Pawley and Rietveld refinements using electron diffraction from L12-type intermetallic Au3Fe1-x nanocrystals during their in-situ order–disorder transition

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A R T I C L E   I N F O

Article history:
Received 23 November 2010
Received in revised form 7 April 2011
Accepted 11 April 2011
Available online 22 April 2011

Keywords:
Electron diffraction
Intermetallic nanoparticle
Long-range order parameter
Order–disorder transition
Pawley refinement
Rietveld refinement

A B S T R A C T

During the in-situ order–disorder transition of intermetallic L12-type Au3Fe1-x nanocrystals, structural information has been retrieved from their electron diffraction patterns based on the Pawley refinement that is unrelated to the electron kinematical or dynamical scattering nature as well as the Rietveld refinement using a kinematical approximation. At room temperature, it was found that the nanocrystals contain approximately 40% vacancies at the Fe site. Based on in-situ heating this phase displayed an irreversible order–disorder transition, with the transition temperature between 553 and 593 K. A sudden increase in lattice parameter was detected during the first heating from the ordered phase, while the second heating of the disordered phase showed only a linear relationship with temperature. From the lattice parameter measurement of the disordered phase, the coefficient of thermal expansion was estimated as 1.462 × 10⁻⁵ K⁻¹. The long-range order parameter S was determined by the refined site occupancies, as well as the integrated intensities of the superlattice (1 0 0) and fundamental (2 2 0) reflections using the Pawley and Rietveld refinements during the order–disorder transition. Considering the dynamical scattering effect, Blackman two-beam approximation theory was applied to corrected reflections using the Pawley and Rietveld refinements during the order–disorder transition. Considering the dynamical scattering effect, Blackman two-beam approximation theory was applied to corrected reflections using the Pawley and Rietveld refinements during the order–disorder transition. It was demonstrated that elemental and structural information could be retrieved through quantitative electron diffraction studies of the nanomaterials. Since the Pawley refinement algorithm does not include the electron scattering event, it is especially useful to refine the electron diffraction data regardless of the sample thickness.

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1. Introduction

Decreasing the crystallite size of intermetallic compounds down to the nanometer scale has become an attractive strategy for accessing ordered structures that are not observed using traditional high-temperature metallurgy techniques [1]. Notable examples include some Au-based compounds. Takanashi et al. [2] prepared an artificial L1₀-type ordered AuFe alloy, with alternating layers of Au and Fe atoms along the c-axis, by depositing alternating monatomic layers of Au and Fe, although such a phase does not exist in the equilibrium Au–Fe system. They found that this ordered AuFe alloy showed ferromagnetism, with a large uniaxial magnetic anisotropy perpendicular to Fe and Au atomic planes. Sato et al. [3] also prepared ferromagnetic L1₀-type AuFe nanocrystals by annealing nanostructured Fe/Au precursor particles, and they observed that the coercivity increased to about 40 kA/m. More recently, L1₂-type ordered Au₃M₁₋ₓ (0 < x < 1) structures, where M represents Fe, Co, or Ni (located at the corner positions of the fcc unit cell), have been synthesized, despite the immiscibility gap that exists between Au and the magnetic 3d elements [4–6]. Magnetic measurements indicated that the Au₃Fe₁₋ₓ and Au₃Co₁₋ₓ nanoparticle powders are superparamagnetic, with a blocking temperature of \( T_B = 7.9 \) and 2.4 K, respectively, while Au₃Ni₁₋ₓ is paramagnetic [6]. Other Au-based intermetallic compounds that have been accessed as nanoparticles using low-temperature solution methods include the AuSn and AuSn₂ in the Au–Sn system [7], AuCu, AuCu₃, and AuCu₃ phases in the Au–Cu system [8], and AuZn, Au₃Zn₃, AuZn, Cu₆Zn₃ type γ-(AuZn), and Mg-type c-(AuZn) in the Au–Zn system [9].

It is known that the order–disorder transition of these intermetallic compounds plays an important role in the physical, chemical, and mechanical properties [10–16]. In the Fe–Al system early work by Taylor and Jones [10] indicated that processing...
by cold working, which reduced the degree of ordering, could increase the magnetic saturation moment and also the lattice parameter. However subsequent short-period annealing at as low as 150 °C caused considerable recovery of the long-range order, which was accompanied by the loss of ferromagnetism and collapse of the lattice parameter to its true equilibrium value. However, in the Fe$_2$Al$_3$ intermetallic compound, Apiñanjiz et al. [12] found that the B$_2$–A$_2$ order–disorder transition produced by ball milling resulted in an increase of the lattice parameter, accompanied by enhanced magnetism. In a further work Nogués et al. [13] reported that the magnetic moment of Fe$_{30}$Al$_{70}$ alloys increases by about 35–45% due to lattice expansion effects induced during the disordering process. In Ni-based engineering alloys the Ni$_3$Al-type L$_1_2$ ordered phase has been used as a primary strengthening phase due to its anomalous strengthening effect at high temperatures, while the stability of the ordered structure is a key issue for alloy applications [15,16].

