

Derivation of Inter-Atomic Force Constants of Cu₂O from Diffuse Neutron Scattering Measurement

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ABSTRACT

Neutron scattering intensity from Cu₂O compound has been measured at 10 K and 295 K with High Resolution Powder Diffractometer at JRR-3 JAEA. The oscillatory diffuse scattering related to correlations among thermal displacements of atoms was observed at 295 K. The correlation parameters were determined from the observed diffuse scattering intensity at 10 and 295 K. The force constants between the neighboring atoms in Cu₂O were estimated from the correlation parameters and compared to those of Ag₂O.

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INTRODUCTION

X-ray and neutron diffraction are the most powerful experimental techniques for material structure analysis. In many cases diffraction intensities consist of Bragg lines and diffuse scattering component. Bragg lines are normally used in the analysis of crystal structure. Recently it was noticed that the diffuse scattering intensity has useful physical properties which includes information about short-order parameters, inter-atomic force constants, and sound waves in crystals, among others. Correlation effects among thermal displacements of atoms have been discussed in the analysis of diffuse scattering of crystalline materials [1-3]. The inter-atomic force constants in Cu, ZnSe, KBr and Ag₂O were obtained from the parameters describing these correlations [4].

The crystal structure of Cu₂O and Ag₂O is of cuprite type as reported by T. Suzuki [5]. Cu₂O and Ag₂O show negative thermal expansion below 200 K [6,7]. Ag₂O is one of the components in AgI-Ag₂O-V₂O₅ super-ionic glass [8]; however, AgI-Cu₂O-V₂O₅ super-ionic glass has not been synthesized yet. In this paper, we discuss the crystal structure and thermal parameters of Cu₂O at 10 K

and 295 K. The Rietveld refinement of measured diffraction patterns was used for structural analysis, whereas the correlation effects among thermal displacements of atoms in Cu₂O were found from the diffuse scattering intensity. The force constants in Cu₂O were calculated from the correlation parameters and compared to those of Ag₂O.

EXPERIMENTAL METHOD

Neutron diffraction measurements were performed at 10 and 295 K from a powder Cu₂O 99% (Kojundo Chemical) by HRPD (High Resolution Powder Diffractometer) installed at JRR-3 in Japan Atomic Energy Agency. The powder sample in a vanadium container with 10 mm diameter was measured at the incident neutron wavelength of 1.823 Å. Neutron diffraction data were collected for 1 day at 0.05° intervals over the 2θ range of 20 to 150°.

RESULTS AND DISCUSSION

Figure 1 shows the measurement result of Cu₂O diffraction intensities at 10 K and 295 K. Several sharp Bragg lines and oscillatory diffuse scattering are observed at 10 K and 295 K. The broad peaks of the oscillatory diffuse scattering

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at 295 K appear around $2\theta \sim 45, 80$ and 150° . However the oscillatory diffuse scattering scheme is not seen at 10 K. There are differences between observed and calculated intensities of diffuse scattering narrowly centered around Bragg peaks at about $2\theta \sim 75$ and 90° in Fig. 3. As the differences increase with the temperature, it appears to be due to the thermal diffuse scattering from acoustic phonons.

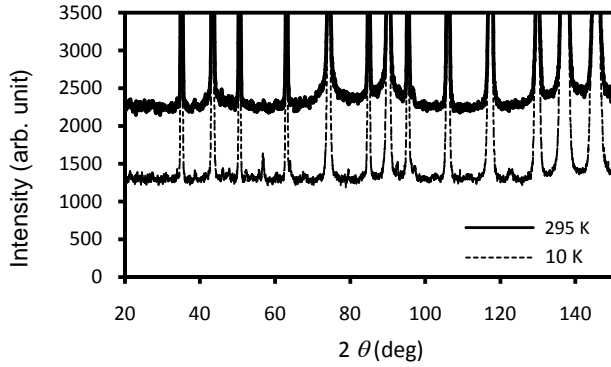


Fig. 1. Observed neutron powder diffraction intensity for Cu_2O at 10 and 295 K. The spectrum at 295 K is shifted up by 1000.

