PHYSICAL REVIEW B VOLUME 21, NUMBER 10 15 MAY 1980

# Neutron diffuse scattering in magnetite due to molecular polarons

Y. Yamada
*Department of Physics, College of General Education, Osaka University, Toyonaka Osaka, Japan*

N. Wakabayashi and R. M. Nicklow
*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

(Received 26 December 1979)

A detailed neutron diffuse scattering study has been carried out in order to verify a model which describes the property of valence fluctuations in magnetite above $T_V$. This model assumes the existence of a complex which is composed of two excess electrons and a local displacement mode of oxygens within the fcc primitive cell. The complex is called a molecular polaron. It is assumed that at sufficiently high temperatures there is a random distribution of molecular polarons, which are fluctuating independently by making hopping motions through the crystal or by dissociating into smaller polarons. The lifetime of each molecular polaron is assumed to be long enough to induce an instantaneous strain field around it. Based on this model, the neutron diffuse scattering cross section due to randomly distributed dressed molecular polarons has been calculated. A precise measurement of the quasielastic scattering of neutrons has been carried out at 150 K. The observed results definitely show the characteristics which are predicted by the model calculation and, thus, give evidence for the existence of the proposed molecular polarons. From this standpoint, the Verwey transition of magnetite may be viewed as the cooperative ordering process of dressed molecular polarons. Possible extensions of the model to describe the ordering and the dynamical behavior of the molecular polarons are discussed.

## I. INTRODUCTION

The charge ordering of magnetite has been subjected to extensive investigations both theoretically and experimentally since Verwey[1] proposed a model of charge ordering within the octahedral Fe sites. In the past decade, there have been substantial developments concerning the crystal structure in the low-temperature phase.[2] It was established that the unit cell is doubled along one of the cubic principal axes.[3,4] This was attributed to small-amplitude internal displacements of the ions which take place at $T_V$ (the Verwey transition temperature) along with the charge ordering. Such a simultaneous ordering of the valence electron configuration and small displacements of atoms strongly suggests the important role of electron-phonon coupling in the process of the Verwey transition.

When approaching the problem of Verwey ordering from the phonon side, we might expect the particular phonon mode which is compatible with the static displacements to become unstable at the transition temperature.[5] In 1975, Fujii *et al.*[6] observed neutron quasielastic scattering just above the transition temperature and analyzed the results in terms of the instability of the TA phonon mode with the wave vector $q = (\frac{1}{2}, 0, 0)$. Later, Shapiro *et al.*[7] carried out more extensive observations of diffuse scattering above the transition temperature. They reported a new type of diffuse scattering which has different characteristics from the previously reported scattering due to soft phonons. The patterns obtained by Shapiro *et al.* are reproduced in Fig. 1. These are drawn somewhat schematically to demonstrate clearly the characteristics of the diffuse pattern. As is seen in the figure, there is strong diffuse scattering which is widely spread in momentum space with its maximum intensity at the $\Gamma$ points (the Brillouin-zone centers) and which has a remarkable anisotropy in the reciprocal space. Moreover, the intensity is not strongly temperature dependent as compared with the diffuse scattering studied by Fujii *et al*. It is observable up to $T_V + 80$ K, while the latter exists only between $T_V < T < T_V + 5$ K. Observation of the same type of diffuse streak pattern by electron diffraction was also reported by Chiba *et al.*[8]

These characteristics do not allow one to make the conventional interpretation of the data as a "critical diffuse scattering" at structural phase transitions. The critical diffuse scattering is usually considered as being due to the correlated fluctuations of the order parameter associated with the phase transition. It has intensity maxima at the positions where new Bragg reflections appear in the ordered phase, because the largest amplitude fluctuation occurs at the wave vector corresponding to the periodicity of the long-range order. In the present case, new Bragg reflections appear at $(\frac{1}{2}, 0, 0)$ corresponding to the doubling of the unit cell along the cubic principal axis. Nevertheless, the maxima of the diffuse scattering are at the $\Gamma$ points. The origin of this type of dif-

