Determination of Phase Angles and Absolute Values of the Structure Potential V_{0002} of Cadmium Sulfide from Equal Thickness Fringes in Electron Micrographs*

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Fringe spacings were measured at the three different diffraction conditions: 0002-Bragg position, 0004-Bragg position and the symmetric position for $000l$ systematic reflections. The absolute value $|V_{0002}|$ and the phase angle Φ_{0002} were determined by analyzing the ratios of fringe spacings with a 15-beam calculation. The values determined were $|V_{0002}| = 6.5 \pm 0.5$ Volt and $\tan \Phi_{0002} = -0.54 \pm 0.04$ on the origin at a cadmium atom. From these values the atom form factors at the position of 0002 reflection were calculated as $f_{\mathrm{Cd}}^{\mathrm{x}} = 42.4 \pm 0.5$ and $f_{\mathrm{S}}^{\mathrm{x}} = 13.0 \pm 0.2$, assuming the parameter u determined by X-ray diffraction.

Introduction

It has long been known that the Fourier coefficients V_{h} of crystal potentials can be determined from the spacing of equal thickness fringes in electron micrographs [1]. For example, Uyeda and Nonoyama [2] determined V_{200} of magnesium oxide using the 90° wedges made by cleaving single crystals. However, a high accuracy could not be attained because of the difficulties in correcting the many-beam interaction and in calibrating the accurate value of the magnification. The former difficulty is overcome by the progress of computer calculation and the latter one can be avoided by the authors' new method [3], where the ratios of fringe spacings are used in the analysis. With these advanced techniques it has become possible to determine the phase angle as well as the absolute value of V_{h}, because in the many-beam theory the extinction distance for the h-reflection includes cross terms of the type

$$V_{\mathrm{h}}^{*} V_{\mathrm{h-g}} V_{\mathrm{g}} = |V_{\mathrm{h}}| \cdot |V_{\mathrm{h-g}}| \cdot |V_{\mathrm{g}}| \exp\{i(-\Phi_{\mathrm{h}} + \Phi_{\mathrm{h-g}} - \Phi_{\mathrm{g}})\}.$$

In the present work the equal thickness fringes were taken from 60° wedges of cadmium sulfide crystal, a noncentrosymmetric crystal, and the absolute value as well as the phase angle of V_{0002} was obtained. The result was further analysed to determine the form factors of cadmium and sulfur atoms at the position of 0002 reflection, and to find the distribution of electrons in the cadmium sulfide lattice.

* The results of this article have been partially referred to in a review article by one of the authors (A. Ichimiya, J. Cryst. Soc. Japan **18**, 13 [1976], in Japanese).

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Experimental

The material used in the present experiment was large cadmium sulfide crystals of wurtzite type made by The Teikoku Tsushin Co., Kawasaki, Japan. Specimens of 60° wedges were prepared by cleaving them along $(10\bar{1}0)$ and $(01\bar{1}0)$. It was fixed on a special holder as described in one of the previous papers [2].

The electron microscope used was JEM-7 operated at 100 kV and with an objective aperture of angular size 7.1×10^{-3} rad. The electron micrographs were taken at (a) 0002-Bragg position, (b) 0004-Bragg position and (c) the symmetric position for $000l$ systematic reflections at the same magnification under bright field. The crystal orientations were adjusted each time in such a way that accidental reflections were excited as little as possible. An example of a set of electron micrographs is shown in Figure 1. The fringe profiles were recorded by a micro-densitometer and the distances $L(n)$ between the first minimum and the $(n+1)$-th minimum were measured. The average fringe spacings $l(n)$ were calculated by dividing $L(n)$ by n, where the numbers n were 5 or 6 for symmetric, 4 or 5 for 0002 and 2 or 3 for 0004. The notation n is abbreviated in the following description. The ratios of the fringe spacings, l_{s}/l_2, l_{s}/l_4 and l_4/l_2, were calculated and used in the analysis, where the suffixes s, 2 and 4 mean symmetric, 0002 and 0004 respectively. The experimental values of l for fringe numbers are shown in Table I.

