

## Scattering of X-Rays by Cold-Worked and by Annealed Beryllium\*

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The intensities of reflection of Mo  $K\alpha$ -radiation by important crystallographic planes in powdered beryllium have been measured by an ionization method under the following conditions: (I) cold-worked particles of average diameter about  $3 \times (10)^{-3}$  cm; (II) the same after  $\frac{1}{2}$  hr. at  $800^\circ\text{C}$ ; (III) cold-worked particles of average diameter about  $(10)^{-2}$  cm; (IV) the same after 1 hr. at  $950^\circ\text{C}$ . In

(II) and especially in (IV) cold-working strains should have been relieved. The atomic structure factors derived from these data show no appreciable change with annealing and further show that Be crystals are rather imperfect. The mass absorption coefficient is found to be 0.26 in good agreement with a value computed according to Compton's empirical formula.

### INTRODUCTION

THE atomic structure factor for x-ray scattering, generally plotted against  $\sin \theta/\lambda$  in so-called  $F$ -curves, is closely dependent upon the charge distribution in the atom.<sup>1, 2</sup> It has been suggested<sup>3</sup> that the charge distribution in the atoms of a cold-worked metal differs from that in the same atoms in annealed crystals, and if so a change in the  $F$ -curve is to be expected when a cold-worked metal is annealed.

Because of its low atomic number beryllium was chosen for test. Since the atomic number  $Z$  is 4, a given change in the position of one electron should have a large proportional effect. The outermost electrons contribute little to the  $F$ -values in the accessible range of  $\sin \theta/\lambda$ , so that changes in their distribution would be much harder to detect than a change in the position of a  $K$  electron.

The crystal structure of beryllium is hexagonal close-packed.<sup>4</sup> In a powder the (101) planes give the strongest reflection. Therefore, measurement of this reflection should furnish the best opportunity for detecting any small change because of

cold-work since errors in the background here have a smaller proportional effect. The (101) planes are unevenly spaced so that their crystallographic structure factor  $S$  is  $\sqrt{3}/2$  instead of 1.

If extinction is negligible,  $F^2$  can be computed from the scattered intensity<sup>5</sup> for the case of transmission of x-rays through a plate of powdered crystals, the normal to which is equally inclined to the incident and emergent beams.  $F$  is usually defined by the equation

$$F = Z \int_{-D/2}^{D/2} p(z) \cos [(4\pi z \sin \theta)/\lambda] dz, \quad (1)$$

$Z$  being the atomic number and  $p(z)dz$  the probability that an electron will be between  $z$  and  $z+dz$  from the lattice plane.

If the initial or final distributions of charge differ, the effect on  $F$ -values will be different for planes with different indices. It is therefore advisable to get  $F$ -values for several planes, even though the precision of the results for some of them may be low. Calculation shows that  $F$  for (101) may vary between 2.0 and 0.8 for extreme assumptions regarding the positions of the two  $L$  electrons. The probable range in  $F$  is much narrower.

### PREPARATION OF SPECIMENS

A 5-gram lot of 99.5 percent Be, produced electrolytically by Siemens and Halske, was obtained in pea-sized lumps from the Metal and

\* Part of a dissertation presented to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

<sup>1</sup> W. Ehrenberg and K. Schäfer, *Phys. Zeits.* **33**, 97 (1932).

<sup>2</sup> E. O. Wollan, *Rev. Mod. Phys.* **4**, 205 (1932).

<sup>3</sup> W. Geiss and J. A. M. van Liempt, *Zeits. f. anorg. Chemie* **133**, 107 (1924); **143**, 259 (1925), have supposed that the normal state of the metal atom is changed by cold-work. This led to the investigation here described. Since its beginning W. A. Wood, *Phil. Mag.* [7] **13**, 355 (1932), has independently proposed a test of this kind.

<sup>4</sup> L. W. McKeehan, *Proc. Nat. Acad. Sci.* **8**, 270 (1922).

<sup>5</sup> A. H. Compton, *X-Rays and Electrons*, Chapter V.

Thermit Corporation. The hardness and brittleness of the metal make plastic deformation difficult, but microscopic examination showed that small particles are flattened by crushing and grinding so that such processes produce some degree of cold-work. Two samples were prepared. A hardened steel crusher and an agate mortar were used to obtain particles of average size about  $3 \times 10^{-3}$  cm (I), the cold-work being done under toluene because of the reputed affinity of Be for oxygen. The surface of the mortar was scratched by the grinding, so to avoid this source of contamination a second cold-worked sample (III) was prepared with the crusher alone. Since larger particles were so obtained the use of toluene to prevent oxidation was dispensed with. The average size of the particles of (III) was about  $10^{-2}$  cm. The crystal powders were packed lightly in flat brass containers, the windows in which were covered with thin cellophane.

In order to obtain Be crystals free from cold-work the powders were subjected to an annealing process in hydrogen at atmospheric pressure. Sample (I) was heated at  $800^\circ\text{C}$  for  $\frac{1}{2}$  hr., sample (III) at  $950^\circ\text{C}$  for 1 hr. The melting point of Be is  $1280^\circ\text{C}$ , so fine powders should have been well annealed by such treatments. After annealing (I) and (III) were designated (II) and (IV), respectively.

#### APPARATUS AND MEASUREMENTS

Molybdenum x-rays from a G.E. water-cooled tube were filtered through  $\text{ZrO}_2$  to give a fairly homogeneous beam. The primary intensity was controlled by a rheostat<sup>6</sup> in the filament circuit. Ionization currents (in  $\text{CH}_3\text{Br}$ ) were measured with a quadrant electrometer at 1000 to 5000 divisions per volt.

