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THE ELECTRON DISTRIBUTION OF MAGNESIUM OXIDE

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Abstract

The *intensity of x-rays reflected* from powdered crystals of magnesium oxide was measured for all lines out to $\theta = 45°$. The values of the structure factor, F, were calculated and plotted against sin θ. Using the values of F from this curve as coefficients in Compton's Fourier series, the *radial electron distribution for the atoms of magnesium and oxygen* was determined. The electron distribution curves for these atoms are very similer to Havighurst's curves for sodium chloride and sodium fluoride. Although it has been generally conceded that crystals of the magnesium oxide type are polar in form, the data here included are more in line with their being non-polar crystals. However, it is not believed possible from x-ray reflection data to prove definitely this point.

Introduction

THE intensity of reflection of the K_α line of molybdenum has been measured for powdered crystals of magnesium oxide. The structure factor curves have been calculated, and the electron density in the crystal and the radial electron distribution in the atoms of magnesium and oxygen have been determined, using the Fourier Series worked out by A. H. Compton.[1] Besides being able to determine the distribution of the electrons in the atoms, the total number of electrons associated with each point of the space lattice can thus be found. This should make it possible to decide whether the crystal is in a polar or non-polar form. In the work of Bragg, James, and Bosanquet, sodium chloride was concluded to be polar and Havighurst has concluded that several crystals with which he worked were of this form. In general the evidence seems to favor this view for crystals of the sodium chloride type, but it can hardly be said to be conclusive.

Magnesium oxide has been chosen for analysis, not only for the interest in determining the electron distribution in the atoms of magnesium and oxygen, but also because it is a very suitable substance for showing the state of ionization of the atoms in the space lattice.

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[1] A. H. Compton, "X-Rays and Electrons."

Experimental Procedure

The accuracy with which intensity measurements can be made with powdered crystals is limited to some extent by the difficulty of obtaining a strictly homogeneous beam of x-rays of sufficient intensity. It was found that the method used by Havighurst[2] was most suitable for obtaining accurate results, especially at large angles, where the intensity is very weak. This method is essentially that first used by W. H. Bragg,[3] and consists in utilizing the focussing effect of randomly oriented crystals pressed into a flat plate, and the use of zirconium oxide filters for cutting out the K_β and K_γ lines and a greater part of the general radiation. The arrangement of the author's apparatus is shown in Fig. 1. A molybdenum target x-ray tube was operated at a potential of 35 kv and 35 m.a., supplied by a transformer with full wave rectification.

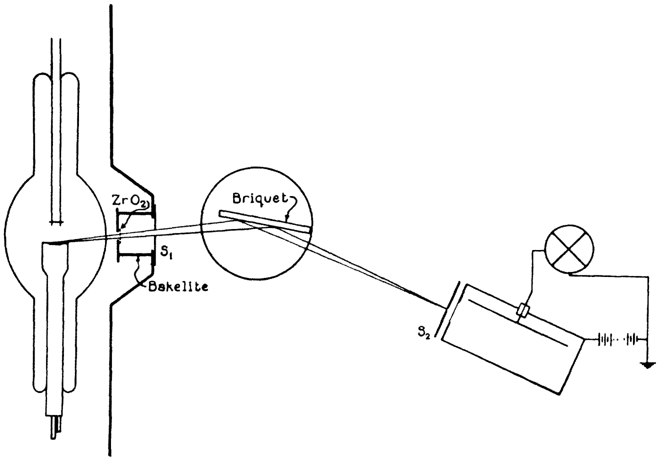

Fig. 1. Diagram of apparatus

The pure magnesium oxide powder was pressed into a brass ring two inches in diameter. The mass per cm^2 of the powder was made just great enough for practically total absorption of the K_α lines of molybdenum. In this way some of the general radiation of shorter wave-length was not effective in scattering and increasing the continuous background.

The slits used in front of the ionization chamber were accurately measured to be of such width that when the briquet was moved through some predetermined increment of arc (generally five to ten minutes) the slit, S_2, moved through its own width. In this way all the reflected energy was received in the ionization chamber.

The ionization current was measured with a Compton electrometer, having a sensitivity of from five to ten meters per volt. The rate of deflection of the electrometer needle was taken at each increment of arc corresponding

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[2] R. J. Havighurst, Phys. Rev. **28**, 832, (1926).