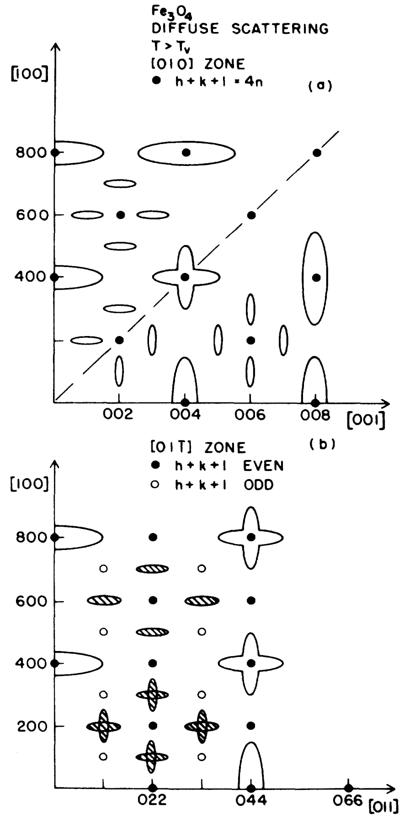

FIG. 1. Schematic representation of the intensity distribution of quasielastic scattering in two different zones as given in Ref. 7.

fuse scattering has not been clarified previously.

The purpose of the present paper is to construct a model to describe the state of valence fluctuations in $Fe_3O_4$ above $T_V$ and, based on this model, to elucidate the origin of this diffuse scattering. The preliminary results of the present investigation have been published elsewhere.[9]

## II. MOLECULAR POLARON MODEL

We notice that the observed intensity distribution in the reciprocal space is strongly anisotropic around each reciprocal lattice point, and moreover, the pattern changes drastically as the reference reciprocal lattice point is changed. (see Fig. 1). These characteristics have certain similarities to the so-called "Huang scattering",[10–12] that is, the scattering due to a single impurity introduced into an elastic medium. We shall apply the concept of Huang scattering to interpret the diffuse scattering in question.

The application has been carried out as follows. In $Fe_3O_4$, there are fluctuating valence electrons above $T_V$. Therefore, we dare to assume that the excess valence electrons essentially play the role of "impurities" in the present case, although the impurities are extremely abundant in the crystal. Further, we assume that local charge neutrality within the unit cell is satisfied in the temperature range under investigation.

Let us consider the symmetry properties of the charge density fluctuation on the octahedral sites in the primitive unit cell. We take the following scalar quantity as the basis function to express the charge fluctuations. $\delta\rho_i$ is the excess charge density over the average value on the $i$th site, $i = \text{I}$, II, III, IV. Owing to the interaction between the charge density on the four equivalent sites (shown in Fig. 2), the possible charge-density fluctuations will be suitably symmetrized according to the symmetry properties of the point group $\bar{4}3m$. Following the conventional procedure, we can construct the basis functions each of which belongs to one of the irreducible representations of the group $\bar{4}3m$:

$$\psi_0 = \delta\rho_{\text{I}} + \delta\rho_{\text{II}} + \delta\rho_{\text{III}} + \delta\rho_{\text{IV}}\,,$$

$$\psi_1 = \delta\rho_{\text{I}} - \delta\rho_{\text{II}} + \delta\rho_{\text{III}} - \delta\rho_{\text{IV}}\,,$$

$$\psi_2 = \delta\rho_{\text{I}} - \delta\rho_{\text{II}} - \delta\rho_{\text{III}} + \delta\rho_{\text{IV}}\,,$$

$$\psi_3 = \delta\rho_{\text{I}} + \delta\rho_{\text{II}} - \delta\rho_{\text{III}} - \delta\rho_{\text{IV}}\,.$$

Among these, we can rule out the totally symmetric function $\psi_0$ as a possible charge-density mode because this does not satisfy the assumption of local charge neutrality,

$$\sum_i \delta\rho_i = 0\,, \quad i = \text{I, II, III, IV}.$$

The remaining three functions belong to the triply degenerate $\Gamma_{15}$ representation. The charge-density distribution represented by one of these functions ($\psi_3$) is depicted in Fig. 2.

