Estimation of Phonon Dispersion Relations Using Correlation Effects Among Thermal Displacements of Atoms

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ABSTRACT

Neutron diffraction measurement of powder α-Fe sample at 295 K was carried out at the high resolution powder diffractometer installed at Japan Proton Accelerator Research Complex (J-PARC). Crystal parameters were determined from Rietveld analysis. The correlation effects among thermal displacements of atoms were estimated from a generalized equation based on the results of fomer diffuse scattering analysis. The force constants among atoms were obtained using an equation for transforming of the correlation effects to force constants. The force constants and the crystal structure of α-Fe were used to estimate the phonon dispersion relations, phonon density of states, and specific heat by computer simulation. The obtained force constants among first-nearest-neighboring atoms is 2.3 eV/$\mathring{A}^2$ at 295 K and the specific heat is 185 meV/K at 150 K. The calculated phonon dispersion relations and specific heat of α-Fe are similar to those obtained from inelastic neutron scattering and specific heat measurements, respectively.

INTRODUCTION

Diffuse scattering data are very important in the analysis of the static and dynamic disorder in crystals[1]. The static disorder is related to atomic arrangements and atomic defects. For instance, the short-range order in binary alloys has been studied for a long time. The application of diffuse scattering measurements to the problems of dynamic disorder has been started by neutron diffraction measurement. Broad oscillations of the diffuse scattering intensity of ordered crystals, where there are no static disorder, were observed and explained by the correlation effects among thermal displacements of atoms[2-6].

The interatomic force constant among first nearest neighboring atoms had been obtained from the thermal displacements of atoms in the extended X-ray absorption fine structure (EXAFS) analysis [7-9]. Recently, neutron diffraction measurement of an aluminum powder sample was carried out at the high resolution powder diffractometer installed at JRR-3[10]. The interatomic force constants among the first-, second-, and third-nearest-neighboring atoms were determined from the correlation effects using a newly introduced equation of transforming. The derived force constants and the crystal structure of fcc Al were used to estimate the phonon dispersion relations, phonon density of states, and specific heat by computer simulation.

In this paper, the correlation effects of bcc Fe (α-Fe) are estimated from interatomic distances using a generalized equation for the former diffuse

scattering analysis. An algorithm for transforming of the correlation effects among thermal displacements of atoms to force constants is applied to determine the force constants. The force constants of α-Fe are used to estimate the phonon dispersion relations, phonon density of states, and specific heat by computer simulation. The calculated phonon dispersion relations and specific heat are compared with those obtained by inelastic neutron scattering and specific heat measurements of α-Fe[11-13].

EXPERIMENTAL METHODS

The powder α-Fe sample (99.9%, Kojundo Chemical) was sealed in V-Ni can with 6 mm diameter. Since the small vanadium Bragg peaks will be detected from a high flux beam experiment in J-PARC, the vanadium sample container alloyed with nickel which cancels the vanadium coherent scattering amplitude was used [14].

Neutron diffraction measurements were performed at 295 K with IBARAKI Materials Design Diffractometer (iMATERIA) installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC [15]. The diffraction intensities were collected by time of flight (TOF) method. The effective *d*-range was from 0.32 Å to 2.8 Å in back scattering bank.

The observed powder diffraction intensities of α-Fe at 295 K are shown in Fig. 1. Calculations by Rietveld analysis were performed using Z-Rietveld [16]. The crystal structure of α-Fe in the Rietveld analysis belongs to a bcc type with the space group Im-3m. The iron atoms occupy 2*a* positions. The refined structural parameters of lattice constant and the parameter of Debye-Waller temperature factor are a=2.866566(2) Å and B=0.270(1) Å^2, respectively. The diffuse scattering intensity of *d* spacing is shown in Fig. 2. There are oscillatory peaks in the diffuse scattering near *d*~0.34, 0.39 and 0.47.
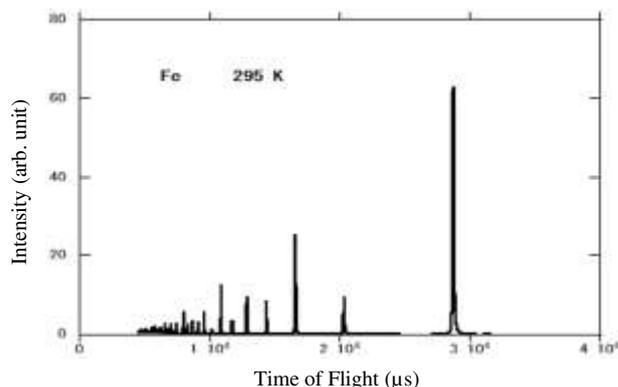

