Iron bcc-hcp transition: Local structure from x-ray-absorption fine structure

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The x-ray-absorption fine-structure technique has been utilized to investigate the pressure-induced bcc-hcp transition in iron from a local structural perspective. Our measurements of the associated lattice constants show a structurally distorted hcp phase with an anomalously large c/a ratio during the transition as reported by previous x-ray-diffraction measurements. We have also observed a structurally distorted bcc phase with an anomalously large lattice constant during the transition. These anomalies are attributed to interfacial strain between the bcc and hcp phases. A transition model based on lattice shearing movements and occurrence of an intermediate fcc structure is consistent with our data and previous results. [S0163-1829(98)04210-6]

I. INTRODUCTION

Since the discovery of the iron bcc to hcp phase transition at 13.0 GPa by Bancroft *et al.* in 1956,¹ a wealth of knowledge has been gained on this transition and the hcp iron phase through numerous studies.^{2–8} The transition starts at 13.0 GPa, and is very sluggish, usually spanning a pressure range of about 8.0 GPa within which the bcc and hcp phases coexist. This transition has a large hysteresis; in some cases, the reverse transformation does not finish until 5.0 GPa.⁶ This transition is an athermal process, in that the amount of the new phase does not change as a function of time, but rather as a function of pressure. It has been argued that this transition is martensitic based upon its highly hysteretic and athermal nature, and upon the irregular shape of the boundary between the coexisting iron bcc and hcp phases.³

One aspect of this transition, however, is still not well understood. Several groups^{2,5–7} have reported different lattice constants for the hcp phase during the transition, yet the results above the transition agree (see Fig. 1). Mao *et al.*² found a similar c/a ratio during the transition and after the transition, while Jephcoat *et al.*⁵ observed a smaller c/a ratio during the transition, At the same time, Bassett and Huang⁶ and Huang *et al.*⁷ found a much larger c/a ratio during the transition. In the latter work,⁷ significant changes of the c/aratio during the transition at different temperatures were found.

The experiments were carried out under different time scales and in high-pressure environments with different degrees of hydrostaticity. In Ref. 2, no pressure transmitting medium was reported and the pressure was held constant for several hundred hours to relax the system after each pressure change. In Ref. 5, argon and neon were used as as pressure transmitting medium and the system permitted to relax for 24 h after each pressure increase. Measurements in both Refs. 2 and 5 lasted 100 h at each pressure. In Ref. 6, no pressure transmitting medium was used and measurements were taken just a few minutes after each pressure change. Similar experiments were reported in Ref. 7, at four different temperatures. Measurements lasted less than 1 h in both Refs. 6 and 7. How the different experimental conditions can affect the observed structure of the hcp phase during the transition and what aspects of the transition mechanism these different behaviors of the hcp phase can reveal needs more study.

X-ray diffraction, which detects long-range order in a crystal, was used by almost all previous researchers to study this transition. In the present work we used the x-ray-absorption fine-structure (XAFS) technique so that we could study the iron bcc-hcp transition from the local structural standpoint. This paper is a followup to an earlier report on this project.⁸

II. EXPERIMENTAL

XAFS spectra in the standard transmission mode were measured at a wiggler side-station at the Stanford Synchrotron Radiation Laboratory (SSRL). Diamond-anvil cells were not used in this experiment because Bragg peaks from the diamond single crystals disrupt XAFS data, and because diamond anvils are very absorbing at the iron *K*-edge x-ray energies (\sim 7 keV). Instead, sintered boron carbide anvils were used to generate the high pressure, with the x-ray beam



FIG. 1. The c/a ratios from the present work (empty circles) compared with previous studies. Typical error bars from the present work are indicated.