[3] W. H. Bragg, Proc. Phys. Soc. London, **33**, 222 (1921).

to the width of the slit, S_2. The reciprocals of these readings were plotted as ordinates against the angle θ and the intensity of the line was taken as proportional to the sum of the ordinates above the base line. If the increments are small the intensity is also proportional to the area under the curve. Different widths of slits, S_2, were found to give results in satisfactory agreement.

Table I, column three, gives the average of the relative intensity measurements where the intensity of the (200) reflection has been taken equal to 100.00. The measurements have been extended to about $\theta=45°$. This is as far as the spectrometer could conveniently be used.

TABLE I. *Measured values of F for magnesium oxide.*

Plane	Sin θ	Rel. Int.	F
111	0.1464	8.55	2.92
200	0.1691	100.00	13.40
220	0.2390	55.10	10.15
311	0.2804	5.80	2.78
222	0.2929	15.20	8.20
400	0.3380	6.00	6.94
331	0.3684	2.53	2.51
420	0.3780	13.20	5.92
422	0.4140	8.72	5.35
511	0.4392	1.07	1.73
333			
440	0.4782	1.71	4.00
531	0.5000	0.83	1.41
600	0.5071	3.31	3.78
442			
620	0.5344	1.84	3.22
533	0.5542	0.25	1.29
622	0.5606	1.30	3.00
444	0.5856	0.37	2.90
551	0.6036	0.19	0.90
711			
640	0.6095	0.89	2.60
642	0.6324	1.40	2.52
553	0.6492	0.16	0.71
731			
800	0.6762	0.12	2.21
733	0.6918		
644	0.6970	0.80	2.05
820			
822	0.7172	0.48	1.86
660			

STRUCTURE FACTOR DETERMINATIONS

Darwin[4] and A. H. Compton[5] have derived equations which relate structure factor and the integrated intensity of x-rays reflected from powdered crystals.

When the relative intensity measurements have been made by reflection from a briquet of powder as they were in this case, the equation for calculating the relative values of the structure factor, F, takes the simple form

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[4] C. G. Darwin, Phil. Mag. **43**, 827, (1927).

[5] A. H. Compton, Phys. Rev. **9**, 29, (1917).

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

where P_s is the intensity of the reflected beam measured on some arbitrary scale, j is the number of planes cooperating in producing the intensity P_s and 2θ is the angle between the primary and the reflected beam. F^2 is the square of the structor factor in which the Debye[6] temperature factor, exp $[(b^2 \sin^2\theta)/\lambda^2]$, is included. The reasons for the inclusion of the Debye factor in the value of F have been pointed out by Havighurst.[2]

The relative values of F can be placed on an absolute scale by comparing the intensity of some line of the substance to be analyzed with the intensity of a line of a substance for which the absolute value of F has been directly determined. The absolute value of F for the (220) reflection of sodium chloride has been measured by James, Bragg and Bosanquet[7] on single crystals, and corrected for secondary extinction. Their value of $F = 15.75$, has been used as a standard for placing the relative F values of magnesium oxide on an absolute basis.

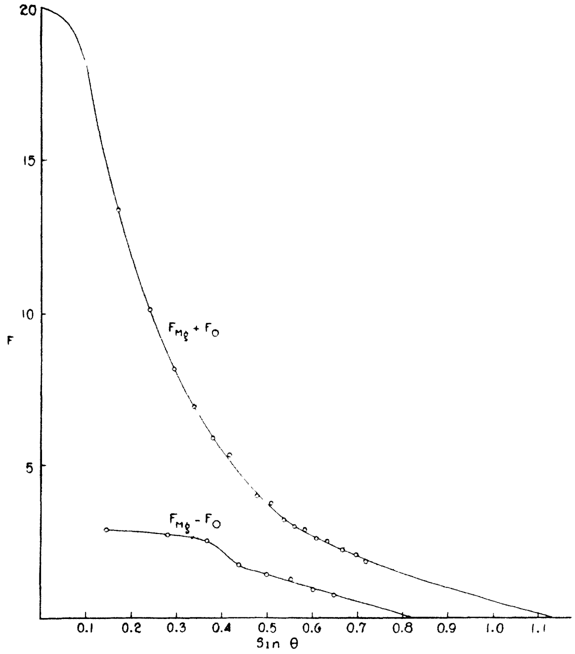

Fig. 2. Structure factor curve for MgO.