Detailed structure studies are crucial for understanding the material properties during the order–disorder transitions. Traditionally the order–disorder transitions are monitored by X-ray diffraction (XRD) using bulk samples, and the long-range order (LRO) parameter S is measured from the intensity ratio of a pair of superlattice and fundamental reflections [17–20]. Due to the electron dynamical scattering event that challenges the accurate structure factor calculation, fewer efforts were made to study LRO using quantitative electron diffraction in a transmission electron microscope (TEM). Matsuhata et al. [21] combined the intersecting Kikuchi-line (IKL) method [22] with convergent-beam electron diffraction (CBED) at a high voltage (761 kV) to determine the structure factor of the intermetallic L$_1_2$-type Cu$_3$Au cast-melting alloy. From the measured structure factor of the superlattice reflections, the S value was estimated as S=0.84 by assuming the sample thickness of 300 nm. Additionally, Kimoto et al. [23] determined S of bulk Cu$_3$Au samples using electron diffraction intensities recorded by a CCD camera. The integrated intensity was estimated by subtracting the averaged background from the averaged peak intensities at equivalent spots. Since the TEM samples were wedge shaped as prepared by electropolishing, the sample thickness was estimated as the distance from the wedge edge using a linear relationship. In order to obtain the intensity ratio $I_{110}/I_{220}$ of the superlattice (1 0 0) and fundamental (2 0 0) reflections they recorded symmetrical diffraction patterns along [0 0 1] zone axis from single-crystal areas, using either selected-area electron diffraction (SAED) with diameter of 270 nm or nanobeam electron diffraction (NBED) with diameter of 10 nm. Along this symmetrical low-index zone axis, as the dynamical scattering effect is very strong, precautions should be taken with the aid of simulations using the multi-slice method. Similar work was done to determine the S parameter of single nanoparticles according to the intensity ratio $I_{110}/I_{220}$ recorded using SAED [24] and NBED [25]. By multi-slice calculations in [24] they found that the ratio $I_{110}/I_{220}$ oscillates strongly with thickness $t$ along [0 0 1] direction as a result of strong dynamical scattering effect, while the ratio keeps an increasing monotonic relationship with $t$ along other high-index zone axes. From the simulations a relationship between $I_{110}/I_{220}$ and S was established, and thus S was determined from the measured intensity ratio $I_{110}/I_{220}$. Note that due to the possible structural and compositional variations as well as the experimental error the measurement of S from single crystals, either by SAED, CBED, or NBED, should be performed on multiple spots for a given sample. Currently the measurement of S as a function of the temperature $T$ using electron beam, as normally done using XRD [17–20], is not observed in the open literature.

The purpose of this work is to study the in-situ order–disorder transition behavior of the newly discovered L$_1_2$-type Au$_3$Fe$_{1–x}$ nanoparticles [4,6] using quantitative electron diffraction. So far the TEM is mainly used as a simple imaging tool for nanoparticle research, while quantitative studies using TEM data are limited. In this work we demonstrate that additional useful information can be retrieved through quantitative studies, specifically quantitative elemental and structural information from electron diffraction data. For the first time, a refinement algorithm proposed by Pawley [26] was applied to refine the electron diffraction data. Interestingly this refinement procedure is not related to the electron kinematical or dynamical scattering behavior, and thus it is perfectly suitable for the electron diffraction data. In addition, by taking advantage of nanoscale particles that exhibit less electron dynamic scattering effect, the Rietveld refinement [27] is also performed using a kinematical approach, for comparison. It is proposed that the S parameter can be determined from these refinements, which is further corrected by taking into account the dynamical effect using the Blackman theory [28]. Finally, a comparison with XRD refinement is made.

