

The Experimental Value of $f(220)$ for Copper

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Abstract

The value of the atomic form factor, $f(220)$, for copper has been determined in recent years by a variety of methods. All the dynamical methods agree on a value in the region of 16.70–16.75. These methods include two X-ray methods, one involving measurement of intensity profiles and the other of Pendellösung beats, and also an electron diffraction measurement using a critical voltage procedure. By contrast, two recent kinematical measurements using γ rays both report a distinctly different value of about 16.45. One of these determinations has already been re-examined by the present authors and the discrepancy removed by an appropriate extrapolation to zero extinction. The present paper shows that the published experimental data for the other γ -ray determination should lead to a value of about 16.69. This value confirms the linearity of our extrapolation and the importance of this extrapolation in deriving experimentally based extinction-free values of structure factors.

1. Introduction

For copper, selected structure factor values, corrected to 0 K, have been determined recently by several groups using different experimental diffraction procedures. In particular, the 220 reflection has been subjected to examination in many cases and we shall focus on this reflection as representative of the results from the various methods and of their mutual consistency. While many values for $f(220)$ have been recorded in the literature from earlier X-ray intensity measurements, we shall concentrate on the more recent results.

Two groups have used X-ray methods. Thus, Nittano *et al.* (1979) have derived a value of 16.75 ± 0.08 for $f(220)$ from fitting the intensity profile of a perfect copper crystal using a triple-axis X-ray diffraction method, while Takamo and Sato (1982) arrived at a value of 16.75 ± 0.08 from Pendellösung intensity beat measurements using white radiation. Using electron diffraction with the critical voltage procedure, C. J. Humphreys (personal communication 1980; see also Smart and Humphreys 1980) has obtained the value 16.696. So, in respect of various dynamical procedures, using either X-ray or electron diffraction, there is close accord with a value for $f(220)$ in the region of 16.70–16.75.

Mackenzie and Mathieson (1979) used the reflectivity curves, obtained by Schneider (1976, 1977) for the essentially kinematic reflection of γ rays, to illustrate the importance of extrapolation to zero interaction (Mathieson 1979) in establishing extinction-free estimates of structure factors. Using the data for all 11 of Schneider's volume

samples, they deduced a value for $f(220)$ of 16.76 by extrapolation of plots of estimated f values against experimental estimates of secondary extinction p_1 to zero extinction. This value is compatible with that derived from the other (dynamical) diffraction procedures. It contrasted, however, with the value 16.46 ± 0.07 derived by Schneider.

Subsequently a second γ -ray study was carried out by Schneider, Hansen and Kretschmer (1981) (SHK), who have reported a value of 16.45 ± 0.05 . There remains therefore an unresolved discrepancy between this latest γ -ray value and the consensus range of values previously derived.

We have used the only published set of data referring to $f(220)$ from SHK, who stated that it is typical. We have arrived at a value of 16.69: a value which supplies a third point on our original line of extrapolation and thereby confirms the validity of this extrapolation for obtaining experimentally based extinction-free values of structure factors.

Table 1. Values of various quantities at 50 K

Constant	Value	Constant	Value
B	0.167 \AA^2	a	3.6035 \AA
$\sin \theta/\lambda$	0.39246 \AA^{-1}	t	0.1839 cm
λ	0.030105 \AA	C	$0.23885 \times 10^8 \text{ cm}$

2. Theoretical Relations

The experimental data presented give r_m , the reflectivity per unit angle corrected for linear absorption at a series of angular positions ω of the crystal. These measurements are values corrupted by convolution with the apparatus ‘window’ function, and so the first step in reducing the experimental data is to obtain the deconvoluted (but extinguished) values r_e . Then, assuming the validity of the Darwin transfer equations, the total integrated reflecting power is given, for the symmetric Laue case, by

$$R = - \int \frac{1}{2} \log \{1 - 2r_e(\omega)\} d\omega. \tag{1}$$

Now the relation of this extinction-free value of R to the structure factor $f(200)$ is given by

$$\{4 f(220) \exp(-M)\}^2 = CR/t = |F|^2,$$

where

$$M = B(\sin \theta/\lambda)^2, \quad C = (V^2/r_0^2 \lambda^3)2 \sin 2\theta \cos \theta/(1 + \cos^2 2\theta),$$

and t is the sample thickness. Thus, using the values of the various constants in Table 1, we have $f(220) = 2923R^{\frac{1}{2}}$ when ω is measured in radians or, more usefully for the present paper,

$$f(220) = 43.18R^{\frac{1}{2}}, \tag{2}$$

when ω is measured in steps of $1/80^\circ$.

In the practical implementation of this procedure, the reflectivity data r_m are first fitted to the sum of one or more gaussians for which the deconvoluted version

is easily written down when the apparatus ‘window’ function is also gaussian. Finally, using these analytic expressions, a numerical integration gives R and hence $f(220)$. For the case discussed below this results in a value of $f(220)$ greater by 0.09 than that calculated from the raw integral of r_m .

