HOMMA, H., ANDO, Y. & KATO, N. (1965). *J. Phys. Soc. Japan*, **21**, 1160.
KATO, N. (1960). *Z. Naturf.* **15**a, 369.
KATO, N. (1961*a*). *Acta Cryst.* **14**, 526.
KATO, N. (1961*b*). *Acta Cryst.* **14**, 627.
KATO, N. (1964). *J. Phys. Soc. Japan*, **19**, 67.
KATO, N. (1968*a*). *J. Appl. Phys.* **39**, 2225.
KATO, N. (1968*b*). *J. Appl. Phys.* **39**, 2231.
KATO, N. & LANG, A. R. (1959). *Acta Cryst.* **12**, 787.
KATO, N. & TANEMURA, S. (1967). *Phys. Rev. Let.* **19**, 22.
YAMAMOTO. K, & KATO, N. (1968). *Acta Cryst.* **A24**, 230.

DISCUSSION

WEISS (TO HART): (*a*) These results are most impressive – it would be excellent if they are indeed as accurate as claimed. We would then have a valuable reference standard.

(*b*) There is one point and that was the relatively large difference between Mo and Ag measurements. Did you consider dispersion corrections?

HART: Yes, the total correction is ~0·4% but the difference is still 0·3%. We have good internal consistency in all measurements. So far we cannot explain this difference. It is the only embarrassing feature.

BATTERMAN (TO KATO): Referring to the table of Debye temperatures where you compare Professor Borrmann's and your own results, you said that Borrmann's measurements were consistent with 296° at room temperature and 330° at 20°K. On the other hand, Professor Borrmann in his talk gave a value of 290° and this appeared to fit over the whole temperature range considered. Have you any comments?

KATO: We do not know the true value of the Debye temperature so I have used the room temperature value derived from our own Pendellösung measurements. Your theoretical values are slightly higher than these and it is possible that the difference between the room and low-temperature values quoted may account for the difference between our value and the theoretical at room temperature.

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Determination of the Atom Form Factor by High Voltage Electron Diffraction

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A new method of determining the atom form factors from the values of accelerating voltages for which the second order Kikuchi line disappears is applied to aluminum, iron, nickel and copper. The accuracy of the method is briefly discussed and the numerical results of the atom form factors are given.

It was reported recently that the second order Kikuchi line in electron diffraction disappears at a certain accelerating voltage E_c due to the many-beam dynamical interaction combined with the relativistic change of electron mass (Watanabe, Uyeda & Kogiso, 1968). The present authors used the effect for determining the Fourier coefficient of the crystal potential for the first order V_1. Thus the corresponding value of the X-ray atom form factor f_1^x was determined also (Watanabe, Uyeda & Fukuhara, 1968). In the present note, an experimental procedure is described and the error in f_1^x obtained by this method is discussed. The numerical results for aluminum, iron, nickel and copper are given.

Thin foils were obtained by electropolishing from 99·9 to 99·99% metal plates annealed in vacuum, and examined with a 500 kV electron microscope. Diffraction patterns were taken from areas of a few microns diameter or smaller by the selected area diffraction technique at various accelerating voltages. The accelerating voltage of each diffraction pattern was determined from the analysis of the Kikuchi pattern with an accuracy of 1% (Uyeda, Nonoyama & Kogiso, 1965). The value of E_c was determined with an accuracy of 10 kV by examining a series of diffraction patterns taken at various accelerating voltages. The values of E_c were measured for the 220 reflexion of iron and the 222 reflexion of aluminum, nickel and copper (Table 1). The X-ray atom form factors f_1^x for the first order reflexion were determined using the measured values of E_c and known values of f_n^x for the second and higher order reflexions ($n=2, 3, \ldots$).

The percentage error in f_1^x thus obtained can be roughly estimated on the basis of the Bethe's second approximation (Bethe, 1928; Uyeda, 1968). It gives the following equation at the voltage E_c,

$$U_2 - R\,.\,d^2 \times \{U_1^2 - \tfrac{2}{3}U_1\,.\,U_3 - \tfrac{2}{8}U_2\,.\,U_4 - \tfrac{2}{15}U_3\,.\,U_5 - \ldots\} = 0\,, \quad (1)$$

where $R = 1 + \dfrac{eE_c}{m_0c^2}$, $m_0c^2 = 511$ kV, $U_i = 2m_0eV_i/h^2$, and d is the lattice spacing for the first order reflexion. From this equation and the well-known formula,

$$f^e = \frac{8\pi^2 m_0 e^2}{h^2}\,\frac{Z - f^x}{s^2}\,, \quad (2)$$

the following equation is obtained for $|\Delta f_1^x/f_1^x|$:

$$\left|\frac{\Delta f_1^x}{f_1^x}\right| \simeq \frac{1}{2}\,.\,\frac{Z - f_1^x}{f_1^x}\left[\frac{eE_c}{m_0c^2 + eE_c}\,.\left|\frac{\Delta E_c}{E_c}\right| + \frac{f_2^x}{Z - f_2^x}\,.\left|\frac{\Delta f_2^x}{f_2^x}\right|\right]. \quad (3)$$

