and, in particular, (20½) poses the vital disagreement. In fact, we have yet to prove that any part of the magnetic cross sections is due to the spin modulation ΔP_j, and not to the magneto-distortive term $\bar{P}(\vec{Q}\cdot\vec{\Delta}_j)$. Table I demonstrates that the observed magnetic cross sections are quite weak. It is conceivable, though very unlikely, that large magnetic peaks exist outside of (h0ℓ) and (hhℓ) zones. If the actual spin modulation is less than $0.15\mu_B$, compared with full $0.5\mu_B$, then the corresponding magnetic intensity ($\sim\Delta P^2$)would be difficult to detect.

Preliminary results of the current structure analysis[18] show several promising aspects. (1) The Δ_j's have been determined by least square analysis without any preassumed model. Yet they

Table I

Comparison of F_M^2(obs) with two model calculations. These are put into absolute units of millibarns per cubic unit cell (Ref. 12). F_M^2(cal) assumes full Fe^{2+} - Fe^{3+} modulations of $\pm 0.5\mu_B$. Total F^2(obs), nuclear plus magnetic, are given for (400) and (40½) for comparison.

	F_M^2(obs)	F_M^2(cal)	
h0ℓ		Verwey model	AB model
402	< 16	10,500	---
002	< 26	17,980	---
20½	< 72	---	3,500
201½	∿ 300	---	3,100
202½	∿ 400	---	2,400
	F^2(obs)		
400	4×10^6		
40½	1.3×10^4		

possess essential features of the Yamada model. (2) The magnetic cross sections based upon this structure give good agreement with the recent polarized beam experiment.[17] (3) The Fe atoms on the octahedral sites may be divided into different kinds with respect to their distances to surrounding oxygens, in accord with NMR and Mössbauer measurements.[20-22] The final step to the spin modulation is still missing.

ACKNOWLEDGMENTS

I would like to thank S. Chikazumi, M. Iizumi, T. Koetzle, S. M. Shapiro, and Y. Yamada for many illuminating discussions during the course of more recent collaboration.

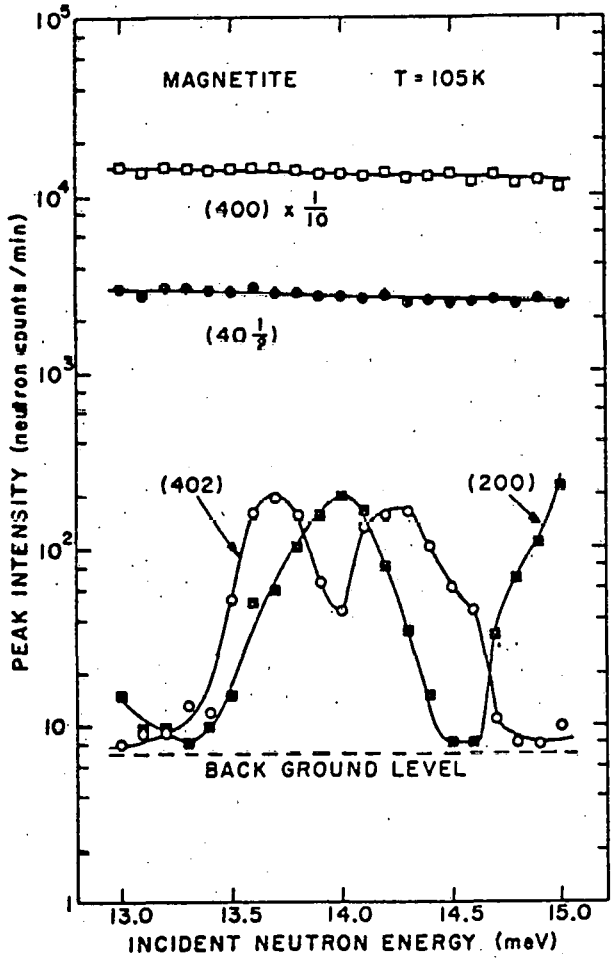

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Fig. 11. Test of simultaneous reflection for selected peaks in Fe_3O_4. (Ref. 12).

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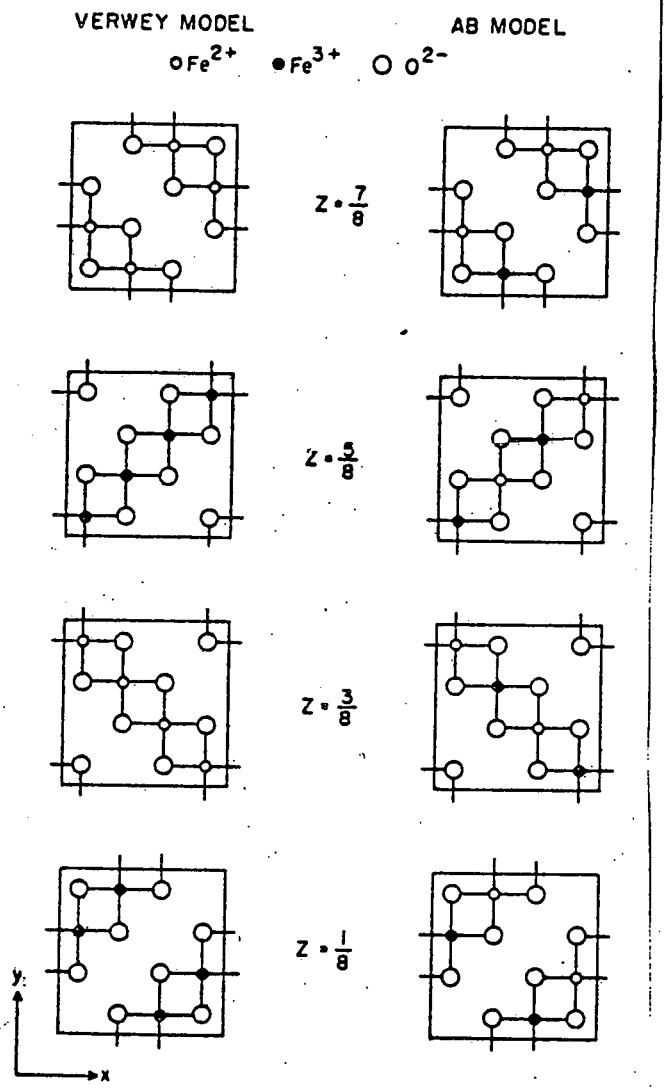

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Fig. 12. Two charge ordering schemes in Fe_3O_4.

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