Study of the 123-K phase transition of magnetite by critical neutron scattering*

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A neutron-scattering study has been carried out on magnetite at temperatures just above the Verwey transition point of $T_V = 123$ K. No critical scattering was observed at the (0,0,2) reciprocal-lattice point where the magnetic scattering appeared below T_V due to the Verwey ordering as previously reported by Hamilton. On the other hand, well-defined critical scattering was observed at the points corresponding to the (4,0,1/2)-type satellites which had been found to result mainly from atomic displacements by Samuelsen *et al.* These results indicate that atomic displacements due to internal lattice modes play an important part in the critical fluctuation of this phase transition. The intensity calculated on the basis of a Δ_5 phonon mode with the wave vector of $\vec{k} = (0,0,1/2)$ qualitatively explains the observed intensity distribution of the critical scattering. The mode of the charge-density fluctuation on the octahedral Fe sites which couples with this phonon mode is quite different from the scheme of the well-known Verwey ordering.

I. INTRODUCTION

Magnetite undergoes a first-order phase transition around 123 K (T_V) accompanying a decrease in electrical conductivity by a factor of 10^2 below T_V. In order to explain this phenomenon Verwey[1] proposed that this phase transition was caused by an electronic charge ordering, in which the random distribution of Fe^{2+} and Fe^{3+} ions on the octahedral sites of the cubic inverse spinel lattice (space group O_h^7) above T_V becomes ordered at T_V. In the ordered phase with the concomitant orthorhombic symmetry, Fe^{2+} and Fe^{3+} ions occupy the alternate (001) layers along the orthorhombic c axis which corresponds to one of the principal axes of the cubic lattice. In 1958 Hamilton[2] carried out neutron-scattering experiments to check this Verwey model, and he reported an observation of the (002) magnetic scattering below T_V. In the Verwey model, this results from the difference between the spin of Fe^{2+} and that of Fe^{3+} ions ordered on alternate (001) layers as shown in Fig. 1. In addition, the space group of D_{2h}^{28} was conclusively assigned to the low-temperature structure from his experiment. Therefore it has since been believed that the Verwey model for this phase transition is basically correct.

Over the past seven years, however, several experiments have shown that this simple scheme of charge ordering must be modified. In neutron and electron diffraction experiments below T_V, Samuelsen *et al.*[3] and Yamada *et al.*,[4] respectively, observed satellites at reciprocal-lattice points with half-integer indexes such as $(4, 0, \frac{1}{2})$ and $(8, 8, \frac{1}{2})$ referred to the cubic lattice. And both groups found that such satellites appeared only along the orthorhombic c axis, which indicates the doubling of the unit cell along this axis. In particular Samuelsen *et al.* noted that the satellite intensity of certain kinds of reciprocal-lattice points are proportional to the square of the reciprocal lattice vector. Based on this fact they concluded that the satellites mainly result from atomic displacements, and they are not directly due to the magnetic ordering of Fe^{2+} and Fe^{3+} ions. Other experiments such as NMR[5] and Mössbauer[5,6] measurements showed the existence of more than two inequivalent octahedral sites in the unit cell below T_V. Also several x-ray diffraction experiments[7] and recent electron microscopic observation[8] showed magnetite was not exactly orthorhombic below T_V. This experimental evidence, which cannot be explained by the simple Verwey model, demands reconsideration of the mechanism of this phase transition as well as the crystallographic and magnetic structures below T_V.

This paper constitutes the first part of two neutron-scattering studies carried out as a joint project across the Pacific. The second paper, to be reported by Shirane *et al.*,[9] will be concerned with the magnetic and structural studies of a single-domain crystal below T_V. We will see that the true nature of the Verwey transition can be fully elucidated only by careful evaluation of the scattering both above and below T_V.

