

Possible Fe/Cu ordering schemes in the $2a$ superstructure of bornite (Cu_5FeS_4)

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ABSTRACT

Based on magnetic structure and TEM studies of bornite we propose a new $2a$ Fe/Cu ordered superstructure model with symmetry $F\bar{4}3m$ and formula $\text{Cu}_8\text{Fe}_4\text{S}_8$. First principles calculations (LAPW implemented in WIEN97 code) of two Fe/Cu ordering schemes indicate that, at the ground state, the Fe atoms should fill the tetrahedral sites of sulfur atoms in the anti-fluorite cube, and the vacancies are associated with Cu atoms in the zincblende cube of the superstructure. The calculated magnetic moment of iron in the Fe/Cu-ordered structure is about $4 \mu_B$, which was not expected from previous work because bornite has both covalent and metallic bonds that make crystal-field theory inappropriate for explaining the magnetic moment of Fe. High-resolution transmission electron microscopy (HRTEM) image simulations for the newly proposed structure model are much closer to experimental HRTEM images than those for the model proposed by Kanazawa et al. (1978).

INTRODUCTION

According to previous investigations, bornite occurs in three different polymorphs: low-, intermediate-, and high-temperature structural forms. The high-temperature form is stable above 265 °C, and the sulfur atoms form face centered cubic (fcc) closest packing whereas the six metal atoms (five Cu and one Fe) and two vacancies are randomly distributed over the eight tetrahedral sites; thus, each tetrahedral site is statistically occupied by 6/8 metal atom. Between 265 and 200 °C, the vacancies and metal atoms are no longer randomly distributed at the tetrahedral sites, but are ordered at particular tetrahedral sites, which doubles the unit cell compared to the high-temperature form (Morimoto and Kullerud 1961). The middle-temperature form can be regarded as being derived from the zincblende and anti-fluorite structures by alternating these two cubes along the three crystallographic axes, thus resulting in the $2a$ superstructure. On cooling below 200 °C, the middle-temperature form is believed to transform to a $2a4a2a$ superstructure with space group $Pbca$ (Koto and Morimoto 1975). In this structure, the vacancies are further ordered along one direction to double the size of the unit cell compared with that of middle-temperature structural form. Though much effort has been expended in trying to explain superstructures in the bornite (Cu_5FeS_4)-digenite (Cu_9S_5) series, fundamental problems still remain. The low-temperature structures of the series and the mechanisms of modulation remain uncertain because of the following challenges: (1) the lack of suitable samples; (2) the large unit cells of the superstructures; (3) anomalous diffraction (non-space-group extinctions); (4) the difficulty of distinguishing Fe from Cu in X-ray and electron diffraction experiments, and (5) non-stoichiometry and structural heterogeneity of samples. One of these fundamental problems is the Fe/Cu ordering in the superstructures of bornite. In the determined structure models, Fe/Cu ordering was neglected and all metal atoms treated as the

same, because Fe and Cu have very similar X-ray and electron scattering factors, though Koto and Morimoto (1975) suggested that Fe could be ordered at sites 4 and 5 in their model. However, the earlier models may not completely represent the true structures of bornite, since our TEM work and magnetic studies reveal that the iron and copper atoms are likely ordered in the low-temperature structures (Ding 2002).

PREVIOUS RESEARCH

Previous experimental results indicate that Fe/Cu are possibly ordered in the low temperature structures of bornite. However, due to the heterogeneity of the samples, the Fe/Cu ordered superstructures of bornite could not be completely determined. In this paper, the consideration of possible Fe/Cu ordered schemes of bornite $2a$ superstructures are motivated by the following brief review of the previous investigations on bornite and their implications.

TEM studies

The most direct evidence for the heterogeneity of bornite is our HRTEM work (Ding 2002). We did not observe the purported $Pbca$ phase but did observe the coexistence of $4a + 2a$ and $6a + 2a$ superstructure domains at room temperature (see Fig. 1). The frequency of observing the various superstructures is $2a > 4a > 6a > 1a$. Thus, the $2a$ and $4a$ structures are probably the most abundant phases, and this could be the reason that the $2a4a2a Pbca$ phase was determined by X-ray study as the low-temperature structure form of bornite, since an apparent $2a4a2a$ diffraction pattern can be produced by superimposing the $2a$ and $4a$ diffraction patterns.