The static approximation of the theoretical treatment of diffuse scattering intensity including the correlation effects among thermal displacements of atoms had been reported by T. Sakuma [1]. The diffuse scattering intensity I_D is calculated from:

$$I_D = I_0 K N_o \sum_s n b_s b_s^* [1 - \exp(-2M_s)] + I_0 K N_o \sum_s \sum_{s'} n b_s b_{s'}^* [\exp\{-(M_s + M_{s'}) (1 - \mu_{ss'})\} - \exp\{-(M_s + M_{s'})\}] Z_{ss'} \frac{\sin(Qr)}{Qr} + I_0 K N_o \sum_s n \sigma_{inc} + C \quad (1)$$

where b_s is the nuclear scattering length for the atom in site s ; $I_0 K$ is a constant which depends on the experimental condition; N_o is the number of unit cells in a unit volume; Z is the number of sites belonging to the s' th neighbor around an s th site; n corresponds to the number of atoms per unit cell; $\exp(-M) = \exp\{-B(\sin\theta/\lambda)^2\}$ is Debye-Waller factor; σ_{inc} is the incoherent scattering cross-section of atoms. The constant C is added for the correction of background noise. The oscillations in diffuse background come from the second term in Eq. (1) which is proportional to $\sin(Qr)/Qr$, where Q equals to $4\pi\sin\theta/\lambda$ and r is distance between site s and site s' . The dimensionless parameter μ is related to correlations among thermal displacements of atoms and defined as follows:

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

where the deviation from an equilibrium position is given by Δr . Correlation effects among thermal displacements of atoms are proportional to displacement correlation function (DCF) [9,10].

The theoretical diffraction intensity graph from crystalline materials in Rietveld analysis consists of Bragg lines and a diffuse background [11]. The background intensity includes several contributions, such as incoherent scattering, thermal vibration, air scattering, multiple scattering, sample cell scattering, background noise and others. In Rietveld analysis the background is usually approximated by Legendre polynomials. In the present analysis the main contribution to the oscillatory diffuse scattering was approximated by Eq. (1) which takes into account thermal correlation effects. The crystal structure was refined by Rietveld method using powder diffraction data. We found that the crystal structure of Cu_2O belongs to cubic cuprite type with space group $Pn\bar{3}m$. The Cu atoms occupy $4b$ positions at (000) and the O atoms occupy $2a$ positions at (1/4 1/4 1/4) in Fig. 2.

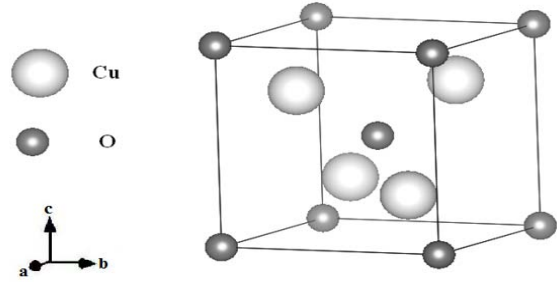


Fig. 2. Crystal structure of Cu_2O at 10 and 295 K.

The refined structural parameters of lattice constant and Debye-Waller temperature factor are shown in Table 1. The inter-atomic distances r and coordination numbers Z are shown in Table 2. The obtained lattice constant $a = 4.2705(9) \text{ \AA}$ at 295 K matches well with the earlier reported value ($a = 4.268(1) \text{ \AA}$) [5]. The lattice constant at 295 K is less than that at 10 K, in agreement with the observation of the negative thermal expansion in this compound.

