zinc-oxygen pairs along the c axis might be due either to the electric field arising from the deviation of the crystal from perfect symmetry or to the existence of some homopolar binding between the zinc-oxygen pairs of nearest neighbors. The most successful model considered places some excess of electrons in the neighborhood of the zinc nucleus (Fig. 4), and hence certainly does not approximate a lattice of the ions Zn^{++} and O^{--}. The indicated intra-crystalline field would be much smaller than that estimated in Section I 1; *it seems then that the concentration of charge indicates that there is homopolar binding of the zinc-oxygen neighbors along the c axis.* Such a binding would account for the deviation of the zinc oxide crystal from perfect symmetry. According to this idea, a zinc oxide molecule would retain its individuality within the crystal, in contrast to the situation in such purely ionic crystals as sodium chloride. These zinc-oxygen pairs, or molecules, are not completely electri-

cally symmetrical; the binding of these molecules into the crystal would thus include electrostatic as well as polarization forces, and possibly some further contribution from homopolar binding as well.

This study of electron scattering from zinc oxide shows that electron diffraction offers a powerful method for the investigation of the structure of crystals, such as zinc oxide, for which the type of binding is not indicated by other methods available.

X-Ray Dispersion in Copper Crystals

E. M. McNatt*
Wayman Crow Hall of Physics, Washington University, St. Louis, Missouri
(Received January 26, 1940)

The diffuse scattering of Cu $K\alpha$ radiation ($\lambda = 1.54A$) from single crystals of copper ($\lambda_k = 1.38A$) has been measured for various scattering angles from $\phi = 40°$ to $120°$. Atomic structure factors, calculated from these measurements by combining them with the average temperature-modified structure factor values obtained by other workers using the powdered crystal reflection method, have been compared with Hartree theoretical atomic structure factor values for $\lambda \to 0$ to obtain the decrement caused by dispersion. The average decrement was found to be $\Delta f = 1.75$ as compared with the Hönl value of 2.8 for this ratio of incident to critical absorption wave-length, $\lambda/\lambda_k = 1.12$. No evidence for a dip in the atomic structure factor curve such as found with zinc was noted. Since copper is a cubic crystal the atomic electron clouds are presumably spherically symmetrical and hence no dip in the S or f curves should be expected.

I. INTRODUCTION

IN a recent paper[1] the writer published experimental results showing the effect of dispersion and atomic electron cloud distortion on the diffuse scattering of Zn and Cu $K\alpha$ radiation from single crystals of zinc. During the course of that experiment similar measurements were made on single crystals of copper ($\lambda_k = 1.38A$), using copper $K\alpha$ radiation ($\lambda = 1.54A$), to determine

whether analogous effects exist in the case of copper. Measurements of the decrement in the reflecting power of copper crystals for Cu $K\alpha$ rays have been made by Rusterholtz[2] and others, using the powdered crystal method. From these measurements the decrement in the atomic structure was calculated with the aid of the Debye-Waller theoretical formula for the temperature correction. However the Debye-Waller formula involves the "characteristic" tempera-

---

[1] E. M. McNatt, Phys. Rev. 56, 406 (1939).

[2] A. A. Rusterholtz, Zeits. f. Physik 65, 226 (1930).

ture, and the uncertainties in the specific heat data from which this is calculated make its use unsatisfactory. On the other hand diffuse scattering measurements combined with experimental reflection intensity data permit the direct calculation of atomic structure factors without the use of the temperature factor. Furthermore, diffuse scattering measurements not only require no corrections for the effects of extinction, but are in general less dependent upon surface conditions than are powdered crystal reflection data because the half-absorption depth in diffuse scattering experiments is from three to thirty times as great as the dimensions of powdered crystals used in reflection experiments.

II. EXPERIMENTAL METHOD

The apparatus and method of measurement used in this research have been described before.[1] Copper crystals used in the experiment were small sections cut from cylindrical single crystals of copper.[3] In order to obtain the required flat surfaces, the crystal rods were first cut lengthwise by slow sawing with a fine jewelers, saw. Next the surface was carefully ground flat with emery powder, and finally the crystal was etched to remove distortion caused by the sawing and grinding. The etching was done by a method described by Underwood,[4] in which the metal is etched with HNO_3, first with 55 percent and then with 74 percent solution. When the stronger solution was not preceded by the weaker, a red oxide which resisted further etching was formed. After the crystal had been properly etched it had the matte surface characteristic of etched crystals, and, if the sample was not single, the different orientations present were clearly distinguishable because of the difference in reflecting power for light incident at various angles. Some of the first crystals so prepared showed small "islands" of polycrystalline copper which made the specimens unsuitable for diffuse scattering measurements, since a Bragg reflection from one or more of the "islands" was likely to occur at almost any angle of scattering. As a result of such stray reflections the

experimental diffuse scattering would be too high, of course, since the reflections might not be strong enough to be detected as such.