At the outset of this study we considered that the basic magnetic ordering was already firmly established by Hamilton's neutron experiment,[2] al-

though it might require a modification. The neutron-scattering experiment by Samuelsen *et al.*[3] also made it clear that this ordering is accompanied by atomic displacements. It appeared, at that point, that the key experiment was to look for critical scattering at both reflections, the $(4, 0, \frac{1}{2})$ type, which is due to atomic displacements and the magnetic $(0, 0, 2)$ reflection. This could give us a clue to the true order parameter of this complex phase transition in magnetite. This type of approach has been quite successful in clarifying many unresolved questions in structural phase transitions.[10]

Section II of this paper is divided into three parts: in the first part, experimental details of the neutron-scattering experiments are presented. The characteristics of the newly observed critical scattering such as temperature dependence, energy distribution, and anisotropy in reciprocal space are given in the second part. The last part of Sec. II presents the intensity distribution of critical scattering observed at various points in reciprocal space. The last section, Sec. III, is devoted to a comparison of the present results with the model calculation which has been recently developed by one of the present authors (Y.Y.).

II. OBSERVATION OF CRITICAL NEUTRON SCATTERING

A. Experimental details

The excellent synthetic crystal of magnetite used in the present experiment was kindly provided by Chikazumi and Todo of the Institute for Solid State Physics, University of Tokyo; this is similar[11] to those previously reported.[4,8] A cylindrical sample 10 mm in diameter, 15 mm in height, with the $[1, 1, 1]$ axis parallel to the cylinder axis was mounted in a variable temperature cryostat with the $[0, 1, 0]$ axis vertical. Measurement of the sample temperature was made with a platinum resistance thermometer which had been previously calibrated. Its temperature could be maintained within ±0.01 K. The mosaic of this crystal was found to be 12 min [full width at half-maximum (FWHM)] at a temperature of 130 K.

Neutron-scattering measurements were performed with a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor. Incident neutron energies of 13.7 and 30.0 meV were used. Monochromator and analyzer crystals were of pyrolytic graphite; the former was vertically bent while the latter was planar. Four horizontal collimators were either 20 or 40 min. Particular care was taken to remove the higher-order contamination of the incident neutron beam by a graphite filter.

B. Nature of critical scattering

According to the neutron-scattering experiments below T_V made by Samuelsen *et al.*,[3] strong satellites which had been found to come mainly from atomic displacements are located at the points $(h, k, l+\frac{1}{2})$ with $h, k, l = 4n$ referred to the cubic lattice. At that stage, however, it was not clear whether the displacements causing these strong satellites were to be considered as the primary-order parameter or a secondary one for the 123-K phase transition of magnetite. In order to clarify this, we concentrated at first on finding critical scattering at temperatures just above T_V. The points $(h, 0, l+\frac{1}{2})$ with $h, l = 4n$ as well as the $(2, 0, 0)$ type were carefully investigated. At the latter point, in the Verwey ordering, magnetic critical scattering should appear as the primary-order parameter because in that model electronic charge ordering of Fe^{2+} and Fe^{3+} ions on the octahedral site causes the phase transition (see Fig. 1). Prior to this measurement, the effect of double scattering was carefully checked and removed by changing the incident neutron energy.

