

THE X-RAY DIFFRACTING POWER OF COPPER AND IRON  
FOR MOLYBDENUM AND COPPER RADIATIONBY ALICE H. ARMSTRONG  
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## ABSTRACT

Ionization spectrometer measurements were made of the intensity of reflection of the  $K\alpha$  doublet of Mo and Cu from copper and iron powders. From the relative intensities of reflection from the different planes of the powdered crystals, the relative  $F$  values for these reflections were calculated. These relative values were placed on an absolute scale by comparison of the intensity of one reflection with that of the (220) reflection of NaCl, for which the absolute value with Mo radiation has been determined by James and Firth. On the assumption that the atomic scattering factors are independent of the wave-length and are proportional to  $\sin\theta/\lambda$ , the same absolute value of  $F$  was used for the (220) reflection of Cu  $K\alpha$  from NaCl. Because of the difficulty experienced in making plates of the copper and iron powders sufficiently thin for use in absorption measurements, previously determined values of absorption were used in the calculation of the absolute values. Calculated values of the absorption coefficient for NaCl were used.

The absolute values of  $F$  are shown as functions of  $\sin\theta/\lambda$ . Those for copper radiation do not lie on the same curve as those for molybdenum. The fact that the two curves do not coincide suggests that the assumption that  $F_{220}$  for NaCl is the same for copper as for molybdenum radiation may not be justified, and that  $F$  is not entirely independent of the wave-length.

## INTRODUCTION

THE atomic scattering factor  $F$  can be obtained by experimental measurements of the intensity of x-ray reflections from crystals. This  $F$  is the ratio of the amplitude of the radiation scattered by the whole atom to the amplitude scattered by a single free electron according to classical wave theory. It is then a pure number which, as a function of wave-length and of angle of reflection, at small angles approaches the total number of electrons in the atom. A knowledge of  $F$  for different atoms is essential to the analysis of complex crystal structures and is of value in studies of atomic structure. The experiments described in this paper form part of an extended investigation of  $F$ -curves being carried out in this laboratory. They were especially chosen as providing a test of dependence of  $F$  on  $\sin\theta/\lambda$ .

## EXPERIMENTAL PROCEDURE

The experimental data consist of measurements<sup>1</sup> with the ionization spectrometer of the intensities of reflections from blocks of iron and copper powders. The study of the intensity of x-ray reflection from a powdered crystal offers a simpler and more direct means of determining the scattering power than reflections from single crystals. If the powder particles are

<sup>1</sup> W. H. Bragg, Proc. Phys. Soc. London **33**, 222 (1921); R. J. Havighurst, Phys. Rev. **28**, 869 (1926); J. A. Bearden, Phys. Rev. **27**, 796 (1926).

sufficiently small, extinction effects are practically eliminated, and no corrections need be applied. Both the copper and iron were obtained in the form of fine impalpable powders, each particle of which was smaller in diameter than  $5 \times 10^{-3}$  cm. The individual crystals were still smaller, and apparently extinction was not operative to an appreciable extent. The powder was compressed, by means of a hydraulic press, into a briquet of a form similar to those used by Havighurst. Effects due to possible orientation of the crystal particles by the pressure were eliminated by scraping off the surface of each briquet with a fine file.

The source of high-tension was a transformer-kenetron-condenser set capable of maintaining a very steady direct-current voltage. For the first series of experiments a water-cooled tube with molybdenum target was run at about 35,000 volts and a tube current of 10 to 14 milliamperes. In order to obtain a monochromatic x-ray beam of sufficient intensity, the x-rays were filtered through a screen of zirconium oxide, which cut out most of the  $\beta$  peak and also considerably reduced the general radiation. The tube with a copper target was run at about 30,000 volts and a tube current of 5 milliamperes. No filter was used. The difference in wave-length between the  $\alpha$  and  $\beta$  peaks was sufficient to prevent any intensity of the  $\beta$  peak from being added to the reflection of the  $\alpha$  peak by the same set of planes; neither did any of the  $\beta$  peaks fall in the neighborhood of the  $\alpha$  peaks reflected by other sets of planes. The intensities of the diffracted beams of x-rays were measured by the usual ionization method. The monochromatic beam—the  $K\alpha$  doublet—was reflected from the powder plate into the ionization chamber. The focussing condition for this method was fulfilled by placing the chamber slit at a distance from the powder equal to the distance from the powder to the target of the tube. The ionization currents were measured by means of a Compton type electrometer and a scale system of high sensitivity. The usual sensitivity was about 12 meters per volt, with the scale 2 meters distant from the electrometer. Reflection from the surface of the powder plate was used rather than transmission through the powder.

