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Independent measurement of the atomic scattering factor and the Debye factor.*

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The usual method for measuring either the atomic scattering factor of an element, f, or its Debye factor, e^{-2M}, is to determine one of them from a set of integrated intensity measurements, assuming the other to be known from theoretical considerations, or to make a set of measurements at more than one temperature. Described here is a method which allows the determination of both of these quantities independently of a knowledge of the other from measurements made at one temperature. The method is illustrated by applying it to copper.

The data required are measurements from a powder sample of the integrated intensities of the Bragg maxima, and of the temperature diffuse scattering, both in absolute units. A Geiger-counter diffractometer was used to obtain these, and molybdenum radiation was employed to extend the $\sin\theta/\lambda$ range. It was found that sufficiently monochromatic radiation may be obtained by the use of a pair of balanced Zr–Sr filters. In such a case, the primary beam intensity as a function of wavelength is the sharp $K\alpha$ doublet superimposed on a short section of continuous radiation bounded on the short wavelength side by the Zr absorption edge and on the long wavelength side by the Sr edge. Under all the strong diffraction maxima the section is clearly visible in the balanced filter difference, superimposed on the diffuse scattering. The shape of the section relative to the primary beam power concentrated in the $K\alpha$ doublet was measured with a rocksalt single crystal, and all measurements of crystalline peaks and diffuse intensities were corrected for this effect.

The diffuse scattering measurements were corrected for air scattering and then converted to absolute units—electron units per atom—by comparing them to the counting rate observed from a wafer of polystyrene (C_8H_8) at a scattering angle sufficiently large that polystyrene may be assumed to be structureless. Values of f^2e^{-2M} in absolute units were obtained from the Bragg reflections also by comparison with the scattering from polystyrene, by a method developed by Warren (1955).

It was assumed that the temperature diffuse scattering for a face-centered cubic element of lattice constant a, in electron units per atom, can be approximated by the relation given by Warren (1953):

$$I = f^2(1-e^{-2M})\left[\frac{(3/\pi)^{\frac{2}{3}}}{6x}\sum_{hkl}\frac{j_{hkl}}{x_{hkl}}\ln\left\{\frac{(3/\pi)^{\frac{1}{3}}}{|x_{hkl}-x|}\right\}\right],$$

where j_{hkl} is the multiplicity for hkl reflections, $x = 2a\sin\theta/\lambda$, and x_{hkl} is the value of x at the reflection hkl. The value of the function in brackets was computed for each diffuse scattering measurement, and after subtracting the Compton modified scattering it was divided out, reducing each measurement to a value of $f^2(1-e^{-2M})$. Shown in Fig. 1(*a*) is a curve of f^2e^{-2M} obtained from the diffraction maxima, and a curve of $f^2(1-e^{-2M})$ from the diffuse scattering, plotted against the scattering angle. The sum of these two curves, then, is f^2, and their ratio is $e^{2M}-1$.

Fig. 1(*b*) compares the resultant f curve for copper obtained from these data, after correction for K electron dispersion by means of Hönl's formula (1933), with f computed by the Hartree–Fock method (Berghuis *et al.*, 1955).

Fig. 1(*c*) shows a plot of the experimentally determined $2M$ values as a function of $\sin^2\theta/\lambda^2$. From the slope of

