

Charge-ordering transition and incommensurate antiphase structure of Fe_2BO_4 as seen via transmission electron microscopy

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The nature of the charge ordering (CO) in Fe_2BO_4 was carefully examined by *in situ* TEM observations from 360 K down to 20 K. An incommensurate structural modulation with the wave vector $q=(1/2,0,\epsilon)$ becomes plainly visible in association with the CO transition at $T_{\text{CO}}\approx 340$ K. Careful structural analysis suggests that this incommensurate structure originates from a well-defined $\text{Fe}^{2+}/\text{Fe}^{3+}$ ionic order along the FeO_6 octahedral ribbons (in the a -axis direction) and from a discommensurate antiphase stripe order along the c -axis direction. The average periodicity of antiphase stripes changes notably with lowering temperature and, via certain intermediate states, toward a superstructure phase with modulation wave vector of $q=(1/2,0,0)$ at ~ 150 K in association with a magnetic phase transition.

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The tendency in transition-metal oxides for charges to order in stripes is a significant phenomenon that is of particular interest for its possible relevance to many notable physical phenomena, such as colossal magnetoresistance^{1,2} and high-temperature superconductivity.^{3,4} Fe_3O_4 , one of the first mixed-valence materials, has been found to possess unusual electronic properties.^{5,6} Selective replacement of the tetrahedral Fe^{3+} in Fe_3O_4 by B^{3+} gives the oxyborate $\text{Fe}^{2+}\text{Fe}^{3+}\text{BO}_4$, which has a warwickite-type structure in which boron bonds to only three of the four oxygen atoms. Numerous experimental investigations have revealed that there are two important phase transitions in Fe_2BO_4 : a charge-ordering (CO) transition at around $T_{\text{CO}}=340$ K in association with a monoclinic to orthorhombic structural phase transformation, and a magnetic transition at about $T_c=150$ K, below which the magnetic structure is found to be almost antiferromagnetic with a small ferromagnetic moment of $0.03\mu_B$ per Fe atom in a 0.05 T field.⁷ Structural investigations have shown a clear incommensurate CO below T_{CO} .⁸ Actually, structural features for the incommensurate (or nearly commensurate) phases have been studied in a variety of materials in past decades—in particular, the charge-ordered domains and discommensurations in the charge-density-wave (CDW) systems.^{9,10} Theoretical study has demonstrated that the average periodicity (L) of discommensurations is related to the incommensurability (ϵ) through the simple relationship $L=2\pi/p\epsilon$, where p is the order of commensurability.¹¹ However, our recent transmission electron microscopy (TEM) study shows that the incommensurate CO modulation in Fe_2BO_4 exhibits a different nature from that of the CDW systems. High-resolution TEM observations often reveal the coexistence of mutual periodic antiphase stripes, the occurrence ratio of the differential antiphase structures changes visibly with temperature, which results in a notable temperature dependence of incommensurability from T_{CO} down to T_c . Previously, the mechanisms for the CO phenomenon in Fe_2BO_4 was analyzed based on electrostatic repulsions between the charges^{7,12} and the strains arising from electron-lattice interactions.¹³ Different localized electronic states have been discussed to account for the alternation of Mössbauer spectra which reveal a visible Fe valence separation at

low temperature.^{7,8,14} In this Rapid Communication, we will report a TEM study of the CO transition in Fe_2BO_4 . We herein present a direct evidence that the incommensurate modulation in Fe_2BO_4 is actually two-dimensional in nature, i.e., a well-defined $\text{Fe}^{2+}/\text{Fe}^{3+}$ order along the FeO_6 octahedral ribbons (the a -axis direction) and a discommensurate antiphase structure along the c -axis direction.

Both polycrystalline and single crystal samples of Fe_2BO_4 were used in the present Rapid Communication. Polycrystalline samples were synthesized by conventional solid-state reactions as reported in Ref. 15. A stoichiometric amount of B_2O_3 , guaranteed reagent grade Fe_2O_3 and Fe were fully mixed in an agate mortar and heated in a sealed quartz tube at 1000 °C for 48 h. Single crystals of Fe_2BO_4 were grown from a flux of PbO and PbF_2 as reported in Refs. 16 and 17. These samples were first well characterized by measuring microstructural and physical properties; magnetic features were found to be in good agreement with the data reported in previous literatures.^{15,18,19} The specimens for TEM observations were prepared by polishing, dimpling, and then ion milling. Microstructure analysis and *in situ* TEM observations were performed on Tecnai F20 and H-9000NA transmission electron microscopes, both equipped with low-temperature holders.