For each reflection the ionization chamber was set first at an angle sufficiently less than that for the maximum reflection so that only general scattered radiation entered the chamber, the powder plate was set at half that angle, and the ionization current measured. Then the ionization chamber was moved successively through given angular distances, the powder plate through half those distances, and the ionization current measured at each setting. Each reflection was mapped out in this way, the peaks were plotted on a large scale, and the relative intensities obtained from the relative areas under the peaks and above the base-line due to general radiation.

#### METHOD OF CALCULATION FROM DATA

The following expression<sup>2</sup> gives the ratio of the power of the rays scattered to the ionization chamber to the power of the primary beam:

$$\frac{P_s}{P} = Q \frac{\rho}{16\pi} \frac{l}{\mu r} \frac{\rho'}{\rho} \frac{1}{\sin \theta}, \quad (1)$$

<sup>2</sup> A. H. Compton, X-Rays and Electrons, p. 131, (Van Nostrand, 1926).

where  $p$  is the number of planes in the crystal belonging to the form which reflects the rays at angle  $\theta$ ,  $l$  is the height of the ionization chamber slit which is distant  $r$  from the powder,  $\rho'$  is the density of the powder mass,  $\rho$  the density of the individual crystals, and  $\mu$  the linear absorption coefficient of the powder plate. In the foregoing equation

$$Q = \frac{1}{2} N^2 F^2 \lambda^3 \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta},$$

where  $N$  is the number of atoms per unit volume of the crystal,  $\lambda$  the wavelength, and  $F$  the structure factor, modified by the effects of thermal agitation.

In the determination of relative  $F$  values all quantities independent of the angle of reflection remain constant. If they are set equal to  $R$ , then

$$F^2 = R \frac{P_s \sin^2 \theta \cos \theta}{P (1 + \cos^2 2\theta)}. \quad (2)$$

In each series of measurements, one particular reflection was chosen as standard, and the structure factors for the other reflections relative to that for the standard were calculated by Eq. (2).

The relative values of  $F$  obtained in this way may be placed on an absolute scale if an absolute value of  $F$  be determined for one reflection. In this investigation the absolute values were obtained by comparison of the intensity of reflection from one plane of each substance with that of the (220) reflection of NaCl powder under the same experimental conditions. W. L. Bragg and his collaborators,<sup>3</sup> who have measured reflections from single crystals instead of from powders, make comparison with the (400) reflection of NaCl in order to avoid primary extinction effects which might occur in reflections at smaller angles. The powders used in these experiments were all so fine that extinction could be neglected for all reflections. Comparisons with the (220) reflections of NaCl were made for the (110) reflection of Fe for both wave-lengths, for the (200) reflection of Cu for both wave-lengths, and also for the (220) reflection of Cu for molybdenum  $K\alpha$ . The absolute value of  $F$  used for the (220) reflection of Mo  $K\alpha$  from NaCl was 15.62, the figure given by James and Firth<sup>4</sup> in their recent study of rock-salt. On the assumption that the atomic scattering factors are independent of the wave-length and are proportional to  $\sin \theta / \lambda$ , the same absolute value of  $F$  was used for the (220) reflection of Cu  $K\alpha$  from NaCl.

The greatest uncertainty in the determination of the absolute value by this method lies probably in the measurements of  $\mu$  and  $\rho'$ , the linear absorption coefficient and the density of the powdered crystal mass. Because of their relatively high atomic numbers and consequent high absorption, only extremely thin plates of Fe and Cu powder would permit the passage of x-rays of measurable intensity. Difficulty was experienced in making such thin plates of uniform thickness and density. As thick plates were

<sup>3</sup> W. L. Bragg and J. West, *Zeits. f. Krist.* **69**, 118 (1928); R. W. James and G. W. Brindley, *Proc. Roy. Soc.* **A121**, 155 (1928).