Table 1. Final refined parameter and obtain R factor in Cu_2O at 10 and 295 K

	295 K	10 K
a (\AA)	4.27050(7)	4.27230(6)
B_{Cu} (\AA^2)	1.521(12)	0.246(9)
B_{O} (\AA^2)	1.448(22)	0.295(16)
R_{wp} (%)	3.551	3.280
R_e (%)	2.191	2.035
S	1.6205	1.6117

Table 2. Coordination numbers Z , inter-atomic distances r and correlation parameter μ of Cu_2O at 10 and 295 K

	295 K			10 K		
	Z	r (Å)	μ	Z	r (Å)	μ
Cu-O	2	1.849	0.88	2	1.850	0.68
Cu-Cu	12	3.020	0.73	12	3.021	0.50
Cu-O	6	3.541	0.27	6	3.543	0.15
O-Cu	4	1.849	0.88	4	1.850	0.80
O-Cu	12	3.541	0.27	12	3.543	0.15
Cu-O	8	3.698	0.05	8	3.701	0.02

The measured diffraction intensity (\times), calculated diffraction intensity (thin solid line), and calculated diffuse scattering intensity (thick solid line) of Cu_2O at 295 K and 10 K are shown in Figs. 3 and 4, respectively. The correlation parameters which have been obtained in the calculation of diffuse scattering intensity in Figs. 3 and 4 are given in Table 2. The calculated total diffuse scattering intensity and its components in Cu_2O at 295 and 10 K are shown in Figs. 5 and 6, respectively. The diffuse scattering intensity is significantly lower at 10K in agreement with experiment. The diffuse scattering contributions from uncorrelated Cu and O atoms in Figs. 5 and 6 correspond to the first term in Eq. (1). It is seen that the oscillatory part in the diffuse scattering intensity corresponds to contributions from correlated thermal displacements of first (Cu-O) and second (Cu-Cu) nearest neighboring atoms. The calculated peaks of oscillatory diffuse scattering at 295 and 10 K appear around $2\theta \sim 45, 80$ and 150° which agrees well with the experiment.

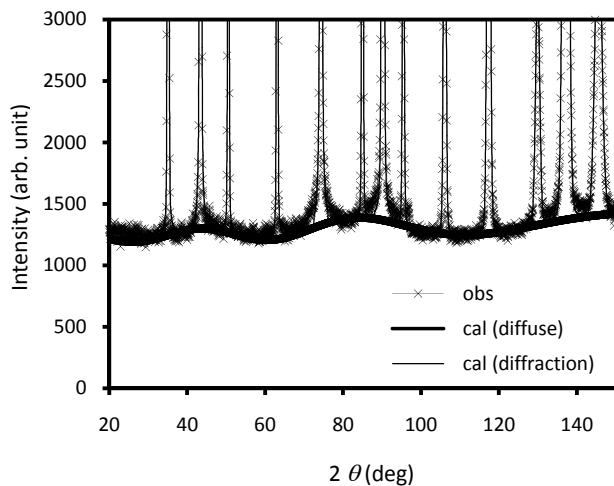


Fig. 3. Rietveld refinements patterns for Cu_2O at 295 K by the neutron diffraction measurement. The crosses (\times) are observed intensities and the thin solid line is calculated intensity. The thick solid lines are calculated diffuse scattering intensity.

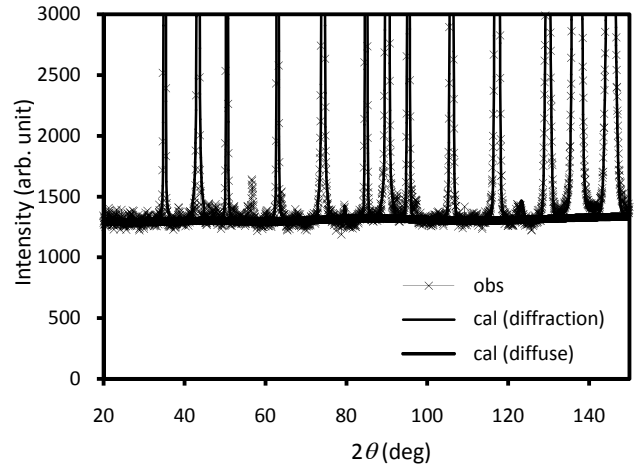


Fig. 4. Rietveld refinements patterns for Cu_2O at 10 K by the neutron diffraction measurement. The crosses (\times) are observed intensities and the thin solid line is calculated intensity. The thick solid lines are calculated diffuse scattering intensity.

