around $\varphi=0$, 180°. This effect influences mostly the 'left–right' reflexion pairs and the R value improvement should be observed on all photographs, as indeed shown in Table 1.

The absorption curve of Fig. 5(c) is again approximately symmetrical around $\varphi=90°$ and 270° and the R value changes are as one would expect.

Fig. 5(d) is an example of a large absorption effect. The R value improvement is particularly high.

This R-value test of equivalent reflexions can, of course, give no indication as to whether the proposed method also provides a proper correction for the absorption variation between diffraction cones; nevertheless it may well do so.

Eventual errors in this correction are, however, no serious problem, as the scaling procedure involves individual scaling factors and temperature factors for each film (Steigemann, unpublished). The 'temperature factor' can take absorption errors of this kind into account.

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Accurate Determination of Atomic Scattering Factors of F.C.C. and H.C.P. Metals by High-Voltage Electron Diffraction

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The accelerating voltage E_c at which the second-order Kikuchi line vanishes has been measured for the 400 reflexions of Al, Ni and Cu and the 0004 reflexion of Ti. The X-ray atomic scattering factors f^x for the first-order reflexion have been determined from the measured values of E_c and the results are compared with theoretical and X-ray experimental data.

Introduction

Two new experimental methods of determining atomic scattering factors have been developed recently. Both methods utilize many-beam dynamical effects in electron diffraction: one uses the effect of the vanishing of the second-order reflexion which occurs due to relativistic enhancement of dynamical interaction among systematic reflexions (Uyeda, 1968; Watanabe, Uyeda & Kogiso, 1968; Watanabe, Uyeda & Fukuhara, 1968); the other uses a similar effect in the accidental many-beam case (Gjønnes & Høier, 1969, 1971). In the former method, the accelerating voltage E_c at which a second-order reflexion vanishes is used to determine the first-order Fourier coefficient, V_1, of the crystal potential; this gives the corresponding value of the X-ray atomic scattering factor f_1^x with high accuracy. The E_c values have been measured so far for the 222

reflexions of f.c.c. metals Al, Ni and Cu, and the 220 reflexions of b.c.c. metals V, Cr and Fe, and the values of f_1^x have been determined by a many-beam calculation with an accuracy as good as that of the most reliable X-ray measurements, and compared with those calculated theoretically for atoms in the solid state (Watanabe, Uyeda & Fukuhara, 1968, 1969; Fujimoto, Terasaki & Watanabe, 1972). The values of E_c for the 400 reflexion of the NaCl type TiO_x crystals ($0.82 \leq x \leq 1.25$) have also been measured and the structure factors for the 200 reflexions have been determined (Watanabe & Terasaki, 1972). In the present study, the values of E_c for the 400 reflexions of f.c.c. metals, Al, Ni and Cu have been measured, and the atomic scattering factors for the 200 reflexions have been determined. The method has also been applied to h.c.p. Ti metal and the atomic scattering factor for the 0002 reflexion has been determined.

Experimental

Thin foils were obtained by conventional electropolishing from rolled sheets 0·1–0·25 mm thick, which were prepared from 99·99%Al, 99·9%Ni, 99·999%Cu and 99·8%Ti and annealed *in vacuo* prior to thinning. Diffraction patterns were taken from regions several thousand Å or more in thickness by the method of selected-area diffraction at various accelerating voltages using 1000 kV as well as 500 kV electron microscopes. Fig. 1 shows examples of diffraction patterns of Ni taken at accelerating voltages 430, 590 and 730 kV. The 400 Kikuchi lines are clearly visible in Fig. 1(a) and (c), but absolutely invisible in (b). Moreover, the middle line of the Kikuchi band is clearly seen in Fig. 1(a) and (c) but not in (b). Asymmetry of the excess-deficient profile of the middle line is reversed from (a) to (c) (Kainuma & Kogiso, 1968; Watanabe, Uyeda & Kogiso, 1968). The values of E_c for the second-order reflexion were determined from a series of such diffraction patterns. The results are shown in Table 1. The diffraction patterns were taken at every 5kV or less in the vicinity of the voltages E_c, in order to minimize the experimental errors. The accelerating voltage in each diffraction pattern was determined from the analysis of the Kikuchi pattern with an accuracy of 1% (Uyeda, Nonoyama & Kogiso, 1965).