2. Experimental procedures and theoretical background

Samples of Au$_3$Fe$_{1–x}$ nanoparticles were synthesized by a previously reported low-temperature solution chemistry technique, using HAuCl$_4$, 3H$_2$O, oleylamine, n-butyllithium, and Fe(acac)$_3$. The synthesis details are identical to those in our previous reports [4,6]. Note that the synthesis uses n-butyllithium in a heated organic solvent, and extreme caution must be taken to avoid dangerous over-pressure situations. Standard glovebox and Schlenk-line techniques were used when carrying out the air-free synthesis. Nanoparticles were deposited on Cu grids with pure carbon as the support film, which can withstand up to 873 K without breaking. The TEM work was done using a JEOL 2010 at 200 kV, which was equipped with a Gatan SC1000 ORIUS CCD camera (4008 × 2672 pixel size), and an Oxford X-ray energy dispersive spectrometer (EDS) for chemical composition analysis. In order to minimize the electron beam damage, observations were made using reduced dose illumination and the view area was moved away from the electron beam during the heating process. The in-situ SAED experiment was performed at a constant camera length in diffraction mode and a constant magnification in the image mode. Altering the camera length or magnification results in camera length error due to the presence of magnetic hysteresis of the microscope used. In addition any necessary refocusing was made by moving the specimen Z-height mechanically, without using the electrical focus knob that interferes with the optical focus length. In the beginning of each TEM experiment, a commercial standard foil containing pure aluminum polycrystals was used to take a SAED pattern to calibrate the camera constant and correct any system distortions. The intensity profiles were produced using the ELD program [29,30] in the Crisp package [31], and then refined using the Reflex module in Materials Studio, Version 5.0, by Accelrys. The XRD data were collected using a Bruker Advance D8 X-ray diffractometer with Cu K$_\alpha$ radiation, and the refinements were performed using the GSAS program [32] with EXPGUI interface [33].

In powder diffraction, the intensity $I(\theta)$ at the scattering angle $2\theta$ is the sum of all $(h k l)$ reflections and the sum of the background function $B$, [34,35]:

$$I_{\text{cal}}(\theta) = \sum_{\text{hkl}} p_{\text{hkl}}(2\theta-2\theta_\text{hkl})I_{\text{hkl}} + \sum_{\text{i}} b_i B_i(\theta)$$

(1)

where $p_{\text{hkl}}$ is the profile function. The integrated Bragg intensity $I_{\text{hkl}}$ is defined by

$$I_{\text{hkl}} = M_{\text{hkl}}P_{\text{hkl}}I_{\text{hkl}}F_{\text{hkl}}^2$$

(2)

where $M_{\text{hkl}}$ is the multiplicity, $P_{\text{hkl}}$ is the preferred orientation factor, and $L_{\text{hkl}}$ is the Lorentz polarization factor. $F_{\text{hkl}}$ is the...
structure factor and is defined by

$$F_{hkl} = \sum_{n} f_n e^{2\pi i (h u_n + k v_n + l w_n)}$$

(3)

where $f_n$ is the atomic scattering factor of the $n$th atom at $(u_n, v_n, w_n)$ coordinate, among the total $N$ atoms in the unit cell.

In the standard Rietveld refinement [27] the structure factor $F$ is determined by the atoms in the unit cell according to Eq. (3), and thus the atomic coordinates and their temperature factors are refinable during the procedure. The X-ray and neutron diffraction refinements largely rely on this kinematical scattering event; however, for electron diffraction from thicker samples, dynamical scattering greatly modifies $F_{hkl}$, which is the major barrier to the quantification of electron diffraction data.

On the other hand the algorithm proposed by Pawley [26] considers the intensities $I_{hkl}$ themselves as refinable parameters, without the calculation of $F_{hkl}$ from Eq. (3) to avoid the dynamical effect on $I_{hkl}$ during the refinement procedure. As the reflection positions are constrained by the unit cell dimensions, as a return, it outputs cell dimensions, fitted background, and integrated Bragg intensities.

In both the Rietveld and Pawley algorithms, the parameters being refined are optimized in order to minimize the weighted profile $R$ factor $R_{wp}$:

$$R_{wp} = \sqrt{\frac{\sum w_i |I_{obs}(\theta_i) - I_{calc}(\theta_i)|^2}{\sum w_i |I_{obs}(\theta_i)|^2}}$$

(4)

where $w_i = 1/I_{obs}(\theta_i)$.

3. Results and discussion

3.1. Room temperature structure

Fig. 1(a) shows a representative TEM image of the nanoparticles. It is observed that the nanoparticles are almost evenly dispersed without overlapping. Quantitative measurements of the nanoparticle size using the program ImageJ [36] result in a mean size of 9.5 nm and a standard deviation of 4.1 nm from a sampling of 627 particles, which represents a fairly narrow size distribution [37]. A magnified image of a single particle is shown in Fig. 1(b), where crystalline lattice fringes are visible. The lattice spacing measurements are consistent with the $L1_2$-type structure. EDS composition measurements reveal an average composition of 84.5 ± 3.0% Au and 15.5 ± 3.0% Fe (both in atomic percent) based on 10 different spots, which deviates from the expected 3:1 ratio in stoichiometric $Au_3Fe$ and is consistent with an earlier report [6].