Similarly, we construct the possible atomic displacement field with the suitable symmetry of $\Gamma_{15}$ as follows, where we have taken into account only

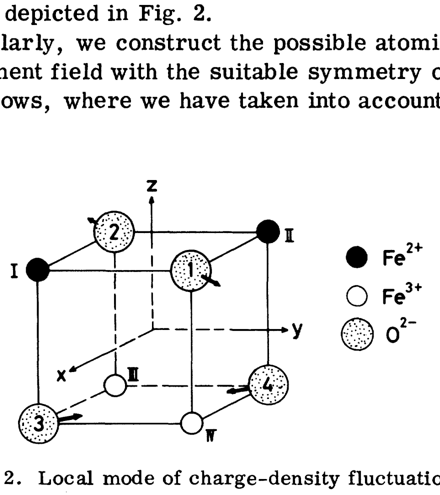

FIG. 2. Local mode of charge-density fluctuation accompanied by small displacements of neighboring oxygens which belongs to the $\Gamma_{15}$ representation. This coupled complex is called a molecular polaron.

the displacements of the oxygen ions for simplicity:

$$\begin{aligned} Q_1 &= (u_{1y}+u_{1z}) + (u_{2y}-u_{2z}) \\ &\quad - (u_{3y}+u_{3z}) - (u_{4y}-u_{4z}), \\ Q_2 &= (u_{1z}+u_{1x}) - (u_{2z}-u_{2x}) \\ &\quad + (u_{3z}-u_{3x}) - (u_{4z}+u_{4x}), \\ Q_3 &= (u_{1x}+u_{1y}) - (u_{2x}+u_{2y}) - (u_{3x}-u_{3y}) + (u_{4x}-u_{4y}), \end{aligned}$$

where $u_{\mu x}$ means the $x$ component of the displacement of the $\mu$th oxygen.

There will be strong linear coupling between the charge-density modes ($\psi_1$, $\psi_2$, $\psi_3$) and the atomic displacement modes ($Q_1$, $Q_2$, $Q_3$) through the electrostatic and other interactions. This leads to the existence of a coupled charge-density-displacement complex belonging to $\Gamma_{15}$. The pattern of the coupled complex is illustrated in Fig. 2. Such a complex may be called a "molecular polaron", since it is considered to be constructed of single-site self-trapped electrons or the simplest of small polarons. Recently, Lakkis *et al.*[13] proposed a concept of "bipolaron" which characterizes a bound state of two electrons accompanied by pairing of ions, in connection with the metal-insulator transition in $Ti_4O_7$. Molecular polaron seems to be essentially the same concept as bipolaron.

Once such a molecular polaron is formed, it would be able to sustain itself for a substantial time interval before eventually changing its state either by hopping to a neighboring site, or by dissociating into independent small polarons by thermal agitation. We assume that the lifetime of a molecular polaron is longer than the inverse frequency of elastic waves in the crystal. Then, each molecular polaron will induce a strain field in the elastic medium whose pattern is determined by the property of the "double force" produced by the molecular polaron. That is, each molecular polaron is "dressed" by a characteristic strain field, and the strain can follow the hopping motion of the central molecular polaron.

Thus, we arrive at the following model describing the system at higher temperatures, $T >> T_V$; there is a random distribution of molecular polarons in the crystal. They are hopping through the crystal independently, and each molecular polaron is inducing an instantaneous strain field around it just as a static impurity does.

## III. HUANG SCATTERING

Based on the model illustrated in Sec. II, we consider that the observed diffuse streaks should be Huang scattering due to the strain fields induced by independent molecular polarons.

The general expression for the cross section of Huang scattering is given elsewhere.[10–12] It is expressed in terms of the elastic constants of the medium and the double-force tensor characterizing the force field produced by an impurity as follows:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{Huang}} = N(|F(K)|^2/V_c^2)|\vec{K}\cdot D^{-1}\cdot \underline{P}\cdot\vec{q}|^2,$$

$$D=\vec{q}\cdot\underline{C}\cdot\vec{q}, \quad \vec{q}=\vec{K}-\vec{K}_h.$$

Here the following notation is used:

$\underline{C}$: fourth rank tensor of elastic constants,
$\vec{K}$: scattering vector of neutrons,
$\vec{K}_h$: reciprocal lattice vector closet to $K$,
$V_c$: unit cell volume,
$N$: number of impurities,
$\underline{P}$: double-force tensor produced by an impurity,
$F(\vec{K})$: structure factor of the undistorted structure.