5647

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Pressure	bcc				hcp			
(GPa)	a (Å)	$\theta_D^{\rm bcc}$ (K)	$\sigma_1^2 \; (10^{-2} \; \text{\AA}^2)$	%	a (Å)	c/a	θ_D^{hcp} (K)	$\sigma_1^2 \; (10^{-2} \; \text{\AA}^2)$
0.0	2.859(1)	418(11)	5.9(2)	100				
5.6	2.830(3)	419(10)	5.8(2)	100				
9.1	2.816(3)	433(12)	5.5(2)	100				
10.5	2.810(3)	428(12)	5.6(2)	100				
11.1	2.804(2)	450(13)	5.1(2)	100				
13.0	2.804(3)	456(18)	5.0(3)	86(2)	2.408(11)	1.667(28)	481(20)	4.6(2)
13.5	2.804(3)	442(6)	5.3(2)	80(2)	2.426(10)	1.634(21)	483(20)	4.6(2)
13.8	2.799(3)	436(10)	5.4(2)	60(2)	2.453(5)	1.601(10)	484(20)	4.6(2)
14.0	2.799(3)	421(10)	5.8(2)	50(2)	2.446(4)	1.604(7)	484(20)	4.6(2)
15.0	2.810(6)	391(15)	6.6(3)	35(2)	2.449(3)	1.600(5)	487(20)	4.5(2)
16.2	2.833(9)	382(28)	6.9(8)	21(3)	2.446(2)	1.603(5)	490(20)	4.5(2)
16.5	2.864(9)	480(70)	4.5(1.8)	12(2)	2.448(3)	1.596(4)	491(20)	4.5(2)
18.6	2.870(11)	465(70)	4.8(1.8)	10(2)	2.449(2)	1.596(3)	497(20)	4.4(2)

TABLE I. XAFS fitting results corresponding to increasing pressure: θ_D is the Debye temperature; σ_1^2 is the σ^2 of the first shell obtained via the Debye model; % is the number percentage of the bcc phase. Quantities without error estimations are set values instead of fitting results.

along the axis. Such anvils do not produce disruptive Bragg peaks and also are less absorbing than diamond. The experimental details of this method have been described elsewhere.⁹ For this experiment, the tips of the anvils were 1.5 mm in diameter. Samples were contained in a 0.4 mm thick, 1.0 mm wide hole in a gasket of Inconel 601. Foils of iron and copper, each $5 \mu m$ thick, were sandwiched between two epoxy pellets and loaded into the gasket. The XAFS spectra of the copper foil were used for pressure calibration while the epoxy pellets served as a quasihydrostatic pressure raising and the pressure releasing processes. Three XAFS scans at the iron *K* edge and two scans at the copper *K* edge were taken at each pressure.

Because there was a small amount of iron impurity in the boron carbide anvils, the measured XAFS spectra consisted of an admixture of iron spectra from both the sample and iron in the anvils. To correct for this effect, iron impurity spectra were measured separately at ambient pressure, without the sample, and subtracted from the measured XAFS spectra to obtain spectra for the sample, itself. The corrected iron XAFS spectra at ambient pressure agree well with that of a standard iron foil outside of the pressure cell. Since we found there was negligible pressure effect on impurity spectra within our experimental pressure range, we made the same correction to the measured XAFS spectra at the other pressures.⁸

The XAFS data were analyzed using programs FEFF6 and FEFFIT from the UWXAFS package.^{10–12} A superposition of single and multiple scattering paths was used to calculate theoretical XAFS spectra generated for a cluster of iron atoms of six Å radius. Theoretical XAFS spectra were then compared with experimental data, and structural information of this cluster was extracted. Local structure of the iron sample was modeled with bcc structure before the transition, and with an admixture of bcc and hcp structures once the transition started. A total of six single scattering paths and 18 double scattering paths were used to construct our model for the bcc phase, while seven single scattering paths and 23 double scattering paths were used to model the hcp phase.

The correlated Debye model was used^{11,12} to calculate the mean-square deviation (σ^2) in the length of the scattering paths.

Two Debye temperatures (θ_D) were used to calculate the σ^2 's for scattering paths in bcc phase and hcp phase separately, and were also allowed to vary with pressure. Fitting results for θ_D for both phases and derived σ^2 's of the first atomic shell are listed in Tables I and II for loading and unloading processes. θ_D of the bcc phase decreases considerably during the transition reflecting increase of local structural disorder, while that of the hcp phase changes slowly and almost linearly with pressure. θ_D of the hcp phase was set at fixed values according to results of a linear regression of θ_D versus pressure data obtained from preliminary analysis. The values of θ_D of the hcp phase listed in Tables I and II are the results of this linear regression instead of direct fitting of data.

