Absolute Measurement of the Atomic Scattering Factors of Aluminum on Powder in Transmission*

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Measurements have been made of the absolute x-ray scattering factors for the first three reflections—(111), (200), and (220)—in aluminum, in symmetrical transmission on a powder sample. Monochromatized Mo $K\alpha$ radiation was applied. The form factors obtained were significantly less than the theoretical Hartree-Fock free-atom values, and even lower than the values calculated for the ten neon-core electrons. These findings were in agreement with previous measurements on powders, and on an imperfect single crystal in transmission. Qualitatively, the x-ray diffraction data correspond to the results of Compton-scattering measurements, which suggest that the momentum density for the aluminum core is more extended in momentum space than that for the Hartree-Fock free-atom calculation.

I. INTRODUCTION

UNDER favorable conditions, absolute structure factors can be measured by x rays to an accuracy of about 1%. The achievement of such accuracy has been reported in the cases of Al, Cr, Cu, and Fe. Briefly, the results in respect of these metals which have similar features can be summarized as follows: Batterman *et al.*,[1] using powder samples, found the absolute form factors of Al, Cu, and Fe to be about 3–4% lower than the theoretical Hartree-Fock (HF) free-atom values. Cooper[2] reported a similar effect of about 5% with respect to Cr powder, and the results obtained by Bensch *et al.*,[3] with Al powder also indicated a lowering of about 1–4% in the structure factors of the first three reflections. The absolute measurements of Jennings *et al.*[4] made on nearly perfect single crystals of Cu, and those of DeMarco[5] with an imperfect single crystal of Al in transmission confirmed the powder results of Batterman *et al.* and Bensch *et al.* However, in studies of Fe powder carried out by Paakkari and Suortti,[6] and those of Cu powder by Hosoya and Yamagishi,[7] it was found that the discrepancies between experimental and theoretical form factors were within the range of experimental error. Furthermore, the scattering factors for the first reflection of Al and Fe determined by Watanabe *et al.*[8] by high-voltage electron diffraction are no more than 0.9% less than the HF values.

It can be hoped that the possibility of systematic deviations of the experimental form factors from HF values is understable on the basis of the scattering factors calculated for a metal atom in the solid by taking account of the band structure. Such calculations made by Wakoh and Yamashita[9] for Fe, and by Wakoh[10] for Cu, yielded form factors in conformity with the measurements of Paakkari and Suortti, and of Hosoya and Yamagishi, respectively. The calculations made by Arlinghaus[11] for Cu and Al gave scattering factors which are, as far as Cu is concerned, in accord with those measured by Batterman *et al.* in indicating that the valence-electron charge density is more widely spread in the solid than in the free atom. For Al, no improvement is gained over HF values by making a solid-state calculation.

The variant results mentioned above suggest a need of further experimental and theoretical studies. In particular, the case of Al is of considerable interest for the following reasons:

(i) In view of the present theoretical considerations, its x-ray results are unexpected in showing such an expansion of the core charge distribution of the Al atom in the solid, that the energy required to effect this is about nine times the cohesive energy.[12]

(ii) The close agreement between theory and experiment for the sequence of elements Ne ($Z=10$),[13] Mg ($Z=12$),[14] and Si ($Z=14$)[15] brings the disagreement in Al ($Z=13$) into sharp focus.

The present study was undertaken with a view to making an independent x-ray scattering-factor measurement with respect to Al. The work was done on a powder sample in transmission. This involved an experimental procedure differing from that for the symmetrical Bragg method applied in previous powder measurements.

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[1] B. W. Batterman, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **122**, 68 (1961).

[2] M. J. Cooper, Phil. Mag. **7**, 2059 (1962).

[3] H. Bensch, H. Witte, and E. Wölfel, Z. Phys. Chem. **4**, 65 (1955).

[4] L. D. Jennings, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **135**, A1612 (1964).

[5] J. J. DeMarco, Phil. Mag. **15**, 483 (1967).

[6] T. Paakkari and P. Suortti, Acta Cryst. **22**, 755 (1967); **A24**, 701 (1968).

[7] S. Hosoya and T. Yamagishi, J. Phys. Soc. Japan **21**, 2638 (1966).

[8] D. Watanabe, R. Uyeda, and A. Fukuhara, Acta Cryst. **A24**, 580 (1968).

[9] S. Wakoh and J. Yamashita, J. Phys. Soc. Japan **21**, 1712 (1966).

[10] See Ref. 7.

[11] F. J. Arlinghaus, Phys. Rev. **153**, 743 (1967).

[12] R. J. Weiss, *X-ray Determination of Electron Distributions* (North-Holland Publishing Co., Amsterdam, 1966).

[13] D. R. Chipman and L. D. Jennings, Phys. Rev. **132**, 728 (1963).

[14] R. J. Weiss, Phil. Mag. **16**, 147 (1967).

[15] J. J. DeMarco and R. J. Weiss, Phys. Rev. **137**, A1869 (1965).

