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Estimation of inter-atomic force constants and phonon dispersion using correlation effects among thermal displacement of atoms in Ge

Takashi Sakuma [a,*], Saumya R. Mohapatra [a], Nobuhiro Isozaki [a], Hiroyuki Uehara [a], Xianglian [b], Khairul Basar [c], Haruyuki Takahashi [d], Osamu Kamishima [e], Naoki Igawa [f]

[a] Institute of Applied Beam Science, Ibaraki University, Mito 310-8512, Japan
[b] College of Physics and Electronics Information, Inner Mongolia University for the Nationalities, Tongliao 028043, China
[c] Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Bandung 40132, Indonesia
[d] Institute of Applied Beam Science, Ibaraki University, Hitachi 316-8511, Japan
[e] Department of Physics, Faculty of Engineering, Setsunan University, Neyagawa 572-8508, Japan
[f] Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai 319-1195, Japan

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ABSTRACT

Neutron diffraction measurements have been performed on powder Ge at 6, 150 and 300 K. Oscillatory diffuse scattering intensity is clearly observed at 150 and 300 K. The diffuse scattering theory including correlation effects among thermal displacements of atoms is applied to background function in the Rietveld analysis. The inter-atomic distance and temperature dependence of the values of correlation effects are discussed. The force constants among the first, second and third nearest neighboring atoms in Ge are obtained from the values of correlation effects and Debye–Waller temperature parameters. A phonon dispersion spectrum in Λ [111] direction for Ge crystal has also been calculated at 80 K using inter-atomic force constants and the crystal structure.

1. Introduction

Diffuse scattering from X-ray and neutron scattering experiments is an important tool for analyzing static and thermally disordered arrangement of atoms in solids. In a disordered structure of AgI, strong and oscillatory diffuse scattering had already been reported [1,2]. Even in many ordered structures of silver halides and copper halides an oscillatory diffuse scattering pattern was observed [3,4]. The oscillatory profile of diffuse scattering from ordered structure has been explained by taking into account the *correlation effects among thermal displacements of atoms* up to the 3rd nearest neighboring atoms. This correlation effect can be useful to predict the force constants among nearest neighboring atoms. Phonon dispersion relation in well defined symmetric directions, Δ[100], Σ[110], Λ[111] can also be evaluated using inter-atomic force constants and the crystal structure [5]. The correlation effect among thermal displacements of atoms was also studied earlier by using extended X-ray absorption fine structure (EXAFS) analysis [6–8]. In the present work, we show that the phonon dispersion relation can roughly be estimated using the results from the analysis of Bragg line and diffuse scattering intensities.

The correlation effect among thermal displacement of atoms is not only specific to ionic crystals. In this paper, we explore such correlation effects in an ideal covalently bonded crystal structure like Ge from its diffuse scattering profile. The Rietveld analysis has been employed along with the background function for inclusion of correlation effects to explain the diffraction intensity. The inter-atomic force constants in Ge are estimated from the values of correlation effects. Further, the phonon-dispersion spectrum of Ge has been plotted at 80 K.

2. Experimental

Neutron scattering experiments have been performed on powder Ge (99.99%, Kojundo Chemical) at 6, 150 and 300 K using HRPD (High Resolution Powder Diffractometer) installed at JRR-3 in Japan Atomic Energy Agency. The sample was put into a cylindrical vanadium container of 1.0 cm in diameter. Incident neutron wavelength of 1.823 Å which was monochromatized by Ge (331) and the data were collected over a 2θ range from 20° to 150° with a step angle of 0.05°.

3. Results and discussion

In Fig. 1 the observed diffuse neutron scattering intensity of powder Ge at 6, 150 and 300 K are shown by plus (+) symbol. The diffraction intensity consists of several strong Bragg peaks and diffuse

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* Corresponding author. Tel./fax: +81 29 228 8357.
E-mail address: sakuma@mx.ibaraki.ac.jp (T. Sakuma).

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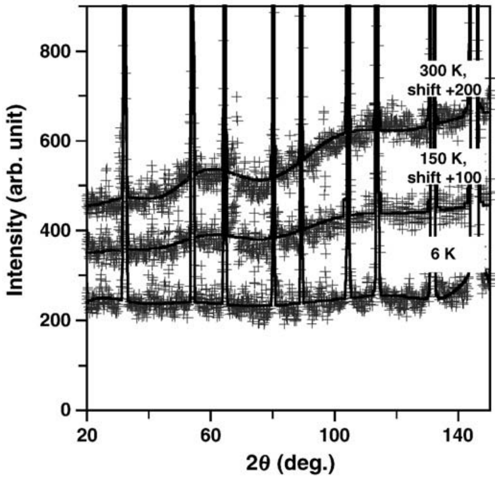

Fig. 1. Observed diffuse neutron scattering intensity of powder Ge at 6, 150 and 300 K. The plus symbol (+) denotes the experimental data and the solid line shows the refined curve.

background. A comparison of the patterns indicates a temperature dependent variation in diffuse scattering intensity. The diffuse scattering intensity increases with the increase of temperature. The diffuse scattering intensity shows oscillatory profile which is more clearly visible at higher temperatures (150 and 300 K). The peaks of the oscillatory profile appear around $2\theta \sim 30$, 60 and 100°.

