Determination of Structure Factors of Al_2O_3 by means of Large Angle Convergent Beam Electron Diffraction

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Intensities of higher order reflections in a large angle convergent beam electron diffraction (LACBED) pattern are measured for $\alpha\text{-Al}_2\text{O}_3$ and are compared with theoretical calculations in order to examine applicability of the kinematical approximation to determination of the structure factors. Effects of specimen thickness, temperature and absorption on the intensities are investigated through the dynamical theory of electron diffraction. A static displacement of Al^{3+} ions from their ideal positions in a unit cell of $\alpha\text{-Al}_2\text{O}_3$ is determined from a relative change between two neighbouring high index reflections. The displacement determined through the kinematical theory of electron diffraction agrees well with the one through the dynamical theory and the ones measured by X-ray or neutron diffraction. The result demonstrates the usefulness of LACBED and the kinematical approximation.

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I. Introduction

Electron diffraction in transmission electron microscopy is quite useful for microcharacterization of materials together with the high resolution multi-beam imaging as well as the conventional bright- or dark-field imaging. In particular, capability of nano-beam or convergent-beam electron diffraction provides us with quantitative information on crystals with high spatial resolution⁽¹⁾⁻⁽⁵⁾. Structure factors are a function of atomic scattering factors, atomic coordinates of unit cell and Debye-Waller factors. Those of alloys, covalent or ionic compounds are also a function of composition through averaged structure factors. We can draw information on solid state effect, ionic state, phonon and composition from measured structure factors. The rocking curve method⁽⁶⁾, the intersecting Kikuchi line method⁽⁷⁾ and the critical voltage method⁽⁸⁾ in electron diffraction have been used for determination of structure factors. These methods utilize phenomena caused by the dynamical diffraction effect and hence need no measurement of diffracted intensity itself, although an analysis based on the dynamical diffraction theory is necessary. Analysis of diffracted intensities has been believed to be hard for the determination of structure factors because of a strong dynamical effect of electrons compared with X-ray diffraction. The technique of X-ray crystallography, in which the kinematical approximation is used, has scarcely been applied in electron diffraction.

Large angle convergent beam electron diffraction (LACBED) may give us countermeasure to overcome some of the weak points in intensity analysis of electron diffraction⁽⁹⁾. The purpose of the present paper is to examine the applicability of the kinematical approximation to determination of structure factors and to demonstrate usefulness of LACBED. We calculate diffraction intensities based on both kinematical and dynamical theories of electron diffraction. Using well known $\alpha\text{-Al}_2\text{O}_3$ as a test specimen, we investigate effects of specimen thickness, specimen temperature, absorption of electrons and accelerating voltage on the diffracted intensity. Then static displacements of Al^{3+} ions from their ideal positions in an unit cell is determined and compared with results by X-ray and neutron diffraction.

II. LACBED and Structure Factors of $\alpha\text{-Al}_2\text{O}_3$

1. LACBED

A radius r of convergent beam disc in a diffraction pattern is proportional to convergence angle α of incident beam. If α is sufficiently large compared with a Bragg angle for lowest order diffraction g , Bragg conditions are simultaneously satisfied for plural reflections, although discs overlap each other (Fig. 1). Discs of higher order diffractions can hardly be visible in practice because of large extinction distance and rapid attenuation of diffracted intensities with a deviation s from a Bragg condition. Only diffracted lines which exactly satisfy Bragg conditions appear for higher order diffractions. An effect of the overlapping of discs turns out to be negligible provided indices of excited diffraction are sufficiently high. In the present experiments, the convergent beam of 8 mrad

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Fig. 1 Schematic drawing of large angle convergent beam electron diffraction (LACBED) for systematic higher order reflections.

is illuminated so as to satisfy Bragg conditions for five or more systematic reflections. A specimen of $\alpha\text{-Al}_2\text{O}_3$ is tilted so that systematic row of $0\ 0\ l$ ($l \geq 30$) diffractions are excited. Then several diffraction lines are recorded on a film with a same electro-optical condition. The specimen thickness of the illuminated area is almost uniform because a probe size adopted is about 20 nm in radius. Electron microscopes used in the present experiments are JEM-2000FX and JEM-4000EX.

