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Original Article

EXAFS Debye-Waller Factors of B2-FeAl Alloys

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Abstract: This work develops the anharmonic correlated Debye model to study the temperature-dependent extended X-ray absorption fine structure (EXAFS) Debye-Waller factors (DWFs) of B2-FeAl alloys. We derived the analytical expressions of the EXAFS DWF and Debye frequency as functions of temperature. Numerical calculations were performed for $Fe_{1-y}Al_y$ alloys with various Al concentration (y = 0.35, 0.40, 0.45 and 0.50) in which Fe-Al alloys still maintained B2 structure. The good agreement between our theoretical results with previous data verifies our developed theory. Our calculations show that DWFs of $Fe_{1-y}Al_y$ alloys increase robustly when temperature and/or Al concentration in $Fe_{1-y}Al_y$ alloys increase. The increasing of DWF will cause the reduction of the amplitude of EXAFS.

Keywords: EXAFS, Debye-Waller factors, Debye model, Anharmonicity, Fe-Al alloys

1. Introduction

Extended X-ray absorption fine structure (EXAFS) is an effective method for investigating the structure and thermodynamic properties of crystalline materials [1]. One of the methods to analyze the EXAFS oscillation is the cumulant expansion approach in which second cumulant $\sigma^2 = \sigma^{(2)}$ is an important factor affecting sensitively amplitudes of EXAFS through the factor $\exp\left(-2\sigma^2 k^2\right)$ [2,3]. The second cumulant, so-called the Debye-Waller factor (DWF), has the form as

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$$\sigma^2 = \left\langle \left[\vec{R}.(\vec{u}_i - \vec{u}_0) \right]^2 \right\rangle = \left\langle u_i^2 \right\rangle + \left\langle u_0^2 \right\rangle - 2\left\langle u_i u_0 \right\rangle, \quad (1)$$

where, the brackets stand for the thermal average, the unit vector $\vec{R}$ pointing from the *0*th site toward the *i*th site, $\vec{u}_0$ and $\vec{u}_i$ are the displacements of the *0*th and the *i*th sites from their equilibrium positions; $\left\langle u_i^2 \right\rangle$ and $\left\langle u_0^2 \right\rangle$ are the uncorrelated mean-square displacements, while $2\left\langle u_i u_0 \right\rangle$ is the correlation function.

EXAFS and EXAFS cumulants including DWF are sensitive to temperature [4]. This fact can lead to uncertainties in physical information taken from EXAFS. In order to consider the temperature-dependent EXAFS cumulants of crystals, Hung and his collaborators proposed the anharmonic correlated Debye model (ACDM) [5] which has been developed further to study thermal disorder of binary alloys [6]. However, the authors just focused on the specific case of FeAl alloys, $Fe_{0.6}Al_{0.4}$. In this work, we apply the ACDM to calculate and analyze the dependence of EXAFS DWFs of $Fe_{1-y}Al_y$ alloys on temperature and Al concentration.

2. Theory

The ACDM is characterized by an anharmonic effective interaction potential $V_{eff}(x)$ which is contributed by the oscillation of absorbing and back-scattering atoms, and their neighbors as [5]

$$V_{eff}(x) = V(x) + \sum_{j \neq i} V\left(\frac{\mu}{M_i} x\hat{\mathbf{R}}_{12}.\hat{\mathbf{R}}_{ij} \right) \cong \frac{1}{2} k_{eff} x^2 + k_3 x^3 + \cdots, \quad (2)$$

where $V(x)$ is the interaction potential between absorber and backscatterer; $i = 1$ and $i = 2$ correspond to absorber and backscatterer, respectively, and the sum j is over all their nearest neighbors, excluding the absorber and backscatterer themselves; k_{eff} is the effective force constant; k_3 is the cubic parameter giving an asymmetry in the pair distribution function; $x = r - r_0$ is the deviation of instantaneous bond length between the two intermediate atoms from equilibrium.