Magnetic structure and X-ray diffraction studies

Allias and Wyart (1965), Townsend et al. (1977), Collins et al. (1980), and Jagadeesh et al. (1981) studied the magnetic structure of bornite from 300 to 4 K using Mössbauer spectra, neutron powder diffraction, and measurements of magnetic

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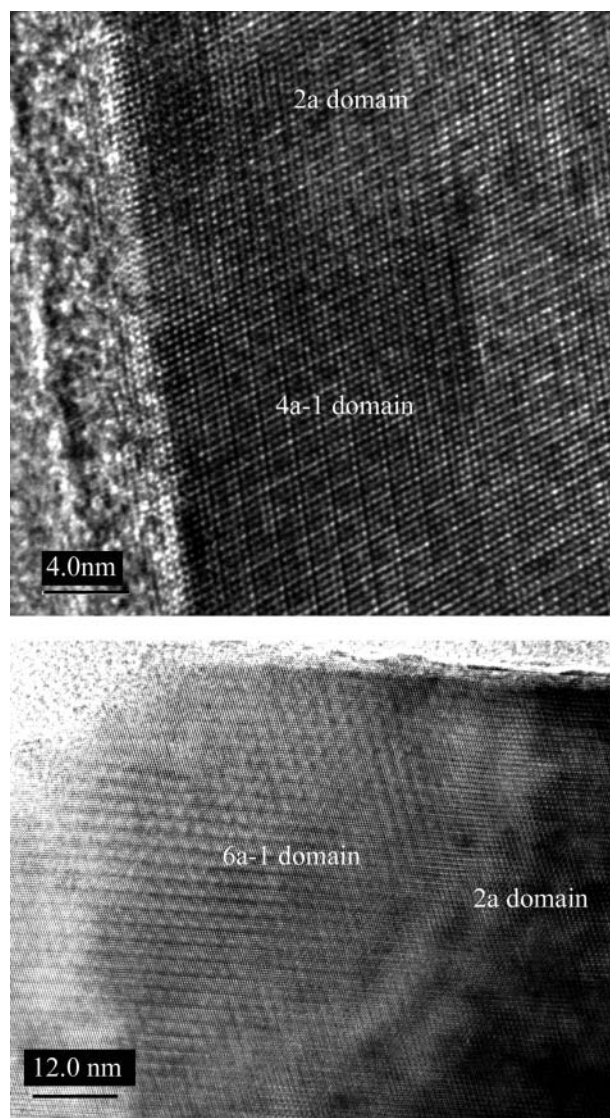


FIGURE 1. Experimental HRTEM images from two different grains of “single-crystal” bornite from Hamley mine, Moonta, South Australia, using a Philips CM300 FEG STEM. (a) HRTEM image shows a 4a-1 domain coexisting with a 2a domain. (b) HRTEM image shows a 6a-1 domain coexisting with the 2a superstructure.

susceptibility.

All of these studies found that bornite remains paramagnetic above 80 K, but below this temperature it has two magnetic ordering transitions occurring at about 67 K (Townsend reported 76 K) and 8 K. At 67 K, bornite became antiferromagnetic, and the magnetic moment changed with temperature. The studies had difficulty explaining the second transition, though Collins et al. (1980) thought it might be related to the electron spin rotation.

Both Townsend et al. (1977) and Jagadeesh et al. (1981) observed additional lines in Mössbauer experiments, but they had different explanations. Townsend et al. (1977) attributed the extra lines to metal-deficient domains in the crystals, whereas Jagadeesh et al. (1981) thought the lines arose from valence

fluctuations between Fe^{2+} and Fe^{3+} , but they didn't explain why there was such a charge transfer in bornite. Jagadeesh et al. (1981) also found that the concentration of Fe^{2+} increased with temperature.

Collins et al. (1980) performed not only Mössbauer spectroscopy but also neutron powder diffraction experiments. However, they could not uniquely determine the Fe/Cu ordering scheme in the low-temperature form (which the authors thought was $Pbca$, $2a4a2a$), because in addition to the ordering scheme proposed by Koto and Morimoto (iron atoms located at sites 4 and 5), there were six additional ordering schemes that were consistent with the experimental results. In general, however, the iron atoms were located in the anti-fluorite cube, according to the work of Collins et al. (1998). Although Koto and Morimoto's (1975) model gave the best fit to neutron diffraction data, the total R value of 10% and profile R value of 22.8% were still large, even though only 68 reflections were used in the calculations of Collins et al. (1998) (2θ between 6.5–34.0 degrees). In Koto and Morimoto's X-ray experiment, R was equal to 14.8% for 1008 superstructure reflections and 27.0% for all 2317 reflections. Collins et al. (1998) also indicated that it was difficult to explain why the ordering scheme in Koto and Morimoto's (1975) low-temperature structure model would have such a high magnetic transition temperature (76 K).

