

Correlation effects among thermal displacements of atoms in VSe by diffuse neutron scattering measurement

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Abstract Neutron diffraction measurements have been performed on powder VSe at 294 K. The diffuse scattering theory including correlation effects among thermal displacements of atoms is applied to background function in the Rietveld analysis. The oscillatory scheme of the diffuse scattering intensity from hexagonal VSe is explained by the correlation effects among far-neighboring Se–Se atoms. The values of the correlation effects depend on the interatomic distance and not on the crystal structure. The relation between correlation effects and force constants is discussed.

Keywords Correlation effects · Diffuse scattering · Force constant · Neutron diffraction · Thermal vibration

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Introduction

Diffuse scatterings contain information about static and dynamic disorders of atoms in crystals [1, 2]. Most of the intensities of the oscillatory diffuse scattering from ionic crystals and semiconductors were from the correlation effects among thermal displacements of the nearest neighboring atoms [3]. The presence of the correlation effects among the second and third nearest neighboring atoms was pointed out from the analysis of diffuse scattering of cubic copper halides. The values of correlation effects decrease rapidly with the increase of inter-atomic distance.

In order to inspect the correlation effects among thermal displacements of atoms in hexagonal crystal, neutron diffraction experiment was performed on VSe at 294 K, where the nuclear scattering length of V ($b_V = -0.0382 \times 10^{-12}$ cm) is much less than that of Se ($b_{Se} = 0.7970 \times 10^{-12}$ cm). We could investigate the contribution from far-neighboring Se–Se pair to the diffuse scattering of hexagonal VSe.

Experimental

Vanadium and selenium were weighed and enclosed in a quartz tube in vacuum condition and reacted at 1,500 K for 3 d. It was annealed at 500 K for 2 d. Subsequently, it was gradually cooled to room temperature. A small excess amount of Se atoms is necessary to compose a sample. The obtained compound was crushed to a fine powder. Neutron diffraction experiment was performed on powder VSe at 294 K using HRPD (High Resolution Powder Diffractometer) installed at JRR-3 in Japan Atomic Energy Agency. The sample was put into cylindrical vanadium

container of 1.0 cm in diameter. Incident neutron wavelength of 0.1823 nm which was monochromatized by Ge 331 was used. The data were collected for 15 m in the 2θ range from 20° to 150° with step angle 0.05° . X-ray diffraction pattern was also measured at 294 K to determine atomic position and thermal parameter of V atoms. Cu- K_α radiation monochromatized with pyrolytic graphite 002 reflection was used. The data were collected for 10 s in the 2θ range from 10° to 90° with step angle 0.02° .

Results and discussion

Many sharp Bragg peaks and diffuse background intensity of VSe were observed by neutron diffraction measurement. The observed diffuse neutron scattering intensity of powder VSe at 294 K is denoted in Fig. 1 by the cross symbol. The maximum intensity of Bragg lines is about 20,000 counts. The diffuse scattering intensity shows oscillatory profile. Some weak peaks of diffuse scattering appeared around $2\theta = 35^\circ, 70^\circ,$ and 120° .

Assuming a hexagonal unit cell the Bragg lines of VSe were indexed [4]. From the possible reflections of Bragg lines, the expected space group of VSe is $P6_3/mmc$. The structure analysis of the observed Bragg intensities of X-ray and neutron diffraction measurements were carried out. The unit cell includes 2 VSe. The crystal contains ordered arrangement, and the atomic positions are as follows:

$$\begin{aligned} 2 \text{ V in } 2a \ 0, 0, 0, \\ 2 \text{ Se in } 2c \ 1/3, 2/3 \ 1/4. \end{aligned}$$

The correlation effects among thermal displacements of atoms μ are defined as [5]:

$$\mu_{ss'} = 2\langle \Delta r_s \cdot \Delta r_{s'} \rangle / (\langle \Delta r_s^2 \rangle + \langle \Delta r_{s'}^2 \rangle), \quad (1)$$