If we assume the Morse pair potential $V(r) = D\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right]$ can be used to describe the interaction between intermediate atoms, the effective potential for B2 structure can be derived as [6]

$$V_{eff}(x) \approx \frac{11}{6} D\alpha^2 x^2 - \frac{3}{4} D\alpha^3 x^3 + \ldots, \quad (3)$$

where *D* and α are the Morse potential parameters, r_0 is the equilibrium distance of two neighbor atoms.

For $Fe_{1-y}Al_y$ alloys, the interatomic effective potential V_{eff} of system is contributed by both Fe-Al pairs and Fe-Fe interactions. The increasing of Al concentration will reduce the number of Fe-Fe nearest-neighbor bonds. The anharmonic effective interaction potential V_{eff} can be approximated as follows: [6]

$$V_{eff} = 2yV_{eff}^{FeAl} + (1-2y)V_{eff}^{Fe} \quad (4)$$

where V_{eff}^{FeAl} and V_{eff}^{Fe} are the effective potential between Fe and Al atoms, and between Fe atoms, respectively.

From Eqs. (3) and (4), the effective force constant k_{eff} of $Fe_{1-y}Al_y$ alloys can be derived as

$$k_{eff} = 2yk_{eff}^{FeAl} + (1-2y)k_{eff}^{Fe}, \quad (5)$$

where

$$k_{eff}^{Fe} = \frac{11}{3}D_0^{Fe}\left(\alpha^{Fe}\right)^2 \; ; \quad k_{eff}^{FeAl} = \left[1+\frac{5}{3}\left(\mu_{Fe}^2+\mu_{Al}^2\right)\right]D_0^{FeAl}\left(\alpha^{FeAl}\right)^2, \quad (6)$$

and

$$\mu_{Fe} = \frac{M_{Fe}}{M_{Fe}+M_{Al}}, \quad \mu_{Al} = \frac{M_{Al}}{M_{Fe}+M_{Al}}. \quad (7)$$

Finally, we obtain the expression of the temperature-dependent EXAFS DWF as [5,6]

$$\sigma^2 = \left\langle \left(r - r_0 - \sigma^{(1)}\right)^2 \right\rangle = \sigma_0^{(2)} \int_0^{\pi/a} \omega(q) \frac{1+Z(q)}{1-Z(q)} dq, \quad (8)$$

where $\sigma_0^{(2)} = -\frac{\hbar a}{2\pi} \frac{1}{2yk_{eff}^{FeAl} + (1-2y)k_{eff}^{Fe}}$; q is the phonon wave number, a is the lattice constant; M is the mass of composite atoms, the correlated Debye frequency is $\omega_D = 2\sqrt{k_{eff}/M}$; $Z(q) = \exp\left(\beta\hbar\omega(q)\right)$ with $\omega(q) = 2\omega_D \left|\sin\left(\frac{qa}{2}\right)\right|$ is the phonon vibration frequency, $\left|q \le \frac{\pi}{a}\right|$.

3. Results and Discussion

In this section, the expressions derived in the previous section are used to numerically calculate DWFs of $Fe_{1-y}Al_y$ alloys with various Al concentration (y = 0.35, 0.40, 0.45 and 0.50) in which Fe-Al alloys still maintain B2 structure. The Morse potential parameters derived within the Möbius lattice inversion scheme [7], describing the Fe-Fe and Fe-Al interactions are shown in Table 1.

Table 1. The Morse potential parameters for B2-type $Fe_{1-y}Al_y$ alloys [7].