Implications of these studies

(1) Fe/Cu are ordered in the low-temperature forms of bornite (Allias and Wyart 1965; Townsend et al. 1977). (2) Consistent with our HRTEM study, the experiments suggest that structural heterogeneity is a common, if not universal, characteristic of bornite: (a) The disagreement between the results of Townsend et al. (1977) and Jagadeesh et al. (1981) can be easily explained if it is assumed that two or more kinds of superstructure domains coexist at low-temperatures. In different superstructure domains, the formal valence of Fe is different and depends on the stoichiometry of the superstructure domain. This can also explain why there is mixing of Fe^{2+} and Fe^{3+} in bornite. (b) The two magnetic ordering transitions are also easy to explain because different Fe/Cu ordered superstructures should have different transition temperatures, i.e., at least two of the magnetic ordering transitions should be observed. The concentration of Fe^{2+} could appear to increase with temperature because the size of one superstructure domain type increases with temperature (i.e., those domains with the valence of iron close to Fe^{2+} would grow). (c) It is noteworthy that the R value of Koto and Morimoto's (1975) model increased when the calculation included all reflections. This suggests that the non-superstructure reflections were not consistent with the superstructure reflections in their experiments, which probably resulted from the presence of more than one type of superstructure domain in their samples. For example, if 4a and 2a superstructure domains coexist in one sample, then the intensities of non-superstructure reflections will be a weighted sum of those for the 2a and 4a structures, and the super-reflections from 4a will not be consistent with the intensities of the non-superstructure reflections.

Thus, if we assume that 4a and 2a are the most commonly occurring phases in bornite at low temperatures, consistent with our TEM observations, then samples used to study the magnetic

structure most likely involved at least $2a$ and $4a$ superstructure domains. This would imply that both the $2a$ and $4a$ superstructures are Fe/Cu ordered structures corresponding to the two magnetic ordering transitions occurring at very low temperatures.

POSSIBLE FE/CU ORDERED 2A SUPERSTRUCTURES

The $2a$ superstructure of bornite was carefully studied by Kanazawa et al. (1978) using the X-ray diffraction method at 185 °C. They described the structure models as having “the space group $Fm\bar{3}m$ with $a = 10.981$ Å. Sulfur atoms form an ideal face centered cubic closest packing, and metal atoms are distributed statistically in the tetrahedral sites of sulfur atoms. The structure consists of two different kinds of cubes with the anti-fluorite type structure; one has a half metal atom in each tetrahedron, and represents disorder of Cu and vacancies, whereas the other has one metal atom in each tetrahedron and represents disorder of Cu and Fe atoms.” However, there are three remaining problems with their model. First, because of anomalous diffraction (non-space-group extinctions), there was ambiguity in the symmetry of the $2a$ superstructure since the space groups $Fm\bar{3}m$, $F\bar{4}3m$, and $F\bar{4}32$ are all consistent with the X-ray diffraction patterns (Kanazawa et al. 1978). Kanazawa et al. chose $Fm\bar{3}m$ only because $Fm\bar{3}m$ is a supergroup of the low-temperature form $Pbca$, whereas the other two space groups are not. However, based on our TEM observations, the $Pbca$ structure form may not even exist but could instead simply be the result of averaging $4a$ and $2a$ domains in the bulk sample used for X-ray studies. Second, the model of Kanazawa et al. (1978) is a Fe/Cu disordered structure. The third problem is that Kanazawa et al. (1978) did not realize that their sample might not be homogenous and that the determined stoichiometry and structure might not represent a single phase, but rather an average over different structural domains. In light of these problems, the $2a$ superstructure model is reconsidered in this paper.

Since there are only three choices of space groups, it is not difficult to determine which symmetry is the best choice for Fe/Cu ordered structures. Table 1 lists all possible sites for sulfur and metal atoms.