Calculation and results

The values of V_1 were calculated from the measured values of E_c by the use of theoretical values of the Fou-

rier coefficients for the systematic reflexion series, V_n ($n \geq 2$). Theoretical atomic scattering factors have been calculated for free atoms by several investigators, *e.g.* Freeman & Watson (1961) (Hartree–Fock wave functions), Doyle & Turner (1968) (relativistic Hartree–Fock wave functions), and Fukamachi (1971) (analytical Roothaan–Hartree–Fock wave functions). Scattering factors for solid Al, Ni and Cu atoms have been calculated by Arlinghaus (1967) and Wakoh & Yamashita (1971). No attempt at theoretical calculation has been made for solid Ti atoms, however. In the present analysis, the values of V_n ($n \geq 2$) calculated from these theoretical scattering factors were used. Since E_c was measured at room temperature (20°C) the values of V_n ($n \geq 2$) including the Debye–Waller factor $\exp(-B \sin^2 \theta/\lambda^2)$ must be used in the calculation of V_1. The Debye characteristic temperatures Θ_D appropriate to crystal diffraction have been measured for many crystals. The following values were chosen from among available experimental data; 395°K for Al, 390°K for Ni and 320°K for Cu. For the Ti crystal, $\Theta_D = 365°K$ was selected; this has been determined for the 000*l* reflexion by the X-ray diffraction experiment of Schoening & Witt (1965). In the present analysis, the corresponding B factors were assumed.

The values of V_1 were calculated by Bethe's second approximation (Uyeda, 1968) taking 11 beams ($n = -4, -3, \cdots, +6$) into account, and by many-beam theory (Fukuhara, 1966) covering 15 beams ($n = -6, -5, \cdots, 8$). In the many-beam calculation, the value of V_1 was determined so that two main branches of the dispersion surfaces contributing to the second-order

Table 1. *Experimental and theoretical X-ray atomic scattering factors for the* 200 *reflexions of* Al, Ni *and* Cu *and the* 0002 *reflexion of* Ti

	Al	Ni	Cu	Ti
E_c	895 ± 15 kV	587 ± 20 kV	593 ± 20 kV	236 ± 10 kV
	(for 400)	(for 400)	(for 400)	(for 0004)
Lattice parameter (Å)	$a = 4·048$	$a = 3·524$	$a = 3·615$	$a = 2·950$
				$c = 4·683$
Θ_D (°K)	395	390	320	365
B (Å²) at 20°C	0·85	0·40	0·54	0·55
	(for 200)	(for 200)	(for 200)	(for 0002)
f_1^* (Present result)	8·36 ± 0·05	19·17 ± 0·17	20·40 ± 0·16	15·47 ± 0·12
f_1^* (Theory)				
Freeman & Watson (1961)*	8·51 ($3s^23p^1$)	19·28 ($3d^84s^2$)	20·76 ($3d^{10}4s^1$)	15·67 ($3d^24s^2$)
			20·54 ($3d^94s^2$)	
Doyle & Turner (1968)	8·50	19·24	20·71	15·64
Fukamachi (1971)*	8·51 ($3s^23p^1$)	19·24 ($3d^84s^2$)	20·71 ($3d^{10}4s^1$)	15·64 ($3d^24s^2$)
			20·49 ($3d^94s^2$)	
Wakoh & Yamashita (1971)		19·05	20·46	
f_1^* (X-ray experiment)				
Bensch, Witte & Wölfel (1955)	8·21			
Batterman, Chipman & DeMarco (1961)	8·25 ± 0·14		19·75 ± 0·34	
Inkinen & Suortti (1964)		19·31 ± 0·07		
Hosoya & Yamagishi (1966)			20·68 ± 0·18	
DeMarco (1967)	8·21 ± 0·07			
Diana, Mazzone & DeMarco (1969)		18·55 ± 0·16		
Hosoya & Fukamachi (1973)		19·29		