3. Examination of SHK Data

Simple scaling of the gaussian curve in Fig. 1 of SHK gives a peak value of $r_m(\omega)$ equal to 0.01383. SHK nominated the full-width-at-half-height (FWHH) of this curve to be 7.5' and that of the (gaussian) apparatus ‘window’ to be 2.8'. Our deconvolution, and correction of this curve according to equation (1), gives a value of $f(220) = 16.66$. This value is significantly higher than 16.45 quoted by SHK, even when the nominated standard deviation of 0.05 is taken into account. Accordingly, it was decided to carry out a closer examination of the available evidence presented by SHK.

Since we do not have available the full record of the experimental results, we cannot offer from this examination a definitive estimate of $f(220)$. We can only show that the published data lead to a much higher value than that nominated by SHK, lying far beyond any value suggested by their standard deviation.

The data which we have examined constitute Fig. 1 of SHK (and also Fig. 5 in preprint material sent to us in 1980). They relate to crystal C which, according to SHK, was the only specimen used to derive 220 data. These two diagrams were carefully measured to an accuracy of about 0.1% (one by J.K.M. and the other by A.McL.M.). These measurements agreed to within about 0.3% which corresponds to a variation in the estimated f values of less than 0.03: an agreement sufficient to encourage further detailed exploration.

Table 2. Reflectivity at 50 K for step number N

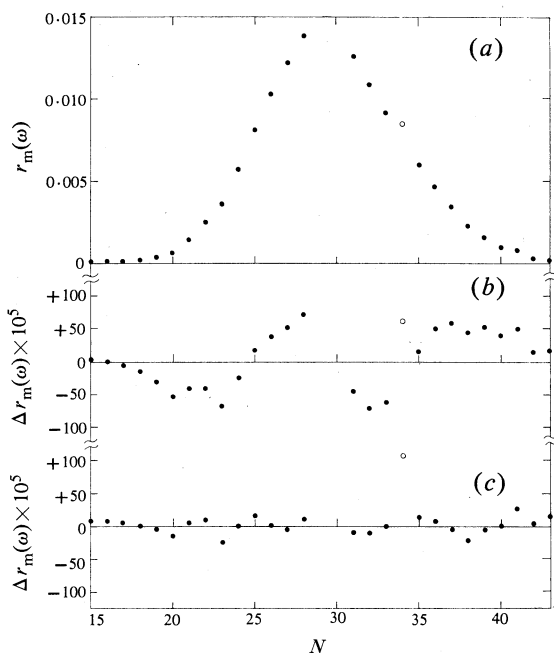
N	Reflectivity	N	Reflectivity	N	Reflectivity	N	Reflectivity
14	0.00006	22	0.00249	30	—	38	0.00225
15	0.00008	23	0.00362	31	0.01259	39	0.00159
16	0.00010	24	0.00575	32	0.01091	40	0.00100
17	0.00012	25	0.00812	33	0.00917	41	0.00082
18	0.00019	26	0.01030	34	0.00848	42	0.00033
19	0.00033	27	0.01226	35	0.00602	43	0.00026
20	0.00059	28	0.01383	36	0.00469	44	0.00017
21	0.00144	29	—	37	0.00342	45	0.00011

By carefully inspecting the angular positions of the data points and taking account of the fact that the ω circle is moved by a stepping motor, it was deduced that 80 equal angular steps correspond to 1° in ω , and that there is usually a reflectivity measurement at each angular step. Thus, the results listed in Table 2 are numbered sequentially by their angular step number N .

When one plots the data in Table 2, as in Fig. 1a, certain features attract attention. Firstly, on the basis of regular reflectivity readings at each unit angular step, two data readings are missing at the data points numbered 29 and 30. Secondly, data point 34 (open circle) appears anomalous and, thirdly, the overall curve is asymmetric.

That the asymmetry of the curve is associated with the crystal substructure and not with the source distribution is evident from comparison of Fig. 3 of SHK with Fig. 19 of Schneider *et al.* (1979). Their Fig. 3 also refers to crystal C and reveals a similar asymmetry, while Fig. 19 deals with the same experimental set-up but refers to a perfect Si crystal and shows the expected symmetrical curve.

Fig. 1. Plots of (a) experimental data recorded in Table 2; (b) differences between the experimental and calculated values for a single gaussian fit given by equation (3); (c) the same differences for the double gaussian fit given by equation (4).



Our first step was to examine how adequately the experimental data are matched by different possible fitted curves. In each case, the curve was fitted by a least-squares procedure to the data points, except for $N = 29, 30, 34$, which were given zero weight. The equation of the fitted single gaussian approximation is

$$r_m(\omega) = 0.01392 \exp[-\{(N - 29.464)/5.958\}^2]. \quad (3)$$

The FWHH of this gaussian is $1.249 \times 5.958 = 7.44'$ which deconvolutes to a width of $6.89'$; the corresponding values quoted by SHK are $7.5'$ and $6.8'$ respectively. The root-mean-square (r.m.s.) error of this fit is 0.00041 and the differences between the experimental and calculated values $\Delta r_m(\omega)$ are plotted in Fig. 1b. It is evident that a single gaussian curve does not constitute a particularly good fit to the experimental data. This approximation leads to a final (extinction corrected) value of $f(220) = 16.65$.