The copper *K*-edge XAFS spectra were fitted using a similar method, and the lattice constant of copper was extracted and used to compute the sample pressure according to published pressure-versus-volume data.¹³

III. RESULTS

XAFS spectra of iron at three different pressures are shown in Fig. 2. Considerable changes caused by the transition can be seen. These changes can be identified and analyzed more easily by studying the Fourier transforms of the XAFS spectra, which closely relate to the radial distribution function about the absorbing atoms. Such Fourier transforms of the data together with theoretical fits, at the beginning, the middle and near the end of the bcc-hcp transition are shown in Fig. 3. The profile of these Fourier transforms changes significantly during the course of the transition, indicating the significant local structural changes that take place during the transition. Structural information was extracted from these XAFS spectra using analysis methods discussed in the previous section. Numerical results from fits corresponding to both increasing and decreasing pressures are listed in Tables I and II, respectively.

Pressure	bcc				hcp			
(GPa)	a (Å)	$\theta_D^{\rm bcc}$ (K)	$\sigma_1^2 (10^{-2} \text{ Å}^2)$	%	a (Å)	c/a	θ_D^{hcp} (K)	$\sigma_1^2 \ (10^{-2} \ \text{\AA}^2)$
18.6	2.872(14)	394(54)	6.5(1.5)	13(3)	2.449(3)	1.595(4)	497(20)	4.4(3)
17.5	2.872(37)	274(54)	13.0(1.5)	17(4)	2.463(5)	1.601(6)	494(20)	4.4(3)
16.5	2.918(40)	267(50)	13.8(1.4)	17(4)	2.463(5)	1.602(6)	491(20)	4.5(3)
16.2	2.877(31)	275(45)	12.9(1.2)	19(4)	2.465(5)	1.603(7)	490(20)	4.5(3)
14.0	2.844(28)	302(48)	10.8(1.2)	20(5)	2.468(6)	1.607(8)	484(20)	4.6(3)
12.1	2.844(31)	276(44)	12.9(1.2)	23(5)	2.476(6)	1.607(9)	479(20)	4.7(3)
11.6	2.864(20)	300(34)	10.9(8)	24(4)	2.480(5)	1.604(8)	477(20)	4.7(3)
11.4	2.879(11)	365(36)	7.5(8)	19(3)	2.477(4)	1.601(6)	477(20)	4.7(3)
10.5	2.830(6)	381(17)	6.9(4)	37(3)	2.474(5)	1.607(8)	474(20)	4.8(3)
10.2	2.816(3)	415(11)	5.9(2)	62(3)	2.476(7)	1.598(13)	474(20)	4.8(3)
8.9	2.816(3)	413(8)	6.0(2)	86(3)	2.485(9)	1.604	470(20)	4.8(3)
6.6	2.830(6)	389(24)	6.7(4)	100				
6.0	2.833(6)	377(16)	7.1(2)	100				
1.9	2.853(11)	366(36)	7.5(6)	100				

TABLE II. XAFS fitting results corresponding to decreasing pressure: θ_D is the Debye temperature; σ_1^2 is the σ^2 of the first shell obtained via Debye model; % is the number percentage of the bcc phase. Quantities without error estimations are set values instead of fitting results.

The fraction of the bcc phase during increasing and decreasing pressure is shown in Fig. 4. The large hysteresis and phase coexistence range are evident. The bcc phase persists until over 18.6 GPa, the highest pressure of our experiment, while the hcp phase persists until below 8.0 GPa, the final data point during the reverse transition. This is consistent with Ref. 6 which reported the hcp phase to persist as low as 5 GPa.

The lattice constants a and c for the hcp phase as a function of pressure are shown in Fig. 5. The values that we find are similar to those of Ref. 6. We observe that the lattice constant a of the hcp phase during the forward transition is quite small at initial stages of the transition and quickly

0.8 P = 18.6 GPa 0.6 P = 15.0 GPa 0.4 $\chi(k)$ P = 13.0 GPa 0.2 P = 0 GPa 0.0 -0.2 0.0 5.0 10.0 15.0 k (Å)

FIG. 2. Typical *K*-edge XAFS spectra $\chi(k)$ of iron at different pressures. The bcc-hcp transition region at pressures higher than 13.0 GPa is evident.

reaches larger and more stable values as the transition progresses. We observe a similarly anomalous effect in the lattice constant c. It is quite large at the initial stage of the forward transition and levels off to smaller and more stable values as the transition progresses. In Fig. 1, we show the c/a ratios obtained in this study plotted against those of the previous reports. We observe a large c/a ratio of the hcp



FIG. 3. Typical Fourier transforms of the iron XAFS spectra $\chi(k)k^2$ (solid line) and corresponding theoretical fits (dashed line). Progressive changes in the radial distribution function as the bcc-hcp transition proceeds are evident.