III. TEMPERATURE-MODIFIED STRUCTURE FACTORS FROM REFLECTION DATA

Experimental values of the diffuse scattering are obtained from electrometer readings and instrumental constants through the formula[1]

$$S = \frac{4R^2 W m^2 c^4}{A N Z e^4 (1 + \cos^2 \chi \cos^2 \phi)} \times \frac{D(\phi, \theta)}{D_0 u(\phi, \theta)} \times \frac{\mu}{\rho}. \quad (1)$$

The theoretical value of S is given by Jauncey's formula[5]

$$S = (f - \Delta f)^2 (1 - e^{-2M})/Z$$
$$+ [1 - (1/Z)\Sigma E_r^2]/R, \quad (2)$$

where f is the atomic structure factor, F is the atomic structure factor modified by the effects of thermal vibrations, E_r is the electronic structure factor for the rth electron, and R is the so-called Breit-Dirac factor to take account of Compton scattering processes. Δf and ΔF are the decrements due to dispersion in the f and F values, respectively.

From Eq. (2) we may express $(f - \Delta f)$ in terms of the measured quantities S and $(F - \Delta F)$, and the incoherent term $[1 - (1/Z)\Sigma E_r^2]/R$. This last term is not an experimentally measured datum, and values of E_r^2 are those obtained by James and Brindley[6] using the Hartree distribution function. Fortunately R is nearly equal to unity, and the contribution of the ΣE_r^2 term is small enough so that a large percentage error in it would but slightly affect the final result. In the case of zinc, measurements of F, S, and the temperature factor have been made for wavelengths considerably shorter than that for the K-absorption edge, in which measurements the effect of the natural frequencies of the electrons is small. Therefore we can say that we know f fairly well, and hence measurements made with $\lambda \approx \lambda_k$ will show the effect of these natural frequencies (anomalous dispersion). However such complete data have not been obtained for copper. Thus to find $(f - \Delta f)$ from the measured S values

[3] The single crystal copper rods from which the samples were cut were presented to the Physics Department through the courtesy of Dr. Foster C. Nix of the Bell Telephone Laboratories, New York.
[4] N. Underwood, Phys. Rev. 47, 502 (1935).

[5] G. E. M. Jauncey, Phys. Rev. 56, 644 (1939).
[6] R. W. James and G. W. Brindley, Phil. Mag. 12, 104 (1931).

we need to know temperature-modified structure factors found using the same wave-length and at the same temperature as that employed in obtaining the diffuse scattering results. Because there are variations in such $(F-\Delta F)$ values published for copper, it was important to investigate the sources of the discrepancies in order to know the best set of values to use.

Perhaps the most conspicuous feature of the published $(F-\Delta F)$ data is that they are not absolute measurements, but have been standardized by comparison with reflections from a standard substance. The fact that the temperature-modified structure factor values of different authors agree well if they are made equal for one value of $(\sin\theta)/\lambda$ indicates that in the standardization of the experiental results lies an important source of error. Several measurements were based on absolute measurements of F for a particular crystal of NaCl, made by James and Firth[7] in 1927. These measurements are not independent of the particular crystal used because of the variation of extinction effects from one crystal to the next, according to James, Brindley and Wood.[8] Consequently measurements standardized by comparison with any other rocksalt crystal may be in error. Another source of uncertainty in the experimental $(F-\Delta F)$ values lies in the preparation of the powders which were used for these experiments. It has been found by Brindley and Spiers[9] for example, that different methods of preparation lead to different results with some materials. Furthermore, the process of packing the powder into briquettes may produce preferred crystal orientation, which would change the experimental results because the orientation is as-

TABLE I. Δf values calculated from experimental S values.

ϕ	$(\text{SIN }\frac{1}{2}\phi)/\lambda$	S_{EXP}	$(F-\Delta F)_{\text{AV}}$	$(f-\Delta f)_{\text{EXP}}$	fH	Δf
40°	0.222A⁻¹	2.09	17.50	18.8	20.55	1.75
60°	0.324	2.40	13.55	15.4	17.10	1.70
70°	0.372	2.42	11.95	14.0	15.90	1.90
80°	0.417	2.76	10.60	13.2	14.80	1.60
120°	0.562	1.62	9.00	10.4	12.20	1.80