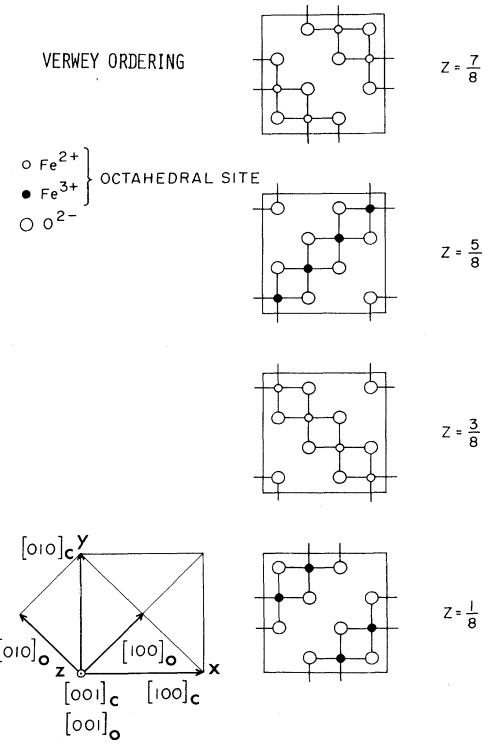

FIG. 1. Charge-ordering scheme of the Verwey model. Fe^{2+} and Fe^{3+} ions on the octahedral site occupy the alternate $(0, 0, 1)$ layers along the orthorhombic c axis (∥ direction). The principal axes of a and b of the orthorhombic lattice are along the $[1, 1, 0]$ and $[\bar{1}, 1, 0]$ directions of the cubic lattice as shown at left.

Although this phase transition is distinctly first order, we succeeded in an observation of strong critical scattering at $(4, 0, \frac{1}{2})$, as shown in Fig. 2. The temperature range where critical scattering can be observed is rather narrow (ca. 4 K). In the same figure the inverse of the observed critical scattering intensity is plotted by open circles in which the intensity at 130 K was taken as background. In the vicinity of T_V, these points show a linear temperature dependence, which crosses over the zero of the ordinate at the temperature of T_V-0.3 K. The phase transition temperature T_V was determined to be 122.6 and 122.8 K on cooling and heating, respectively, from a discontinuous change in intensity of the fundamental (4, 0, 0) Bragg reflection as shown at the bottom of Fig. 2. This intensity change at T_V is mainly due to the change of the extinction effect because a formation of multidomains below T_V increases the mosaic of the crystal.

On the other hand, no appreciable critical scattering was observed at (2, 0, 0) and (4, 0, 2), the temperature dependence of which is very similar to that of (6, 0, 0) shown in Fig. 2. At some other type points such as $(2, 0, 4+\frac{1}{2})$ and (4, 0, 1), the latter of which is shown in Fig. 2, critical scattering was also observed although its intensity is weak in comparison with the $(4, 0, \frac{1}{2})$ type. The existence of a satellite at (4, 0, 1) below T_V was also previously confirmed by Samuelsen *et al.*[3]

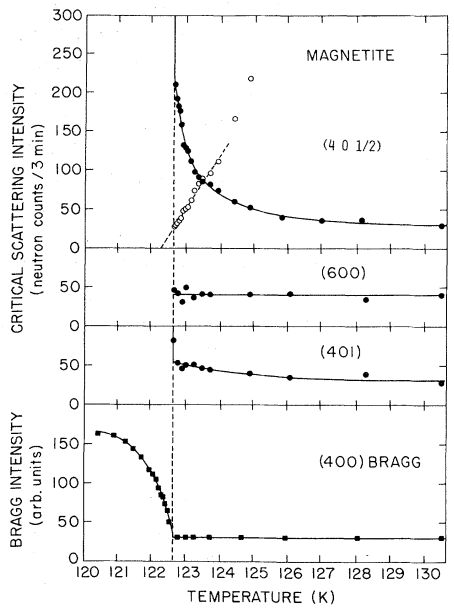

FIG. 2. Temperature dependence of critical scattering observed at three kinds of points in reciprocal space (black circles) together with the fundamental (4, 0, 0) Bragg reflection (black squares). Open circles represent the temperature dependence of the inverse of the critical scattering observed at $(4, 0, \frac{1}{2})$ in which the intensity at 130 K was taken as background. A distinct discontinuity of intensity was observed at T_V for the (4, 0, 0) reflection though it is not clearly observable from the figure.

