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High-pressure EXAFS Debye-Waller Factors of Metals

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Abstract: The anharmonic correlated Debye model has been developed to investigate the pressure effects on the extended X-ray absorption fine structure (EXAFS) Debye-Waller factors of metals. The recent well-established Grüneisen parameter expressions have been applied to formulate the pressure-dependent analytical expressions of the effective spring constant, correlated Debye frequency and temperature. Combing with the anharmonic correlated Debye model, the expression of EXAFS Debye–Waller factor under pressure can be derived. Numerical calculations, performed for Fe and Cu metals show reasonable agreement with experiments.

*Keywords:*EXAFS, Debye-Waller factors, Debye model, Anharmonicity, Pressure

1. Introduction

One of the most effective methods for investigation the structure and thermodynamic properties of crystals is extended X-ray absorption fine structure (EXAFS) [1]. The anharmonic EXAFS provides information on structural and thermodynamic properties of substances. The EXAFS oscillation has been analyzed by means of cumulant expansion approach containing the second cumulant $\sigma^2 = \sigma^2$ which is an important factor in EXAFS analysis since the thermal lattice vibrations affect sensitively on the XAFS amplitudes through the factor $\exp -2\sigma^2 k^2$. The second cumulant corresponds to the parallel mean square relative displacement or Debye-Waller factor (DWF).

The EXAFS is sensitive to temperature and pressure [2] which can make changes of cumulants including DWF, which in turn lead to uncertainties in physical information taken from EXAFS. In the recent years, the remarkable developments of EXAFS techniques permit the experiments with unprecedented accuracy under extreme conditions of high pressure and temperature. In 2011, Hung et al. have developed the anharmonic correlated Einstein model to determine the DWF of crystals at high pressure [3]. However, this model is still limited. Recently the anharmonic correlated Debye model

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(ACDM) has been used to calculate the temperature dependence of EXAFS cumulants of crystals at zero pressure [4]. The purpose of this work is to develop the ACDM for calculation and analysis of pressure effects on EXAFS DWF of metals at a given temperature.

2. Theory

On the theoretical determination of EXAFS DWF, many great ideas has been put forward such as correlated Einstein model [5], statistical moment method [6],.... In line with the Debye model, Hung et al. developed the ACDM and successfully investigated the temperature-dependent EXAFS cumulants, including DWF [4]. In this model, the second cumulant has been derived as

$$\sigma^2 = -\frac{\hbar a}{2\pi k_{eff}} \int_0^{\pi/a} \omega\ q\ \frac{1+Z\ q}{1-Z\ q} dq \quad , \tag{1}$$

where q is the phonon wave number, a is the lattice constant, M is the mass of composite atoms, and k_{0eff} is the effective local force constant, $Z\ q = \exp\ \beta\hbar\omega\ q$ with $\omega\ q$ is the phonon vibration frequency and has the form as $\omega\ q = 2\sqrt{\frac{k_{0eff}}{M}}\left|\sin\left(\frac{qa}{2}\right)\right|$, $\left|q \le \frac{\pi}{a}\right|$. The correlated Debye frequency ω_{0D} and temperature θ_{0D} are $\omega_{0D} = 2\sqrt{k_{0eff}/M}$; $\theta_{0D} = \hbar\omega_{0D}/k_B$, respectively.

In this work, the ACDM will be developed to investigate the pressure (and volume) dependence of EXAFS DWF through the local force constant $k_{eff} = M\omega_D^2/4$ by considering the definition of the Grüneisen parameter in Debye model as

$$\gamma_G = -\frac{\partial \ln \omega_D}{\partial \ln V} \quad , \tag{2}$$

where V is the volume of crystal, ω_D is the Debye frequency depending on V (and also pressure P).

At low pressure, the Grüneisen parameter of material can be seen as constant. However, previous works [7, 8] showed that the Grüneisen parameter reduced gradually when pressure increased. Recently, through the consideration of low- and ultra-high-pressure limits in the Thomas-Fermi approximation, Burakovsky et al. proposed an analytic model of the Grüneisen parameter of solid at all densities as[9, 10]

$$\gamma_G = 1/2 + \gamma_1\eta^{1/3} + \gamma_2\eta^q \quad \text{with } \gamma_1, \gamma_2, q = \text{const},\ q > 1 \quad , \tag{3}$$

here V_0 and $\eta = V/V_0$ are the crystal volume at zero pressure and volume compression, respectively.