In order to understand the microstructure features of Fe_2BO_4 in the CO states below T_{CO} , we performed an extensive structural investigation by means of selected-area electron-diffraction and high-resolution TEM. Due to its fine spatial resolution, TEM has played a very important role in the structural characterization of the local CO states. In comparison with the x-ray and neutron diffraction revealing average structural features, its capability to obtain both structural and chemical information from an area as small as a few nanometers makes it a powerful tool for microstructure analysis that is, as yet, little exploited in present system. Figures 1(a)–1(d) show a series of electron-diffraction patterns taken along the relevant [100], [010], [001], and [101] zone-axis directions at room temperature. The main diffraction spots with relatively strong intensity can be well indexed by a monoclinic cell with $P2_1/c$ symmetry, its lattice parameters, consistent with the x-ray diffraction results, are a

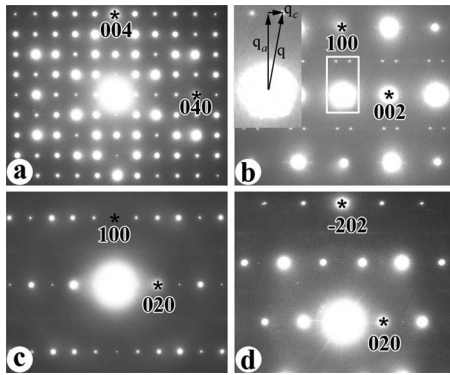


FIG. 1. Electron diffraction patterns at room temperature taken along (a) [100], (b) [010], (c) [001], and (d) [101]. The incommensurate modulation is written as $q=q_a+q_c$ as shown in inset of (b), $q_a=(1/2,0,0)$ and $q_c=(0,0,\varepsilon)$.

$=3.168 \text{ \AA}$, $b=9.384 \text{ \AA}$, $c=9.250 \text{ \AA}$, and $\beta=90.22^\circ$. In this work, we made no attempts to systematically measure the monoclinic distortion through this CO phase transition due to the very small angular distortion for the average structure across the T_{CO} transition, i.e., $\beta=90^\circ$ in the orthorhombic phase and $\beta=90.22^\circ$ in monoclinic phase.^{7,20} On the other hand, the most striking structural phenomenon observed below T_{CO} is the appearance of a series of superlattice satellite spots aligned with the main diffraction spots, as clearly illustrated in Fig. 1(b). Careful examination reveals that these satellite spots in general are only clearly visible in the a^*-c^* plane of reciprocal space and can be characterized by a unique modulation wave vector, $q=(1/2,0,\varepsilon)$, where ε is the incommensurate parameter and depends distinctly on temperature as discussed in the following context. Experimental measurements show that ε has an average value of ~ 0.32 at room temperature and often varies slightly from one area to another within the range of 0.30–0.34—similar variations were also observed in samples prepared by different methods.

Previously, there have been a number of structural studies of Fe_2BO_4 , mainly by neutron^{14,21} and x-ray diffraction,^{8,16} these works mainly focused on the monoclinic CO phase of $2a \times b \times c$ below $T_c=150 \text{ K}$. This superstructure phase can be well interpreted by a long-range order from the alternating $\text{Fe}^{2+}/\text{Fe}^{3+}$ arrangement on the four edge-sharing FeO_6 octahedral chains along the a -axis direction. We actually spent considerable time trying to characterize the CO behaviors between $T_{CO}=340 \text{ K}$ and $T_c=150 \text{ K}$ in a few well-characterized samples and saw certain interesting structural phenomena in connection with a discommensurate antiphase structure of the CO state along the c -axis direction, which shows a notable thermal dynamic nature and changes markedly within the temperature range between T_{CO} and T_c .

In order to directly observe the charge-order behaviors in the present system, we carried out an extensive investigation by high-resolution TEM on the incommensurate structural modulation within the a - c plane. However, it was found that the CO modulation in thin regions of a crystal is extremely sensitive to the electron beam and often shows clear changes during the TEM observations. Figure 2(a) shows a high-resolution TEM image taken in a relatively thicker area with

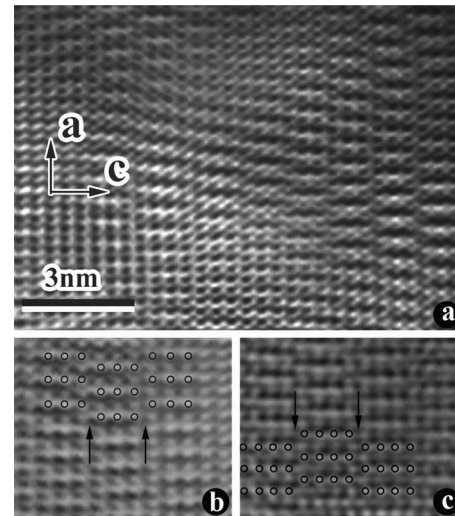


FIG. 2. (a) High-resolution TEM image taken at room temperature, showing the CO and antiphase stripes in a - c plane. (b) and (c) Images of antiphase structures with different local periodicities of $3c$ and $4c$.

