atmospheric pressure and 450°K at 150 kbar (estimated from Lindemann or Grüneisen relations) the recoilless fraction increases from 0.77 to 0.81 over this pressure range.[16] Under the experimental conditions of high background and uncertain self-absorption in the source it is difficult to determine f precisely enough to measure a change of this size.

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Measurement of the Scattering Factor of Copper in a Perfect Crystal

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Several studies of the scattering factors of metal powders have shown that the charge distribution is more spread out than that calculated by the Hartree-Fock (HF) method for free atoms. On the other hand, measurements on gases have yielded agreement with the HF calculations. In order to distinguish whether the disagreement in the case of the metals arises from the powder measurement technique or from solid-state effects, we have measured the scattering factor of copper in a nearly perfect crystal and compared the result with that obtained previously on copper powder; we find agreement within experimental error. The inference from this result is that the previous powder measurements on aluminum, which yielded a scattering factor even lower than that calculated for the core electrons by the HF method, are also reliable.

INTRODUCTION

ONE of the most direct ways of studying the accuracy of approximate wave functions in solids or atoms is to determine the electron density through a study of the x-ray scattering. Several considerations have, however, limited the extensive use of the x-ray technique. For example, it is not at present possible to obtain the higher order Fourier components of the charge density, given through the scattering factor, because of wavelength limitations and increasingly serious uncertainties in the Debye-Waller factor. As a result, it is not possible to completely synthesize the charge distribution from the experimental results. Instead, one may compare the observed values for the low-order components with those given on the basis of various theories. Unfortunately, many recent theoretical discussions[1] do not include values for the scattering factor, or even for the charge density, although such information is available within the framework of the theory. Furthermore, because of difficulties in technique and in interpretation, it is not always clear that the scattering factor may be derived from the measured results to the accuracies which at first sight seem possible.

To elucidate this latter point, there have recently been a number of projects whose purpose has been not only to investigate the electron distribution in solids, but also to examine the applicability of the experimental method.[2] Some of the first such experiments made use of imperfect single crystals for which it was necessary, however, to make corrections for extinction.[3] Since such corrections are most in doubt for the lowest reflections, which are the very ones which most distinguish the solid from the free atom, much recent work has been done on powders.[4–9] In this case, it is easier to prepare an extinction free sample, but one must avoid porosity and preferred orientation effects. Nevertheless, a number of experiments on powders have given scattering factors within an accuracy of the order of 1%. Since some of these results, notably those for Al,[4,5] were somewhat surprising, it has seemed desirable to us to check these results with a different experimental technique. Such a check has recently been made possible by the production of nearly-perfect copper cyrstals.[10] We have measured the scattering factor of the (111), (222), and (333) reflections from nearly perfect copper single crystals kindly supplied to us by Dr. F. W. Young, and

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[1] G. A. Burdick, Phys. Rev. **129**, 138 (1963); and B. Segall, Phys. Rev. **125**, 109 (1962) are representative of recent work on copper.

[2] As an example of the extensive considerations which are required for such a simple case as LiH, see R. S. Calder, W. Cochran, D. Griffiths, and R. D. Lowde, Phys. Chem. Solids **23**, 621 (1962).

[3] R. J. Weiss and J. J. DeMarco, Rev. Mod. Phys. **30**, 59 (1958).

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

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

[6] S. Gottlicher, R. Kuphal, G. Nagorsen, and E. Wölfel, Z. Physik. Chem. **21**, 133 (1959).

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

[8] M. J. Cooper, Phil. Mag. **8**, 811 (1963).

[9] S. Hosoya, J. Phys. Soc. Japan **19**, 235 (1964).

[10] F. W. Young, Jr., Bull. Am. Phys. Soc. **7**, 215 (1962); M. C. Wittels, F. A. Sherrill, and F. W. Young, Jr., Appl. Phys. Letters **1**, 22 (1962); and **2**, 127 (1963); and Phys. Letters **5**, 183 (1963).

find agreement, within experimental error, with the previous results on copper powders.[4] The supposition is then that the former results on Al[4,5] are also valid.