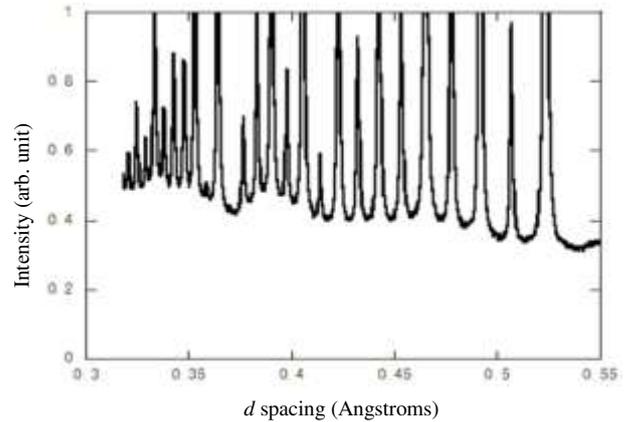**Fig. 1.** Powder diffraction pattern of α-Fe at 295 K.

Fig. 2. Diffuse scattering of α-Fe at 295 K.

RESULTS AND DISCUSSION

The correlation effects had been determined from the analysis of oscillatory diffuse scattering intensity. The values of correlation effects of fcc metals (Cu [6], Al[10]) and semiconductor (Ge [2]) near room temperature are shown in Fig. 3. The correlation effects decrease with the increase of interatomic distance. The values of the correlation effects are about 0.6 for the interatomic distance 2.5 Å and about 0.2 for 4 Å near room temperature. The correlation effects do not depend significantly on the type of crystal structure and crystal binding. From the results we suppose an equation between correlation effects μ ($\gtrsim 0$) and interatomic distance r (Å) as

$$\mu = -0.32r+1.44 \qquad (1)$$

The quantitative analysis of diffuse scattering intensity by TOF diffractometer is difficult. The diffuse scattering intensity includes undefined contributions besides thermal disorder. Although oscillatory diffuse scattering intensity can be observed below *d*<0.55 in Fig. 2, the diffuse scattering intensity is weak in the region of *d*>0.55. The oscillatory diffuse scattering part in Figure 2 is mainly from the thermal disorder. The oscillatory peak positions (*d*~0.34, 0.39 and 0.47) correspond to the calculated values with interatomic distance (r_1=2.864) of first-nearest-neighboring atoms: $\sin(2\pi r_1/d)$=1 [1]. In this paper we estimate the correlation effects of α-Fe using Eq. (1) without analyzing observed diffuse scattering intensity. The obtained correlation effects among first-, second-, and third -nearest-neighboring atoms in α-Fe at 295 K were 0.65, 0.52, and 0.14, respectively (Table 1).
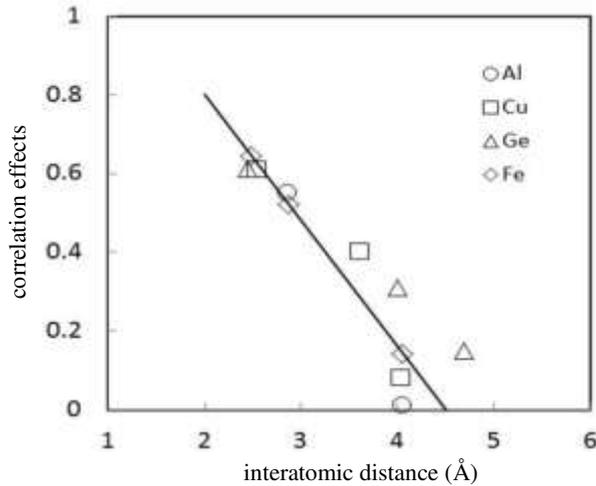
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Fig. 3. Correlation effects reported from the analysis of metal and semiconductor at room temperature. A generalized equation (Eq. (1)) is shown by solid line.