The detailed theoretical treatment of diffuse scattering intensity from ordered and disordered crystals was reported earlier [2,9]. In the case of ordered crystals, the mathematical expression to explain the profile of diffuse background scattering intensity is written as follows:

$$I_B = kN_o\left[\sum_i n_i b_i^2(1-\exp(-2M_i)) + \sum_i\sum_j\sum_{s'}{}' n_i b_i b_j \times\left[\exp\left(-\left(M_i+M_j\right)\left(1-\mu_{r_{s(i)s'(j)}}\right)\right)-\exp\left(-\left(M_i+M_j\right)\right)\right]Z_{r_{s(i)s'(j)}} \times\sin(Qr_{s(i)s'(j)})/(Qr_{s(i)s'(j)}) + \sum_i \sigma_i^{\mathrm{inc}}\right] + C \quad (1)$$

where k is the proportionality constant and N_o is the number of unit cell in a unit volume. n_i, b_i and σ_i^{inc} are number of atoms in unit cell, neutron scattering length and incoherent scattering cross section of atom i, respectively. Z_r is the number of sites belonging to the s'th j-type neighbor around an sth i-type site. Two sites $s(i)$ and $s'(j)$ are apart by distance r. The prime added in the summation symbol in the second term is to omit the term of $r_{s(i)s'(j)}=0$. The Debye–Waller factor for atom i, $\exp(-M_i)$, is equal to $\exp(-B_i(\sin\theta/\lambda)^2)$, where B_i is the Debye–Waller temperature parameter of atom i. The constant C is added for taking into account the corrections of background noise. The correlation effect among atomic thermal displacements μ_r is defined as:

$$\mu_{r_{s(i)s'(j)}} = 2\left\langle \Delta r_{s(i)}\cdot\Delta r_{s'(j)}\right\rangle / \left(\left\langle \Delta r_{s(i)}^2\right\rangle + \left\langle \Delta r_{s'(j)}^2\right\rangle\right). \quad (2)$$

The deviation from an equilibrium position is shown by Δr. The values of correlation effects among thermal displacements of atoms i and j are 0 in the case of no correlation and $2(B_i\,B_j)^{1/2}/(B_i+B_j)$ in the case of perfect correlation. As Ge is a mono-atomic crystal, the perfect correlation case would be $\mu=1$.

Rietveld refinement analysis has been performed on the observed intensity of Ge using RIETAN-94 [10], where we used the background intensity function of Eq. (1). The crystal structure of Ge is cubic (diamond type) with the space group $Fd\bar{3}m$. The obtained lattice constants a, Debye–Waller temperature parameters B and reliability factors R at 6, 150 and 300 K from the refinement of Bragg lines and diffuse scattering are recorded in Table 1. The inter-atomic distances and the numbers of neighboring atoms Z for the first, second and third neighboring atoms in the structure of Ge are also presented in Table 1.

The values of correlation effects μ up to third nearest neighboring atoms has been obtained using B parameters from Rietveld refinement analysis and recorded in Table 1 for different temperatures and inter-atomic distances. The obtained value of correlation effects for first nearest neighboring atoms in Ge is almost the same as that recorded by Yoshiasa et al. by EXAFS analysis [8]. The variation of μ as a function of inter-atomic distances is shown in Fig. 2. The values of correlation effects among thermal displacements of atoms are

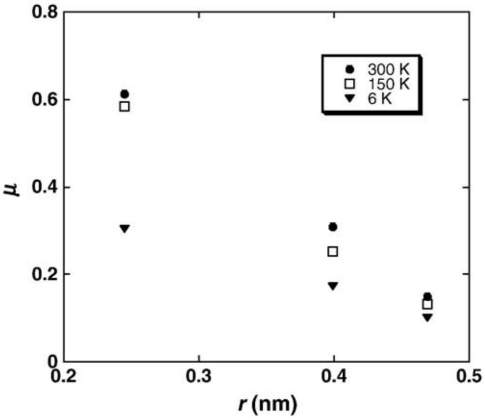

Fig. 2. Inter-atomic distance dependence of the correlation effects among thermal displacements of atoms in Ge.

Table 1
Lattice constant a, Debye–Waller temperature parameter B and reliability factors R from refinement analysis of Bragg lines and diffuse scattering of Ge. Z, r and μ show coordination number, inter-atomic distance and value of correlation effects, respectively.

		6 K		150 K		300 K	
		$a=0.5652$ nm;		$a=0.5654$ nm;		$a=0.5657$ nm;	
		$B_{\mathrm{Ge}}=0.00105$ nm^2		$B_{\mathrm{Ge}}=0.00225$ nm^2;		$B_{\mathrm{Ge}}=0.00340$ nm^2;	
		$R_{\mathrm{wp}}=8.49\%$;		$R_{\mathrm{wp}}=7.44\%$;		$R_{\mathrm{wp}}=7.13\%$;	
		$R_I=4.12\%$;		$R_I=3.32\%$;		$R_I=3.81\%$;	
		$R_F=1.99\%$		$R_F=1.59\%$		$R_F=1.93\%$	
	Z	r (nm)	μ	r (nm)	μ	r (nm)	μ
1st nearest neighboring atom	4	0.2447	0.303	0.2448	0.583	0.2449	0.612
2nd nearest neighboring atom	12	0.3996	0.173	0.3998	0.253	0.3999	0.310
3rd nearest neighboring atom	12	0.4686	0.100	0.4688	0.132	0.4689	0.150