The matrix element of the double-force tensor is defined by

$$P_{ij}=\sum_{\nu} f_i^\nu u_j^\nu, \quad i,j=x,y,z$$

where $\vec{f}^\nu$ is the force acting at the position $\vec{u}^\nu$. In the present case it is readily shown that the tensor describing the double force produced by a molecular polaron depicted in Fig. 2 ($\psi_3 - Q_3$) is given by

$$\vec{P}=p_0\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Here $p_0$ is a constant which is considered to be a scalar parameter in the present treatment. The tensors corresponding to the other two cases ($\psi_1 - Q_1$ and $\psi_2 - Q_2$) are easily obtained by cyclic permutation of the $(x,y,z)$ coordinates. The elastic constants of magnetite are given by Moran and Luthi[14] and Kino.[15] Making use of these values along with the above expression for the double-force tensor, and superimposing the scattering cross sections due to independent polarons in the states $\psi_1$, $\psi_2$, and $\psi_3$, we can calculate the intensity of Huang scattering from the whole system explicitly.[16] Some of the results are summarized in Fig. 3. When compared with the patterns given in Fig. 1, the calculated results seem to show overall agreement. However, there are several noticeable points: (i) In the experimental pattern around the $(HH0)$ type of lattice points in Fig. 1(a), the directions of elongation of the contours are along the ⟨100⟩ directions, while in the calculated contours they are definitely off these symmetric directions. (ii) The experimental pattern around the $(2H, H, 0)$ type of lattice points shows a simple

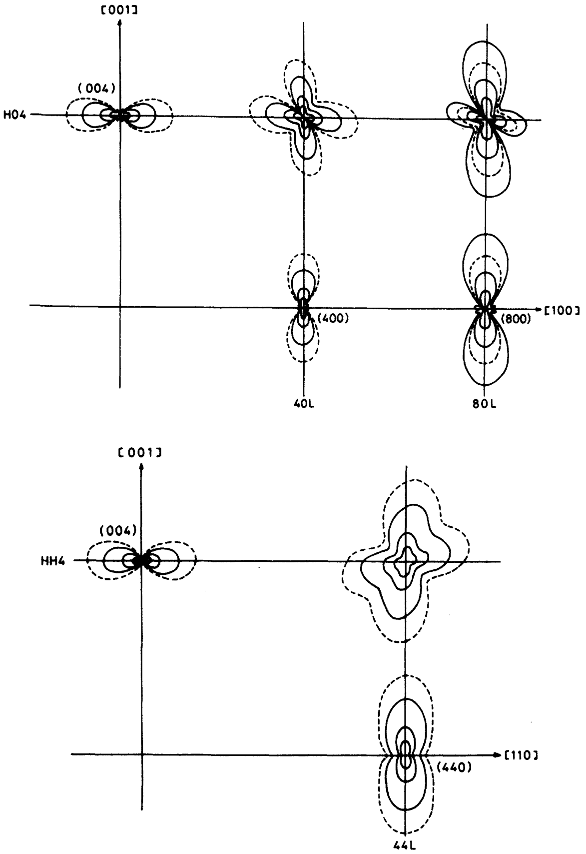

FIG. 3. Calculated intensity distributions of the Huang scattering in the two zones corresponding to Fig. 1.

ellipse, while in the calculation there are minor lobes sticking out in the direction of about 14° off the symmetric [$\bar{1}$00] direction. Therefore, in order to verify the molecular polaron model, it is important to investigate the distribution of the diffuse scattering at various types of reciprocal lattice points more precisely and to check the existence of such characteristics seen in the calculated patterns.

## IV. EXPERIMENTAL RESULTS

We reexamined the diffuse scattering distributions in more detail. Measurements were carried out on a single crystal provided by the Chikazumi laboratory at the University of Tokyo. The sample has a cylindrical shape with the axis of the cylinder parallel to the [010] axis, and it is 1 cm in diameter and 1.5 cm in height. It was mounted in a cryostat with the [010] axis vertical. The observations were made mainly at $T = 150$ K. This temperature was chosen so that we could observe strong enough diffuse intensity while avoiding the effect of the development of correlations between molecular polarons.

The measurements were carried out on a triple-axis spectrometer located at the High Flux Isotope Reactor of the Oak Ridge National Laboratory. The (002) and (101) planes of Be crystals were used as monochromator and analyzer. All measurements were carried out with a neutron energy of 12 THz (49.6 meV) and with a beam collimation of 20′ before and after the samples. With this high energy, higher-energy contamination of the incident beam was negligible owing to the very low flux of neutrons with energies above 200 meV in the reactor spectrum. Since we wanted to confine our attention to the intensity of elastic scattering, the use of an energy analyzer in the scattered beam enabled us to eliminate the inelastic scattering from being measured.