2. Structure factors of $\alpha\text{-Al}_2\text{O}_3$

Oxygen ions in corundum are ideally arranged in a close packed hexagonal layer, while Al ions occupy centers of octahedra formed by oxygen ions⁽¹⁰⁾. One-third of octahedral interstices are vacant to keep electrical neutrality. Consequently, Al ions are actually displaced by δ to the vacant sites from ideal centers of the octahedra, as shown in Fig. 2. While oxygen ions are displaced in a c -plane from their ideal positions. A structure factor of $0\ 0\ l$ diffraction is a function of δ alone as given by

$$F_{0,0,l} = 18f_{\text{O}} \exp(-B_{\text{O}}S^2) + 2f_{\text{Al}} \exp(-B_{\text{Al}}S^2) \times \sum_{j=1}^3 \cos\{2\pi l((2j-1)/12 \pm \delta/c)\} \quad (1)$$

where $c = 1.2991$ nm, or the lattice dimension along the c -axis, f_{O} and f_{Al} are the atomic scattering factors of oxygen and aluminum, respectively. B_{O} and B_{Al} are the B factors of oxygen and aluminum atoms, and $S = \sin \theta / \lambda$,

Fig. 2 Ideal structure of $\alpha\text{-Al}_2\text{O}_3$ and static displacement of Al ions. Oxygen ions are omitted for simplicity. ● : Al ions, ○ : vacant sites.

or the magnitude of scattering vector.

III. Calculation of Intensities

Intensities of diffractions in $\alpha\text{-Al}_2\text{O}_3$ are calculated through a usual matrix method with 24-beams of systematic $0\ 0\ l$ reflections. We use atomic scattering factors of Doyle and Turner⁽¹¹⁾, because the effect of ionicity on atomic scattering factors can be neglected for higher order reflections. Absorption parameters of Humphreys and Hirsch⁽¹²⁾ and B -factors of Aldebert and Traverse⁽¹³⁾ are used. Figure 3 shows intensities at 200 kV as a function of specimen thickness t . An intensity of $0\ 0\ 12$ oscillates with t , while those of $0\ 0\ l$ with $l \geq 36$ are approximately proportional to t . Thus the kinematical approximation seems to be applicable for reflections higher than $0\ 0\ 30$ in specimens less than a few hundred nm in thickness. In the present experiment we use a specimen with a thickness less than 200 nm. Intensities of $0\ 0\ 36$ and $0\ 0\ 42$ reflections shown in Fig. 3 are nearly equal irrespective of thickness. Relative changes of these reflections are, however, sensitive to a change in a value of static displacement δ as shown in Fig. 4. An intensity ratio $I_{0,0,36}/I_{0,0,42}$ is a good measure for determination of a value of the displacement δ . The temperature dependence of the relative intensities is also indicated in Fig. 4 where B -factors for 300, 110 and 0 K are adopted. The uncertainty of the specimen temperature does not bring about large errors as is clear from Fig. 4.

The effect of absorption on diffracted intensities is expressed in terms of V'_g/V_g , or a ratio of imaginary and real parts of crystal potential⁽¹²⁾. The absorption effect changes with a magnitude of reciprocal lattice vector g and consequently the effect varies from reflection to reflection. It is predicted from Fig. 3 that the ratio $I_{0,0,36}/I_{0,0,42}$ is insensitive to a change in specimen thickness and hence seems to be insensitive to the effect of absorption of elec-

Fig. 3 Intensities of 0 0, l reflections as a function specimen thickness. Calculation with accelerating voltage of 200 kV, B -factors of 300 K, and absorption parameter of $V'_g/V_g=0.02$. Enlarged portion of (a) is shown in (b).

Fig. 4 Change in intensity ratio $I_{0,36}/I_{0,42}$ with static displacement of Al ions and specimen temperature. Systematic 24 beams are taken into account, but the effect of absorption is ignored in calculation. Accelerating voltage is assumed to be 200 kV.

trons. An intensity ratio $I_{0,36}/I_{0,42}$ calculated for absorption parameters of $V'_g/V_g=0.0, 0.02$ and 0.05 shows no appreciable change as shown in Fig. 5. Thus the effect of absorption on the determination of δ is negligible, provided intensities of neighboring reflections are compared.

An effect of accelerating voltage on intensities of higher order 0 0, l reflections is given in Fig. 6. The ratio $I_{0,36}/I_{0,42}$ calculated with a fixed value of δ decreases with an increase in accelerating voltage due to the many-beam dynamical effect. It appears from Fig. 6 that an accelerating voltage below 200 kV is desirable for an analysis with the kinematical approximation.

Fig. 5 Effect of absorption on $I_{0,36}/I_{0,42}$. Absorption parameters used in calculation are $V'_g/V_g=0.0, 0.02$ and 0.05 . Accelerating voltage and specimen temperature are assumed to be 200 kV and 300 K, respectively.

Fig. 6 Change in intensities of 0 0, l reflections with accelerating voltage. Specimen thickness and temperature are assumed to be 150 nm and 300 K, respectively.

Above results indicate that we can determine a value of the δ with the kinematical approximation by measuring the intensity ratio $I_{0,36}/I_{0,42}$.