By making the combination of the Eq. (3) with Eq. (2) and taking the integration, we derived the volume-dependent expressions of the Debye frequency ω_D and temperature θ_D, respectively, as

$$\omega_D\ \eta\ = \omega_{0D}\eta^{-1/2} \exp\left[-3\gamma_1\ \eta^{1/3} - 1\ - \frac{\gamma_2}{q}\ \eta^q - 1\right], \tag{4}$$

$$\theta_D\ \eta\ = \theta_{0D}\eta^{-1/2}\exp\left[-3\gamma_1\ \eta^{1/3}-1\ -\frac{\gamma_2}{q}\ \eta^{q}-1\right], \tag{5}$$

where the Debye frequency ω_{0D} and temperature $\theta_{0D}=\hbar\omega_{0D}/k_B$ of material at ambient pressure can be gathered from experiments or determined from the correlated Debye model [4].

In pursuance of investigation of the pressure effects on the thermodynamic quantities, we need to know the equation-of-state (EOS) of crystal. There are many EOSs that have been used on studying thermodynamic properties at high pressure of materials such as Birch-Murnaghan [11], Holzapfel [12]... In the work of Cohen et al. [13], the Vinet equation is found to be the most accurate one at high compression. The well-established Vinet EOS has the form as [14]

$$P=3K_0\eta^{-2/3}\ 1-\eta^{1/3}\ \exp\left[\frac{3}{2}\ K_0^{'}-1\ \times\ 1-\eta^{1/3}\ \right], \tag{6}$$

where K_0 and K_0' are correspondingly the isothermal bulk modulus and its first-pressure derivative.

3. Results and discussion

In this section, the expressions derived in the previous section will be used to numerically calculate thermodynamic quantities including the Debye frequency and temperature, and DWF of copper and iron metals.

For the sake of simplicity, in the present work, the interatomic potential between two intermediate atoms is assumed to be the Morse potential $V\ r\ = D\left[e^{-2\alpha\ r-r_0}\ -2e^{-\alpha\ r-r_0}\ \right]$, where α describes the width of the potential, D is dissociation energy, and r_0 is the equilibrium distance of the two atoms. It is obviously that the indispensable input parameters required to determine the thermodynamic quantities as functions of compression η (and pressure P) are the isothermal bulk modulus K_0, the first-pressure derivative K_0' and γ_1,γ_2,q of Grüneisen parameter. The bulk modulus and its first-pressure derivative can be gathered from experiments while the values of γ_1,γ_2,q could be obtained by fitting Eq. (3) with experimental data of copper [15] and iron [16]. The Morse potential parameters, K_0 and K_0', and fitting parameters γ_1,γ_2,q of copper and iron are shown in the Table 1.

Table 1. Morse potential parameters D, α [17]; isothermal bulk modulus K_0 and its first-pressure derivative K_0'; and fitting parameters γ_1,γ_2,q of copper and iron.

Metals	γ_1	γ_2	q	α (Å^{-1})	D (eV)	K_0 (GPa)	$K_0^{'}$
Cu	-2.6667	4.1935	1.1941	1.3588	0.3429	133.41	5.37
Fe	-0.1603	1.4092	1.0003	1.3885	0.4174	148.4	6.126

In Fig. 1, we display the experimental Grüneisen parameters of copper [15] and iron [16] and our fitting curves. As it can be seen in this figure, the Grüneisen parameters of metals can be well described by the Eq. (3) up to high compression. Using the derived parameters γ_1, γ_2, q, we continue calculating the pressure-dependent Debye frequency and temperature, and then the EXAFS DWF of copper and iron.