FIG. 4. Relative abundance of the iron bcc phase during the bcc-hcp transition. Filled (open) circles correspond to increasing (decreasing) pressure.

phase at the beginning of the transition, and an almost constant value of 1.604 as the transition continues, which agrees qualitatively with the results of Ref. 6. The lattice constant of the bcc phase is plotted in Fig. 6. It is observed to increase significantly near the end of the forward transition, and stay relatively large upon release of pressure, only returning to normal value when the reverse transition almost completely finishes. This anomalous behavior of the bcc lattice constant observed in this study has not been reported previously and underscores the ability of XAFS to probe local structure.



FIG. 5. Lattice constants a and c of the hcp phase as a function of pressure. Filled (open) circles correspond to increasing (decreasing) pressure. Typical error bars are indicated.



FIG. 6. Lattice constant of the bcc phase as function of pressure. Filled (open) circles correspond to increasing (decreasing) pressure. Typical error bars are indicated.

IV. DISCUSSION: PHASE TRANSITION MECHANISMS

According to the discussion in the previous section, the hcp phase behaves anomalously in the initial stage of the forward transition, while the bcc phase behaves anomalously in the final stages. We conclude that the lattice constants of each phase behave anomalously only when their relative amount is minimal. This kind of behavior suggests that the observed anomalous structures during the transition are very likely caused by the interfacial strains between the two phases. These distorted structures only become measurable when the fraction of the interfacial regions becomes significant compared to that of the bulk of either minority phase. Understanding the mechanism of the transition and such interfaces will shed light on the cause of these structural anomalies. By the same token, knowledge of these distorted structures will help us to differentiate plausible transition mechanisms from implausible ones.

The iron bcc-hcp transition is a martensitic or displacive transition. During such a transition, the newly formed martensitic phase (in this case, hcp) is derived from the parent phase (bcc) via collective shear movements of atomic planes. One important characteristic of such transitions is that the martensitic phase has a unique crystallographic orientation relationship with its parent phase. For example, in the case of the temperature-driven iron fcc-bcc martensitic transition, the following relationships were found to be true: $(111)_{fcc} || (011)_{bcc}$ and $[10\overline{1}]_{fcc} || [\overline{1}1\overline{1}]_{bcc}$, which are the so-called Kurdjumov-Sachs relations.¹⁵ We shall name lattice planes, such as $(111)_{fcc}$ and $(011)_{bcc}$, which are parallel to each other during the transition, the "conjugate" planes of the transition.

Another associated characteristic of martensitic transitions is that, in most cases, the martensitic phase has uniquely oriented coherent interfaces with its parent phase. Coherent interfaces have similar or identical atomic arrangements in parent and martensitic phases, and hence, have



FIG. 7. Hypothetical hysteresis loops of mismatching base vectors during a martensitic transition: \mathbf{X}_P from the parental phase (dashed lines) and \mathbf{X}_M from the martensitic phase (solid lines). P_0^f and P_1^f are the starting and finishing pressures of the forward martensitic transition, while P_0^r and P_1^r are that of the reverse transition.

small or no interface strain. One can use two noncollinear lattice vectors in the interface planes, which we shall name "base" vectors, to characterize their structure. If the interface planes are not identical in the two phases, one or both of the base vectors in one phase will be different from that of the other phase. If both phases have significant presence in the system, interface effects will not be important and one should be able to measure one or both of the undistorted base vectors of the two phases that are different from each other. If however, either martensitic or parent phase has only a minimal presence in the system, then the minority phase will be distorted in a way to match the other phase, and have intermediate base vector dimensions between that of the undistorted martensitic and parent phases. During a martensitic transition, the martensitic phase will develop from minimal to significant and finally to dominant presence in the system. and the measured base vectors of martensitic phase and parent phase will change accordingly due to interfacial strain effects. Figure 7 shows a hypothetical evolution of one pair of base vectors during a martensitic transition, which exhibits overlapping hysteresis loops. One looks for this kind of behavior as a signature of coherent interfacial strain during a martensitic transition.