Table I, column IV gives the absolute values of F for all the lines measured, where F (220) was found equal to 10.15 by comparison with the same reflection from sodium chloride.

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[6] P. Debye, Verh. d. D. Phys. Ges. **15**, 678, (1913).

[7] W. L. Bragg, James, and Bosanquet, Phil. Mag. **42**, 1, (1921).

Fig. 2 shows the F curves plotted from the above values of F. The upper curve is due to even order reflections and corresponds to $F_{Mg}+F_O$, while the lower curve corresponds to $F_{Mg}-F_O$. The values of F for the separate atoms can be found from the relations

$$F_{Mg} = \tfrac{1}{2}(F_{Mg} + F_O) + (F_{Mg} - F_O) \text{ and}$$
$$F_O = \tfrac{1}{2}(F_{Mg} + F_O) - (F_{Mg} - F_O). \qquad (2)$$

Since magnesium and oxygen are bivalent and have atomic numbers of 12 and 8, respectively, the ions would have 10 electrons each. This means that for ions the lower F curve is dependent on the different electron distributions and not on the number of electrons in the two ions. If the scattering centers are neutral atoms this curve would be a function of both the distribution and the number of electrons.

ELECTRON DISTRIBUTION CURVES

For the determination of the radial electron distribution curves the equation derived by Compton was used. This is a one dimensional Fourier series and much easier to evaluate than the three dimensional series of Duane. The series has the form

$$U = \frac{8\pi r}{D^2} \sum_{1}^{\infty} nF_n \sin \frac{2\pi n r}{D} \qquad (3)$$

where U is equal to the number of electrons per Angstrom and r is the distance from the center of the atom in Angstroms. If both sides of this equation are multiplied by dr and integrated from 0 to $D/2$ one gets an expression for Z, the total number of electrons in the atom included between these limits,

$$Z = -2 \sum_{1}^{\infty} (-1)^n F_n. \qquad (4)$$

In calculating the electron distribution curves for magnesium and oxygen, spherical symmetry has been assumed in the atoms, and the values of F were read directly from the F curves, assuming a grating space of 2.5A for the sake of convenience in calculations. This gives a series of only seven terms, but it was found that the distribution in the K and L shells was only very slightly different if a larger number of terms were used.

TABLE II. *Values of F from F-curves on basis of D = 2.5A.*

Indices	Sin θ	$(F_{Mg}+F_O)$	$(F_{Mg}-F_O)$	F_{Mg}	F_O
111	0.142	15.00	2.92	8.96	6.04
222	.284	8.40	2.76	5.58	2.82
333	.426	5.10	2.00	3.55	1.60
444	.568	2.94	1.14	2.04	0.90
555	.710	1.94	0.44	1.19	0.75
666	.852	1.24	0.00	0.62	0.62
777	.994	0.60	0.00	0.30	0.30

Table II gives the values of $F_{Mg}+F_O$ and $F_{Mg}-F_O$ which have been taken from the F curves of Fig. 2 and the values of F_{Mg} and F_O, which have been calculated with the aid of Eq. (2). Using these values of F as coefficients in the series 3, given above, the electron distribution curves of magnesium and oxygen have been plotted in Figs. 3 and 4.

MAGNESIUM

Fig. 3 shows the curve for the radial electron distribution in magnesium. The area under the curve corresponding to the K and L shells is about 9.5 electrons, unless a part of the adjoining hump is included. If the distribution is calculated on the basis of $D=5.00$A the area under this part of the curve is 10 electrons and its distribution is very nearly the same with a slightly better resolution of the hump at $r=0.5$A. The distribution in these shells is very similar to Havighurst's[8] curves for sodium in NaCl and NaF, except that in this case the average distance of the electrons from the nucleus is less. This could be expected from the fact that magnesium has a higher atomic number and also that the grating space of Mg is less than for either of the other two substances mentioned.