In the observed temperature range, the critical scattering is quasielastic, with an energy width less than the instrumental resolution. This response may be interpreted either as due to overdamped phonons or as due to order-disorder type fluctuations. A typical example of the former case is observed in $KMnF_3$,[12] in which the phonon sidebands gradually merge into the central peak. In the latter, phonon peaks do not show appreciable change even at the transition point, as is observed in ND_4Br.[13]

As is discussed in Sec. III, a possible candidate for the soft phonon is considered to be the low-lying Δ_5 mode (TA mode) with wave vector $\vec{k} = (0, 0, \frac{1}{2})$. The temperature dependence of the phonon response of the [1, 0, 0] TA mode was observed at $(8, 0, \frac{1}{2})$ in order to check possible softening of the TA mode. As is shown in Fig. 3, no appreciable change either in energy or in line profile of the well-defined phonon (scan B) was observed in the temperature range between $T_V + 0.3$ and $T_V + 8.2$ K. During the course of the present experiment, Samuelsen and Steinsvoll[14] reported that they did not observe any softening of the [1, 0, 0] TA phonon. On the other hand, the scan A in Fig. 3 indicates that critical scattering is located at the point of zero energy transfer, and there is no appreciable broadening in energy compared with the energy width of the instrumental resolution drawn by the horizontal bar. The intensity observed at 130.8 K was found to come from other origins, as mentioned in Sec. III. At this temperature, critical scattering already disappears, as demonstrated in the case of $(4, 0, \frac{1}{2})$ in Fig. 2. These experimental results show that the

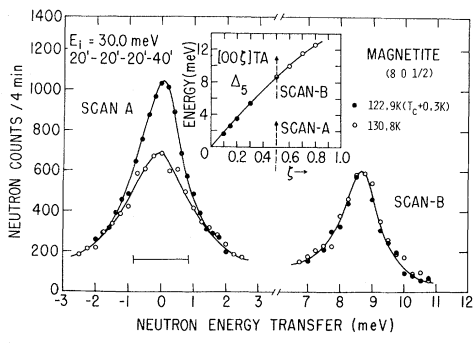

FIG. 3. Temperature dependence of the [1, 0, 0] TA phonon (scan B) and energy distribution of the critical scattering located at the point of zero energy transfer (scan A). Measurements were made at $(8, 0, \frac{1}{2})$.

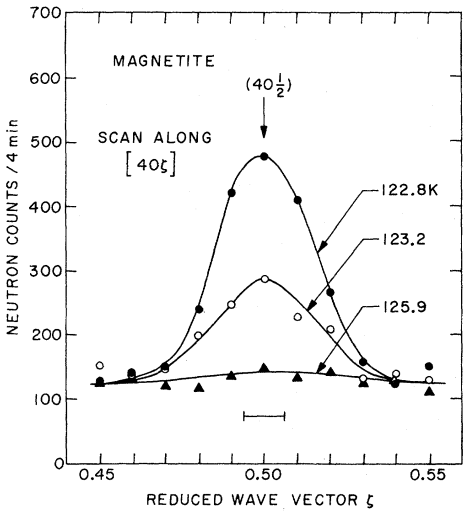

FIG. 4. Intensity distribution of the critical scattering along the [0,0,1] direction through $(4,0,\frac{1}{2})$. It has wider width than that of the instrumental resolution shown by the horizontal bar.

critical scattering should be interpreted as order-disorder type rather than overdamped phonons.

The critical scattering was found to be considerably anisotropic in reciprocal space. Figure 4 displays the line profile of the critical scattering observed at $(4,0,\frac{1}{2})$ along the $[0,0,1]$ direction. The horizontal bar in the figure indicates the resolution width (FWHM) along this direction in reciprocal space which was experimentally determined by using Bragg reflection. Evidently the critical scattering has wider distribution than the resolution width. On the other hand, the width along the $[1,0,0]$ direction was found to be nearly equal to that of the resolution. Therefore, one can conclude that critical scattering at the point of $(h,0,l+\frac{1}{2})$ has anisotropy in reciprocal space in which the intensity distribution elongates in the direction of [001].

C. Intensity distribution

In order to determine the atomic motion in the lattice mode contributing to the phase transition, the intensity distribution of critical scattering was measured at various points on the (0,1,0) zone in reciprocal space. The results are plotted as solid circles in Fig. 5, in which two types of points with half-integer index and integer one are separately displayed. The solid line drawn for the former-type points represents the values calculated based on the Δ_5 phonon mode with wave vector of $\vec{k}=(0,0,\frac{1}{2})$, which will be described in Sec. III.