Fig. 1 is a curve for sample (III), showing the strongest reflections. The lower curve is for the NaCl (220) reflection which was used to standardize the measurements, the  $F$ -values for NaCl (220) being well known.<sup>2</sup> The standard curve is low because of the thickness of the specimen used, but is convenient for comparison with the majority of the Be peaks.

Effective absorption coefficients  $\mu'$  were found

<sup>6</sup> P. Kirkpatrick, J.O.S.A. and R.S.I. 7, 195 (1923).

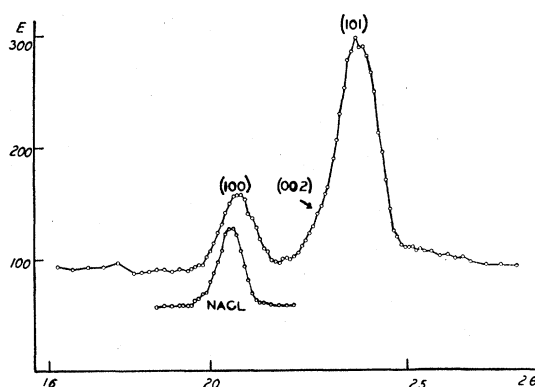


FIG. 1. Principal peaks for Be and NaCl standard. X-ray intensities in divisions per sec.  $\times 10^2$  are plotted along the ordinate, scattering angle in degrees along the abscissa.

by placing each of the Be samples in the primary beam while measuring the intensity of NaCl (220). By taking the integrated area of the peak above background this measurement is limited, as is desirable, to the Mo  $K\alpha$  wave-lengths.

#### RESULTS

Absolute values of  $F$  can be found if the known value of  $F$  for NaCl (220) is used to eliminate measurement of the x-ray power input which is difficult with such a sensitive instrument as the electrometer. Then

$$F^2 = (C/S^2\chi(\theta))(\rho/\rho')e^{\mu'h \sec \theta}R, \quad (2)$$

where  $C$  is a constant for all reflections,  $\chi(\theta)$  a function of the angle of scattering only,  $h$  is the thickness of the plate of powder,  $\rho'$  is the apparent density,  $\rho$  the density of the particles,  $R$  the ratio of the intensity of the Be reflection to the standard NaCl reflection and  $S$  the crystallographic structure factor.

The value found for  $\rho$  by weighing in air and in toluene was  $1.85 \text{ g cm}^{-3}$ . This value of  $\rho$  agrees with most others,<sup>7</sup> but differs from that given by Jaeger and Rosenbohm<sup>8</sup> ( $1.90 \text{ g cm}^{-3}$ ), who used metal from the same supplier.

Values of  $F$  for the four samples are given in Table I. The values for (002) reflections are of low precision because of poor resolution and

<sup>7</sup> Siemens-Konzern (Beryllium), Chem. Catalog Co. (1932).

<sup>8</sup> F. M. Jaeger and E. Rosenbohm, Proc. Roy. Acad. Amst. 35, 1055 (1932).

TABLE I. Values of  $F$  for the four samples.

| Plane          | $(\sin \theta)/\lambda$ | $F_1$ | $F_2$ | $F_3$ | $F_4$ |
|----------------|-------------------------|-------|-------|-------|-------|
| 100            | 0.254                   | 2.3   | 2.0   | 2.3   | 2.1   |
| 002            | .277                    | 1.4   | 1.4   | 1.3   | 1.3   |
| 101            | .289                    | 2.08  | 2.11  | 2.05  | 2.03  |
| 102            | .376                    | 1.6   | 1.5   | 1.7   |       |
| 110            | .438                    | 1.62  | 1.75  | 1.69  |       |
| 103            | .486                    | 1.3   | 1.4   | 1.3   |       |
| 112 }<br>201 } | .517                    | 1.41  | 1.44  | 1.39  |       |

uncertainty of background. Relative values of  $F$  (101) for the cold-worked and annealed samples indicate that the cold-work to the degree here attained had no appreciable effect upon charge distribution in the atom.

One can only conclude, from the fact that a 2 percent change in  $F$ , which could have just been detected, was not actually observed in the case of the (101) reflection, that the average effect of cold-work of this limited sort is small. If large local changes in  $F$  exist they must be limited to a small fraction of the total volume. It is conceivable that Be is self-annealing at the temperature of experiment<sup>9</sup> though this would

<sup>9</sup> L. Thomassen and J. E. Wilson, Phys. Rev. **43**, 763 (1933), found Al to show line-broadening when worked at  $-75^\circ\text{C}$ , but not when worked at room temperature.

be anomalous in view of its melting temperature.

The effect of change in particle size from  $3 \times 10^{-3}$  to  $10^{-2}$  cm was very small. This is evidence that Be is a rather imperfect crystal since the sizes were near those which are minimum for primary extinction in the notably imperfect crystal NaCl.<sup>10</sup>

The average values for  $F$  for all samples agree fairly well with theoretical values given in a paper by James and Brindley.<sup>11</sup>

The data also furnish values for  $\mu/\rho$  which are computed from the experimentally measured  $\mu'/\rho'$  by correcting<sup>12</sup> for known impurities, in this case 0.4 percent iron. The same result  $\mu/\rho=0.26$  was so obtained from samples (III) and (IV). This agrees well with  $\mu/\rho=0.28$  as given by Compton's empirical formula.<sup>13</sup>

In conclusion the author wishes to express his thanks to Professor L. W. McKeenan, who suggested the problem and gave much helpful advice, and to Professor C. D. Cooksey for his constant interest and assistance in designing the apparatus.

<sup>10</sup> R. J. Havighurst, Phys. Rev. **23**, 882 (1926).

<sup>11</sup> R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

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

<sup>13</sup> Reference 5, p. 189.