<sup>4</sup> R. W. James and E. M. Firth, *Proc. Roy. Soc.* **A117**, 62 (1927).

used in the determination of the relative intensities of reflections from different planes, it was considered that more reliable results would be obtained from known values of the absorption coefficients. The values of  $\mu$  used for copper were taken from the recent determinations of Backhurst,<sup>5</sup> and were calculated from the formulas which he found to fit his experimental values for copper. These gave  $\mu = 459$  for Mo  $K\alpha$ ,  $\lambda = .710$ , and  $\mu = 474$  for Cu  $K\alpha$ ,  $\lambda = 1.537$ . Allen<sup>6</sup> has also quite recently measured the absorption coefficient of copper. His values are  $\mu(\text{Mo}K\alpha) = 464$ ,  $\mu(\text{Cu}K\alpha) = 446$ . As determinations made here gave a ratio of the absorption of Mo radiation to that of Cu radiation in agreement with the ratio obtained from Backhurst's figures, his values were used rather than those of Allen.

The values of  $\mu$  for iron, however, were taken from Allen's tables. He gives  $\mu/\rho = 38.4$  for  $\lambda = 0.709$ , or  $\mu(\text{Mo}K\alpha) = 302$ ; and  $\mu/\rho = 330$  for  $\lambda = 1.537$ , or  $\mu(\text{Cu}K\alpha) = 2594$ .

No experimental determinations of the absorption of NaCl have evidently been made at long wave-lengths. Allen states that the  $K$  absorption of Na probably obeys the 2.92 relation in the general formula:

$$\mu/\rho = C\lambda^{2.92}N^4/A + \sigma/\rho,$$

where  $N$  is the atomic number,  $A$  the atomic weight, and the best value of  $C$  for the  $K$  series is  $1.32 \times 10^{-2}$ .  $\sigma/\rho$ , the scattering coefficient, is about 0.1 for elements of low atomic number, and has been neglected here. Since Na and other substances near it in the periodic table obey the 2.92 relation, Cl has been assumed to obey it likewise, and absorption of NaCl has been calculated accordingly. The value obtained is 17.6, in good agreement with Havighurst's<sup>7</sup> observed value of 17.5. Havighurst, using the  $\lambda^3$  relation and a numerical value for  $\sigma/\rho$ , also calculated the absorption coefficient for NaCl and obtained 18.0, whereas Windgardh found 18.1. The value 17.6 was used

TABLE I. Intensities of reflection and the resultant  $F$ -values of metallic copper.

Reflection	(sin $\theta$ )/ $\lambda$	$P_s(\text{Mo } K\alpha)$	$F(\text{Mo } K\alpha)$	$P_s(\text{Cu } K\alpha)$	$F(\text{Cu } K\alpha)$
111	0.241	222.	19.81	233.	16.05
200	.278	100.	17.85	100.	14.41
220	.392	60.7	14.28	52.	11.15
311	.461	55.7	11.62	54.2	9.25
222	.481	16.1	11.35	15.8	8.80
400	.556	5.7	9.27		
331	.607	14.9	8.30		
420	.620	11.2	7.41		
422	.681	7.1	6.63		
511}	.723	7.6	6.37		
333}					
440	.785	1.5	5.10		
531	.822	5.4	5.11		
600}	.832	2.7	4.64		
442}					
620	.879	1.7	4.35		

<sup>5</sup> I. Backhurst, *Phil. Mag.* **7**, 353 (1929).

<sup>6</sup> S. J. M. Allen, *Phys. Rev.* **28**, 907 (1926).

<sup>7</sup> R. J. Havighurst, *Proc. Nat. Acad. Sci.* **12**, 477 (1926).

here. The absorption coefficient for copper radiation calculated in the same way is 168.

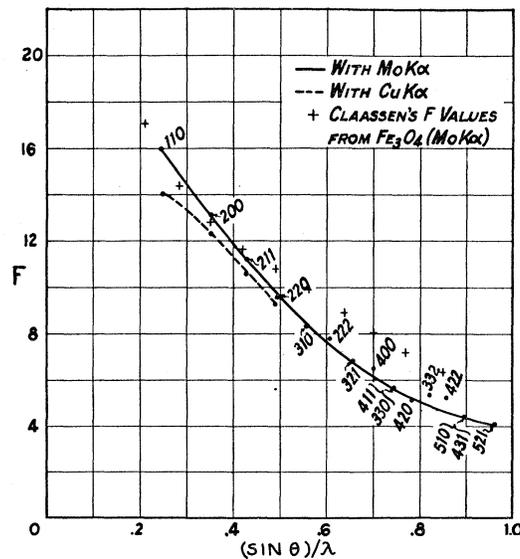
## EXPERIMENTAL RESULTS

In Table I are given the experimental values of the relative intensities of reflection  $P_s$  and the consequent values of  $F$  for Cu for Mo  $K\alpha$  and Cu  $K\alpha$  radiation. Comparison of Cu (220) with NaCl (220) for Mo  $K\alpha$  gave the

TABLE II. Intensities of reflection and the resultant  $F$ -values of metallic iron.