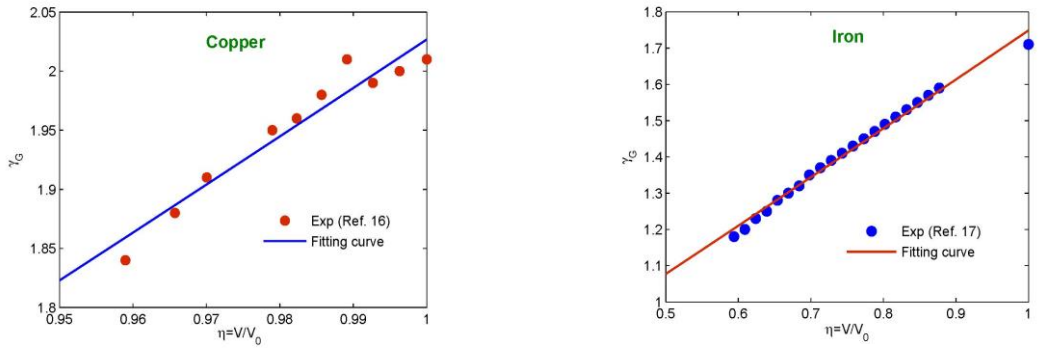

Fig1. Experimental Grüneisen parameters of copper and iron and our fitting curves.

The pressure dependence of EXAFS second cumulants of copper and iron at room temperature are presented in Fig. 2 & 3. From the Fig. 2, we can see that the DWF curves of metals are almost similar and diminish gradually when pressure increases. These results will affect the EXAFS amplitude. Here, we should be noted that in the pressure below 12 GPa, iron is in the $\alpha-$phase with body-centered cubic structure while copper is in face-centered cubic structure. At pressure $P=0$, the DWF of Cu and Fe are, 8.6×10^{-3} Å^2 and 9.2×10^{-3} Å^2, respectively. Up to pressure 12 GPa, the DWF σ^2 are reduced and have the values 6.6×10^{-3} Å^2 and 7.5×10^{-3} Å^2, correspondingly. This phenomenon can be explained that when pressure increases the vibration of atoms will be limited and it results in the reduction of atomic mean-square relative displacement (or DWF). In Fig. 3, because of the lack of DWF experimental data of these two metals, we present the change in DWF $\sigma^2\ P\ -\sigma^2\ 0$ along with those of calculations for metallic copper by Freund et al. [18]. It can be seen in this figure, results of our developed ACDM are in very good agreement with those of previous studies up to 10 GPa but with lower values.

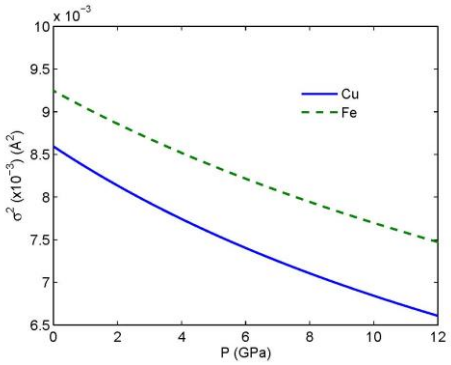

Fig. 2. EXAFS DWF of copper and iron as functions of pressure.

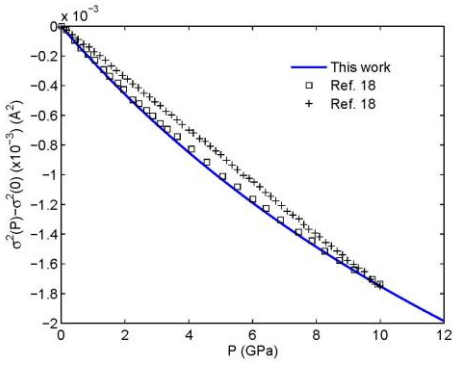

Fig. 3. Change in DWF $\sigma^2\ P\ -\sigma^2\ 0$ of copper as a function of pressure.

4. Conclusions

In this work, the ACDM has been developed to investigate the EXAFS Debye-Waller factors of metals at pressure. The pressure-dependent analytical expressions of the Debye frequency and temperature, EXAFS Debye–Waller factor have been derived. We have performed numerical calculations for copper and iron metals. Theoretical calculations are in very good agreement with those of previous data verifying our developed theory. Our calculations show that the Debye-Waller factor of metals diminish gradually, and then reduce the EXAFS amplitude when pressure increases. This approach could be used to verify as well as analyze the future high-pressure experiments. It also could be applied to study other thermodynamic parameters in EXAFS theory in the near future.

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