Guided by the form of asymmetry of the profile curve, we examined the possibility that crystal C consists of more than one component distribution. Provisionally, as the next simplest possibility, we took a major and a minor distribution and fitted two gaussians. The resulting approximation is

$$r_m(\omega) = 0.01418 \exp[-\{(N - 28.973)/5.237\}^2] + 0.00224 \exp[-\{(N - 35.981)/4.050\}^2]. \quad (4)$$

The r.m.s. error of this fit is 0.00011 and the differences $\Delta r_m(\omega)$, which are plotted in Fig. 1c, show a considerable improvement over those for the single gaussian curve. This approximation leads to a final value of $f(220) = 16.69$.

It is very clear from the overall close fit that the recorded reading at data point 34, namely 0.00848, is anomalous and must be regarded as dubious. If this reading had occurred due to the presence of a *third* and very peaked component [as occurs for sample 5 in Schneider (1976, 1977)], there should be evidence of the wings of this third peak in the adjacent data points 33 and 35, since the step resolution is 0.75' while the instrument resolution is 2.8'. Fig. 1c shows no evidence of such wings.

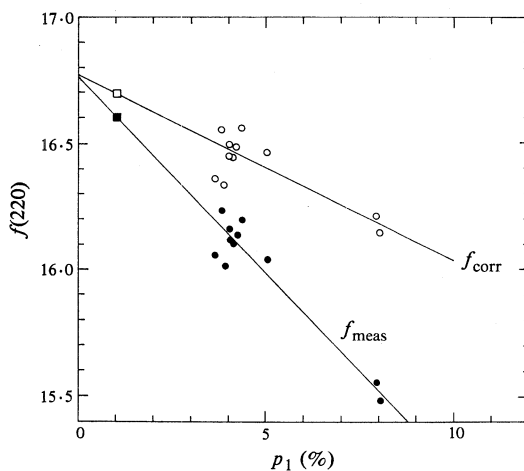


Fig. 2. Plots of the atomic scattering factor $f(220)$ for Cu against an experimental estimate of the effect of secondary extinction p_1 . The solid symbols are for the raw measured values and the open symbols are for those corrected for secondary extinction according to equation (1). The circles and the lines are from Mackenzie and Mathieson (1979); the squares refer to the results of the present paper.

4. Importance of Extrapolation

Our earlier paper (Mackenzie and Mathieson 1979) used the published curves of Schneider (1976, 1977) and, by applying the same data-handling treatment as that of Schneider, arrived at essentially the same numerical results [compare Table 2 of Mackenzie and Mathieson with Fig. 5 of Schneider (1977)]. Whereas Schneider arrived at his nominated value of 16.46 by rejecting two of his eleven sets of measurements on essentially subjective grounds, we accepted the validity of *all* his measurements and demonstrated that, with estimates of secondary extinction p_1 (see Table 2 of Mackenzie and Mathieson) derived from his measured curves, extrapolation to zero extinction indicated that $f(220)$ was in the region of 16.76: the same value was obtained by extrapolation of either the data nominally corrected for extinction or the uncorrected data. This result was obtained before the values reported in Section 1 were available from dynamical techniques, all of which fall in the range 16.70–16.75.

In the case of SHK, accepting that the available published experimental data are as typical as they are stated to be, we have applied the treatment for deconvolution

and correction for secondary extinction which is specified in SHK. Depending on whether a single or double gaussian distribution is fitted to the data, we derive a value of either 16.65 or 16.69 for $f(220)$. The higher value, which is derived from the closer fit to the experimental data, lies well outside the range permitted by the SHK value (16.45) with a standard deviation of 0.05.

The estimate of p_1 is 1.1% and, when we place the extinction-corrected value 16.69, and the corresponding extinguished value 16.60, on the graph from our earlier paper [see Fig. 2 both here and in Mackenzie and Mathieson (1979)], we find that the two points are perfectly consistent with the earlier ones. This confirms the linearity of the extrapolations and strengthens our earlier conclusions (a) that the value of $f(220)$ for Cu lies in the region of 16.76 rather than 16.45 and (b) that the correction for secondary extinction made according to Darwin's transfer equations appears not to constitute complete correction. It is indeed evident that, whether uncorrected values or partially corrected values are used, extrapolation is a necessary operation to ensure an 'absolute' structure factor value.

The procedure used by SHK to correct for secondary extinction is based on the original simple form of Darwin's transfer equations. However, recent work by Wilkins (1981) and by Suortti (1982) has pointed to inadequacies in this model arising from the omission of the effect of beam spread after the first (and subsequent) diffraction process has occurred. Failure to take account of this effect could lead to substantial underestimation of the nominally corrected value of the structure factor. Again, in his original paper, Darwin (1922) discussed whether an imperfect crystal should best be modelled as warped or cracked. Although he leaned towards the former model as probably the more realistic, he adopted the latter as being the more tractable mathematically. Thus, he recognized the limitations of the simple set of transfer equations. In the absence of an appropriate theory, our extrapolation procedure remains the only practicable alternative for reduction of the experimental data.

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