IV. Experimental Results and Discussion

An example of LACBED patterns observed at 200 kV and at room temperature is shown in Fig. 7 along with its intensity profile recorded by a microdensitometer. A peak of the left-hand at 0 0, 36 reflection in Fig. 7(b) is due to the nonsystematic reflection as apparent from the pattern in Fig. 7(a). The thickness of the specimen used for Fig. 7 is measured to be about 150 nm from a usual

Fig. 7 Example of LACBED pattern observed at 200 kV and 300 K (a) and its micro-densitometer trace (b).

Fig. 8 LACBED patterns observed at different specimen thickness but with the same accelerating voltage of 200 kV and temperature of 300 K. (a): $t = 150$ nm, (b): $t = 300$ nm.

CBED pattern. It is seen in Fig. 7 that intensities of 0 0, 36 and 0 0, 42 reflections are weaker than those of 0 0, 30 and 0 0, 48, but they are nearly equal to each other corresponding well with the calculated results of Fig. 3. It is also apparent that the darkness of the film is not saturated among reflections higher than 0 0, 32. In the present experiment we paid special caution to the exposure or developing time to minimize errors originated from non-linearity between darkness and the electron intensity. LACBED patterns obtained from different specimen thicknesses, different temperatures and different

Fig. 9 LACBED patterns observed at different temperatures. Specimen thickness is 150 nm and accelerating voltage is 200 kV. (a): 300 K, (b): 110 K.

Fig. 10 LACBED patterns observed at different accelerating voltages. Specimen thickness and temperature are 150 nm and 300 K, respectively. (a): 100 kV, (b): 200 kV, (c): 400 kV.

accelerating voltages are shown in Figs. 8, 9 and 10, respectively. Similar intensity profiles in Fig. 7(b) are obtained from Figs. 8 ~ 10, as predicted by calculation. We obtain the intensity ratio $I_{0,36}/I_{0,42}$ assuming that the effect of inelastic scattering is eliminated by subtracting a background intensity fitted by a smooth curve. This assumption is reasonable for two neighboring higher order reflections, because the difference in magnitude of scattering vectors is not large and consequently the effect of temperature diffuse scattering is similar for both reflections. Comparing a measured $I_{0,36}/I_{0,42}$ with the calculated one we determine the value of δ as shown in Table 1.

Figure 11 shows intensities for various 0 0, l reflec-

Table 1 Comparison of static displacements of Al ions measured with different methods.

Method	Displacement δ (nm)	Reference
LACBED (K)	0.02435 ± 0.00020	Present result
(D)	0.02445 ± 0.00020	Present result
X-ray	0.02461 ± 0.00007	Ishizawa <i>et al.</i> ⁽¹⁴⁾
	0.02430 ± 0.00040	Newnham <i>et al.</i> ⁽¹⁵⁾
Neutron	0.02463 ± 0.00024	Aldebert <i>et al.</i> ⁽¹³⁾

K: Kinematical approximation.

D: Dynamical approximation.

Fig. 11 Intensities of 0 0, l reflections calculated as a function of displacement δ (nm) through the kinematical approximation. B -factors at 300 K are considered.

tions calculated with the kinematical diffraction theory. A relative change of intensities between 0 0, 36 and 0 0, 42 reflections is very sensitive to a change in δ as clear from Fig. 11. The value of δ determined with the kinematical approximation is 0.02435 ± 0.00020 nm which agrees well with the result obtained by applying the dynamical theory. The present results are listed in Table 1 along with those in the literatures (13)~(15). Our results are in good agreement with those by X-ray and neutron diffraction demonstrating the adequateness of the present kinematical treatment.

V. Concluding Remark

Diffraction intensities of a LACBED pattern were analyzed through the dynamical and kinematical diffraction theories in order to determine a structure factor of α -Al₂O₃. LACBED is very useful for observing several

diffraction lines from the same specimen thickness and with the same electro-optical conditions. By comparing an intensity ratio of higher order reflections with the calculated one, a value of the static displacement of Al ion from its ideal position was determined. Applicability of the kinematical approximation to the determination of structure factors is well demonstrated. The method presented here is useful for refinement of crystal structures such as high T_c oxide superconductors. In the present experiment we compared two neighbouring reflections which have intensities not much different each other, in order to minimize errors caused from crude subtraction of the background intensity and from weak points of films such as non-linearity and a small dynamic range. Feasibility and accuracy of the present treatment will be much improved by the use of new recording systems such as an imaging plate⁽¹⁶⁾ or a slow scan CCD camera⁽¹⁷⁾ which overcomes some of weak points of films. Furthermore an energy filtering system which enables us to subtract the contribution of inelastic scattering will provide us with more quantitative information⁽¹⁸⁾. A study by using these systems is under progress and the results will be soon reported.

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