II. SAMPLE

Atomized powder No. 140 from The Aluminum Company of America was selected from a variety of aluminum products. The purity of the powder was 99.5%, and the average particle diameter 4–6 μm. Several samples were prepared by the insertion of a suspension of aluminum powder and ether into a cylindrical sample holder, and compression between highly polished plates after the suspension had dried. The amount of powder was such that $\mu T \approx 1$ [see Eq. (1)], since variations in the thickness of the sample then introduce only second-order variations in the diffracted energy. The distribution of thickness over the surface of the sample was determined by a narrow pinhole beam of monochromatized Cu $K\alpha$ radiation. Samples could be prepared with smooth variation in the thickness of less than 0.5%.

On examination of the variation in integrated Bragg intensities of several reflections with moulding pressure, and by measuring the diffracted intensities as a function of the sample polar angle, no effects of preferred orientation were discernible when the pressure was less than 500 kg/cm^2. For the final measurements, a sample pressed with 300 kg/cm^2 was used; the density of the sample was about 0.6 relative to bulk density. No extinction effects were expected since the powder evidenced considerable line-broadening. Furthermore, the effect of porosity was found to be negligible in the present study.[12]

III. MEASUREMENTS

In the symmetrical Laue case, the integrated intensity of a reflection from an ideal powder sample is given by[12]

$$\frac{E\omega}{P_0} = \frac{r_e^2 \lambda^3 j l d F^2 T \exp(-\mu T/\cos\theta)(1+K\cos^2 2\theta)}{16\pi R^2 V^2 \sin 2\theta \sin\theta}, \quad (1)$$

where E is the total diffracted energy for a reflection, ω is the angular velocity of the detector, P_0 is the total power in the primary beam, $r_e^2 = e^2/mc^2$ is the classical electron radius, λ is the x-ray wavelength, R is the distance from the receiving slit of height l and breadth d to the sample of thickness T, j the multiplicity, μ the linear absorption coefficient, θ the Bragg angle, K the polarization ratio of the monochromator placed behind the receiving slit, and F the structure factor of a cell of volume V.

The total energy diffracted from the monochromator into the counter when driven with an angular velocity ω across the transmitted incident beam is given by

$$E_{\text{in}} = \frac{P_0 d e^{-\mu T}(1+K)}{2\omega R A}, \quad (2)$$

where A is the attenuation factor of the absorber used for reducing the intensity of incident x rays. Thus, for the absolute structure factor of a reflection hkl there is derived from Eqs. (1) and (2):

$$F(hkl) = \frac{4V}{r_e}\left[\frac{\pi R \sin^2\theta \cos\theta e^{-\mu T}(1+K)}{\lambda^3 j l (1+K\cos^2 2\theta) T e^{-\mu T/\cos\theta}} \frac{E(hkl)}{A E_{\text{in}}}\right]^{\frac{1}{2}}. \quad (3)$$

Initially, the integrated intensities were measured with reference to that of the 111 reflection, which was then measured on an absolute scale. The line focus of a molybdenum anode tube served as the x-ray source. The x-ray generator was operated at 30 kV and 20 mA, which did not excite the half-wavelength harmonic. The recording apparatus comprised a NaI(Tl) scintillation counter, followed by a pulse-height analyzer and a digital printout. The dead time of the detector and associated electronics was found to be 2.5 μs. The dynamic component of the bent ground quartz crystal which served as the monochromator has been proved negligible.[16] Thus, $K = \cos^2 2\theta_m$, where θ_m is the Bragg angle of the monochromator. The wavelength distribution in the monochromatized beam was determined with a single crystal reflection; the relative fractions of the $K\alpha_1$ and $K\alpha_2$ wavelengths were 0.67 and 0.33, respectively ($\lambda = 0.71069$ Å).

As the transmission method is not a focusing one, the horizontal divergence of the incident beam was adjusted to $\frac{1}{8}°$, to achieve optimum conditions for the resolution and the integrated intensities of the neighboring reflections 111 and 200. The vertical divergence was small, the height of the incident beam being only 2 mm at the sample site. Both the horizontal and vertical divergences were symmetrical. The accuracy of the zero alignment for the x-ray focus, the goniometer axis, the normal of the sample surface, and the receiving slit was better than 0.05° in 2θ. The center of the sample was placed on the goniometer axis, applying the 180° rotation-shift method.[17] The sample-displacement error was less than 0.05 mm. Corrections of the integrated intensities due to measuring geometry and diffractometer alignment were thus negligible. The receiving slit of length 4 mm and breadth 0.1 or 0.2 mm was scanned with an angular velocity of $\frac{1}{8}°$ per minute through the reflections and the primary beam. The true background was established by making a separate study outside the angular range of integration. The scans were repeated, so that statistically an accuracy of better than 1% was attained for the integrated intensities. The sample was rotated in its own plane at 30 rpm, to suppress statistical fluctuations in particle sampling.