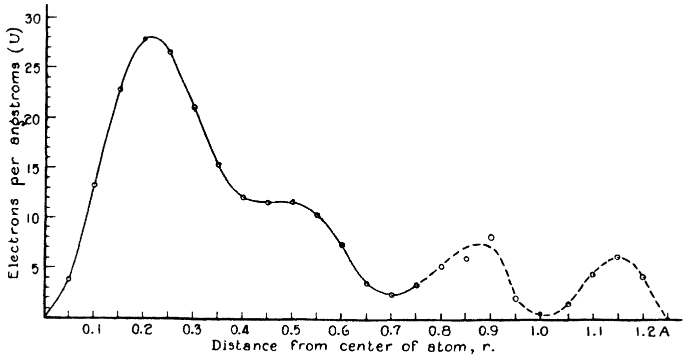

Fig. 3. Electron distribution in Mg.

In this curve there is also an indication of the two valence electrons, and these, as might be expected, are more loosely bound than the other electrons. Little significance can be placed in the positions of these humps, however, since they are not the same when calculated on the basis of $D=5.0$A.

The total number of electrons in the atom, according to this analysis is 11.50. This is the area under the curve and also the value as given in Table II, calculated from Eq. (4). In all cases the area under the curve checks the value from Eq. (4) as, of course, should be the case if no error is made in working out the Fourier series. The existence of only 11.50 electrons using the F values corresponding to $D=2.5$A and 11.04 electrons for $D=2.424$A indicates that some of the electron atmosphere is at a distance greater than

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[8] R. J. Havighurst, Phys. Rev. **29**, 1, (1927).

$D/2$ from the nucleus, beyond which the series does not hold, since it drops to zero at this value.

OXYGEN

Fig. 4 shows the radial electron distribution curve for oxygen. Here the electron shells in oxygen have areas corresponding to 3, 3.5 and 1.5 electrons with a small erratic variation near $D/2$. The fact that the humps do not represent an integral number of electrons may be due to experimental error, but there is no reason, from the idea of elliptic and interpenetrating orbits, that the distributions should be made up of humps representing integral numbers of electrons.

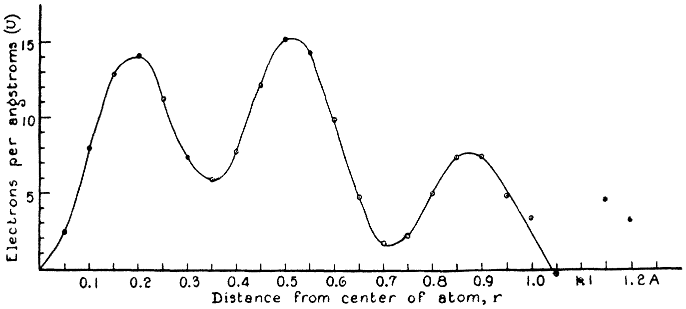

Fig. 4. Electron distribution in O.

The total area under the curve is equal to 8.7 electrons, which also checks the value in Table II, as calculated from Eq. (4). This curve for oxygen closely resembles Havighurst's curve for fluorine.

ELECTRON DENSITY IN THE MgO CRYSTAL

Compton has derived a series which represents the number of electrons in a plane at any height above some atomic layer. This series has the form

$$P = \frac{Z}{a} + \frac{2}{a} \sum_{1}^{\infty} \left(F_n \cos 2\pi n \frac{z}{a} \right) \tag{5}$$

where P is equal to the number of electrons per Angstrom, z is the distance above the reference plane in Angstroms, and Z is the total number of electrons per molecule of the substance.

Using the values of F_{111}, F_{222}, etc., given in Table I and the value of F_{666} extrapolated from the F curve, as coefficients in this series and plotting P against z/a, one gets the curve shown in Fig. 5.