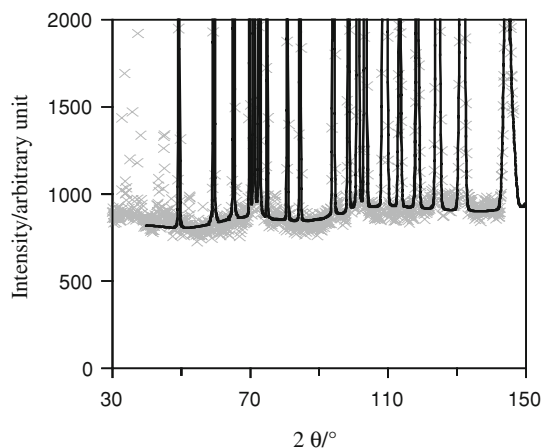


Fig. 1 Neutron scattering intensity of powder VSe at 294 K. The cross symbol denotes the observed intensity and the solid line the calculated refined intensity

where Δr is the displacement of atoms from equilibrium positions. When the atoms in crystals vibrate independently, the value of correlation effects is equal to zero. Rietveld refinement analysis was performed on the observed intensity of VSe using RIETAN-94 [6], in which we used the background intensity function including the correlation effects among thermal displacements of atoms. The calculated neutron diffraction intensities are denoted in Fig. 1 by solid lines. The observed Bragg lines and background intensities are explained by the calculation. The obtained lattice constants a and c , Debye–Waller temperature parameters B , the correlation effects μ , the interatomic distance r , the number of neighboring atoms Z , and the reliability factor R at 294 K are shown in Table 1.

To estimate the contribution to the oscillatory part of diffuse scattering intensity, the oscillatory intensity I_{corr} is divided into three components:

$$I_{\text{corr}} = I_{\text{V-Se}} + I_{\text{V-V}} + I_{\text{Se-Se}}, \quad (2)$$

where $I_{\text{V-Se}}$, $I_{\text{V-V}}$, and $I_{\text{Se-Se}}$ are the oscillatory components of V–Se and Se–V, V–V, and Se–Se, respectively. The calculated intensities of the three components at 294 K are shown in Fig. 2. It is found that the oscillating scheme in the diffuse scattering intensity of VSe is mainly from the contribution of Se–Se pair. Although the value of the correlation effects of far-neighboring Se–Se atoms is less than that of the nearest neighboring V–Se and Se–V, the large contribution to diffuse scattering from Se–Se atoms was caused by the value of nuclear scattering length of atoms. The peak positions of the oscillatory diffuse scattering intensities in Fig. 2 coincide with those of $\sin(Qr_{\text{Se-Se}}) = 1$, where $r_{\text{Se-Se}}$ is the inter-atomic distance between neighboring Se–Se atoms in VSe. The contribution to the diffuse scattering from far-neighboring Se–Se atoms was clearly confirmed by the experiment.

Table 1 Lattice constants (a , c), Debye–Waller temperature parameter (B), value of correlation effects (μ) and reliability factors (R) from Rietveld analysis of diffraction profile of VSe at 294 K

		Z	r/nm	μ
$a = 0.3675 \text{ nm}$	V–Se	6	0.2598	0.74
$c = 0.5994 \text{ nm}$	Se–V	6	0.2598	0.74
$b_{\text{V}} = 0.00109 \text{ nm}^2$	V–V	2	0.2997	0.65
$b_{\text{Se}} = 0.00755 \text{ nm}^2$	Se–Se	8	0.3673	0.45
$R_{\text{wp}} = 5.45\%$	V–V	6	0.3675	0.45
$R_{\text{I}} = 4.32\%$	Se–Se	4	0.3677	0.45
$R_{\text{F}} = 2.48\%$	V–Se	6	0.4500	0.20
$S = 2.13$	Se–V	6	0.4500	0.20
	V–V	12	0.4742	0.10

Z and r are coordination number and inter-atomic distance, respectively

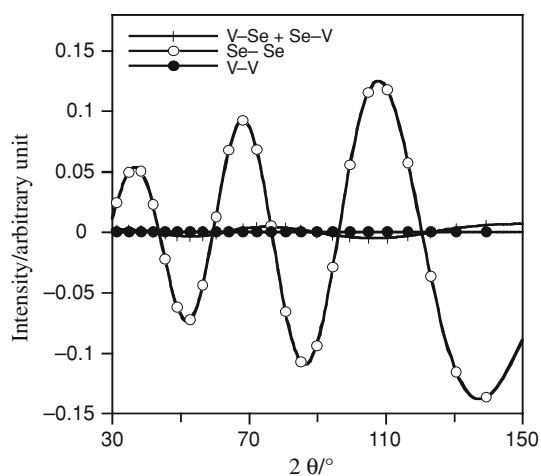


Fig. 2 Calculated components of oscillatory diffuse scattering of VSe at 294 K

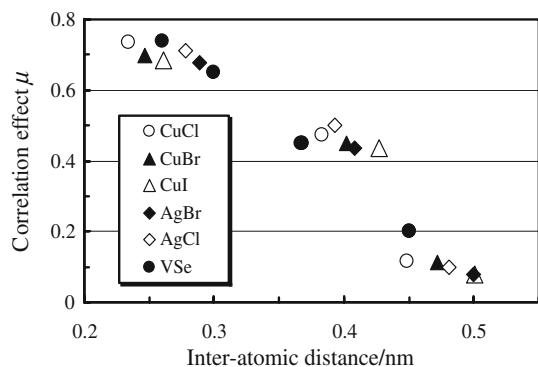


Fig. 3 Inter-atomic distance dependence of the correlation effects among thermal displacements of atoms in cubic ionic crystals and hexagonal VSe at room temperature