The intensity of the transmitted beam was reduced to a measurable rate by the use of two zirconium absorbers, of which the combined attenuation factor was found to be $A = 67.19 \pm 0.30$. A small correction of 0.1%, due to the difference in absorption for the $K\alpha_1$ and $K\alpha_2$ wavelengths, was taken into account. The

[16] P. Suortti and T. Paakkari, J. Appl. Cryst. 1, 121 (1968).
[17] P. M. de Wolff, Acta Cryst. 13, 835 (1960).

TABLE I. Absolute atomic scattering factors of aluminum measured in the present work, f_{pres}, theoretical Hartree-Fock free-atom values f_{HF},[a] neon core values f_{core},[b] and form factors measured by Batterman *et al.*,[c] by Bensch *et al.*,[d] by DeMarco,[e] and by Watanabe *et al.*,[f] f_{BCD}, f_{BWW}, f_D, and f_{WUF}, respectively.

hkl	f_{pres}	f_{HF}	f_{core}	f_{BCD}	f_{BWW}	f_D	f_{WUF}
111	8.74±0.06	8.95	8.88	8.70±0.14	8.63±0.13	8.69±0.04	8.88±0.08
200	8.24±0.10	8.51	8.55	8.33±0.14	8.32±0.08	8.21±0.07	
220	7.17±0.09	7.32	7.39	7.18±0.13	7.25±0.07	7.25±0.06	

[a] Reference 19.
[b] Reference 20.
[c] Reference 1.
[d] Reference 3.
[e] Reference 5.
[f] Reference 8.

attenuation of the incident beam in the sample, $e^{-\mu T}$, was 0.407±0.002. The average thickness of the sample was determined by measurement of the mass, and the diameter of the sample. With the measured distribution of thickness taken into consideration, $T=0.0670 \pm 0.0004$ cm was obtained for the irradiated middle part of the sample. For the ratio R/l, the value proved to be 45.08±0.25. On insertion into Eq. (3) of the above values, the experimental result $(4.96\pm0.04)\times10^{-3}$ for the ratio $E(111)/E_{in}$, and other parameters, $F(111)=34.10$ is obtained.

By application of the formula derived by Chipman and Paskin,[18] the contributions of thermal diffuse scattering (TDS) to the total measured integrated intensities were found to be 2.3% (111), 3.8%(200), and 4.2% (220). On subtraction of the correction for TDS, $F(111)=33.71\pm0.24$ is obtained for the absolute structure factor $F(111)$ of aluminum for Mo $K\alpha$ radiation.

The error given in $F(111)$ includes the uncertainties attributable to the following factors: statistical accuracy (0.3%), background subtraction (0.3%), sample thickness (0.3%), attenuation factor of the absorbers (0.2%), ratio R/l (0.3%), and TDS correction (0.2%). (The error in $e^{-\mu T}$ exercises a negligible influence on the structure factor.) Thus, the total error (square root of sum of squares) is about 0.7%.

IV. DISCUSSION OF RESULTS

To compare the present results with other works, the values of $F(hkl)$ have been converted to the atomic scattering factors $f(hkl)$ which correspond to the atom at rest, and are independent of the x-ray wavelength. The values $B=0.8822$ Å^2 (Ref. 5) and $\Delta f'=0.04$ (Ref. 12) were adopted for the temperature parameter and for the real part of the dispersion correction, respectively. The resulting scattering factors f_{pres} are indicated in Table I, together with the HF free-atom values f_{HF},[19] and the neon core values f_{core}.[20] The form factors measured by Batterman *et al.* and by Bensch *et al.* on powders, f_{BCD} and f_{BWW}, respectively, by DeMarco on a single crystal in transmission, f_D, and by Watanabe *et al.* with the Kikuchi-line method, f_{WUF}, are also listed, after adjustment for the values of B and $\Delta f'$ mentioned above.

Comparison of the experimental form factors in Table I shows that they are in satisfactory mutual agreement. The largest variation appears in $f(111)$, the difference between the extreme values f_{WUF} and f_{BWW} being about 3%. It is to be noted that the values f_{BWW} do not include the correction for TDS. The present results agree, within the range of their experimental error, with the values f_{BCD} and f_D.

Table I indicates that the results of different measurements have a common attribute, that the experimental scattering factors are less than the values f_{HF}. The x-ray results are even lower than the values calculated for the ten neon core electrons, whereas, the electron-diffraction result coincides with f_{core}. Consequently, a real discrepancy exists between the experimental scattering factors in aluminum and the HF free-atom calculation. Qualitatively, an expansion of the core-charge distribution of the aluminum atom in the solid indicated by the x-ray data corresponds to results of Compton-scattering measurements of Phillips and Weiss,[21] which suggest that the measured momentum density for the aluminum core is more extended in momentum space than that for the HF free-atom calculation.

Absolute measurements of the atomic scattering factors of aluminum on powder samples in symmetrical reflection are in progress in this laboratory. The results of this study will be reported in the near future.

[18] D. R. Chipman and A. J. Paskin, J. Appl. Phys. **30**, 1998 (1959).

[19] *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, 1962), Vol. III.

[20] See Ref. 5.

[21] W. C. Phillips and R. J. Weiss, Phys. Rev. **171**, 790 (1968).