From Table 1, it can be seen that the sulfur atoms occupy the same crystallographic sites in the structures having the three different symmetries, if the origin of the unit cell is assigned to a sulfur position. Thus, for sulfur atoms, the three symmetries make no structural difference. In structures with symmetries $Fm\bar{3}m$ and $F\bar{4}32$, there are only two nonequivalent metal atom sites, whereas in the structure with symmetry $F\bar{4}3m$, there are four nonequivalent sites. With the stoichiometry of bornite Cu_5FeS_4 (or $Cu_{10}Fe_2S_8$ for the $2a$ superstructures), symmetries $F\bar{4}32$ and

$Fm\bar{3}m$ cannot produce fully Fe/Cu and vacancy/metal ordered structures, since in this stoichiometry there are more Cu atoms than any set of equivalent tetrahedral sites, and there could be two kinds of structures: (1) the one proposed by Kanazawa et al. (1978), where $3/4Cu + 1/4 Fe$ occupy one metal atom site, and $1/2Cu$ occupies the other metal atom site; (2) with the Cu atom fully occupying one metal atom site, and the other site occupied by $1/4Cu + 1/4Fe$. However, with symmetry $Fm\bar{3}m$ or $F\bar{4}32$, only Fe/Cu, vacancy/metal disordered structures can form.

In contrast, in structures with symmetry $F\bar{4}3m$, there are four non-equivalent sites for two different atoms, and thus there could be two kinds of Fe/Cu ordered structures. One ordering scheme is Cu at 0.125, 0.125, 0.125 and 0.375, 0.125, 0.125 with occupancy equal to 1, and Fe at 0.625, 0.125, 0.125, or 0.875, 0.125, 0.125 with occupancy equal to 1. In this model, Cu atoms fill anti-fluorite cubes, and Fe atoms fill the zincblende cube. Another ordering scheme involves exchanging the Fe position with one of the Cu positions in the anti-fluorite cube, either at 0.125, 0.125, 0.125, or at 0.375, 0.125, 0.125. For convenience, we call the first ordering scheme Cu(anti) and the second CuFe(anti), and both structures are shown in Figure 2. However, either of these two models produces the structural formula $Cu_8Fe_4S_8$ and not $Cu_{10}Fe_2S_8$, which is believed to be the stoichiometry of bornite. We will discuss this problem later in this paper. According to the first formula, the formal valence of Cu is 1+ and Fe is 2+. To determine which ordering scheme is energetically preferable, we applied first-principles methods to calculate the total energy of the ground state of these two structures by using full potential linearized augmented plane wave (FLAPW) methods.

CALCULATION METHODS

The calculation method applied in this paper is the well-known full potential LAPW method written in WIEN97 code by Blaha et al. (1999), in which no shape approximation is made for either potential or charge density. The exchange correlation effects are treated in density functional theory (DFT) with either the local (spin) density approximation (LSDA) (Perdew and Wang 1992) or the generalized gradient approximation (GGA) (Perdew et al. 1996). In the calculations, the sphere radii of Cu, Fe, and S were 2.2, 2.2 and 1.9 a.u. respectively. The plane wave cutoff was $R_{\text{m}}K_{\text{max}} = 6$, and the k -points sampling in the irreducible Brillouin zone was 10 for both structures. The first mesh point R0 and the number of the radial mesh points were also kept the same for each chemical element in the two structures. The GGA was applied in the calculations, and spin-polarization effects and volume optimization were also included.

RESULTS AND DISCUSSION

The calculations for two structures converged after 20 [Cu(anti)] and 17 [CuFe(anti)] self-consistent field (SCF) iterations respectively, with the charge convergence criterion of 0.0001 eV. After performing the volume optimizations, the

TABLE 1. Structural information used for calculations

Formula	Symmetry	Unit cell	Cu				Fe				S			
			x	y	z	O	x	y	z	O	x	y	z	O
$Cu_{10}Fe_2S_8$	$Fm\bar{3}m/F\bar{4}32$	2a (model 1)	0.125	0.125	0.125	0.75	0.125	0.125	0.125	0.25	0	0	0	1
			0.625	0.125	0.125	0.5	0.625	0.125	0.125	0	0.5	0	0	1
		2a (model 2)	0.125	0.125	0.125	1	0.625	0.125	0.125	0.25	0.25	0.25	0	1
			0.625	0.125	0.125	0.25								
$Cu_8Fe_4S_8$	F-43m	2a Cu(anti)	0.125	0.125	0.125	1	0.625	0.125	0.125	1	0	0	0	1
			0.375	0.125	0.125	1	0.875	0.125	0.125	0	0.5	0	0	1
	F-43m	2a FeCu(anti)	0.125	0.125	0.125	1	0.375	0.125	0.125	1	0.25	0.25	0	1
			0.625	0.125	0.125	1	0.875	0.125	0.125	0				

Note: O = occupancy.