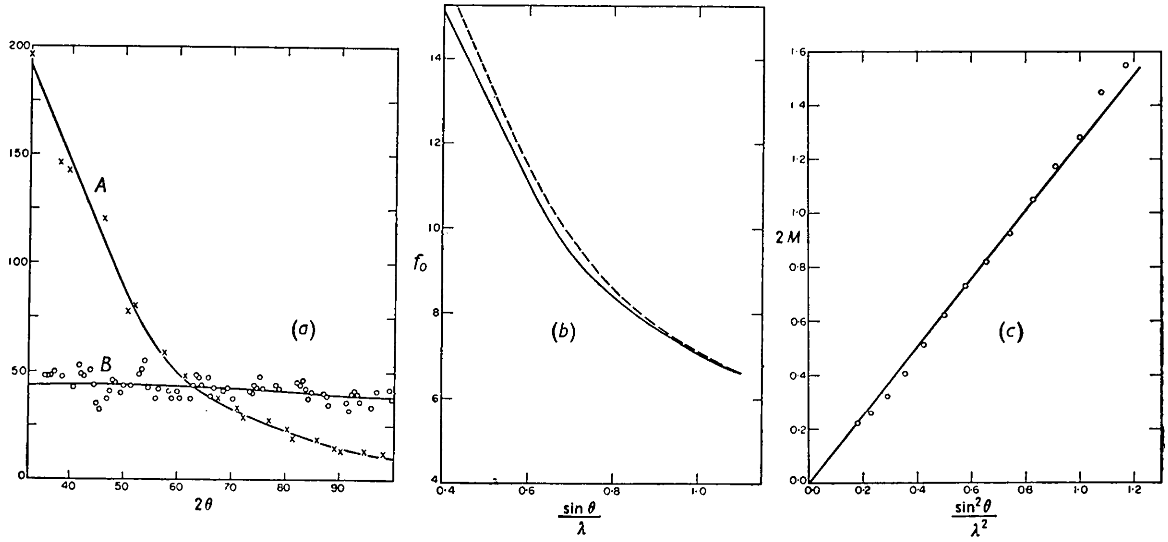

Fig. 1. (*a*) Curve *A*: values of f^2e^{-2M} for copper, $T = 298°$ K.; curve *B*: values of $f^2(1-e^{-2M})$ for copper, $T = 298°$ K. (*b*) Comparison of f values for copper. Full line: experimentally determined; broken line: computed by the Hartree–Fock method. (*c*) Values of $2M$ for copper, $T = 298°$ K., determined from the data of Fig. 1(*a*).

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this line the effective Debye temperature of copper is computed to be 299° K. This may be compared with the value 313° K. computed from the vibrational frequency spectrum of copper as measured by Jacobsen (1955).

The advantage of this method is that f^2 and e^{-2M} are obtained from measurements made at only one temperature. The disadvantage is that it involves the diffuse scattering and hence a correction for Compton modified scattering which must be taken from tables computed from a theoretically determined radial distribution of electrons. However, since the Compton scattering is a small fraction of the total diffuse scattering for most measurements, the method should be fairly insensitive to errors introduced from this source.

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Guanidinium aluminum sulfate hexahydrate: crystallographic data.

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The discovery of ferroelectricity in guanidinium aluminum sulfate hexahydrate, $C(NH_2)_3Al(SO_4)_26H_2O$, was reported by Holden, Matthias, Merz & Remeika (1955) and some of the properties of this crystal have been discussed in a later paper (Holden, Merz, Remeika & Matthias, 1956).

Morphology and cleavage

The colorless, transparent crystals grow from aqueous solutions as hexagonal prisms terminated by basal planes. There is perfect cleavage parallel to $\{0001\}$ and much less perfect cleavage parallel to $\{11\bar{2}0\}$.

Although most crystals show only the prisms, $\{11\bar{2}0\}$ and $\{2\bar{1}\bar{1}0\}$, and the base $\{0001\}$, some crystals also show the pyramid faces $\{11\bar{2}1\}$, $\{2\bar{1}\bar{1}\bar{1}\}$, $\{11\bar{2}\bar{1}\}$ and $\{2\bar{1}\bar{1}1\}$. Of these, the first two are commonly well developed compared to the second two. The well developed faces are those related by a center of symmetry and the outward form of these crystals thus shows the symmetry D_{3d}–$\bar{3}m$.

Optical properties

The crystals are uniaxial, negative. The indices of refraction for sodium light have been given by Ferraboschi (1908) from measurements made by the minimum-deviation method, using two natural prism faces, with the following results: $n_o = 1{\cdot}5423$, $n_e = 1{\cdot}4540$.

Etch pits

Etch pits produced with water on the $\{0001\}$ faces of these crystals are triangular with edges parallel to three edges of the (0001) face, normal to the a axes of the crystal. The orientation of the triangular etch pits and secondary cleavage relative to the crystallographic axes was established by taking a Buerger precession photograph of an etched crystal. Etch pits on $(000\bar{1})$ are related to those on (0001) by twofold axes normal to the a axes, thus again exhibiting symmetry D_{3d}–$\bar{3}m$, higher symmetry than that of the crystal which cannot have a twofold axis normal to c since the c axis is electrically polar. Thus the point group indicated is C_{3v}–$3m$.

A description of etch pits differently 'cocked' in different parts of these crystals has been given by Holden *et al.* (1956). Examination of the optic figure and X-ray precession photographs shows no deviation from parallelism of the crystal structure in these different parts. No difference of any sort has as yet been detected among them by X-ray diffraction or optical methods. The apparent 'cocking' of these etch pits results from the translation of the stepped walls in the deeper parts of the pit, relative to those of the shallower parts, in a direction parallel to the (0001) face and apparently parallel to the a axes.

Unit cell and space group

The diffraction symmetry is D_{3d}–$\bar{3}m$ with no systematic absences. The lattice constants are:

$$a_0 = 11{\cdot}77 \pm 0{\cdot}04,\ c_0 = 8{\cdot}98 \pm 0{\cdot}03\ \text{Å}\,.$$

Both from the precession photographs and from the etch pits we see that the symmetry planes are parallel to the crystallographic axes. Therefore the probable space groups are as follows: D_{3d}^1–$P\bar{3}1m$; C_{3v}^2–$P31m$; D_3^1–$P312$; D_3^2–$P321$. On the basis of our knowledge that the crystal is ferroelectric, we can eliminate space group D_{3d}^1–$P31m$, which requires a center of symmetry, and also D_3^1–$P312$ and D_3^2–$P321$, which require twofold axes normal to c. This leaves C_{3v}^2–$P31m$ uniquely determined as the space