An example of the EDS spectrum is shown in Fig. 1(c). Further inspection of the nanoparticle structure using NBED confirms that they indeed possess the $L1_2$-type ordered structure, as shown in the two representative NBED patterns from single nanoparticles in Fig. 1(d) and (e), which exhibit weak $L1_2$ superlattice reflections between the strong fundamental reflections of the face-centered cubic (fcc) structure. Such $L1_2$ ordering is caused by the Fe atoms occupying the corner site, while Au atoms sit at the face center, as shown in the structure model in Fig. 1(f). Occasionally a few Au nanoparticles (Au rich in EDS) can also be found, which possess an fcc structure that coexists with the $L1_2$-ordered $Au_3Fe$ nanoparticles in the sample. In addition, impurity particles of iron oxides (Fe rich in EDS) can also be found, although they are very few.

In order to study the $Au_3Fe_{1-x}$ structure, precautions were made to choose areas without impurity particles as determined by the EDS measurements. An SAED pattern from the $Au_3Fe_{1-x}$ nanoparticles only is shown in Fig. 2(a), which contains both $L1_2$ superlattice and fundamental reflections as marked by vertical bars above and below the radial horizontal line, respectively. The intensity profile of the SAED pattern is shown in Fig. 2(b). In the low angle range, it is seen that the superlattice and fundamental reflections are superimposed upon the high background contributed by the strong center beam. Since the sample is very thin, the center beam is very strong. In order to remove the high background, the ELD program [29,30] offers background subtraction using a straight line. A closer fitting of the background intensity $I$ at 2θ scattering angle is to use the curve fitting of a power law, i.e.

$$I = b(2\theta)^c$$

(5)

where $b$ and $c$ are fitting parameters; here $b=51.422$, and $c=-0.89902$. The resulting intensity profile after subtracting the background clearly presents the weak $L1_2$ superlattice reflections among the fcc fundamental reflections, as shown in Fig. 2(b), although the background contribution is not completely removed.

Firstly, the Pawley refinement is performed on this pattern using the intensity profile in Fig. 2(b). Since the refining program can provide polynomial background fitting, the original profile without background removal was used as the input. After refining all necessary parameters (see Supplementary information) with sufficient cycles a good fit is achieved, with a weighted profile $R$-factor $R_{wp}=0.688$, background-corrected weighted profile $R$-factor $R_{wpb}=4.28\%$, and profile $R$-factor $R_p=0.48\%$, as shown in Fig. 2(c). The refined lattice parameter is $a=0.40554 \pm 0.00003$ nm, which is close to that in the previous report [4,6] as well as the XRD result in the following text. The refinement also outputs the fitted background, as shown in Fig. 2(c). After subtracting this background the experimental and simulated reflection intensities, as well as their difference curve, are plotted in Fig. 2(d). Note that as mentioned previously the intensity calculation is performed using Eq. (1) considering $I_{obs}$ as a refinable parameter, without calculating $F_{hkl}$ in Eq. (3). The high background, mainly from the strong center beam, is sufficiently removed. It is important to mention that since the SAED pattern contains high background from the center beam, $R_{wp}$ and $R_p$ are typically very low due to the high background contribution. However, $R_{wpb}$ is a good measurement of the similarities since it excludes the background contribution [34].

By NBED examination of single nanoparticles it is found that the nanoparticles are randomly oriented and most of them are off from their major diffraction zone axes, in which case the dynamical scattering effect is not dominant. Considering the small mean particle size, the Rietveld refinement [27] is performed, on the basis of the refined results available from the previous Pawley refinement, using a kinematical approximation as previously reported [38–40]. A trial using the ideal 75% Au–25% Fe model, i.e. where Au and Fe fully occupy the A (face center) and B (corner) sites, respectively, yields $R_{wpb}=6.39\%$ (refer to the Supplementary information Fig. S1). However further refinement of the Au and Fe occupancies results in a better agreement with $R_{wpb}=5.39\%$, as shown in Fig. 2(e) (refined parameters are provided in the Supplementary information). The refined occupancies are $1.0000\text{Au}$ at the A site, but only $0.603 \pm 0.005\text{Fe}$ at the B site, with about 40% vacancy. This configuration would result in an alloy composition of $83.3\%\text{Au}–16.7\%\text{Fe}$, which is in good agreement with the EDS measurement here and in the previous report [6]. The refined lattice parameter is $a=0.40049 \pm 0.00004$ nm, consistent with the Pawley refinement. Attempts at fitting the EDS data with any other compositional model, e.g. 100% Au at site A and a mixture of 60% Fe and 40% Au at site B, resulted in much higher $R$ value of $R_{wpb}=9.96\%$ (refer to Supplementary 1 If a lattice (lattice parameters and space group) is given, the Pawley refinement can be done even without atoms in the unit cell.
Fig. 1. (a) TEM image of Au$_3$Fe$_{1+x}$ nanoparticles; (b) magnified image from the framed area in (a) showing crystalline lattice fringes; (c) EDS spectrum; (d) and (e) NBED patterns from single nanoparticles (arrows indicate fundamental reflections); and (f) model crystal structure of Au$_3$Fe with the $L_{12}$ structure.