A – B	D_0^{A-B} (Å)	α^{A-B} (eV)	r_0^{A-B} (Å^{-1})
Fe–Fe	0.346	2.562	2.507
Fe–Al	0.269	1.850	2.656

Applying our developed ACDM model, we derive the force constants k_{eff} , k_3 , Debye frequency ω_D (see Table 2), and anharmonic effective potential V_{eff} of Fe-Al alloys. In Figure 1, we show the anharmonic effective potentials V_{eff} of $Fe_{1-y}Al_y$ alloys as functions of $x = r - r_0$ with various Al concentration. As can be seen in Figure 1, these potential curves are asymmetric due to the anharmonic contributions described by the third order force constant k_3 of these potentials. The effective potential curve of FeAl alloys is opened out when Al concentration increases. These anharmonic effective potentials of FeAl alloys are going to be used for calculating the EXAFS DWF.

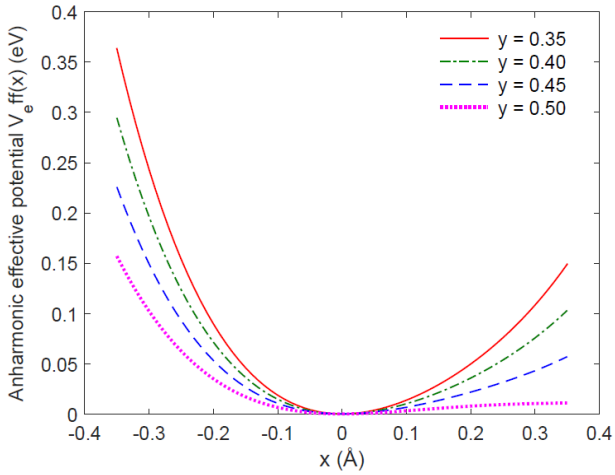

Figure 1. Anharmonic effective potential V_{eff} of $Fe_{1-y}Al_y$ alloys.

Table 2. The force constants and Debye frequencies of B2-type Fe-Al compounds.

Alloys	k_{eff} (eV/Å^2)	k_3 (eV/Å^3)	ω_D (′ 10^{13} Hz)
$Fe_{0.65}Al_{0.35}$	3.1427	-2.5014	5.1528
$Fe_{0.60}Al_{0.40}$	2.4020	-2.2353	4.5776
$Fe_{0.55}Al_{0.45}$	1.6613	-1.9693	3.8705
$Fe_{0.50}Al_{0.50}$	0.9207	-1.7032	2.9311

The temperature dependence of EXAFS second cumulants of Fe-Al alloys is presented in Figure 2. It can be observed from this figure that the DWF curves of Fe-Al alloys are almost similar and rise linearly when temperature increases. The rapid development of DWF indicates the significant contributions of thermal lattice vibrations at high temperature. This phenomenon can be explained that when temperature rises the thermal vibration of atoms increases resulting in the enhancement of mean-square relative displacement or DWF, which causes the reduction of the EXAFS amplitude at high temperature. Furthermore, as can be seen from Figure 2, when we increase the Al concentration, the DWFs of $Fe_{1-y}Al_y$ also increases. At temperature lower than 50 K the values of the second cumulants are very small but different from zero due to the zero-point vibration contributions (a quantum effect). In our calculations, the zero-point contributions to DWFs of $Fe_{0.65}Al_{0.35}$, $Fe_{0.60}Al_{0.40}$, $Fe_{0.55}Al_{0.45}$, $Fe_{0.50}Al_{0.50}$ alloys are 0.0032 Å^2, 0.0035 Å^2, 0.0040 Å^2 and 0.0048 Å^2, respectively.

In Figure 3, due to the lack of experimental EXAFS DWFs of Fe-Al alloys, the change of DWF of FeAl alloy (y = 0.50) is shown. The measurements of the change of EXAFS DWF $\Delta\sigma^2$ relative to the lowest temperature value for the first three-shell distances of FeAl have also been presented for comparison [8]. The composition of this bulk sample of FeAl was not analyzed, but the material was weighed before and after melting, with minimal weight loss. The structure was verified by X-ray diffraction with no extraneous peaks. The authors measured EXAFS spectra at beam line X-11 of the National Synchrotron Light Source [8]. As can be observed from Figure 3, our theoretical results of FeAl alloy (y = 0.50) are consistent with experimental measurements for the second-neighbor shell up to temperature of 300 K. It is worth mentioning that by comparing the change of EXAFS DWF relative

to the lowest temperature value, we can eliminate errors in calculation of the structural disorder which is caused by strain or alloying.