[7] R. W. James and Elsie M. Firth, Proc. Roy. Soc. 117, 62 (1928).
[8] R. W. James, G. W. Brindley, and R. G. Wood, Proc. Roy. Soc. 121, 154 (1928).
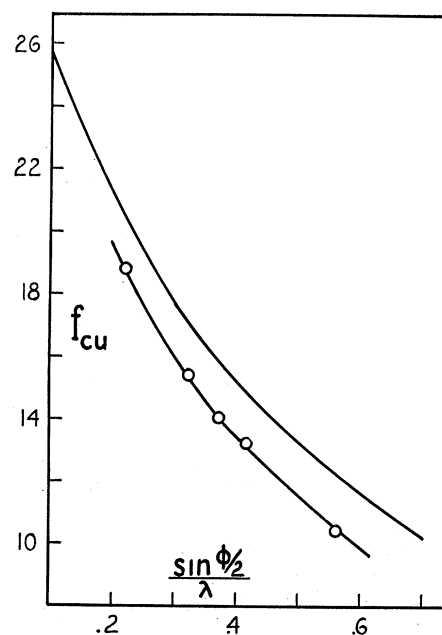[9] G. W. Brindley and F. W. Spiers, Phil. Mag. 20, 882 (1935).

FIG. 1. Atomic structure factors for copper. Upper curve, Hartree theoretical values for $\lambda/\lambda_k\to 0$. Lower curve joins experimental points for $\lambda=1.54$A.

sumed to be random in the calculation of $(F-\Delta F)$ values from the reflection coefficients.

One of the earliest measurements of copper $(F-\Delta F)$ values using Cu $K\alpha$ radiation was made by Armstrong[10] in 1929. Miss Armstrong used blocks of powdered crystal which had been compressed and then scraped to remove the preferred orientation effect, and standardized her relative values by comparison with the (220) reflection from a NaCl crystal. As mentioned above, this reflection had been calibrated by James and Firth, but with molybdenum $K\alpha$ radiation. She assumed that $(F-\Delta F)$ was independent of wave-length and a function of $(\sin\theta)/\lambda$, and used their absolute value as standard. The powder used was fine enough so that she believed a correction for extinction was unnecessary. In 1930 Wyckoff[11] restandardized the copper (220) reflection and used Armstrong's data to give a new set of $(F-\Delta F)$ values. Rusterholtz[2] used the absolute calibration of aluminum powder by James, Brindley and Wood[8] to standardize his relative measurements on copper using Cu $K\alpha$ radiation. He neglected extinction effects.

[10] A. H. Armstrong, Phys. Rev. 34, 931 (1929).
[11] R. W. G. Wyckoff, Phys. Rev. 36, 1116 (1930).

Brindley and Spiers[12] in 1935 published $(F-\Delta F)$ data obtained by measurements made on copper powder which was produced by adding finely powdered zinc to $CuSO_4$ solution. The resulting precipitate was carefully washed, dried, and sieved through a screen of 350 mesh per inch. Microscopic examination showed the particle size to be of the order of 5×10^{-4} cm. The measurements were standardized by comparison with reflections from precipitated KCl. In 1936, however, Brindley [13] recalculated these values on the basis of a standardization employing aluminum powder as standard rather than KCl. Brindley makes his aluminum values "absolute" by fitting them to the theoretical curve at one point. This procedure seems hardly to be justified in the light of the uncertainties mentioned above. At any rate, his new values of f for copper turned out to be about ten percent higher than those previously published.

IV. EXPERIMENTAL RESULTS

In view of the nature of the discrepancies noted, it was judged that an unweighted average of the values obtained by the authors cited above constitute the best set of $(F-\Delta F)$ values available. This average set was consequently used in calculating $(f-\Delta f)$ values from the experimental diffuse scattering (S) values and Eq. (2). Table I

shows the experimental values of S, the average $(F-\Delta F)$ values and f values calculated therefrom. Also shown are the atomic structure factors calculated by Hartree's method. The values of Δf shown in the last column are obtained using the Hartree factors as standard. The average value is $\Delta f=1.75$ as compared with $\Delta f=2.8$ from Hönl's theory for $\lambda/\lambda_k=1.12$.

No high degree of accuracy is claimed for the value of Δf obtained, but it is consistent with results from other methods. (See, for example, Fig. 3 of reference 1, which is a plot of results for Δf by various authors.) As shown in Fig. 1 there is no evidence for such a dip in the atomic structure factor curve as was found for zinc. However the experimental difficulties—chiefly low scattered intensity—made it necessary to limit the number of values of $(\sin\theta)/\lambda$ for which the diffuse scattering measurements were made, and additional data would be helpful in proving more conclusively that no such dip exists. The absence of the dip in the curve for a copper crystal adds support to the opinion that the dip in the $\psi=0°$ curve for a zinc crystal is a result of a similar dip in the corresponding f values for zinc.

[12] G. W. Brindley and F. W. Spiers, Phil. Mag. 20, 865 (1935).
[13] G. W. Brindley, Phil. Mag. 21, 778 (1936).