a thickness estimated to be 8 nm, clearly displaying the structural features of a Fe_2BO_4 crystal with visible structural modulation. Though this image could not clearly show the detailed atomic structure of the Fe_2BO_4 crystal, we can undoubtedly recognize the rich structural feature resulting from the CO order along FeO_6 chain direction and discommensurate antiphase stripes along the c -axis direction. Our careful examinations suggest that the CO state commonly adopt a well defined $2a$ periodicity corresponding with the Fe^{2+} and Fe^{3+} order along the a -axis direction, and the incommensurability is essentially in connection with the complex feature of the antiphase stripes going periodically along the c -axis direction. For instance, according to our TEM observations at room temperature, the antiphase stripes could have the local periodicities of $3c$ and $4c$, as clearly shown in the images of Figs. 2(b) and 2(c), the coexistence of the antiphase structure could give rise to an average superstructure with the periodicity of $3.2c$, consistent with our diffraction observations at room temperature.

To further characterize the incommensurate structural modulation in the present system, we made a comprehensive examination along several relevant orientations in many areas over the temperature range of 360 K down to 20 K. Remarkably, the *in situ* TEM observations of the a^*-c^* reciprocal plane reveal visible temperature change in the incommensurability. Figure 3(a) shows a series of diffraction patterns illustrating the progressive alterations of the superstructure reflections. Generally, the superstructure reflections appear as weak broad reflections and become detectable as the temperature is reduced below $T_{CO} \approx 340 \text{ K}$, signifying the occurrence of CO in the observed area. Then both the intensity and position of the satellite spots undergo continuous evolutions. Moreover, careful examinations of the periodicity of the structural modulation with lowering temperature suggest that the CO states in the present system, via a few intermediate superstructure phases, go toward the well-defined CO phase of $2a \times b \times c$ at about 150 K. Previ-

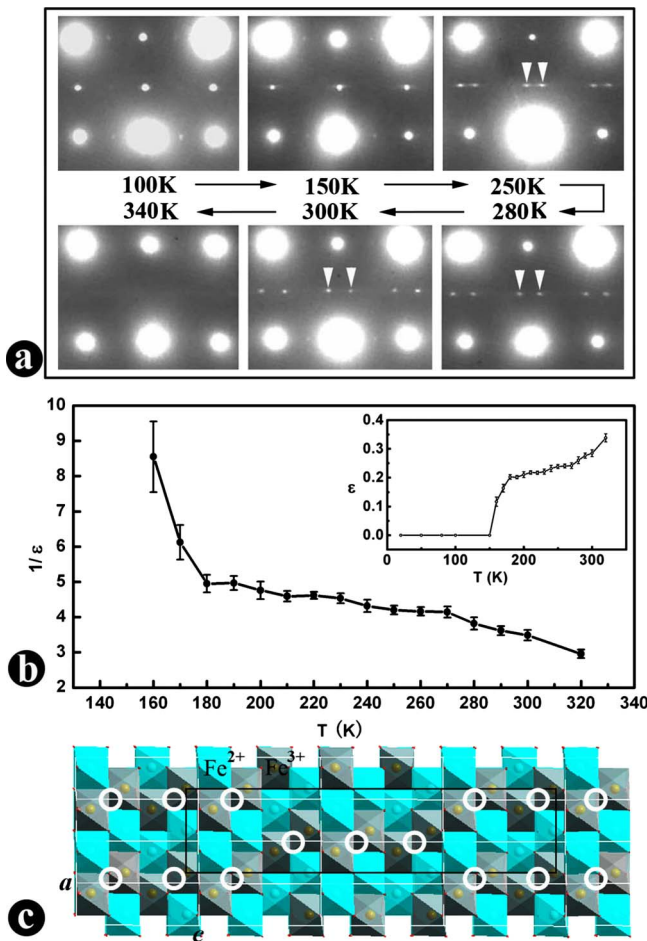


FIG. 3. (Color online) (a) Electron-diffraction patterns taken at different temperatures: 100, 150, 250, 280, 300, and 340 K. Changes in superlattice reflections are illustrated. (b) Temperature dependence of $1/\epsilon$, inset shows the temperature dependence of incommensurate parameter ϵ . (c) Structural model schematically illustrating the Fe^{2+} - Fe^{3+} charge-order and antiphase structures. White lines indicate a unit cell and black frame indicates the superstructures.

ously, this low-temperature monoclinic CO phase was examined by means of x-ray^{8,16} and neutron diffraction¹⁴ to characterize its crystal structural features and magnetic structural phase.