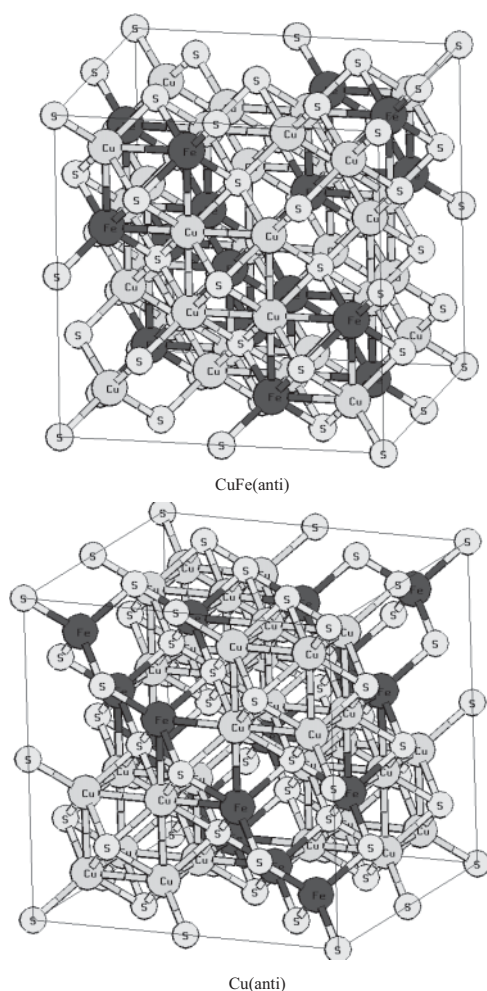


FIGURE 2. Atomic structural models of two possible ordering schemes for $2a$ superstructures with symmetry $F\bar{4}3m$.

equilibrium volumes were 2061.203 a.u.³/f.u. and 2071.936 a.u.³/f.u., which correspond to the unit-cell parameters $a = 10.70$ and 10.71 Å, respectively. The total energy of the Cu(anti) structure is -43049.222850 eV/unit cell, and that of CuFe(anti) is -43049.275563 eV/unit cell, with a difference of about 52.7 meV/unit cell. The calculated magnetic moment of iron in the Cu(anti) structure is $3.70 \mu_B$ (the moment inside the spheres is $2.785 \mu_B$, and the interstitial moment is $0.915 \mu_B$), and the moment of iron in the CuFe(anti) structure is $4.02 \mu_B$ (the moment inside the spheres is $2.984 \mu_B$, and the interstitial moment is $1.122 \mu_B$). Thus, the FLAWP calculations suggest that the CuFe(anti) structure is more stable than Cu(anti) structure, at the ground state, and that iron in the CuFe(anti) structure has a higher magnetic moment than Fe in the Cu(anti) structure.

Calculation method and the stability of the structures

The ground state total energy and the charge distribution are the only values that can be rigorously calculated by DFT, and the only major approximation made in the calculations is the exchange-correlation effect. Since there are no calculations performed by other methods or experimental data to compare,

it is hard to estimate the accuracy of the absolute value of total energies calculated with this code. However, what is important in this study is which structure is more stable, which involves the difference between the ground state total energies; the accuracy of the absolute values is not critical. Since both calculations were made with exactly the same conditions, except for the position of iron in the structures, the calculated difference of energy and charge distribution between the structures should be caused only by the different ordering schemes. We also performed the calculations using LSDA, different k -points sampling, and different convergence criteria, and all the results indicate that the total energy of the CuFe(anti) structure is about 40–50 meV/unit cell lower than that of the Cu(anti) structure.

According to our calculations, the energy difference between the two Fe/Cu ordering schemes is only 50 meV/unit cell (around 6.25 meV/atom), which is very small. Thus, at certain elevated temperatures, the $2a$ superstructure could be disordered.

Magnetic moment of Fe²⁺

Our calculations indicate that iron in both structures has significant magnetic moment, and this result is in contrast to the conclusion of Jagadeesh et al. (1981). According to Jagadeesh et al. (1981), since the Fe²⁺ is at a tetrahedral site of ligands, it is in low-spin state and the magnetic moment is zero. The conclusion of Jagadeesh et al. (1981) was based on crystal field theory, though the author didn't specifically indicate that. However, since bornite involves covalent bonds (metal-sulfur bonds) and metallic bonds (Ding 2002), crystal field theory is no longer appropriate and only complex band structure calculations are likely to give reasonable results.