The complex morphology of martensitic transitions makes the task of identifying and studying the interfaces during the transition very difficult especially under high pressure environment. A forming martensitic phase from temperature quenching could take the shape of plates, needles, or bamboo leaves depending on chemical composition, such as the carbon concentration in the steel, or on the experimental condition, such as the temperature quenching rate. It is observed that conjugate planes of a martensitic transition are very often also the interface planes of the transition.¹⁵ Without knowing the exact morphology of the iron bcc-hcp transition, we limit ourselves to only considering conjugate planes of the transition as possible interface planes between bcc and hcp phases.

In the following subsections three possible transition models for the iron bcc-hcp transition are discussed. Possible interface planes will be selected from the various conjugate



FIG. 8. Model I suggests a two-step process: (a) \rightarrow (b) \rightarrow (c) for the iron bcc-hcp transition, where (a) and (c) are projected views from the [110]/[0001] direction of the bcc and hcp structure, and (b) is that of an intermediate structure obtained by compressing (a) along the [001] and stretching (a) along the [110] direction.

planes predicted by these models. Evolution of the base vectors of the interface planes from bcc to hcp phase and back is examined to see if they exhibit the hysteresis behavior of coherent interface planes as shown in Fig. 7.

A. Model I

We first describe the model proposed in Refs. 2 and 6, which is pictured as a two-step process leading from the bcc structure to the hcp structure (see Fig. 8). Firstly, the bcc lattice contracts along the [001] direction, and expands along the $[1\overline{1}0]$ direction so that the (110) planes become hexagonally arranged atomic planes corresponding to the (0002) planes in the hcp phase. Secondly, every other (110) plane shifts toward the $[1\overline{10}]$ direction while the interplane distance d(110) is unchanged. In this model, there are three sets of conjugate planes during the transition: (A) atomic arrangement in the two structures, and will be considered as possible interface planes. In set (A) two orthogonal base vectors \mathbf{X}_{bcc} , \mathbf{Y}_{bcc} can be found for $(002)_{bcc}$ planes in the bcc phase, while corresponding base vectors \mathbf{X}_{hcp} , \mathbf{Y}_{hcp} can be found for $(\overline{2}110)_{hcp}$ planes in the hcp phase. The actual directions and lengths of these base vectors are listed in Table III. Since d(110) is invariant during the transition in this model, base vectors X_{bcc} and X_{hcp} should not change during the transition. The evolution of X_{bcc} and X_{hcp} is plotted in Fig. 9(a). We observe changes in \mathbf{X}_{bcc} and \mathbf{X}_{hcp} while we expect them to be invariant through the transition. The other pair of base vectors \mathbf{Y}_{bcc} and \mathbf{Y}_{hcp} are different in magnitude. Their evolution versus pressure is plotted in Fig. 9(b). Instead of the expected fully overlapping hysteresis as shown in Fig. 7, we observe that the two hysteresis loops hardly overlap. Therefore the evolution of both base vectors of conjugate planes (A) does not give the signature of structural distortion caused by interfacial strain. We find the same to be

TABLE III. Base vectors of conjugate planes $(002) \| (\overline{2}110)$.

	$X_{\rm bcc}$	$Y_{\rm bcc}$	$X_{\rm hcp}$	Y _{hcp}
Direction	[110]	[110]	[0001]/[110]	[0110]/[110]
Length	<i>d</i> (110)	$2d(1\bar{1}0)$	d(0002)	$2d(0\overline{1}10)$



FIG. 9. (a) and (b) are hysteresis loops for base vectors of conjugate planes $(002)_{bcc} \| (\bar{2}110)_{hcp}$ in model I; (a) and (c) are hysteresis loops for base vectors of conjugate planes $[\bar{1}1\bar{1}]_{bcc} \| [11\bar{2}0]_{hcp}$ in model II. The circles represent the bcc phase while the diamonds represent the hcp phase. Filled circles and diamonds and solid lines correspond to increasing pressure while empty circles or diamonds and dashed lines correspond to decreasing pressure.

true of conjugate planes (B). Thus our simplified methods described in this section and based on the assumptions of model I, do not enable us to find interface planes and corresponding interfacial structural distortion compatible with the anomalous behavior we observed during the transition.