Fig. 2. (a) SAED pattern of Au$_3$Fe$_{1+x}$ at RT; (b) intensity profile, as well as the difference after subtracting the simulated background using the power law as described in the text; (c) the Pawley refinement (refined background is shown); (d) reflection intensities after subtracting the refined background in (c); (e) the Rietveld refinement (refined background is shown); and (f) reflection intensities after subtracting the refined background in (e).
information Fig. S2), where the superlattice reflection intensities are very weak, as the occupation of Au at the B site largely reduced the superlattice reflection intensities. This indicates that it is unlikely that Au can occupy the B site. The refined background is shown in Fig. 2(e). After subtracting this background the experimental and simulated reflection intensities, as well as their difference, are plotted in Fig. 2(f). The low R factor of $R_{wpb}=5.39\%$ is an indication for the validity of the kinematical approximation applied for the sample.

3.2. In-situ heating

An in-situ heating experiment is performed from room temperature (RT, 295 K) to 633 K, with a heating rate of about 10 K/min and a dwell time of $\sim$5 min at each temperature where a measurement is made, to ensure sample stability. The series of SAED patterns is shown in Fig. 3(a). It is seen that during the heating process the superlattice reflections remain visible up to 523 K, become very faint at 553 K, and then disappear at 593 K. The Rietveld refinements were made on each diffraction pattern, using the procedure as demonstrated previously in Fig. 2. The refined intensity profiles after background subtraction are shown in Fig. 3(b), while the refined occupancies of Au and Fe are shown in Fig. 4. At 338–553 K, the refinements are made based on the $L_1_2$ structural model. It is seen that from 338 to 523 K the refined occupancies remain essentially the same as at RT, although with some fluctuations due to experimental error. At 553 K very faint superlattice reflections are present, and the refinement is also made using this $L_1_2$ model. This results in 75.98% Au at site A and 75.38% Au at site B. With the presence of Au with large scattering factor $f$ at the A and B sites, the structure factor $F$ is dominated by Au. Fe, therefore, has a minimal contribution to the refinement and is thus unable to be refined. Hence, Fe is assigned as 14.6% at both A and B sites to maintain the same composition. The validity of this assignment is verified by the low R factor $R_{wpb}=6.95\%$. At this temperature, the disordering of Au and Fe atoms is almost completed. At 593 and 633 K the refinements are made based on the fcc structure, with 75% Au and 14.6% Fe randomly occupying each site. The remaining 10.4% is likely due to vacancies or light elements (e.g. Li) that are not detected.

Refined lattice parameter $a$ is plotted in Fig. 5(a). It is seen that $a$ essentially maintains a linear relation with temperature $T$ although with the presence of measurement error. A sudden
change occurs during the order–disorder transition, followed by a linear relationship again. Such linear relationships are fitted with straight lines, as indicated with arrows. The increased lattice parameter of the disordered structure is commonly present in other systems, such as Cu3Au [14,41], NiAl [41], and Ni3Al [41]. After cooling down to RT the SAED exhibits only the fundamental reflections without evidence of superlattice reflections, indicating that the order–disorder transition is irreversible. A second heating cycle is made in a similar manner with the disordered sample.

Since no superlattice reflections are present the refinements are made using the fcc model with 75% Au and 14.6% Fe, and the refined lattice parameter is given in Fig. 5(b). The refined lattice parameter of the disordered sample exhibits a nearly linear relationship again. Such linear relationships are fitted with regression result in Eq. (6), taking \(a_0=0.4005\) nm at 295 K and \(da/dT=5.8637 \times 10^{-6}\) in Eq. (6), the CTE is thus \(\alpha=1.46 \times 10^{-5}\) K\(^{-1}\), which is consistent with the CTE data \(\alpha_{Au}=1.42 \times 10^{-5}\) m m\(^{-1}\)K\(^{-1}\) and \(\alpha_{Fe}=1.18 \times 10^{-5}\) m m\(^{-1}\)K\(^{-1}\) [43] measured from bulk materials. The measure \(\alpha\) is slightly greater than \(\alpha_{Au}\) or \(\alpha_{Fe}\) or their mixture of the bulk materials, possibly because of size effects that have been observed in other studies [44,45], e.g. that nanoparticles exhibited greater CTE’s.