EXPERIMENTAL

Technique

We had at our disposal three copper single crystals, each about 1 in. in diameter and $\frac{1}{4}$ in. thick. The faces were approximately parallel to a (111) plane. These faces had been acid-sawed, acid-polished, electropolished, and etched, according to procedures described by Young,[11] before we received them. The three crystals had been chosen to display varying degrees of perfection. Microscopic examination revealed that the most imperfect crystal, designated C, had about 3×10^4 etch pits per cm^2 in most areas, but displayed, in addition, lines of great density of pits. The intermediate crystal B had about 2×10^4 pits per cm^2 and the best crystal A about 1.5×10^3 pits per cm^2. Inasmuch as the copper contained less than 10 ppm total impurity,[11] it is clear that, to our experimental accuracy, any deviations from ideal perfect-crystal scattering arose from imperfections, rather than from impurities *per se.* To prepare the crystals for use, we merely washed them in dilute HCl to remove the oxide film, and rinsed with water.

The obvious method for measuring the integrated intensity in absolute units from a perfect crystal is to use a two-crystal spectrometer, for then the diffracted beam power is comparable to the incident power for the second crystal. However, the range of reflection encompasses a very small angle and a very fine instrument is required to produce the necessary constant, known angular velocity. Instead, we mounted the sample on a Norelco goniometer which had been modified to accept a bent LiF monochromator. Mo $K\alpha$ radiation was used because the Hönl correction is more exactly calculable in this case than for softer radiations for which the crystals would appear more perfect. The beam divergence was limited to about 0.05 deg with slits. The average angular velocity of the goniometer over a range of $\frac{1}{2}$ deg was checked with an optical method. Final results were obtained by averaging runs with the diffraction peak centered at each of ten positions throughout this $\frac{1}{2}$-deg range.

Because of the geometry, the direct beam power was some 20 times greater than the peak power in the diffracted beam. We reduced the direct beam to a measurable rate with the help of Zr foil absorbers as previously described.[4] This technique requires that the beam be sensibly monochromatic, and suitable measurements were made to insure that such was the case.

The direct beam was monitored via the scattering from a Mylar foil. Both the monitor and the data channel utilized scintillation counters in conjunction with the pulse-height analyzers. The characteristics of the data channel were such that it was possible to place the base line between the copper fluorescence peak and the Mo $K\alpha$ peak. Furthermore, it was found that there was no appreciable shift in the pulse-height distribution up to counting rates of 10 000 counts per second, and that in this range the lost counts could be accounted for with the help of a simple dead-time correction.

After the experiments were completed on the crystals which had been prepared as described above, we made further tests to ensure that there was negligible effect from the etch pits on the surface and that the crystals had not been damaged in handling. We acid-polished the crystals, using a manual technique, rather than the mechanical technique of Young, and then electropolished them. Runs were made on these polished surfaces and the results were indistinguishable from those on the original surfaces for crystals B and C. The crystals were then etched. In the case of B and C the etch-pit patterns were indistinguishable from the as-received crystals, and we concluded that the degree of surface polish did not affect the integrated intensity. In the case of A we found an increased density of etch pits. In view of integrated intensity measurements then made on this crystal, we concluded that the imperfections had been introduced during the manual acid polishing. By varying our polishing technique we were able to prepare surfaces which yielded 2.5×10^3 and 5×10^3 etch pits per cm^3, and measurements were made on these two surfaces. We were then able to extrapolate our results to zero etch-pit density.

Interpretation

Using the results of Hirsch and Ramachandran,[12] whose nomenclature we use, we may relate the integrated reflection to the scattering factor through the formula

$$\rho_H=\frac{1}{|b|^{1/2}}\frac{K}{\sin2\theta_B}\frac{e^2\lambda^2}{\pi mc^2}N|F_H'|R_H{}^y(g,k)\,, \qquad (1)$$

where K is the polarization factor, b is the ratio of the direction cosines of the incident and emergent beams with respect to the crystal surface, F_H' (considered as the unknown) is the real part of the structure factor for the Bragg reflection H as corrected for thermal motion, and $R_H{}^y(g,k)$ is a complicated integral which gives the effect of absorption. The parameters g and k are defined by

$$g=-\frac{1-b}{4K|b|^{1/2}}\frac{mc^2}{e^2\lambda N}\frac{\mu(1+k^2)^{1/2}}{|F_H|}\,, \qquad (2)$$

$$k=F_H''/F_H'.$$

We evaluated K assuming that the initial x-ray beam was unpolarized, that the LiF monochromator reflected

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[11] F. W. Young, Jr., J. Appl. Phys. **32**, 192 (1961); and F. W. Young, Jr., and T. R. Wilson, Rev. Sci. Instr. **32**, 559 (1961).