III. DISCUSSION

In Fig. 3 we show the scattering which is located at the point of zero-energy transfer and still remains at 130.8 K. This was found to be part of a ridgelike diffuse scattering in reciprocal space and is different from the critical scattering mentioned above. The latter can be called spotlike located at $(8,0,\frac{1}{2})$, although it has an anisotropy as described in Sec. II. The former ridgelike diffuse scattering is elongating between $(8,0,\bar{1})$ and (8,0,1) through (8,0,0), while along the [1,0,0] direction it shows a peak on the line of $[8,0,\zeta]$ with a width of about $0.35a^*$ which is much wider than resolution width. As the temperature is lowered to T_V, its intensity slowly increases in comparison with the critical scattering. A similar ridgelike diffuse scattering was observed also along the line between (8,0,3) and (8,0,5) through (8,0,4). This diffuse scattering was first discovered in electron diffraction by Chiba, Suzuki, and Chikazumi.[15] However, a relation between the spotlike critical scattering and the ridgelike

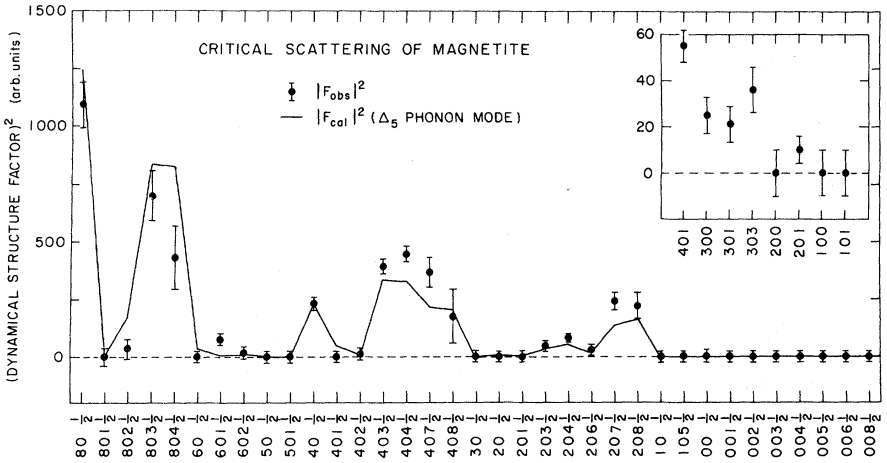

FIG. 5. Comparison between the observed structure factor of critical scattering (black circles) and the dynamical structure factor calculated on the basis of the Δ_5 phonon mode (solid line) (Ref. 16). Vibrational amplitudes of atoms for this mode used in the calculation are displayed in Fig. 6(b). Data at the integer-type reciprocal-lattice points are also shown in insert.

diffuse scattering has not been clarified yet.

Strong critical scattering observed at $(h,0,l\pm\frac{1}{2})$ with $h,l=4n$ does not show a decay of intensity at the higher-index points. Thus the observed critical scattering is not mainly of magnetic origin but due to the atomic displacements. As for the corresponding satellites below T_V, it was previously confirmed by Samuelsen *et al.*[3] Therefore, one can conclude that atomic displacements play an important part in the critical fluctuations. This result is in contrast to the concept of the Verwey ordering in which charge ordering is accomplished by electron-electron interaction.

Recently one of the present authors (Y.Y.)[16] has developed a theory of the 123-K phase transition of magnetite based on the electron-phonon coupling. According to his theory, there are two possibly condensing phonon modes Δ_4 and Δ_5 with wave vector of $\vec{k}=(0,0,\frac{1}{2})$. The Δ_4 mode is nondegenerate while the Δ_5 mode is doubly degenerate. Figure 6 shows the atomic displacements for each mode together with the scheme of charge-density fluctuation on Fe ions located at octahedral site which couples with these phonon modes by the cooperative Jahn-Teller effect. The charge density mode of Δ_4 is identical with the Verwey ordering (Fig. 1) except that it is modulated by wave vector $\vec{k}=(0,0,\frac{1}{2})$. On the other hand, the charge-density mode with Δ_5 symmetry leads to a new type of charge ordering below T_V, in which Fe^{2+}-Fe^{3+} ordering is accomplished *within* the (0,0,1) atomic plane.