In comparison with experimental magnetic measurements for the Fe_2BO_4 system, it is likely that the magnetic transition at around 150 K occurs in association with the formation of the commensurate phase $2a \times b \times c$. It is known that the CO phenomena in a variety of materials are in correlation with magnetism. For instance, the double exchange process in $\text{La}(\text{Ca})\text{MnO}_3$ (Refs. 22 and 23) requires transfer of a charge carrier (hole) from a Mn^{3+} ion across an intervening oxygen ion to an adjacent Mn^{4+} ion. The magnetic coupling induced by itinerant charge carriers is totally incompatible with the localized charges in a commensurate CO state. Hence, it is also expected that certain electrons in Fe_2BO_4 could divert from Fe^{2+} to Fe^{3+} at around 150 K and result in some change in the “up” and “down” spins lying on structurally inequivalent Fe(1) and Fe(2) and give rise to a ferro-

magnetic moment. In addition, theoretical analysis suggests that, in contrast with the Fe_3O_4 material, the presence of both relatively weak magnetic interaction and frustrated superexchange pathways in Fe_2BO_4 constrains the electron hopping in the paramagnetic structure to a degree, which leads to a lower magnetic ordering temperature (~ 155 K) and a relatively high CO temperature (~ 317 K).⁷

The notable changes in the incommensurability ϵ associated with the antiphase structure along the c -axis direction clearly suggest the existence of complex intermediate phases from valence fluctuation—this fluctuation is not static but dynamic. The continuous alternation of temperature dependence for the incommensurate parameter ϵ implies that the antiphase stripes move easily in the intermediate states due to thermal excitation. Another remarkable structural phenomenon observed in our *in situ* TEM investigations is the presence of a few terraces in the temperature dependence curve of $1/\epsilon$ as shown in Fig. 3(b). Actually, our experimental results obtained from both the cooling and heating runs demonstrate that the incommensurability corresponding to the discommensurate antiphase stripe order along the c -axis direction depends significantly on the temperature—especially, a plateau in the temperature range 270 K down to 180 K is commonly obtained. This fact likely suggests that electron hopping below 270 K is very weak,^{7,8} which means electrons are more localized and the antiphase stripes adopt a relatively steady state. Careful examination suggests that this plateau often contains two or three terraces in association with certain superstructure phases with the periodicities of $L = 4, 4.5$, and $5c$. The inset of Fig. 3(b) shows statistical data obtained from a Fe_2BO_4 crystal in several cooling runs from 340 K down to 20 K, illustrating the presence of three terraces at low temperatures. The antiphase stripe orders at these terrace positions are schematically shown in Fig. 3(c) for $L=3c$, in which the charge order in a single ribbon is clearly illustrated. Though the Coulomb interaction plays the critical role for the charge ordering,⁷ the existence of these intermediate superstructure phases demonstrates that the interaction between the crystal lattice and the local structural distortions also visibly affects the CO behaviors in the present system.^{8,13} As a result, the charge-ordering tendency is particularly pronounced near certain periodicities, where the charge modulation is commensurate with the underlying lattice, as shown in Fig. 3(c).

Moreover, *in situ* TEM observations also reveal certain changes of the intensity of satellite spots with decreasing temperature. Upon cooling from 360 K, the charge-ordering superlattice reflections first become visible just below the $T_{\text{CO}} \sim 340$ K, and then, with decreasing temperature, the intensity of the satellite spots increases rapidly and become clearly visible at about 320 K, below which no clear intensity changes have been detected within the experimental uncertainties. On the other hand, as mentioned above, the CO modulation is extremely sensitive to the electron beam and often shows clear changes during the TEM observations. Therefore, a careful measurement of the superstructure intensity is still in progress. In comparison with the previous experimental results, our TEM observations of the temperature dependence of the incommensurate CO state are fundamentally in agreement with results obtained from a thermoelec-

tric power experiment²⁴ on charge localization at low temperatures, which suggests that the fully realized CO state is reached at the Neel temperature $T_c=150$ K, and a spin ordering seems to be necessary for a complete CO in this system. On the other hand, measurements of Mössbauer spectra on Fe_2BO_4 reveal that no notable electron hopping below 270 K,⁸ and x-ray diffraction suggests that the incommensurability disappears at the same temperature.⁸ We suspect that the inconsistency among the experimental results is very likely caused by sample differences due to fabrication conditions.

In summary, *in situ* TEM observations of the nature of the CO in Fe_2BO_4 reveal a rich variety of structural phenomena from 360 K down to 20 K. Careful TEM examinations while lowering temperature show that this structural modulation in general becomes visible gradually at around $T_{\text{CO}}=340$ K,

via a few intermediate superstructure phases, goes toward the well-defined CO phase of $2a \times b \times c$ at about 150 K. This incommensurate structure is found to consist of a well-defined $\text{Fe}^{2+}/\text{Fe}^{3+}$ ionic order along the FeO_6 octahedral ribbons (the *a*-axis direction) and a discommensurate antiphase stripe order along the *c*-axis direction. The average periodicity of antiphase stripes changes notably within the temperature range of 340 K down to 150 K.

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