It will be noticed that the electron density does not fall to zero between the atoms. This means that the atoms overlap, and in order to tell how many electrons belong to each atom it is necessary to extrapolate the curve of one atom into the space of the other. This, in general, can be only a good guess; but in this case there is considerable difference in the size of the humps, and the most obvious extrapolation would be to give magnesium more electrons than oxygen. In Fig. 5 extrapolations have been made for the two extreme cases of the neutral atom and the ion. The broken line shows how the curve can be extrapolated to give Mg 12 electrons and oxygen 8 electrons, while the dot and dash line gives the ions with 10 electrons each. From the fact that the radial electron distribution curves for magnesium do not contain 12 electrons between 0 and $D/2$, however, one is led to the conclusion that the valence electrons of magnesium spend part of the time nearer to the nucleus of oxygen than to that of the magnesium atom. It is, however, probable that the distribution for large values of r in the radial distribution curves, is no more reliable than a logical extrapolation of the curves in Fig. 5.

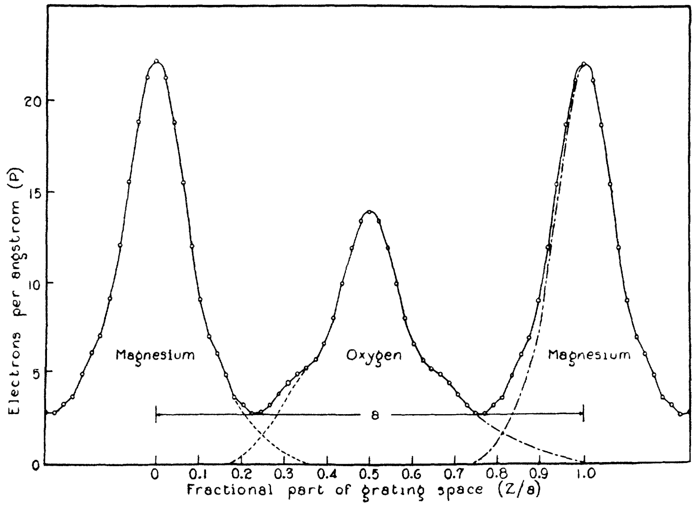

Fig. 5. Electron density in MgO.

Using the table of F values worked out by Havighurst as coefficients in series 4, the total number of electrons associated with the atoms in various crystals has been determined and the results are shown in Table III. It will be seen that the analysis of these data by the use of Compton's series leads to no definite conclusions regarding the state of ionization of the atoms in the crystals considered.

TABLE III.

	Mg	O	
$D=$ 2.5A	$Z=11.52$	$Z=$ 8.70	
2.424A	$Z=11.04$	$Z=$ 8.42	
5.00A	11.56	8.34	
	Havighurst's Data		
NaCl	NaF	CaF_2	LiF
$Z_{Na}=10.82$	$Z_{Na}=10.48$	$Z_{Ca}=19.04$	$Z_{Li}=1.42$
$Z_{Cl}=17.54$	$Z_F=$ 9.12	$Z_F=10.46$	$Z_F=8.38$

CONCLUSION

There seems to be fairly good agreement in the data of different observers for the distribution of the electrons in the K and L shells of various atoms. For magnesium there is no overlapping of these shells for neighboring atoms. In the shells of larger radius, where there is overlapping of the electrons for the two or more atoms considered, it is quite likely that the analysis of the distribution is less reliable.

From the data at hand, one is hardly justified in drawing definite conclusions regarding the location and the behavior of the valence electrons in the atoms of crystals. To say that an atom is ionized in the crystal presumably means that the electrons are revolving about the nucleus of the other atom. Since a large portion of each atom overlaps its neighbor, this implies that the analysis can detect whether an electron scattering at a point near the nucleus of one atom is actually revolving about the nucleus of the other. This can, at best, be only a good guess as to what is actually occurring.

The calculation of the distribution of diffracting power in some direction in the crystal is considerably more straightforward. Hence, a curve of the type of that shown in Fig. 5 would be more reliable than the radial distribution curves. In the case of magnesium oxide it would be easier to extrapolate this curve to give 12 and 8 electrons to the atoms of magnesium and oxygen, respectively, than to make an extrapolation giving these atoms each 10 electrons.

Since there is a considerable amount of overlapping of the neighboring atoms, it would be more reasonable to conclude from the data at hand that the valence electrons are shared by the atoms of magnesium and oxygen and that neither of the conclusions regarding the existence of ions or neutral atoms in the points of the crystal lattice is altogether correct.

In conclusion, the writer wishes to express his appreciation to Professor A. H. Compton for his helpful suggestions throughout the work.