Stoichiometry, symmetry, and disordered structures

Although the stoichiometry of the proposed the Fe/Cu $2a$ superstructure is different from that of bornite (Cu_5FeS_4), as mentioned earlier, only this stoichiometry could produce a completely Fe/Cu ordered structure among the three choices of symmetries derived from X-ray experiments ($Fm\bar{3}m$, $F\bar{4}32$, and $F\bar{4}3m$). The stoichiometry $\text{Cu}_{10}\text{Fe}_2\text{S}_8$ could occur only for Fe/Cu disordered structures, and the formal valence 3+ of Fe also makes it difficult to understand why there is Fe²⁺ in the structure. Actually, there is an inconsistency between the symmetries ($Fm\bar{3}m$, $F\bar{4}3m$, and $F\bar{4}32$) and the requirement of Fe/Cu ordered structures for the stoichiometry Cu_5FeS_4 . That is, if we require a Fe/Cu ordered structure with the stoichiometry $\text{Cu}_{10}\text{Fe}_2\text{S}_8$, the symmetry must be lower than any of the three symmetries mentioned above, and if we want to keep any of the three symmetries with the stoichiometry $\text{Cu}_{10}\text{Fe}_2\text{S}_8$, Fe/Cu must be at least partially disordered. Thus, if we wish to keep any symmetry from the three choices ($Fm\bar{3}m$, $F\bar{4}32$, and $F\bar{4}3m$) and Fe/Cu ordered structures, the stoichiometry must be $\text{Cu}_8\text{Fe}_4\text{S}_8$. In fact, the stoichiometry of naturally occurring bornite could be $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$ (Jagadeesh et al. 1981), which is very close to our proposed stoichiometry. Moreover, this proposed structure can explain why there is Fe²⁺ in the structures. As a result, we suggest that the stoichiometry of the $2a$ Fe/Cu ordered bornite superstructure is not $\text{Cu}_{10}\text{Fe}_2\text{S}_8$ but $\text{Cu}_8\text{Fe}_4\text{S}_8$, and this deviation of the stoichiometry from the traditionally accepted stoichiometry of bornite may explain the non-stoichiometry observed for bornite, which could be the result

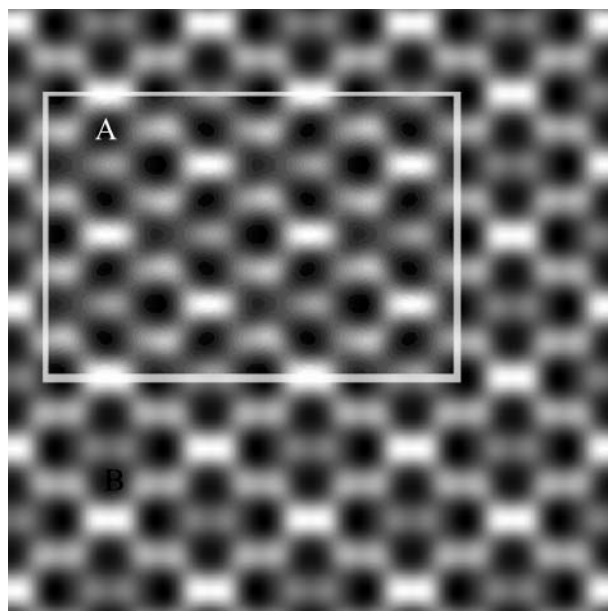


FIGURE 3. (a) HRTEM simulation of CuFe(anti) structure using MacTempas, and (b) the processed experimental HRTEM image from CRISP. The dark areas in the HRTEM images represent the regions of high charge potential in the structure.

of averaging different superstructure domains, the stoichiometry and sizes of which vary in different samples.

HRTEM simulation of the newly proposed 2a model of bornite

HRTEM image simulations for the newly proposed 2a superstructure model were performed using MacTempas to compare with experimental 2a HRTEM images processed with CRISP (Hovmöller 1992; Zou et al. 1996) (see Fig. 3), and the results of the simulations are very close to the experimental images. The defocus and thickness for the simulation in Figure 3 are close to the Scherzer condition and 150 Å, respectively. We also simulated HRTEM images for the model proposed by Kanazawa et al. (1978) within the focus range from -1000 and 1000 Å and thickness range from 50 to 500 Å, but no simulated image is closer to the experimental image than that for newly proposed

2a model, which implies that at room temperature (even under electron radiation for short time) the 2a can still be Fe/Cu ordered. Besides, we have never observed the expected low structural form of bornite [2a4a2a (*Pbca*)] from any of the different zone axes in this experiment (Ding et al. 2005).

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