* The outer electron configurations corresponding to each calculated value are shown in parentheses.
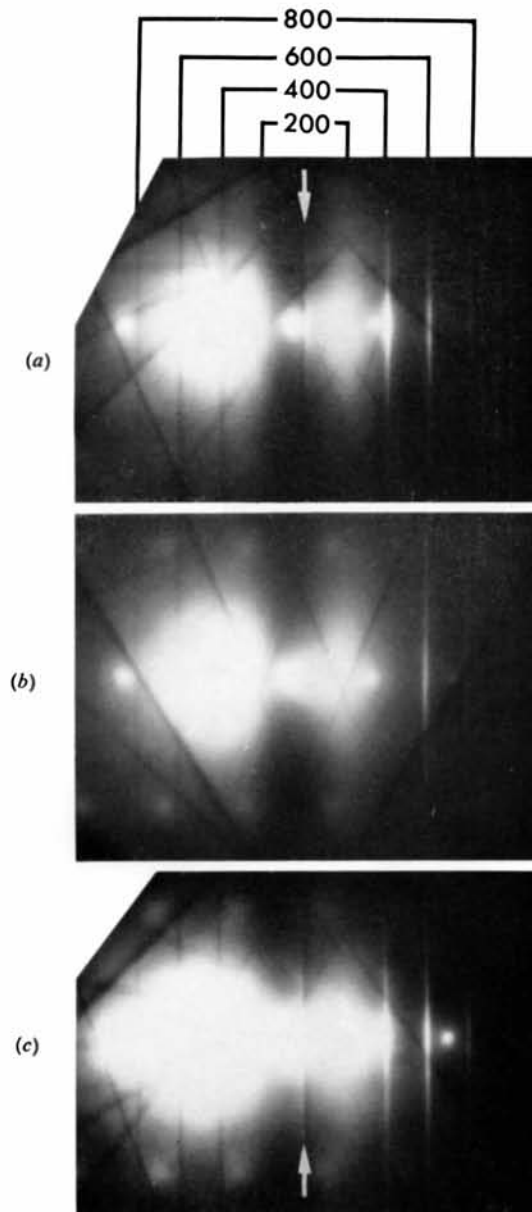
PLATE 23

Fig. 1. Electron diffraction patterns of nickel taken at (a) 430 kV, (b) 590 kV and (c) 730 kV. Arrows in (a) and (c) show the middle line of the Kikuchi band.

reflexion touch each other at the voltage E_c. The results of the two calculations agreed very well, the difference being less than 0·1 %, although the result given by the former method of calculation cannot be theoretically justified. Calculations covering 3 beams ($n=0$, +1, +2) to 15 beams were performed, and it was confirmed that a 7-beam calculation gives the results with sufficient accuracy for the present case. It should be noted that the above-mentioned theoretical scattering factors for the second and higher-order reflexions calculated using different wave functions give almost identical results for the V_1 values. Table 1 shows the f_1^x values without thermal-vibration effect converted from the V_1 values calculated with the use of theoretical V_2 etc., of Doyle & Turner (1968), together with other available data for comparison. The estimated errors in f_1^x are 0·6–0·9 % (Table 1), which include those arising from experimental errors in E_c and errors in the f_2^x and B values assumed in the calculation. The errors of f_2^x estimated from reliable theoretical and X-ray experimental data are 1·4 % for Ni, 1·3 % for Cu and less than 0·5 % for Al and Ti. The errors of assumed B factors are estimated to be 0·05 Å^2 for Al, Ni and Cu and 0·1 Å^2 for Ti. The range of the Θ_D value corresponding to these errors is 405–380 °K for Al, 415–365 °K for Ni, 335–305 °K for Cu and 405–335 °K for Ti, and the contribution to the error of f_1^x is estimated to be only 0·25 % for Al, Ni and Cu and 0·45 % for Ti. The present values of f_1^x are smaller than those for free atoms in the ground states by about 1·6 % for Al and Cu, 0·5 % for Ni, and 1·2 % for Ti. For each metal the rate of decrease is about the same as that obtained for the innermost reflexion (Watanabe et al., 1969).