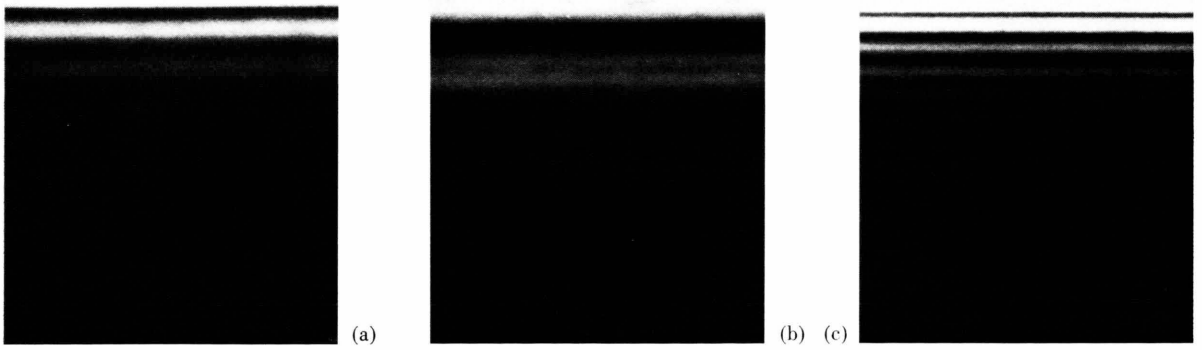

Fig. 1. Electron micrographs of equal thickness fringes of a cadmium sulfide crystal.
(a) 0002 Bragg position, (b) 0004 Bragg position and (c) symmetric position for 000l systema tic reflections.

Table I. Values of l_s, l_2 and l_4 and the correction parameters C_s, C_2 and C_4 for various fringe numbers.

n	l_s (mm)	C_s	n	l_2 (mm)	C_2	n	l_4 (mm) *	C_4 *
5	1.20±0.014	1.001	3	2.01±0.030	0.988	1	4.55±0.13	1.011
6	1.19±0.017	1.018	4	1.90±0.045	1.026	2	4.55±0.08	0.997

* Average values from first and second fringe positions.

Relation Between the Structure Potential and the Atom Form Factor

The Fourier coefficients V_{000l} of cadmium sulfide, where l is even, are given as

$$V_{000l} = (h^2/2\,m\,e)\,(2/\pi\,\Omega)\,[f^e_{Cd} + f^e_S \exp\{2\pi i u l\}] = V_{000l} \exp\{i\,\Phi_{000l}\}\,, \quad (1)$$

where h, m and e are the usual notations, Ω is the unit cell volume, $f^e_{Cd\,or\,S}$ the atom form factor for electrons of cadmium or sulfur atom, and u the parameter giving the position of sulfur atoms relative to cadmium atoms. The atom form factor for electrons f^e is related to that for X-rays through the Mott formula

$$f^e = (2\,m\,e^2/h^2)\,[(Z - f^x)/(\sin\Theta/\lambda)^2] \quad (2)$$

where Z, Θ and λ are respectively the atomic number, one half of the scattering angle and the wavelength of the electrons. The absolute value $|V_{000l}|$ and the phase angle Φ_{000l} are given as

$$|V_{000l}| = (h^2/2\,m\,e)\,(2/\pi\,\Omega) \cdot \sqrt{f^{e2}_{Cd} + f^{e2}_S + 2\,f^e_{Cd} f^S_e \cos(2\pi u l)} \quad (3)$$

and

$$\Phi_{000l} = \tan^{-1}[f^e_S \sin(2\pi u l)/(f^e_{Cd} + f^e_S \cos(2\pi u l))]\,,$$

where the origin of the co-ordinate is taken at a cadmium atom. There are three unknowns, f^e_{Cd}, f^e_S and u, in Equation (3). Therefore, two of them can be determined if $|V_{000l}|$ and Φ_{000l} are obtained by some means. In the present work $|V_{0002}|$ and Φ_{0002} were obtained by experiment, and f^e_{Cd} and f^e_S were calculated by Eq. (3), adopting the value $u = 0.375$ known in X-ray diffraction [4].

Method of Analysis

According to the dynamical theory, each of the three ratios of the equal thickness fringes is given as a function of V_{000l}'s. However, the unknown variables are essentially V_{0002} and Φ_{0002}, because satisfactory values of V_{000l} for $l \geqq 4$ can be obtained theoretically.

Since the fringe spacings were not uniform, the analysis proceeded in the following way. At first approximate formulas

$$l_s/l_2 = \Delta_2/\Delta_s\,,\ l_s/l_4 = \Delta_4/\Delta_s\,,\ l_4/l_2 = \Delta_2/\Delta_4\,, \quad (4)$$

were assumed, where Δ_s, Δ_2 and Δ_4 are the separations of the two most strongly excited dispersion surfaces at three specified diffraction conditions. The right-hand sides of the above equations were

calculated by a systematic 15-beam calculation with various trial values of $|V_{0002}|$ and $\tan\Phi_{0002}$. Figure 2 shows the variation of Δ_2/Δ_s against $\tan\Phi_{0002}$ for several values of $|V_{0002}|$. The experimental value of l_s/l_2 is shown by a broken line (a) in Figure 2. From the intersections of the solid curves and the broken line (a), the relation between $|V_{0002}|$ and $\tan\Phi_{0002}$ was obtained as a broken curve a′ shown in Figure 3. Through the same treatment for the other ratios, the curves b′ and c′ shown in Fig. 3 were drawn. From the intersection of the curves, the first approximate values of $|V_{0002}|$ and $\tan\Phi_{0002}$ were obtained.