The observed distributions of diffuse scattering at 150 K around (8 0 8), (8 0 4), and (8 0 0) are given in Figs. 4–6, respectively. We see that they definitely reproduce the important characteristics which we noticed in the calculated patterns. That is: (i) around (8 0 8), the direction of maximum intensity is off the ⟨100⟩ directions. This is more clearly seen in Fig. 7(a), which gives the profiles of the intensities scanned through (7.5, 0, $8-\zeta$) and ($8+\zeta$, 0, 7.5). The deviations of the peaks are consistent with the calculated peak positions indicated by the arrows. (ii) Around (8 0 4), the minor lobes are observed. As for the intensity profiles, it is remarkable that the asymmetric deviations of the peaks with respect to the two scans, along

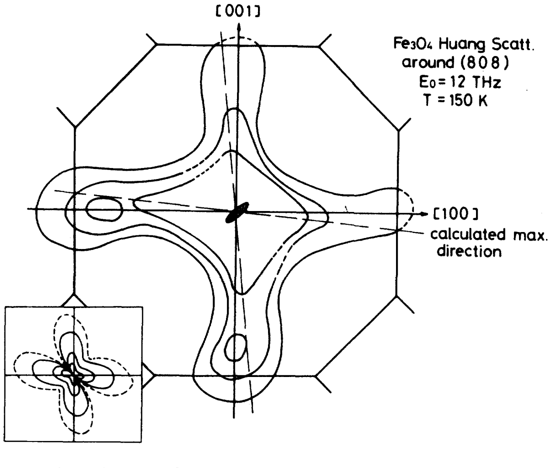

FIG. 4. Observed intensity distribution of the neutron quasielastic scattering around the (8 0 8) reflection. The small ellipse at the lattice point indicates the size of the experimental resolution. The inset figure is the calculated contour to be compared with the observed pattern. The dashed lines show the direction of maximum intensity of the calculated contour.

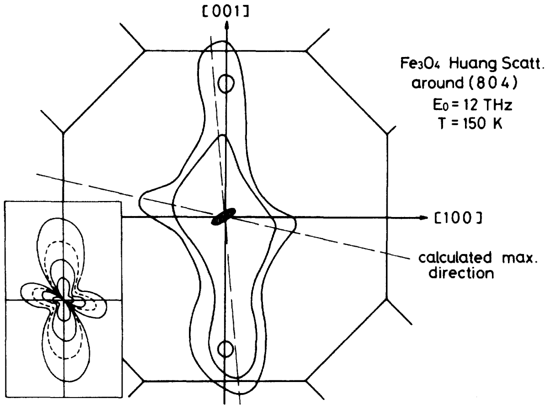

FIG. 5. Observed intensity distribution of the neutron quasielastic scattering around the (8 0 4) reflection. The dashed lines indicate the direction of maximum intensity of the calculated contour given in the inset.

$(7.5,\ 0,\ 4-\zeta)$ and $(8+\zeta,\ 0,\ 3.5)$, are in quantitative agreement with the calculated results [see Fig. 7(b)]. Thus, in the region of $|\vec{q}| < 0.5a^*$, the observed results are in agreement with the calculations based on the model of "dressed molecular polarons".

In the outer regions, $|\vec{q}| \geq 0.5a^*$, there are significant deviations from the calculations. The outer lobes of the intensity contour around (8 0 8) seem to have a tendency to restore the symmetry around the ⟨100⟩ directions. Particularly important is the fact that maxima in the diffuse scattering are observed at $\vec{q} = (0.8,\ 0,\ 0)$ and $q = (0,\ 0,\ 0.8)$. The existence of these maxima has already been pointed out by Shapiro *et al.* They performed extensive investigations including the temperature dependence of the intensity profile scanned along [100], and clearly observed the increase of the "humps" at $\vec{q} = (0.8,\ 0,\ 0)$ as the temperature is decreased towards $T_V$ (Ref. 17). As will be discussed in Sec. V, we conjectured that this is due to the effect of interactions between individual molecular polarons which eventually give rise to the cooperative ordering at the Verwey transition temperature. In order to obtain a more complete agreement with the simple model calculation, we tried to reduce the effect of correlation by raising the temperature. The extra peaks did decrease as the temperature was raised. However, the intensity of the Huang scattering itself also decreased rapidly with increasing temperature, which limited the highest temperature at which we could make these measurements to about 190 K. We carried out measurements around (8 0 8) at 190 K. The results, however, did not show any substantial improvement from those in Fig. 4.