The relation between the value of correlation effects μ and the inter-atomic distance r in AgBr, CuCl, CuBr, and CuI crystals is shown in Fig. 3. It is found that the value of μ is ~ 0.7 for $r \sim 0.25$ nm in silver and copper halides. The value is ~ 0.5 for $r \sim 0.4$ nm. The values of correlation effects decrease with the increase of inter-atomic distances. AgBr and AgCl belong to NaCl-type structure, whereas CuI, CuBr, and CuCl belong to zinc blend-type structure [7, 8]. The values of correlation effects in hexagonal VSe are almost the same as those in ionic crystals shown in Fig. 3.

The values of the correlation effects do not depend so much on the type of the crystal binding and the crystal structure. Recently, the temperature dependence of the values of correlation effects of the nearest neighboring atoms was studied [9]. The values of the correlation effects do not change so much in the high temperature region $T/\Theta_D > 0.5$, where Θ_D is the Debye temperature. However, the values of correlation effects decrease with the decrease of temperature in the low temperature region

$T/\Theta_D < 0.5$. The value of correlation effects of first nearest neighboring atoms in ZnSe changes from 0.7 at room temperature to 0.3 at 15 K [9]. The similar tendency of correlation effects of first nearest neighboring atoms had also been reported by Beni and Platzman by theoretical approach in the EXAFS analysis [10]. They pointed out that, with a simple Debye model, the value and the temperature dependence of correlation effects for bcc are similar to those for fcc. The obtained values of correlation effects by their calculation were $0.7 \sim 0.8$ near $T \sim \Theta_D$. Therefore, the values of the correlation effects would depend not so much on the type of the crystal structure at near room temperature.

The average of the thermal displacements of atoms is obtained by cumulant expansion. The value of $\langle \Delta u_{ss'}^2 \rangle$, that is usually expressed by δu^2 in EXAFS measurements, is written as

$$\begin{aligned} \langle \Delta u_{ss'}^2 \rangle &= (\langle \Delta r_s^2 \rangle + \langle \Delta r_{s'}^2 \rangle) \left(1 - 2 \frac{\langle \Delta r_s \Delta r_{s'} \rangle}{\langle \Delta r_s^2 \rangle + \langle \Delta r_{s'}^2 \rangle} \right) \\ &= \frac{1}{8\pi^2} (B_s + B_{s'}) (1 - \mu_{ss'}). \end{aligned} \quad (3)$$

The values of $\langle (\Delta u)^2 \rangle$ are obtained from the values of B_s , $B_{s'}$ and $\mu_{ss'}$. Through the use of the equation $\langle (\Delta u)^2 \rangle = k_B T / \alpha$, we could estimate the force constant α among first, second, and third nearest neighboring atoms from the diffuse scattering measurements. It is found that the force constant is related to correlation effects and Debye–Waller temperature parameters. As the values of correlation effects do not change so much on the crystal structure, the force constant of the crystal would mainly depend on the values of temperature parameters.

The phonon dispersion relation is calculated by the force constants among atoms [11]. The force constant of the first nearest neighboring atoms is obtained by EXAFS measurement, whereas the force constants of the first, second, and third nearest neighboring atoms are obtained by the analysis of diffuse scattering. Therefore, we would estimate the phonon dispersion relation from the analysis of diffuse scattering by X-ray and neutron diffraction measurements with a higher accuracy than by the method of EXAFS measurement. The derivation of phonon dispersion relation from the correlation effects is in progress.

Conclusions

The oscillatory diffuse scattering intensity of hexagonal VSe was observed by neutron scattering measurement. The main contribution to the oscillatory diffuse scattering of VSe was from the correlation effects among thermal

displacements of far-neighboring Se–Se atoms. The values of the correlation effects depend on the inter-atomic distance and not on the crystal structure. From the values of Debye–Waller temperature parameters and correlation effects, we could estimate a phonon dispersion relation.

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