B. Model II

Another mechanism, model II, was proposed by Burgers for the bcc-hcp transition of zirconium upon quenching from high temperature.¹⁴ Several other metals, such as lithium, titanium, and hafnium, have this type of bcc-hcp martensitic phase transition.¹⁵ In each case the following crystallographic orientation relationships between the bcc and the hcp phases were found: $(110)_{bcc} || (0002)_{hcp}$ and $[\bar{1}1\bar{1}]_{bcc} \| [11\bar{2}0]_{hcp}$. They are very likely following the same two-step process as proposed by Burgers¹⁴ in transforming from the bcc to hcp structure (see Fig. 10). The first step involves a shearing toward the $[\overline{1}1\overline{1}]$ direction and along the $(\overline{1}12)$ plane, so that (110) planes can be changed to hexagonally arranged atomic planes which correspond to (0002) planes. In the second step every other (110) plane shifts in the $[0\overline{1}10]$ direction, while keeping the (110) interplane distance unchanged. The result of the first step of this model is the same as that of model I except the lattice is rotated by approximately 5°. Because martensitic transitions are usually driven by collective shear movements of lattice planes, we believe the shearing process of model II to be more plausible than the compressing and stretching process



FIG. 10. Model II suggests a two-step process: (a) \rightarrow (b) \rightarrow (c) for the iron bcc-hcp transition; model III suggests a three-step process: (a) \rightarrow (b) \rightarrow (d) \rightarrow (e)/(c) for the the same transition. (a) and (c) are projected views from the [110]/[0001] direction of bcc and hcp structure, while (b) is that of an intermediate structure during the bcc-hcp transition obtained by shearing of ($\overline{1}12$) planes along the [$\overline{1}1\overline{1}$] direction; (d) and (e) are projected views from the [$2\overline{1}\overline{1}0$] direction, where (d) is an intermediate fcc phase obtained from (b) by shearing of (110)/(0001) planes along the [$0\overline{1}10$] direction, and (e) is the hcp structure obtained from (d) by slipping of two (0001) and (0002) planes together (indicated by arrows) along the [$01\overline{1}0$] direction. (c) and (e) are the same hcp structure view from two different directions. Note the angle between [001] and [$2\overline{1}\overline{1}$] is 185° instead of 180°.

of model I. The second step of model II is the same as that of model I, except for the direction of the shifting relative to the bcc lattice. We can identify two sets of conjugate planes from model II: (A) $(\overline{1}12)_{bcc} \| (1\overline{1}00)_{hcp}$ and (B) $(110)_{bcc} \| (0002)_{hcp}$. Of these two sets, only (Å) has similar atomic arrangements in the two phases, and will be considered as a candidate for the interface planes. As in the discussion of model I, two orthogonal base vectors \mathbf{X}_{bcc} , \mathbf{Y}_{bcc} in the $(\overline{1}12)_{bcc}$ planes in the bcc phase and the corresponding vectors \mathbf{X}_{hcp} , \mathbf{Y}_{hcp} for $(1\overline{1}00)_{hcp}$ planes in the hcp phase need be considered. The directions and lengths of these base vectors are listed in Table IV. The evolution of base vectors \mathbf{X}_{bcc} and \mathbf{X}_{hcp} is the same as plotted in Fig. 9(a), because the $d(110)_{bcc}$ is kept constant during the transition as in model I. Therefore $(\overline{1}12)_{bcc} \| (\overline{1}100)_{hcp}$ interfacial planes could not translate the observed structural anomaly in \mathbf{X}_{bcc} and \mathbf{X}_{hcp} directions into an interfacial strain-driven structural distortion. In contrast the evolution of base vectors \mathbf{Y}_{bcc} and \mathbf{Y}_{hcp} versus pressure, as shown in Fig. 9(c), yields the desired fully overlapping hysteresis loops. These findings mean that although model II is not able to explain the anomalously

TABLE IV. Base vectors of conjugate planes $(\overline{1}12) ||(1\overline{1}00)$.

	$X_{\rm bcc}$	Y _{bcc}	$X_{\rm hcp}$	Y _{hcp}
Direction	[110] d(110)	$\begin{bmatrix} \overline{1}1\overline{1} \end{bmatrix}$	[0001]/[110]	[1120]/[111]
Lengui	<i>u</i> (110)	$\frac{\sqrt{3}}{2}a_{\rm bcc}$	u(0002)	$u_{\rm hcp}$

large c at the beginning of the transition, it is nevertheless able to predict both the correct amount of reduction of a of the hcp structure at the beginning of the transition as well as the correct amount of increase of a of the bcc phase near the end of the transition. Model II therefore allows us to identify interface planes that are consistent with the anomalous behavior of the lattice constant a of the bcc and hcp phases, via interfacial strain, but not with lattice constant c of the hcp phase.