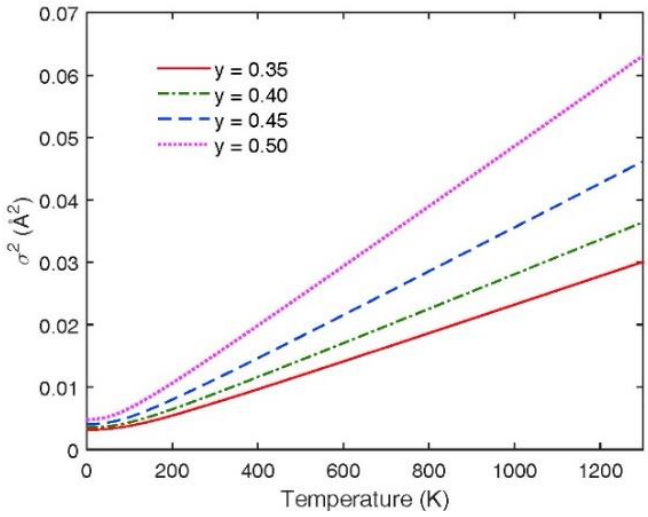

Figure 2. The EXAFS DWFs of $Fe_{1-y}Al_y$ alloys with various Al concentration.

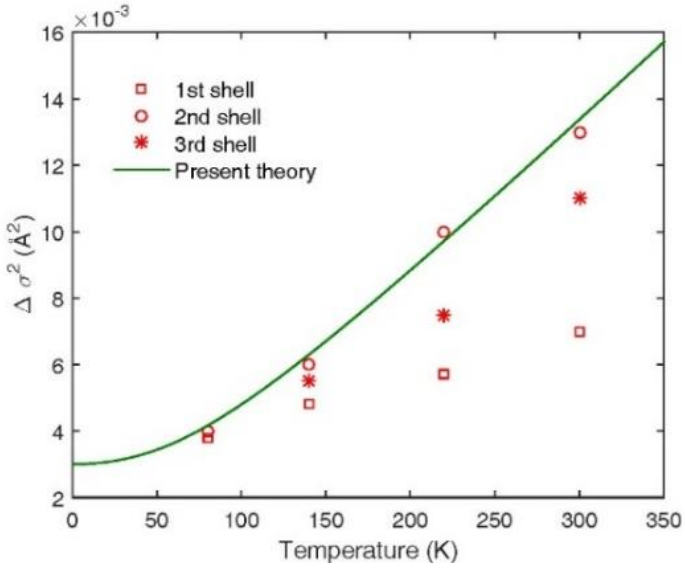

Figure 3. The change of EXAFS DWF of FeAl alloy.
The experimental measurements are shown for comparison [8].

4. Conclusion

In this work, we applied the ACDM to investigate the dependence of EXAFS DWFs of $Fe_{1-y}Al_y$ on temperature and Al concentration. The analytical expressions of the EXAFS DWF and

Debye frequency have been derived. We performed numerical calculations for $Fe_{1-y}Al_y$ alloys with various Al concentration (y = 0.35, 0.40, 0.45 and 0.50) in which Fe-Al alloys still maintain B2 structure. The theoretical calculations are in good agreement with those of previous data verifying our developed theory. Our calculations show that the DWFs of $Fe_{1-y}Al_y$ alloys increase rapidly when temperature and/or Al concentration in $Fe_{1-y}Al_y$ alloys increase. The increasing of DWFs reduces the amplitudes of the EXAFS spectra.

Acknowledgments

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