Here, it should be emphasized that the percentage error in f_1^x is very small compared with the error in the experimental value of E_c and the uncertainty in the value of f_2^x. Since

$$\frac{Z - f_1^x}{f_1^x} \simeq 0{\cdot}45 \sim 0{\cdot}30\,,\; \frac{f_2^x}{Z - f_2^x} \simeq 1{\cdot}0 \sim 0{\cdot}8,$$

and

$$\frac{eE_c}{m_0c^2 + eE_c} = 0{\cdot}37 \text{ to } 0{\cdot}46$$

for metals examined in the present study, contributions of ΔE_c and Δf_2^x to $|\Delta f_1^x/f_1^x|$ are less than one tenth of $|\Delta E_c/E_c|$ and about one fifth of $|\Delta f_2^x/f_2^x|$, or less, respectively. Contributions of Δf_3^x *etc.* are less because the factors multiplying $|\Delta f_3^x/f_3^x|$ *etc.* are much smaller. In the present analysis, the theoretical Hartree–Fock values of f_2^x, f_3^x *etc.* for the free neutral atoms (Freeman & Watson, 1961; *International Tables for X-ray Crystallography*, 1962) were used. The errors of f_2^x estimated from reliable theoretical and X-ray experimental data are about 1·4 % or less for iron, nickel and copper, and less than 2 % for aluminum (Bensch, Witte & Wölfel, 1955; Hosoya & Fukamachi, 1968; Hosoya & Yamagishi, 1966; Inkinen & Suortti, 1964, Jennings, Chipman & DeMarco, 1964; Paakari & Suortti, 1967; Sachs, 1967; Wakoh, 1968).

The values of V_1 were calculated from the measured values of E_c using the theoretical V_2 *etc.* derived from the assumed f_2^x, *etc.* by Bethe's second approximation, equation (1), taking eleven beams ($i = -4, -3, \ldots, +6$) into account, and by an orthodox many-beam theory (Fukuhara, 1966) covering nine beams ($i = -3, -2, \ldots, +5$). The results of both calculations agreed almost exactly. Table 1 shows the results for f_1^x at the first order reflexion which were derived from the values of V_1 calculated by the many-beam theory, together with other available theoretical and X-ray experimental data for comparison. The estimated errors of f_1^x are about 0·6 % for iron, nickel and copper and 0·9 % for aluminum, which include those arising from ΔE_c, Δf_2^x and the assumed temperature factors B.

References

Batterman, B. W., Chipman, D. R. & DeMarco, J. J. (1961). *Phys. Rev.* **122**, 68.

Bensch, H., Witte, H. & Wölfel, E. (1955). *Z. Phys. Chem.* **4**, 65.

Bethe, H. A. (1928). *Ann. Phys.* **87**, 55.

Freeman, A. J. & Watson, R. E. (1961). *Acta Cryst.* **14**, 231.

Fukuhara, A. (1966). *J. Phys. Soc. Japan*, **21**, 2645.

Hosoya, S. & Fukamachi, T. (1968). *J. Phys. Soc. Japan.* To be published.

Table 1. *Experimental and theoretical X-ray atom form factors for aluminum, iron, nickel and copper at the first order reflexion*

	Al	Fe	Ni	Cu
E_c	430 kV (for 222)	305 kV (for 220)	295 kV (for 222)	325 kV (for 222)
Debye temperature Θ (°K)	395	425	390	320
Temperature factor B (Å^2)	0·85	0·36	0·40	0·54
f^x (Present result)	(for 111) 8·87 ± 0·08	(for 110) 18·34 ± 0·11	(for 111) 20·48 ± 0·12	(for 111) 21·78 ± 0·13
f^x (Theory)				
Freeman & Watson (1961)	8·95	18·51	20·57	22·14
Wakoh (1968)		18·34	20·28	21·72
f^x (X-ray experiment)				
Bensch, Witte & Wölfel (1955)	8·55			
Batterman, Chipman & DeMarco (1961)	8·63 ± 0·14	17·63 ± 0·20		21·29 ± 0·34
Inkinen & Suortti (1964)			20·46 ± 0·13	
Jennings, Chipman & DeMarco (1964)				21·52 ± 0·1
Hosoya & Yamagishi (1966)				22·07 ± 0·09
Paakari & Suortti (1967)		18·19 ± 0·20		
Hosoya & Fukamachi (1968)		18·44 ± 0·15	20·78 ± 0·26	