### 3.3. Determination of LRO parameter S

It is known that the LRO parameter \(S\) is defined as [17]

\[
S = \frac{3}{2} S_A + \frac{1}{2} S_F = \frac{3}{4} \left( \frac{\gamma_A - m_{Au}}{1 - m_{Au}} \right) + \frac{1}{4} \left( \frac{\gamma_F - m_{Fe}}{1 - m_{Fe}} \right)
\]

where \(\gamma_A\) and \(\gamma_F\) are the fractions occupied at the A and B sites, respectively, and \(m_{Au}\) and \(m_{Fe}\) are the proportions of Au and Fe in the alloy. The calculated \(S\), as well as \(S_A\) and \(S_F\) calculated from Au and Fe based on the refined occupancies (Fig. 4), is shown in Fig. 6, which shows the change of \(S\) as a function of temperature that is similar to those in other systems [14,17,18]. Note that due to the Fe vacancy, \(S<1\) even at room temperature. At 593 K, \(S\) is zero and thus the transition temperature \(T_c\) is within 553–593 K.

An alternative easier way to calculate LRO \(S\) is from the reflection intensities, which is normally done using XRD [17–20]. Here we calculate \(S\) using the integrated intensities of (1 0 0) and (2 2 0) that are not overlapped with others, as shown in Fig. 2(d) and (f). The refined (1 0 0) and (2 2 0) intensities and their ratio \(I_{100}/I_{220}\) by the Pawley and Rietveld methods are plotted in Fig. 7(a) and (b), respectively. Note that the (2 2 0) intensity varies at 523 K during the transition; such a variation was also present in the XRD intensity measurement [18]. The LRO parameter \(S\) can be obtained from the

![Fig. 6. LRO S determined from refined occupancies of Au and Fe, respectively, during the in-situ heating process.](image)

![Fig. 7. Refined (1 0 0) and (2 2 0) integrated intensities and their \(I_{100}/I_{220}\) ratios by the Rietveld (a) and Pawley (c) refinements, and the LRO S determined by the (1 0 0)/(2 2 0) pairs in (b) and (d), respectively.](image)
intensity ratio of (1 0 0) and (2 2 0) as follows:

\[ S^2 = \frac{I_{(100)}^0}{I_{(220)}^0} \left[ \frac{M^2}{e^{-2M}} \right] \frac{I_{(1220)}^0}{I_{(100)}^0} \]

where \( e^{-2M} \) is the temperature factor, and the Lorentz polarization factor \( L \) is expressed as

\[ L = \frac{1}{\sin \theta \sin 2\theta} \]

for electrons [34]. Note that the \( L \) for electrons is different from that for X-rays, which should be taken into account in the intensity calculation of powder electron diffraction. The structure factor is

\[ F = \begin{cases} |\gamma_{Fe}F_{Fe} + 3F_{Na}|, & \text{when } hkl \text{ are unmixed (all odd or all even)} \\ |\gamma_{Fe}F_{Fe} - F_{Na}|, & \text{when } hkl \text{ are mixed} \end{cases} \]

Therefore, \( S \) has a dependence on the Fe occupancy \( \gamma_{Fe} \) according to Eqs. (9) and (11). To compute \( S \), temperature factors are taken from Ref. [46], and the electron atomic scattering factors \( f_{Fe} \) and \( f_{Na} \) are taken from Ref. [47]. The calculated \( S \) at different \( \gamma_{Fe} \) levels is shown in Fig. 7(c) and (d) from the intensities by the Pawley and Rietveld refinements, respectively. At 553 K, the Rietveld refinement still gives low (1 0 0) intensity, \( I_{(100)}^0 = 0.34 \), while the Pawley refinement gives \( I_{(100)}^0 = 0.0 \). When \( \gamma_{Fe} \) is between 0.5 and 0.7, \( S \) is considerably close to the calculated value from the refined occupancies in Fig. 6. However, at higher \( \gamma_{Fe} \) levels, \( S > 1 \), which is untenable. Thus, this intensity calculation also supports the possibility of Fe vacancies at site B.

### 3.4. Dynamical effect correction of the LRO parameter \( S \)

To determine the LRO parameter \( S \) more accurately using electron diffraction, dynamical effects should be taken into account. In the past, by dynamical calculations using wedge-shaped NiAl as an example, Urban [48] demonstrated the sample thickness effect on the relationship between the intensity ratio \( I_{(100)}^0/I_{(220)}^0 \) and \( S \). It was shown that when the sample is thin (25 nm at 100 keV, or 50 nm at 1 MeV) the intensity ratio is proportional to \( S^2 \) over the entire range of \( 0 \leq S \leq 1 \), while for thicker samples the linear \( S^2 \) dependence only holds for \( 0 \leq S \leq 0.3 \). Currently, to correct for the dynamical effect of poly-ring diffraction patterns, the two-beam approximation theory proposed by Blackman [28] has been widely used in a variety of studies [49–54]. By introducing a correction factor \( D \), the structure factor \( F_{corr} \) and the observed \( F_{obs} \) agree [53]:

\[ F_{corr}^2 = F_{obs}^2 / D \]