C. Model III

Model III is a three-step process, also proposed by Burgers,¹⁴ as an alternative mechanism for the zirconium bcc-hcp transition (see Fig. 10). The first step is similar to the first step in model II. However for the second step an intermediate fcc structure is first obtained by shearing in the $[0\overline{1}10]_{hcp}$ direction along the $(110)_{bcc}$ plane. This is followed by a third step in which the fcc structure is converted to hcp structure by a slipping of pairs of (110)-type planes in the $[01\overline{1}0]$ direction. Instead of going directly from the bcc to hcp phase, this model thus requires that the bcc phase first transform to the fcc phase followed by a further transformation to the hcp phase. Even though there is an extra phase and an extra step in this model, the whole transition process consists of shearing and slipping movements, which are very common in martensitic transitions, compared with the less energetically favorable shifting of alternate plane movements in models I and II. We therefore believe model III is more favorable from a physical standpoint.

In model III, after a small quantity of the bcc phase transforms to the fcc phase, it is possible that lattice matching between bcc and fcc phase makes the fcc phase metastable, so that the next step of the transition could not proceed without additional pressure or a long waiting time. If such a system is measured and interpreted as bcc+hcp, a larger lattice constant c would be detected because the fcc structure has the same c/a ratio, 1.633, as an ideal hcp whereas the normal c/a ratio for pure hcp iron is 1.604. The c/a ratio reported in Ref. 6, and which we also find, is close to 1.633 at beginning of the transition (see Fig. 1), supporting the possibility of a metastable fcc structure. In conclusion, model III not only yields an energetically preferable route from the bcc structure to hcp, it also is able to explain both the larger c value and the smaller a value observed in the hcp phase in Ref. 6 and the present work.

D. Conclusions

Of the experiments mentioned in the Introduction that reported different hcp lattice constant behavior during the transition under different experimental conditions, the present study and Ref. 6 both observe an anomalously large c/a ratio. It is possible that the structural anomalies observed in these two experiments are metastable structures, such as an intermediate fcc phase or structurally distorted interfaces, which disappear after a long enough waiting period. The experiments that used long waiting times would not be expected to be able to observe this anomaly.

As reported in Ref. 7, the anomalously large c/a ratio decreases with increasing temperature. At 300 °C, c/a re-

sumes its normal value. Higher thermal energy may enable the system to more easily overcome the energy barrier between a metastable fcc phase and stable hcp phase or to get rid of structurally distorting interfaces, hence making the metastable structure less observable.

It is interesting that in Ref. 7 at even higher temperature (450 °C), the c/a ratio was again found to become anomalously large. This also supports the existence of a metastable fcc phase during the bcc-hcp transition. Since fcc iron itself becomes stable above 500 °C at the transition pressure, a metastable fcc phase will become more stable as the temperature approaches 500 °C, making the energy barrier to the stable hcp phase higher. This effect could make a metastable fcc phase observable again at 450 °C, which is very close to its stable temperature. Hence the existence of a metastable fcc phase during the transition could explain the reverse of the decreasing trend of the c/a ratio as temperature increases, which was observed in Ref. 7. In Ref. 5 were reported normal c values and large a values which resulted in smaller c/a ratios. This effect can be explained by an argument given in Ref. 6. The volume of hcp phase nuclei is reduced after transforming from bcc phase; the void generated by this transition cannot be effectively filled by surrounding grains of bcc phase because of a dome effect under isotropic stress; therefore, the eventual volume of these hcp phase nuclei tend to be a little larger than its usual volume at the nominal pressure. The lattice constant c of the hcp nuclei is fixed by interfacing with the bcc phase. The net result would be a larger than usual lattice constant a.

V. SUMMARY

We have reported XAFS studies of the iron bcc-hcp transition, finding similar lattice constants for the hcp phase as the diffraction study in Ref. 6. We have also found an anomalously large lattice constant for the iron bcc phase when the relative amount becomes less than approximately 10%. Several transition mechanisms have been considered in which interfacial strain between the bcc and the hcp phases can explain the anomalous value of the lattice constant a in both bcc and hcp structure. We also suggest that a transition mechanism involving an intermediate fcc phase may explain the anomalously large value of the lattice constant, c, in the hcp structure during the transition. These anomalous lattice constants are apparently only observed in experiments in which the measurements are made shortly after the pressure change.

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