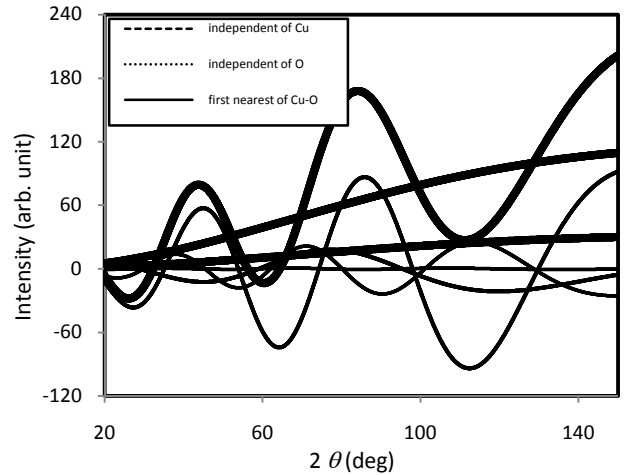


Fig. 5. Calculated diffuse scattering intensity oscillatory and components of Cu_2O at 295 K.

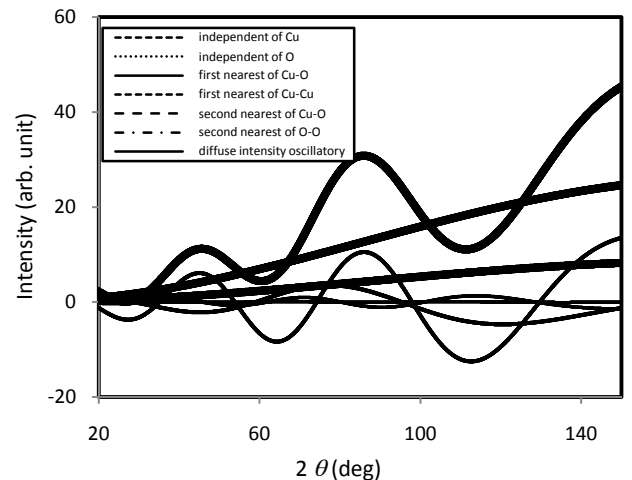


Fig. 6. Calculated diffuse scattering intensity oscillatory and components of Cu_2O at 10 K.

The correlation parameters of Cu_2O in Table 2 decrease with the inter-atomic distance as

for Ag₂O, ZnSe [12] and Cu [13]. The values of the correlation parameters of Cu₂O are about 0.88 for the inter-atomic distance of $r \sim 1.8 \text{ \AA}$ and ~ 0.73 for $r \sim 3.0 \text{ \AA}$ at 295 K. The Debye-Waller temperature factor B and mean square displacement (MSD) $\langle \Delta r^2 \rangle$ are related directly as $B = 8\pi^2 \langle \Delta r^2 \rangle$. The mean square of the thermal displacements of atoms $\langle \Delta u_{ss}^2 \rangle$ can be written in terms of correlation effects and Debye-Waller parameters with the definition of mean-square displacements (MSD) and displacement correlation function (DCF) [5,8],

$$\langle \Delta u_{ss}^2 \rangle = (\langle \Delta r_s^2 \rangle + \langle \Delta r_{s'}^2 \rangle) \left(1 - 2 \frac{\langle \Delta r_s \Delta r_{s'} \rangle}{\langle \Delta r_s^2 \rangle + \langle \Delta r_{s'}^2 \rangle} \right) \quad (3)$$