Here, \( D \) at the thickness \( t \) is defined from

\[ D(t) = \frac{1}{A} \int_0^A J_0(2x)dx \]

where \( J_0(x) \) is the zero-order Bessel function, and \( A \) is defined as [28,54]

\[ A = \frac{2\pi m|e| V_F t^2}{\hbar^2 K^2} \]

where \( m \) and \( e \) are the electron mass and charge, respective, \( h \) is Planck’s constant, \( V_F \) is the Fourier coefficient of the crystal potential [55], \( K \) is the wave vector, \( F_F \) is the structure factor, and \( D \) is the unit cell volume. Here, the wave vector \( K \) inside the crystal is expressed as

\[ K^2 = \frac{2me|e| E}{\hbar^2} + U_0 \]

where \( E \) is the acceleration voltage and \( U_0 \) is the mean inner potential [56]. If one ignores \( U_0 \) then \( K = 1/\lambda \) and \( A \) is simplified to \( A = (\pi F_F / D) \), which are widely used in other studies [49–53], where \( \sigma \) is the interaction constant.

Using the calculated structure factor \( F \) of (1 0 0) and (2 2 0) with the temperature factor included the correction factors \( D_{100} \) and \( D_{220} \) are calculated, as plotted in Fig. 8(a). It is seen that the (1 0 0) beam, with smaller \( F \), decreases slower than (2 2 0) with larger \( F \). Therefore, the corrected intensity ratio \( I_{(100)}^0/I_{(220)}^0 \) is

\[ I_{(100)}^0 / I_{(220)}^0 \]

The ratio \( D_{220}/D_{100} \) is plotted in Fig. 8(b). At the thickness \( t = 9.5 \) nm, the ratios \( D_{220}/D_{100} \) at different \( \gamma_{Fe} \) levels are calculated as 0.9810 (\( \gamma_{Fe} = 0.4 \)), 0.9788 (\( \gamma_{Fe} = 0.5 \)), 0.9767 (\( \gamma_{Fe} = 0.6 \)), 0.9730 (\( \gamma_{Fe} = 0.7 \)), and 0.9744 (\( \gamma_{Fe} = 0.8 \)). After applying this

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**Fig. 8.** (a) Blackman correction factor \( D \) of (1 0 0) and (2 2 0) reflections; (b) ratio of \( D_{220}/D_{100} \); (c) corrected \( S \) by the Pawley refinement; and (d) corrected \( S \) by the Rietveld refinement.
3.5. Comparison with X-ray diffraction data

Generally, structural refinement by X-ray diffraction strongly depends on the sample purity. However, in our Au$_x$Fe$_{1-x}$ samples, the fcc Au phase always accompanies the L1$_2$ phase as an unavoidable impurity. Fig. 9(a) and (b) shows two XRD patterns from two samples synthesized using different procedures [4,6]. In Fig. 9(a), the fcc phase is very evident. After subtracting the background using a smoothing procedure [57] an enlarged part is shown in the inset, where the fcc peaks, as indicated by arrows at the left side of (1 1 1) and (2 0 0) peaks, are almost at the same height as that of the L1$_2$ phase. Note that the lattice parameter of the fcc Au is slightly larger than that of the L1$_2$ phase, since it does not contain Fe with a smaller atomic radius. Therefore, the fcc peaks appear at the left side of the L1$_2$ peaks.

In Fig. 9(b), the L1$_2$ phase is the predominant phase. As shown in the inset after subtracting the background, however, the two major (1 1 1) and (2 0 0) peaks are not symmetrical, due to the existence of secondary fcc phase, as indicated by arrows. The Rietveld refinements are made based on this pattern. The first attempt using the single L1$_2$ phase results $R_{wpb}=7.82\%$ without background contribution. As shown in Fig. 9(c) a relatively large error is present before the (1 1 1) peak, since the simulated peak is symmetrical. However, if both L1$_2$ and fcc phases are considered, the refinement yields a better fit, with $R_{wpb}=5.56\%$. The refined intensity ratio is 15.53:1, which yields weight fraction of 92.46 wt% L1$_2$ and 7.54 wt% fcc Au phase. By the addition of the fcc phase the error before the (1 1 1) peak is significantly reduced, as shown in Fig. 9(d). The refinement results are listed in Table 1. The XRD refinements also show that site B is not fully occupied with Fe, $\gamma_{fe}=0.5624$. For the secondary fcc phase, the refinement indicates no Fe inclusion. Since its lattice parameter $a=0.40682$ nm is slightly smaller than that of pure Au ($a=0.40783$ nm), as well as the observation of low Fe signals from the EDS measurement, the possible small fraction of Fe that may exist in the fcc phase cannot be refined since Au has a much larger atomic radius.