In order to compare these models with the present experimental results, we have analyzed the intensity of critical scattering at various $(h,0,l+\frac{1}{2})$-type points in reciprocal space. Only the phonon contributions have been taken into account as the first approximation. The systematic tendency that intensity is strong when $h,l=4n$ definitely suggests that the condensing phonon mode belongs to Δ_5. By adjusting the parameters of atomic displacements we can come to a good agreement between the model calculation and experiment as shown in Fig. 5. Eigenvectors of each atom except for Fe^{3+} ions on the tetrahedral site used in the calculation are displayed in Fig. 6(b). In this particular case of magnetite, a charge-density wave is accompanied by an equivalent spin-density wave because the spin degeneracy is already lifted due to magnetic ordering. Therefore, the above-stated results imply that there should be the *spin*-density fluctuations with Δ_5 symmetry, which is, in principle, detectable as magnetic critical scattering of neutrons. However, the intensity at $(2,0,\frac{1}{2})$, where the magnetic scattering is expected, was too weak to be observed.

The direct evidence of this new type of charge-(spin-) density ordering will be more easily observable by investigating the static magnetic structure in the low-temperature phase. If the condensing mode is doubly degenerate, the static structure in the low-temperature phase cannot be uniquely determined from the information of critical scattering above T_V, because any linear combination of the degenerate mode is equally probable. Therefore careful evaluation of scattered intensity *both* above and below T_V with a single-domain crystal can give full information about the mechanism of the phase transition and the static charge density as well as the atomic structure in the low-temperature phase. Such an experiment of the low-temperature phase of magnetite by using a single-domain crystal is now in progress and it will be reported separately by Shirane *et al.*[9]

We have presented the successful observation of critical scattering at the Verwey transition. The intensity distribution shows a good over-all agreement with the Yamada model based on electron-phonon coupling. It should be emphasized, however, that the present experiment by no means establishes the uniqueness of the model. Many important questions remain unsolved; these include the origin of (4,0,1)-type critical scattering and the ridgelike diffuse scattering around (8,0,0).

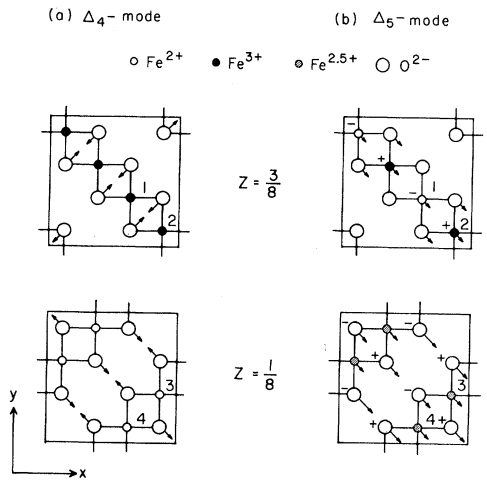

FIG. 6. (a) The coupled phonon-charge density mode with symmetry Δ_4. Only the displacements of oxygens are illustrated. (b) One of the doubly degenerate phonon-charge density modes with symmetry Δ_5. The length of the arrow represents the relative vibrational amplitude of atoms for this phonon mode used in the present calculation (Fig. 5). The sign ± shows the vibration along the z direction. The charge ordering in sites 3 and 4 is coupled to the other Δ_5 mode. The low-temperature structure is determined as a linear combination of these two degenerate modes.

Probably the most challenging problem is to separate out the magnetic component in the critical scattering by application of a magnetic field.

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