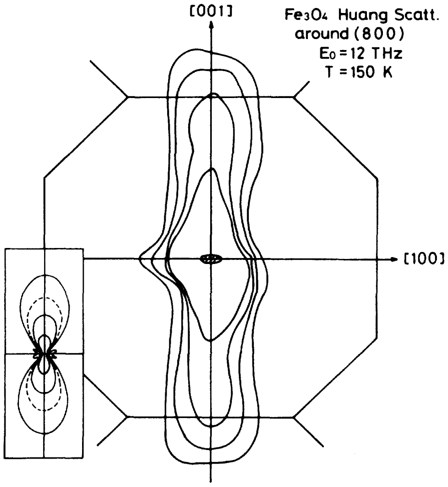

FIG. 6. Observed intensity distribution of neutron quasielastic scattering around the (8 0 0) reflection. In this case, the symmetry with respect to the ⟨100⟩ direction is retained.

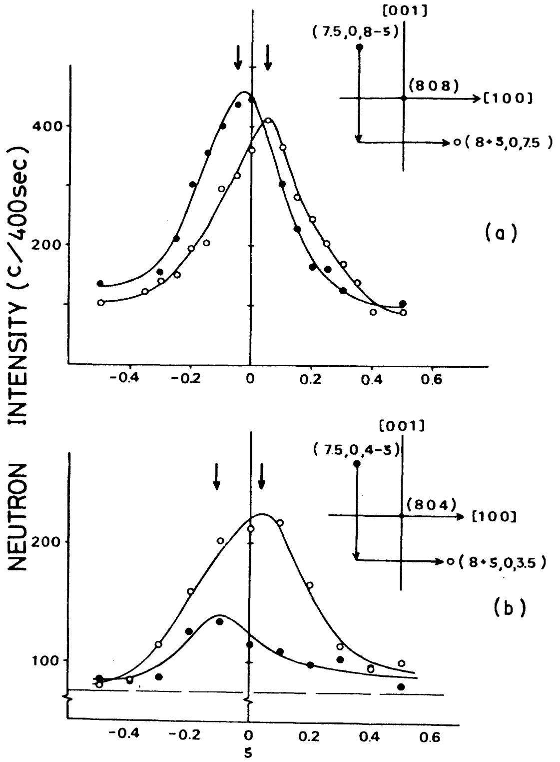

FIG. 7. (a) Observed intensity profiles of the quasielastic scattering around the (8 0 8) reflection. The inset shows the lines along which the scans were made. Solid curves are drawn through experimental points for guides to the eye. The arrows indicate the calculated positions of the maximum intensity for the corresponding scans. (b) Observed intensity profiles of the quasielastic scattering around the (8 0 4) reflection. The inset and the arrows give similar information as in (a). The dashed line gives the background level.

## V. DISCUSSION

From the model developed above, the Verwey transition may be viewed as the ordering process of dressed molecular polarons. In order to discuss the phase transition itself, however, the treatment developed in Sec. II is inadequate in the following two points.

(i) Neglect of the interaction between molecular polarons. We have calculated the diffuse scattering due to randomly distributed (independent) dressed polarons. Actually, however, there will be finite interactions between neighboring polarons either through direct coupling such as the electrostatic interaction or through indirect coupling via strains. Therefore, as the temperature is decreased towards the transition point, a spatial correlation with a particular wavelength develops between molecular polarons, which gives rise to diffuse peaks at the corresponding wave vector in the diffraction pattern.

(ii) Neglect of exact translational symmetry of the lattice. The calculation of the Huang scattering is based on the assumption that the crystal lattice can be approximated by an elastic medium. This is valid for long-wavelength displacement fields (or in the $\vec{q} \simeq 0$ region of the reciprocal space). On the other hand, the observed diffuse intensity extends to the boundaries of the first Brillouin zone. It is not surprising that there are significant differences between the observations and the calculated Huang scattering in the region of $|\vec{q}| \geq 0.5a^*$ even in the absence of correlation effects.