Fig. 9. XRD patterns of two Au$_x$Fe$_{1-x}$ samples with large (a) and minor (b) fcc phase impurities. The Rietveld refinement of the data from (b) using (c) a single L1$_2$ phase and (d) using a mixture of L1$_2$ and fcc phases. Insets are the magnified portion after subtracting the background. Arrows indicate the peaks from the fcc phase.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Single L1$_2$ Phase</th>
<th>Mixture of L1$_2$ and fcc phases</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>L1$_2$</td>
<td>fcc</td>
</tr>
<tr>
<td>Lattice parameter $a$ (nm)</td>
<td>0.3986687</td>
<td>0.3986558</td>
</tr>
<tr>
<td></td>
<td>Au: 1.0000, Fe: 0.5211</td>
<td>Au: 1.0000, Fe: 0.5624</td>
</tr>
<tr>
<td></td>
<td>Au: 1.0000, Fe: 0.05935</td>
<td>Au: 1.0000, Fe: 0.0000</td>
</tr>
<tr>
<td>Occupancies (Au at site A and Fe at site B for L1$_2$, and identical site for fcc)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotropic temperature factor $U_{iso}$ ($\AA^2$)</td>
<td>0.0257, Fe: 0.05935</td>
<td>Au: 0.02647, Fe: 0.08617</td>
</tr>
<tr>
<td>Scale factors: histogram scale $S_h$, phase fraction scale $S_{ph}$, weight fractions $W_p$</td>
<td>$S_h=0.50949$, $W_p=100%$</td>
<td>$S_h=175.56$, $S_{ph}=0.284682$, $W_p=92.46%$</td>
</tr>
<tr>
<td>$R$ factors</td>
<td>$R_{wpb}=7.82%$, $R_{wp}=7.33%$</td>
<td>$R_{wpb}=5.56%$, $R_{wp}=5.67%$</td>
</tr>
<tr>
<td></td>
<td>$R_{wp}=5.89%$, $R_p=7.75%$</td>
<td>$R_{wp}=4.44%$, $R_p=5.53%$</td>
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</tbody>
</table>
In summary, we have studied the in-situ order–disorder transition of Au$_3$Fe$_{1-x}$ nanoparticles by retrieving their structure information from the electron diffraction data. The major results are summarized as follows:

(1) Both Pawley and Rietveld refinements were made on the electron diffraction data. Since the Pawley refinement is unrelated to the electron kinematical or dynamical scattering nature, it was especially useful to process the diffraction data to achieve useful information such as lattice parameters, background subtraction, and reflection intensities. Considering the small nanoparticle size, the Rietveld refinement was also made using a kinematical approximation, and the results are consistent with those of the Pawley refinement as well as the XRD refinement.

(2) The material that was studied, nanoparticles of Au$_3$Fe$_{1-x}$, possesses an $L_1_2$-type ordered structure, but contains about 40% vacancies at the Fe site, based on the Rietveld refinement as well as EDS measurements. Upon in-situ heating this ordered phase displayed an irreversible order–disorder transition, with the transition temperature between 553 and 593 K.

(3) The lattice parameters were measured using the refinements. During the order–disorder transition, a sudden change in lattice parameter was detected during the first heating from the ordered phase, while the second heating of the disordered phase showed only a linear relationship with temperature $T$. From the lattice parameter measurement of the disordered phase, the coefficient of thermal expansion could be estimated.

(4) The long-range order parameter $S$ during the order–disorder transition was determined from the refined site occupancies using the Rietveld refinement, as well as the integrated intensities of the superlattice $(100)$ and fundamental $(220)$ reflections using both Pawley and Rietveld refinements. Further, the Blackman two-beam approximation theory was used to correct the dynamical scattering effect.

Since the interaction of electrons with the specimen is much stronger than with X-rays, studies using electron beams may be made on limited local areas without the strong requirement of sample purity as for XRD refinement. In the present sample, as the fcc phase (similar to a disordered structure from $L_1_2$) is unavoidable with the $L_1_2$ structure, electron diffraction is more feasible than XRD refinement. Especially the refinement using electron beam can be combined with other TEM techniques such as EDS, electron energy loss spectroscopy, scanning TEM, and in-situ TEM experiment to obtain additional structural and chemical information.

Acknowledgment

The Reflex module in Materials Studio for simulating the powder electron diffraction patterns was provided by the Laboratory for Molecular Simulation, Department of Chemistry, Texas A&M University. The synthesis work (R.E.S., Y.V., J.F.B., and materials) was supported by the U.S. Department of Energy (DE-FG02-06ER46333).

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ultramic.2011.04.003.

References