The refinement was carried out as follows: The fringe profile for each diffraction condition was

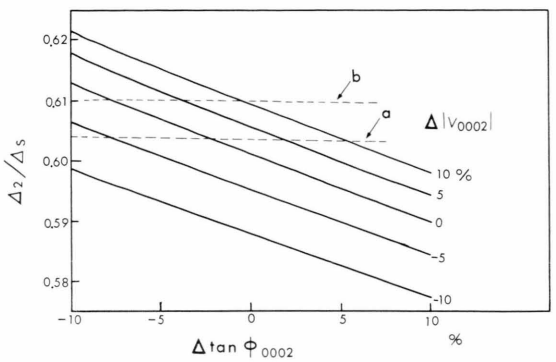

Fig. 2. The variation of Δ_2/Δ_s against $\tan\Phi_{0002}$ for several values of $|V_{0002}|$. The broken line (a) shows experimental value of l_s/l_2. The broken line (b) shows the final value of Δ_2/Δ_s by iteration.

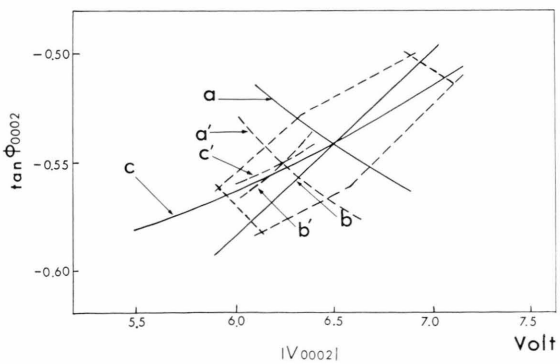

Fig. 3. Diagram of $|V_{0002}|$ vs. $\tan\Phi_{0002}$. The broken curves (a′), (b′) and (c′) were drawn for the first approximate values of Δ_2/Δ_s, Δ_4/Δ_s and Δ_2/Δ_4, respectively. From the third iteration, the curve (a) is drawn for $\Delta_2/\Delta_s=0.61$, the curve (b) for $\Delta_4/\Delta_s=0.263$ and the curve (c) for $\Delta_2/\Delta_4=2.32$. The intersection of these curves gives the values of $|V_{0002}|$ and $\tan\Phi_{0002}$. The area bounded by the broken curves gives the experimental error.

drawn by the systematic 15-beam calculation using the values of $|V_{0002}|$ and $\tan\Phi_{0002}$ obtained in the above analysis. In the calculation of the profile, the fourier coefficients of imaginary potential V'_{000l} were taken as $V_0'=1.1$ Volt and $V'_{000l}=0.03\,(0.5+l)\,V_{000l}$ Volt[5–7], where V_0' was determined from the profiles obtained in the present experiment. The average values of fringe spacings l^{calc}'s were obtained from the calculated profiles, and the correction parameters C are defined as

$$C_s=1/(\Delta_s l_s^{\mathrm{calc}}),\quad C_2=1/(\Delta_2 l_2^{\mathrm{calc}}),\quad C_4=1/(\Delta_4 l_c^{\mathrm{calc}}). \qquad (5)$$

Each parameter was multiplied on each experimental value of the average fringe spacings. Then, starting from the equations

$$C_s l_s/C_2 l_2=\Delta_2/\Delta_s,\quad C_s l_s/C_4 l_4=\Delta_4/\Delta_s,\quad C_4 l_4/C_2 l_2=\Delta_2/\Delta_4, \qquad (6)$$

the second approximate values of $|V_{0002}|$ and $\tan\Phi_{0002}$ were obtained. In the same way as in the first step, the iteration of the same process was carried out until the result converged. In the present work three iterations were sufficient.

Results

The ratios $C_s l_s/C_2 l_2$, $C_s l_s/C_4 l_4$ and $C_4 l_4/C_2 l_2$ determined by the third iteration are:

$$C_s l_s/C_2 l_2=0.61\pm0.014, \qquad (7\,a)$$
$$C_s l_s/C_4 l_4=0.263\pm0.0077, \qquad (7\,b)$$
$$C_4 l_4/C_2 l_2=2.32\pm0.074, \qquad (7\,c)$$

where the values of C_s, C_2 and C_4 are shown in Table I for various fringe numbers.