It is important that we observed extra peaks at $\vec{q}_0 = (0.8,\ 0,\ 0)$ [and its equivalence, $\vec{q}_0 = (0,\ 0,\ 0.8)$]. We consider that, as commented in (i), these are due to the correlated fluctuation of molecular polarons, which implies that the interpolaron interaction tends to stabilize a charge-density wave with the wave vector $\vec{q}_0 \simeq (0.8,\ 0,\ 0)$. Since the inverse of $|\vec{q}_0|$ does not seem to give a simple multiple of the fundamental cubic lattice constant, we may say that the Verwey transition is inherently an incommensurate phase transition.[18]

Another important point in connection with the comment (ii) is that $q_0$, the wave vector of the large-amplitude fluctuation, is far from the zone center, or is even closer to the zone boundary. It is definitely inappropriate to discuss the physical properties in this $\vec{q}$ region on the elastic continuum model. Therefore, in order to investigate the ordering process properly, we have to adopt a microscopic standpoint by describing the displacement field by the coordinates of individual atoms, or the phonon field, instead of the strain field of an elastic continuum.

Microscopic treatments with a close analogy to the present system have been developed in the problems of cooperative Jahn-Teller ordering[19–21] as well as the impurity ordering in metals.[22,23] In fact, these systems are formally identical, being treated in the same framework of the "coupled pseudospin-phonon" system.[24] In this connection, it is worthwhile to notice that recently an incommensurate Jahn-Teller ordering has been reported to take place in some of the hexanitrocuprate complexes.[25–27] Mori *et al.*[28] studied x-ray and neutron scattering from these substances and observed similar phenomena to those reported in the present investigation. They analyzed the experimental results on a microscopic basis and discussed the origin of the incommensurate Jahn-Teller ordering in terms of the electron-phonon coupling.[29] One of the possible extensions of the present investigation is to follow the same procedure in order to understand the microscopic mechanism of the Verwey transition in magnetite.

Another important extension which should be carried out is the investigation of the dynamical behavior of the molecular polaron. In the calculation of Huang scattering carried out in Sec. III, we have simply superimposed the effects due to $\psi_1 - Q_1$, $\psi_2 - 0_2$, and $\psi_3 - Q_3$ with equal weight. However, this does not mean that the molecular polaron takes on these three states as the stationary states. On the contrary, we consider that the true ground state would be a vibronic state. That is, when we express the vibrational state of the "molecule" as a vector in the three-dimensional Hilbert space spanned by the $Q_1$, $Q_2$, and $Q_3$ coordinates, the vector is "rotating" rapidly on the surface of minimum potential and the electronic state is adiabatically following this motion. This is supported by the observation of the Mössbauer effect, where no splittings of spectra due to different site symmetry within the octahedral site above $T_V$ has been reported, implying that each octahedral site is equivalent within the frequency resolution of Mössbauer spectra ($10^7\ \mathrm{sec}^{-1}$). As far as Huang scattering is concerned, such a dynamical behavior would have little effect on the intensity distribution, as is discussed in the case of the dynamical Jahn-Teller effect in hexanitrocuprate.[27] In order to obtain information on the dynamical behavior of molecular polarons, experiments with various characteristic frequency ranges should be carried out.

## VI. CONCLUSIONS

In conclusion, we propose a model of molecular polaron which describes the properties of the valence fluctuations in magnetite above $T_V$. A molecular polaron is assumed to be a complex of two excess electrons and a local displacement mode of oxygens within the fcc primitive cell. At sufficiently high temperatures, there is a random distribution of molecular polarons which are fluctuating independently by hopping through the crystal or by dissociating into smaller polarons. The lifetime of each molecular polaron is long enough to induce an instantaneous strain field around it. Based on this model, the neutron diffuse scattering cross section due to independent dressed molecular polarons was calculated. In order to verify the validity of the model, precise measurements of quasielastic scattering of neutrons were carried out at 150 K. In the region of $|q| < 0.5a^*$, the observed results show the characteristics predicted by the model calculation.