[12] P. B. Hirsch and G. N. Ramachandran, Acta Cryst. **3**, 187 (1950).

as an imperfect crystal, and that the copper sample reflected as a perfect crystal. We measured values for b in the following way. If the sample is uniform, values for the amount and orientation of the miscut of the crystal may be obtained by measuring the integrated intensity for various values of the angle of rotation φ of the sample about an axis perpendicular to the reflecting planes. From this result, approximate values of b may be obtained, and a simple calculation shows that negligible error is introduced by the use of these values for b if integrated intensities for values of φ which differ by 180° are averaged after the correction has been applied. This situation may be contrasted to that in imperfect crystals where such averaging is adequate, without correction for b. As an example, for our most extreme case, averaging without correcting for b would have led to an error in F_H of about 0.5%, whereas b could easily be measured to an accuracy such that this error was reduced to less than 0.02%.

For the cases which we are considering, R_H^y does not differ greatly from the value 8/3 which it assumes when there is no absorption, and it is not very sensitive to the values of g and k. It is permissible, for example, to set b equal to its average value, -1, in evaluating g. For the mass absorption coefficient μ we used the value 49.1 g/cm^2, which we measured for our wavelength distribution, which was nearly the natural ratio of Mo $K\alpha_1$ and Mo $K\alpha_2$. To estimate values for k, we calculated F_0'' (the value in the forward direction) from the absorption coefficient and made use of the result that the angular dependence of F'' arises mostly from the thermal motion.[13] We thus assumed that $F_H''=F_0''e^{-M}$, with e^{-M} calculated as described below.

To obtain ρ_H from the measured integrated power, one must correct for various background contributions arising from Compton scattering, from that part of the fluorescence which is not discriminated against by our pulse-height analyzer, and from thermal diffuse scattering (TDS). We assumed that all such effects except TDS are slowly varying functions of the scattering vector and may be accounted for by measuring the background when this vector is off a reflection. On the other hand, the TDS peaks at a reflection and must be taken into account explicitly. We made use of the formulation of Nilsson,[14] which applies to mosaic crystals, to calculate the amount of power which would be contained above background in the range of our scan [rotation of the crystal by $\frac{1}{2}$ deg in the case of (111)]. Of this power, only a few percent is contained within the angular range of strong reflection for a perfect crystal; one would expect that only within this range does the diffuse scattering differ between perfect and mosaic crystals. We therefore assumed that, to the accuracy required, the TDS power contained within a scan was that given by Nilsson. Since many of the same parameters enter into this calculation as enter into the expression for the integrated intensity, it is convenient to give the result as a multiplicative factor, $1+\gamma$, by which the integrated intensity must be corrected. Our γ is then larger than Nilsson's corresponding quantity, α, by the ratio of the integrated intensity for the imperfect to that for the perfect crystal.[15]

TABLE I. Values of some subsidiary parameters.

	(111)	(222)	(333)
γ	0.002	0.016	0.052
k	0.060	0.093	0.136
$-g_{\perp}$	0.062	0.106	0.182
$R_{H\perp}^y$	2.358	2.187	1.935
$-g_{\parallel}$	0.066	0.137	0.380
$R_{H\parallel}^y$	2.338	2.057	1.412

In using Eq. (1) to evaluate F_H', it is in principle necessary to use an iterative procedure since the unknown is contained implicitly in R_H^y. Such iteration was however not required in our case. To convert this measured structure factor to the usual scattering factor f_H for an atom at rest, it is necessary to correct for the thermal motion in the actual sample. Noting that there are four equivalent atoms per cubic unit cell and making use of Debye-Waller theory, we write $f_H=\frac{1}{4}F_He^M$ with $M=B(\sin^2\theta_B)/\lambda^2$, a result which, from available theory and experiment, obtains for both mosaic and perfect crystals. The value of B was calculated using Debye theory to be 0.55 Å^2, based on the temperature-dependent measurements of Chipman and Paskin.[16]

Furthermore, to compare our results to the theoretical values of the scattering factor f_0, it is necessary to make the dispersion correction. As a check on the approximate method[17] used previously,[4] we performed the necessary integration of the absorption coefficient[18] and found that $\Delta f'=0.35$, in agreement with the previous estimate. In summary, we obtain ρ_H by correcting our measured integrated powers for background and then dividing by $1+\gamma$. We then list as our experimental result $f_0=\frac{1}{4}F_H'e^M-0.35$, with F_H' determined from Eq. (1), using values of subsidiary parameters given in Table I.

DISCUSSION OF RESULTS

Measurements on crystal B and C revealed that their integrated intensities were greater than that of crystal A and that these intensities were dependent on the portion of the crystal illuminated by the beam. Since our purpose was not to examine the effect of imper-

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[13] H. Wagenfeld, J. Appl. Phys. **33**, 2907 (1962); B. Okkerse, Philips Res. Rept. **17**, 464 (1962); B. W. Batterman, Phys. Rev. **134**, A1354 (1964).