HOSOYA, S. & YAMAGISHI, T. (1966). *J. Phys. Soc. Japan*, **21**, 2638.
INKINEN, O. & SUORTTI, P. (1964). *Ann. Acad. Sci. Fennicae*, A VI. No. 147.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JENNINGS, L. D., CHIPMAN, D. R. & DEMARCO, J. J. (1964). *Phys. Rev.* **135**, A1612.
PAAKARI, T. & SUORTTI, P. (1967). *Acta Cryst.* **22**, 755.
SACHS, L. M. (1967). *Acta Cryst.* **22**, 931.
UYEDA, R. (1968). *Acta Cryst.* A**24**, 175.
UYEDA, R., NONOYAMA, M. & KOGISO, M. (1965). *J. Electronmicroscopy*, **14**, 296.
WAKOH, S. (1968). To be published.
WATANABE, D., UYEDA, R. & FUKUHARA, A. (1968). *Acta Cryst.* A**24**, 580.
WATANABE, D., UYEDA, R. & KOGISO, M. (1968). *Acta Cryst.* A**24**, 249.

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Experimental Determination of the Extinction Factor by the use of Polarized X-Rays

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The problem of estimating the extinction factor by the use of polarized X-rays has been re-examined in the light of the theory of X-ray diffraction in real crystals developed recently by Zachariasen. Expressions are given for deriving the extinction-free structure factors in terms of the observed integrated intensities for perpendicular and parallel polarizations. A simple attachment to a diffractometer for analysing the polarization of the diffracted beam is described. Measurements on quartz are presented; the extinction-free structure factors so obtained are in excellent agreement with Zachariasen's calculated values based on new *f* curves.

Theory

The theory of X-ray diffraction in real crystals developed recently by Zachariasen (1967, 1968) provides a basis for evaluating large extinction effects to a greater precision than has been possible so far. According to the theory, the integrated intensity of reflexion from a symmetrically shaped crystal of volume v, assumed to consist of nearly spherical domains of radius r, is given by

$$P = P_k y \tag{1}$$

for unpolarized X-rays, where

$$P_k \text{ (the kinematical value)} = I_0 v A Q_0 \left(\frac{1+\cos^2 2\theta}{2}\right). \tag{2}$$

y (the extinction factor)

$$= \frac{(1+2x_0)^{-\frac{1}{2}} + \cos^2 2\theta (1+2x_0 \cos^2 2\theta)^{-\frac{1}{2}}}{1+\cos^2 2\theta}. \tag{3}$$

$$x_0 = Q_0 \lambda^{-1} T r^*, \tag{4}$$

$$Q_0 \lambda^{-1} = \left|\frac{e^2 \lambda F}{mc^2 V}\right|^2 \Big/ \sin 2\theta,$$

$$r^* = r[1+(r/\lambda g)^2]^{-\frac{1}{2}},$$

$$T = -\frac{1}{A}\frac{dA}{d\mu} = \frac{1}{A^*}\frac{dA}{d\mu}.$$

I_0 is the incident intensity, $A^* = A^{-1}$ the absorption factor, g the factor determining the disorientation of the perfect domains in the crystal, and the other symbols have their usual meanings. We shall show in this paper that the extinction factor can be determined experimentally by the use of polarized X-rays.

That the polarization factor of a reflexion depends critically on the state of perfection of the crystal was demonstrated experimentally for the first time by Ramaseshan & Ramachandran (1953, 1954). A method of applying a first order correction for extinction errors using polarized X-rays was developed by Chandrasekhar (1956, 1963). We reconsider this method in the light of Zachariasen's new formulae. For perpendicular polarization (1)–(4) give

$$P_\perp = P_{k\perp} y_\perp \tag{5}$$

where

$$P_{k\perp} = I_0 v A Q_0$$

and

$$y_\perp = (1+2x_0)^{-\frac{1}{2}}.$$

For parallel polarization

$$P_\parallel = P_{k\parallel} y_\parallel \tag{6}$$

where

$$P_{k\parallel} = P_{k\perp} \cos^2 2\theta$$

$$y_\parallel = (1+2x_0 \cos^2 2\theta)^{-\frac{1}{2}}.$$

From (5) and (6)

$$P_{k\perp}^2 = \frac{P_\perp^2 P_\parallel^2 (1-\cos^2 2\theta)}{P_\perp^2 \cos^4 2\theta - P_\parallel^2 \cos^2 2\theta} \tag{7}$$

and

$$x_0 = \tfrac{1}{2}[(P_{k\perp}/P_\perp)^2 - 1]. \tag{8}$$