## ACKNOWLEDGMENTS

The authors wish to thank Professor Chikazumi of the University of Tokyo for providing excellent single crystals of magnetite. Thanks are due to S. M. Shapiro, M. Iizumi, and G. Shirane of Brookhaven National Laboratory for their valuable discussions. One of the authors (Y. Y.) wishes to express his sincere thanks to Dr. W. C. Koehler and to the Solid State Division, Oak Ridge National Laboratory for facilitating the neutron scattering experiments at the HFIR reactor. Research for this project was sponsored in part by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

---

[1] E. J. W. Verwey and P. W. Haayman, Physica 8, 979 (1941); E. J. W. Verwey, P. W. Haayman, and N. C. Romeijin, J. Chem. Phys. 15, 181 (1947).

[2] As the review, refer to S.Chikazumi, in *Proceedings of the 21st Annual Conference on Magnetism and Magnetic Materials*, edited by J. J. Becker and G. H. Lander (AIP, New York, 1976), p. 382; G. Shirane, in *Electron-Phonon Interactions and Phase Transitions*, edited by T. Riste (Plenum, New York and London, 1977).

[3] T. Yamada, K. Suzuki, and S. Chikazumi, Appl. Phys. Lett. 13, 172 (1968).

[4] E. J. Samuelson, E. J. Bleeker, L. Dobrzynski, and T. Riste, J. Appl. Phys. 39, 1114 (1968).

[5] Y. Yamada, in *Proceedings of the 20th Annual Conference on Magnetism and Magnetic Materials*, edited by C. O. Graham and G. H. Lander (AIP, New York, (1975), p. 79.

[6] Y. Fujii, G. Shirane, and Y. Yamada, Phys. Rev. B 11, 2036 (1975).

[7] S. M. Shapiro, M. Iizumi, and G. Shirane, Phys. Rev. B 14, 200 (1976).

[8] K. Chiba, K. Suzuki, and S. Chikazumi, J. Phys. Soc. Jpn. 39, 839 (1975).

[9] Y. Yamada, M. Mori, Y. Noda, and M. Iizumi, Solid State Commun. 32, 827 (1979).

[10] M. A. Krivoglaz, *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969).

[11] P. H. Dederichs, J. Phys. F 3, 471 (1973).

[12] H. Trinkaus, Phys. Status Solidi b51, 307 (1972).

[13] S. Lakkis, C. Schlenker, B. K. Chakraverty, R. Buder, and M. Marezio, Phys. Rev. B 14, 1429 (1976).

[14] T. J. Moran and B. Luthi, Phys. Rev. 187, 710 (1969).

[15] Y. Kino, private communication.

[16] We have assumed that each molecular polaron is independent, whence the total scattering intensity is obtained by simply superimposing the cross sections due to the polarons in the states $\psi_1$, $\psi_2$, and $\psi_3$ with equal weight.

[17] Shapiro *et al.* analyzed this diffuse intensity in terms of one-dimensional short-range order of the same displacement pattern as given in Fig. 2. In the region of $q \geqslant 0.5$, they found good agreement with the experimental results along the [100] direction. In their treatment, however, the effect of the induced strain field was not taken into account. This entails the lack of the intensity distribution around the $\Gamma$ points. We may interpret that they calculated the correlation between bare (undressed) polarons.

[18] This possibility was first pointed out by M. Iizumi, in *Proceedings of the International Conference on Modulated Structures*, edited by J. M. Cowley, J. B. Cohen, M. B. Salamon, and B. J. Wuensch (AIP, New York, 1979), p. 184.

[19] J. Kanamori, J. Appl. Phys. 31, 14S (1960).

[20] M. Kataoka and J. Kanamori, J. Phys. Soc. Jpn. 32, 113 (1972).

[21] R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. R. Soc. London A328, 217 (1972).

[22] H. E. Cook and D. DeFontaine, Acta Metall. 17, 915 (1969).

[23] A. G. Khachaturyan, Kristallografiya 10, 303 (1965) [Sov. Phys.—Crystallogr. 10, 248 (1965)].

[24] In the present problem the pseudospin variable stands for the triply degenerate electronic states of molecular polarons.

[25] Y. Noda, M. Mori, and Y. Yamada, Solid State Commun. 19, 1071 (1976).

[26] M. Mori and Y. Yamada, J. Phys. Soc. Jpn. 46, 1673 (1979).

[27] Y. Noda, M. Mori, and Y. Yamada, J. Phys. Soc. Jpn. 45, 954 (1978).

[28] M. Mori, Y. Noda, and Y. Yamada (unpublished).

[29] M. Mori, Y. Noda, and Y. Yamada (unpublished).