[14] N. Nilsson, Arkiv Fysik **12**, 247 (1957).

[15] This result has been pointed out by D. R. Chipman and B. W. Batterman, J. Appl. Phys. 34, 912 (1963).

[16] D. R. Chipman and A. Paskin, J. Appl. Phys. **30**, 1992 (1959).

[17] L. G. Parratt and C. F. Hempstead, Phys. Rev. **94**, 214 (1954).

[18] R. W. James, *The Optical Principles of the Diffraction of X Rays* (G. Bell and Sons, Ltd., London, 1948).

fections on intensity, we do not report these variable results. We did find, however, that reasonably consistent measurements could be made on crystal A with each of the surface preparations previously described. These results are given in Table II along with our extrapolation to the value appropriate to a completely perfect crystal. One should note that the total extrapolation is less than our experimental error and therefore cannot affect our conclusions. For the higher order reflections there are numerous corrections, as detailed previously, and we did not feel that it was worthwhile to make such extensive measurements. For these reflections we merely quote our best value.

The significant feature of our results is that they agree with the previous results obtained from powder data as shown in Table II, and that both sets of experimental values lie below the HF values, which are listed in Table II for comparison. Such low results are especially significant in the case of the perfect crystal data, for in this case virtually every reasonable difficulty would raise the measured values of the scattering factor. We are thus led to the conclusion that the techniques used in the powder experiments were reliable, in contrast to the recent suggestion of Hosoya[9] that the powders deteriorate with time.

It is perhaps worth while at this point to summarize the present situation with regard to measurement of scattering factors. We feel that the consistency of recent work taken together with the results on gases,[19] where it was possible to extrapolate to zero angle at which $f=Z$, shows that the x-ray technique is capable of giving results within a fraction of one percent. This accuracy is obtainable, however, only for the lowest order reflections, for the uncertainties in interpretation increase greatly at the higher orders. Because of these uncertainties, we feel that it is essential that all necessary corrections be established on the basis of other measurements than those which determine the scattering factor itself. This limitation restricts, at present, accurate scattering-factor measurements to only the simplest of materials.

Because it is probably the most accurate available method for calculating wave functions, except for the lightest atoms, the Hartree-Fock calculation for the free atom forms a convenient starting point for discussion of the scattering factor. In the case of the rare gases, a closed shell, free atom case, the HF method yields the scattering factor within the experimental accuracy. Unfortunately, no experimental studies have been made of nonclosed shell, free atom cases. The results of the present experiment allow one to state with some confidence that the scattering factor is low compared with the free atom value in some metals, results being available on Al,[4,5] Cu,[4] Fe,[4] and Cr,[7] although the Cr result has been questioned.[9] In the case of the transition metals, one can understand the possibility of such lowering on the basis of band calculations, although a detailed comparison is not yet available. In the case of Al, the scattering is less than that which would be yielded by the core alone, according to the HF calculations. In this case, then, it is germane to inquire whether this discrepancy arises from a failure of the HF method for the nonclosed Al atom, or whether the solid-state effects give rise to an appreciable core redistribution. It should be noted that the semiconductor, Si,[6,20] and the alloys CoAl and NiAl [8] appear to yield scattering factors which are in agreement with the HF free atom calculations. Also, Hosoya and his co-workers[9] report agreement in the case of Cr and several compounds, but the time dependence found for Cr is not supported by other powder measurements.[4,5,7] These conflicting results suggest the need for further experimental work; in particular, it would be fruitful to study a specific atom in materials having several different types of binding.

TABLE II. Scattering factors of copper. The quoted errors represent estimates of the experimental error. For the (222) and (333) reflections there are additional uncertainties in the interpretation, as discussed in the text.

Etch-pit Density (cm^{-2}) or source	$f_0(111)$	$f_0(222)$	$f_0(333)$
5000	21.77		
2500	21.64		
1500	21.58	14.01±0.1	9.41±0.1
0(extrapolated)	21.52±0.1		
Powders[a]	21.29±0.34	13.70±0.3	8.37±0.4
HF theory[b]	22.14	14.19	9.54

[a] See Ref. 4.

[b] A. J. Freeman and R. E. Watson, Acta Cryst. 13, 403 (1960).

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

[20] R. J. Weiss and J. J. DeMarco, unpublished measurements on Si perfect crystals.