Table 1. Interatomic distances r, coordination numbers Z, correlation effects among thermal displacements of atoms, and force constants of first-, second-, and third-nearest-neighboring atoms of α-Fe at 295 K.

	1st	2nd	3rd
r (Å)	2.483	2.867	4.054
Z	8	6	12
μ	0.65	0.52	0.14
α (eV/ Å^2)	2.3	1.4	0.20

An equation for transforming of the correlation effects to force constants has been introduced in the analysis of diffuse scattering of fcc Al [10]. The force constant α between s and s' sites is shown as

$$\alpha = \frac{8\pi^2 k_B T \mu_{ss'}}{3(B_s + B_{s'})(1 - \mu_{ss'})} \tag{2}$$

where k_B is Boltzmann constant and T temperature. In the absence of correlation effects ($\mu=0$), the force constant is also zero in Eq. (2). The values of correlation effects between the first-, second- and third-nearest- neighboring atoms calculated using Eq. (2) for α-Fe at 295 K are given in Table 1. We estimate the phonon dispersion relations from the force constants using the method described in Ref.[9]. The calculated phonon dispersion relations propagating in the [100], [110], and [111] directions at 295 K are shown in Fig. 4. From the phonon dispersion relations, the phonon density of states and specific heat of α-Fe were also derived. The results are shown in Figs. 5 and 6. The phonon dispersion relations calculated with force constants determined by Eq. (2) are qualitatively in agreement with the results of inelastic neutron scattering measurements at room temperature [11,12]. For example, there are two transverse acoustic branches T_1 and T_2 in the dispersion relations in the [110] direction in Fig. 4. A separation into two transverse acoustic branches of [110] direction and the maxima in LA modes of [100] and [111] directions are strongly related to correlation effects of first- and second-nearest-neighboring atoms. The specific heat of Fe below 200 K is from the contribution of lattice vibrations which corresponds to the calculation of the present phonon dispersion relations. Above 200 K specific heat related to α–γ phase transition is added [13]. The difference between observed ($\square$) and calculated (solid line) values is mainly from the contribution of α–γ phase transition..

As the interatomic distance of first-nearest-neighboring atoms for α-Fe (r_1=2.483) is less than that for Al (r_1=2.864), the correlation effects among first-nearest-neighboring atoms for bcc α-Fe (μ_1=0.65) are greater than that for fcc Al (μ_1=0.55). Young's modulus E of α-Fe is 15.23×10^{10} N/m^2 and that of Al 7.03×10^{10} N/m^2 [17]. The ratio of force constant among first-nearest- neighboring atoms for α-Fe to that of Al is similar to the ratio of Young's modulus.