Discussion

Many experimental determinations of atomic scattering factors have been made so far by absolute measurements of X-ray intensities diffracted from powder samples and single crystals, for the purpose of studying the discrepancy between the f^x values for atoms in solid state and those for free atoms. Theoretical calculations have shown that this discrepancy is very small for metals. That is, the former values are estimated to be smaller than the latter by the order of 1–2 % or less (Wakoh & Yamashita, 1971). This difference is called the reduction due to the solid-state effect. The X-ray experimental results obtained at different places are not consistent with each other, however, as seen in Table 1, and it is difficult to estimate quantitatively the order of magnitude of the reduction from the X-ray intensity measurements. The reproducibility of the data from the present method is fairly good, on the other hand, because of the essentially simple experimental procedure using a zero method. As a matter of fact, the values of E_c for the 220 reflexion of Fe, the 222 of Al and Cu and the 400 of Cu, which were measured by Lally, Humphreys, Metherell & Fisher (1972) independently, agree with those obtained by the pres-

ent authors (Watanabe et al., 1969) within experimental error.* The error in f_1^x values obtained by the present method is substantially small, as already discussed in a previous paper (Watanabe et al., 1969), and it is considered that the values of f_1^x given in Table 1 are fairly reliable experimental scattering factors and the deviations from those for free atoms are due to the intrinsic solid-state effect.

In the present analysis, only the systematic reflexions were taken into consideration and the effects of accidental reflexions and inelastic scattering of electrons were not considered. It has been shown by Fujimoto & Fukuhara (1973) that the effect of inelastic scattering on the value of E_c is very small, i.e. within the experimental error of E_c. The effect of simultaneous reflexions was avoided with great care in the present experiment. However, the effect of weak accidental interactions should be studied in more detail, in order to improve the accuracy of the results. Many-beam calculations including the effects of absorption and weak accidental interactions are in progress and the results will be published shortly.

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* It should be mentioned, however, that the scattering factor values for the 111 reflexion of Al and Cu derived by Lally et al. (1972) are different from those given by Watanabe et al. (1969). It seems that temperature corrections has not been properly made in the analysis of Lally et al.

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A Monte Carlo Method for Calculation of Transmission Factors

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An alternative approach to the calculation of transmission factors is given. Several variance-reducing techniques are discussed. A comparison with earlier attempts is made. Description of a program is given. Some results are listed. Typical computing time is 0·3 sec per reflexion (cpu) on an IBM 360/65.

Introduction

One of the major difficulties in the derivation of correct structure factors from observed intensity values for diffracted X-rays is the correction for absorption. The transmission factor A^{-1} (A being the absorption factor) is given by

$$A^{-1} = V^{-1} \int \exp\left[-(l_i + l_d)\mu\right] \mathrm{d}V, \qquad (1)$$

where V is the irradiated crystal volume, μ is the linear absorption coefficient and l_i and l_d are the path lengths of the incident and diffracted beam respectively.

The integral (1) can be evaluated in three ways:

(1) The numerical method called Gaussian quadrature (Busing & Levy, 1957);

(2) The analytical method (De Meulenaer & Tompa, 1965);

(3) The Monte Carlo method (Alberti & Gottardi, 1966).

An excellent review on the relative merits and demerits of methods (1) and (2) is given by Coppens (1970). Since these methods are rather expensive in terms of computer time, we decided to investigate the third alternative.

Principles of the Monte Carlo method

Assume that we want to integrate a function $F(x)$ of x within the interval $a \le x \le b$, and furthermore assume

that the integration cannot be executed by conventiona means. We denote the estimand θ

$$\theta = \int_b^a F(x)\mathrm{d}x . \qquad (2)$$

Now the expression

$$t = \frac{1}{N} \sum_{i=1}^{N} F(\xi_i) \qquad (3)$$

is an unbiased estimator of θ if, and only if, ξ_i are N independent random numbers distributed rectangularly between a and b. Its variance is given by

$$\mathrm{var}\,(t) = \frac{\sigma^2}{N} = \frac{1}{N} \int_a^b (F(x) - \theta)^2 \mathrm{d}x . \qquad (4)$$

Let the desired standard deviation of t have the value p, then the number of values $F(\xi_i)$ to be computed is

$$N = \sigma^2/p^2. \qquad (5)$$

In general integral (4) will not be known. An unbiased estimator of σ^2 is

$$s^2 = \frac{1}{k-1} \sum_{i=1}^{k} F[(\xi_i) - \bar{F}]^2, \qquad (6)$$

where $\bar{F}$ denotes the mean of k $F(\xi_i)$ values. Determine $N = s^2/p^2$ and compute, if necessary, $N - k$ additional values $F(\xi_i)$. Again evaluating (3) gives the desired result t.

This procedure is called 'Crude Monte Carlo' (hereafter CMC). A Fortran program for the calculation of