Reflection	$(\sin \theta)/\lambda$	$P_s(\text{Mo } K\alpha)$	$F(\text{Mo } K\alpha)$	$P_s(\text{Cu } K\alpha)$	$F(\text{Cu } K\alpha)$
110	0.247	100	15.87	100	13.96
200	.350	16.6	13.23	16.6	12.29
211	.428	30.6	11.24	31.6	10.56
220	.494	8.0	9.55	10.8	9.33
310	.553	9.2	8.27		
222	.605	2.2	7.84		
321	.655	8.3	6.82		
400	.699	.8	6.56		
411 } 330 }	.741	3.2	5.68		
420	.780	1.6	5.18		
332	.821	1.5	5.43		
422	.857	.9	5.29		
510 } 431 }	.891	2.5	4.42		
521	.956	1.2	4.02		

same absolute values as those obtained from the (200) comparison. Table II contains the experimentally determined relative intensities and the values of  $F$  obtained for Fe for Mo  $K\alpha$  and Cu  $K\alpha$  radiation.

Fig. 1. Experimental  $F$ -values for metallic iron.

Figs. 1 and 2 show the absolute values as functions of  $(\sin\theta)/\lambda$ . Too much reliance should not be placed on the figures at large values of  $(\sin\theta)/\lambda$ , as the intensities of these weak reflections could not be measured with great accuracy. In Fig. 1 are shown also the interpolated values of  $F$  obtained by Claassen<sup>8</sup> for Fe from  $\text{Fe}_3\text{O}_4$ . The agreement is not at all satisfactory. Claassen's figures are for divalent and trivalent iron ions, whereas this investigation was made for metallic iron.

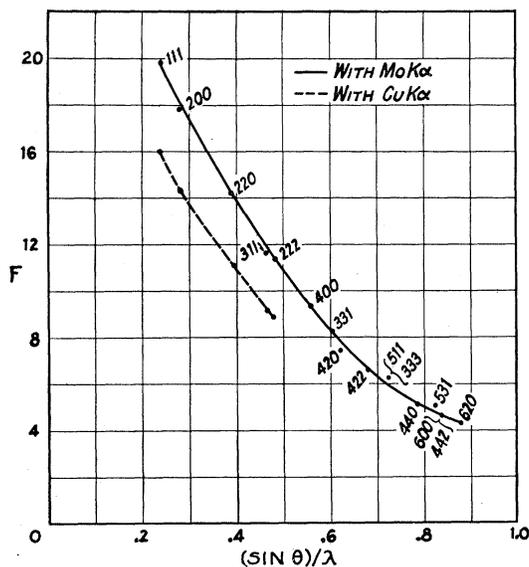


Fig. 2. Experimental  $F$ -values for metallic copper.

Of special interest is the fact that the  $F$  values for copper radiation do not lie on the same curves as those for molybdenum. The  $F$  values for  $\text{Cu } K\alpha$  may not be the true absolute ones, as they were obtained on the assumption that  $F_{220}$  for  $\text{NaCl}$  was the same for copper radiation as for molybdenum. The fact that the two curves do not coincide indicates that this assumption may not be justified and that  $F$  is not independent of the wave-length. James and Firth<sup>4</sup> found that their absolute determinations of the intensity of reflection of  $\text{Mo } K\alpha$  from rock-salt confirmed earlier unpublished measurements by Bosanquet with rhodium radiation. The wave-length of  $\text{Cu } K\alpha$  radiation differs so much from those of the other two that the results of this experiment are not necessarily in conflict with these earlier investigations.<sup>9</sup> This investigation was suggested by Dr. Ralph W. G. Wyckoff, to whom the author is indebted for much helpful criticism.

<sup>8</sup> A. Claassen, Proc. Phys. Soc. London **38**, 482 (1926).

<sup>9</sup> Cf. E. Wagner and H. Kulenkampff, Ann. d. Physik **68**, 369 (1922), who found values of  $F$  for the (100) and (200) reflections of rock-salt with copper and iron radiation in agreement with the values given by Bragg, James, and Bosanquet (Phil. Mag. **41**, 309 (1921)) for rhodium radiation. Their results with calcite, however, were not in agreement with the assumption that  $F$  is independent of the wave-length.