The diagram of $|V_{0002}|$ vs. $\tan\Phi_{0002}$ were given as shown in Figure 3. The curves a, b and c were drawn for the above values of Eqs. (7 a), (7 b) and (7 c) respectively. The area bounded by the broken curves gives the experimental error. From the intersection of the curves, the values of $|V_{0002}|$ and $\tan\Phi_{0002}$ were determined as

$$|V_{0002}|=6.5\pm0.5\ \text{Volt},\quad \tan\Phi_{0002}=-0.54\pm0.04.$$

With these values $f_{\mathrm{Cd}}^{\mathrm{e}}$ and $f_{\mathrm{S}}^{\mathrm{e}}$ were calculated by Eq. (3) as given in Table II. These values included the Debye-Waller factor. After correcting for this factor with $B=0.8$ Å^2 (see [8]), the atom form factors for X-rays f^{x} were obtained as given in Table II. The theoretical values of the neutral atoms by Cromer and Mann[9] are also given in Table II. The

Table II. Values of atom form factors for 0002 reflections.

	f^e (exp) Å	f^x (exp) $u=0.375$	f^x (exp) $u=0.379$	f^x (theory)
Cd	6.0 ± 0.6	42.4 ± 0.5	42.9 ± 0.5	41.97
S	3.3 ± 0.2	13.0 ± 0.16	12.7 ± 0.2	12.63

present values for sulfur is a little larger than the theoretical value, while that for cadmium agrees with the theoretical value.

Discussions

Figure 4 shows that an arbitrarily introduced change of 10% in the value of $|V_{0004}|$ as a trial produces a change of less than 1% in the result of $|V_{0002}|$ and $\tan\Phi_{0002}$. No detectable change results in the values of $|V_{0002}|$ and $\tan\Phi_{0002}$, when B is changed from 0.0 to 1.0 Å^2. Therefore, no significant error has arisen either from the use of the theoretical values of V_h for higher orders or from the inaccuracy in the temperature parameter. The effect of accidental reflections is estimated to be smaller than 1% under the present experimental condition [10].

The change of $|V_{0002}|$ and $\tan\Phi_{0002}$ caused by the change of the parameter u in the range from 0.370 to 0.380 is also shown in Figure 4. Since this change is very sensitive, it is planned to carry out

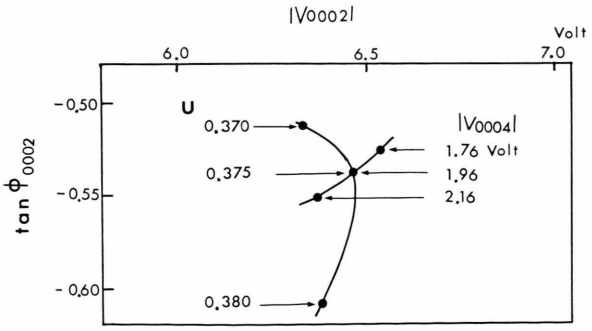

Fig. 4. The change of $|V_{0002}|$ and $\tan\Phi_{0002}$ caused by the change of $|V_{0004}|$ and parameter u.

the present method at various acceleration voltages. Then the parameter u can also be determined from experiment [3].

The value of u can be determined also from the intensity of higher order reflections of X-ray diffraction. If the unpublished data of Takeuchi [8], are adopted, the atom form factors become as given in the third column of Table II. The value of f_S^x changes relatively sensitively with the value of u.

We are interested in the deviation of the electron distribution from the theoretical one obtained by the superposition of neutral atoms. From the present experimental results of the first order 0002, the deviation of the one-dimensional distribution along the axis can be roughly reproduced. In Fig. 5, the

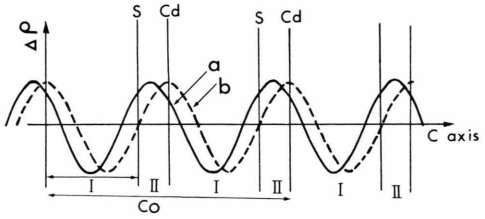

Fig. 5. The difference of the experimental and theoretical one-dimensional electron distributions $\Delta\varrho$ along the c-axis. The curve a is for $u=0.375$ and the curve b for $u=0.379$. Cd and S indicate the atomic planes parallel to (0001).

deviation is shown for the result of $u=0.375$ (solid curve) and for $u=0.379$ (broken curve). Both results in Fig. 5 show a higher electron density in region II than the theoretical one. This can be interpreted by the build up of bonding electrons as well as by the contraction of the electron distribution around each atom. These two possibilities cannot be distinguished from the present data.

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