At room temperature in the case of classical limit there is the following relation between MSD and inter-atomic force constants : $\langle (\Delta u)^2 \rangle = k_B T / \alpha$ (α is the force constants between the nearest neighboring atoms) [4]. Using this formula we could estimate the force constants α . At low temperatures the quantum effects should be taken into account to estimate the force constants [14]. The obtained force constant for first nearest neighbors in Cu₂O at 295 K is $\alpha_{\text{Cu-O}} = 5.6 \text{ eV/\AA}^2$. The force constant for second and third nearest neighbors are $\alpha_{\text{Cu-Cu}} = 2.5 \text{ eV/\AA}^2$ and $\alpha_{\text{Cu-O}} = 0.9 \text{ eV/\AA}^2$, respectively. The force constant for first nearest neighbors in Cu₂O at 295 K is greater than that of Ag₂O (1.37 eV/\AA^2) and KBr (1.45 eV/\AA^2), less than that of ZnSe (6.16 eV/\AA^2), and close to observed in Cu (5.58 eV/\AA^2). In our treatment the first three of radial force constants were determined. The transverse force constants and the long-range Madelung-type forces were omitted. Using the first three of radial force constants and crystal structure of Cu₂O, computer simulations of phonon dispersion relation, phonon density of states and specific heat of Cu₂O were performed. The estimated phonon density of states of Cu₂O almost agrees with observed values [16]. The peak of the phonon density of states appears in the region of $10 \sim 20 \text{ meV}$. The details of the computer simulations are to be published later.

At 295 K the lattice constant of Cu₂O and Ag₂O are 4.2705 \AA and 4.7183 \AA respectively in same crystal structure that belongs to cubic cuprite with space group $Pn\bar{3}m$. The peaks of calculated diffuse scattering in Cu₂O appear at $2\theta \sim 45, 80$ and 150° and shifted in comparison to that of Ag₂O ($2\theta \sim 40, 70$ and 130° [17]) (Fig. 7) due to the differences in the lattice constant.

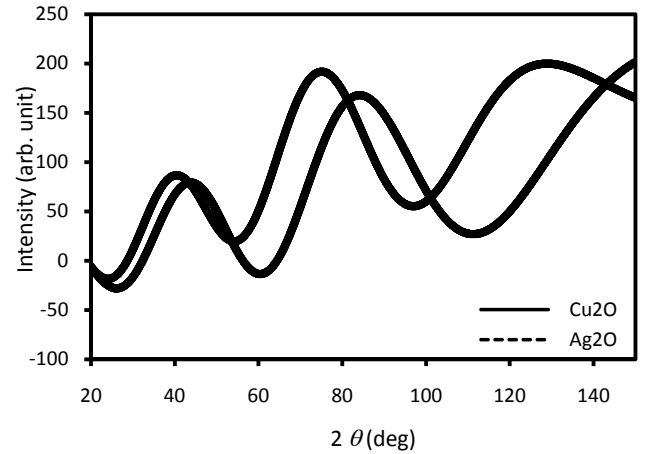


Fig. 7. Comparison of calculated diffuse scattering intensity oscillatory of Cu₂O and Ag₂O at 295 K.

In contrast to Cu₂Se a noticeable oscillatory diffuse scattering has been observed in Ag₂O at 8 K [15]. This indicates that correlation effects and thermal parameters of Ag₂O are larger than those in other ionic crystals, metals and semiconductors which do not show diffuse scattering intensity at low temperature. There might be two contributions to diffuse scattering at low temperature. One is from the thermal vibrations of atoms and the other contribution comes from the static displacements of atoms from the regular atomic positions. These two contributions could be separated by scattering measurements using triple-axis spectrometer in diffractometer two-crystal configuration and in three-axis elastic scattering mode with analyzer crystal [17].

CONCLUSION

Oscillatory diffuse scattering was observed at 295 K in Cu₂O in neutron diffraction patterns. The diffuse scattering in Cu₂O are related to correlations among thermal displacements of atoms. The calculated intensity of diffuse scattering is significantly lower at 10 K in agreement with experiment. The inter-atomic force constant in Cu₂O was greater to that of Ag₂O at room temperature.

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