The estimation of correlation effects in other metals would be possible from Eq. (1). The force constants are obtained from the correlation effects. By a computer simulation the phonon dispersion relations and specific heat of metals can be estimated.
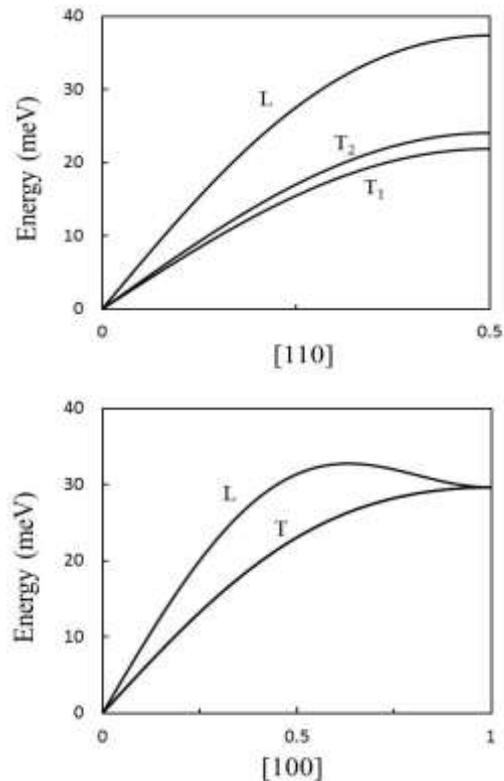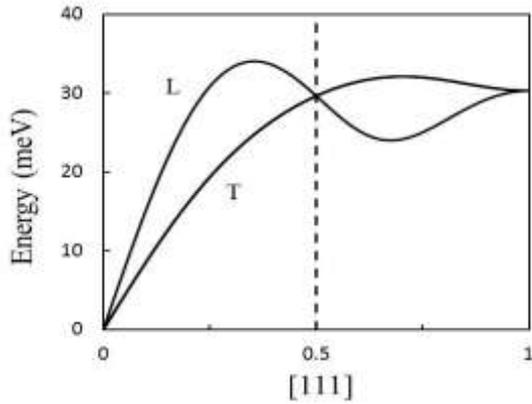
Fig. 4. Phonon dispersion relations of α-Fe in the [100], [110], and [111] directions at 295 K calculated using the force constants determined using Eq. (2). The dashed line in [111] direction shows zone boundary.
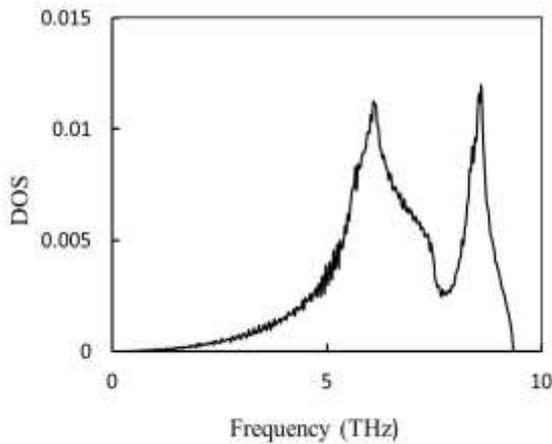

Fig. 5. Phonon density of states of α-Fe calculated by computer simulation using the force constants determined using Eq. (2).
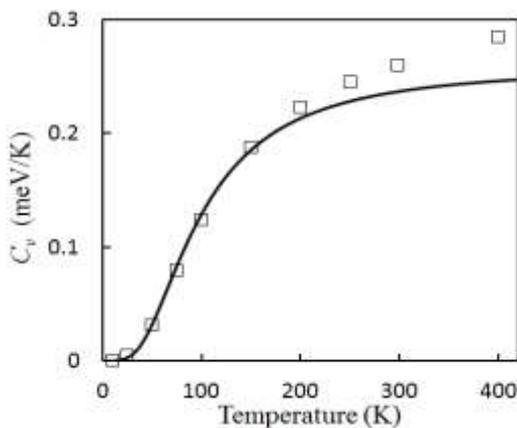

Fig. 6. Specific heat of α-Fe calculated by computer simulation using the force constants determined using Eq. (2) (solid line) and values observed by specific heat measurement (□). The difference between observed and calculated specific heat above 200 K is mainly from the contribution of α–γ phase transiton of Fe [13].

CONCLUSION

The correlation effects of atomic thermal displacements in α-Fe were estimated from a generalized equation based on the former diffuse scattering analysis. A transformation from correlation effects to force constants was applied. The derived force constants were used to calculate the phonon dispersion relations, phonon density of states, and specific heat of α-Fe by computer simulation. The calculated phonon dispersion curves and specific heat agree well with the results of inelastic neutron scattering and specific heat measurements, respectively.

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