

white line could escape notice, but the remainder of the structure is also quite out of agreement with that of the calcium. Thus, the distance from the middle of the first absorption line to the middle of the second broad and strong absorption line, ignoring the division of the first line in the case of calcium, is 7.2 volts for Ca, and 12.8 volts for Ti.

In the case of perovskite ( $\text{CaTiO}_3$ ), although the separations of the first two white lines agree very well, as may be seen from the table, yet on examining the plates one is not convinced that they are alike, for the two white lines are of nearly equal intensity for Ti, while for Ca the first line is much stronger than the second (see photometer curves).

The absorption due to Cr in chromite differs much from that due to Fe in the same compound.

The two strong white lines in the case of Cr are distinct and should be plainly observed a little closer together for Fe on account of the lesser dispersion. The second line is not observed for Fe, but there is another white line of moderate intensity about 57 volts from the first one. No white line appears for Cr at this distance. It seems therefore evident that the secondary structure in absorption, while greatly influenced by crystal structure, is not wholly controlled by that factor.

The x-rays were reflected from the rhombohedral face of a quartz crystal, the grating constant thus being 3336 x.u. The absorbing material was ground into a fine powder and suspended as uniformly as possible in a thin film of collodion. This screen was then placed between the slit and the crystal.

## A Quantitative Test of the Waller-Hartree Theory of X-Ray Scattering Applied to the Diffuse Scattering from Crystals

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The effect of the extra term in the incoherent part of the scattered radiation due to the operation of the Pauli exclusion principle is calculated for neon. It is shown that the inclusion of this term gives considerably better agreement with experimental results for NaF; it is further pointed out that it is probably only in the case of the diffuse scattering from crystals that the effect of this term can be detected experimentally.

A QUANTUM-mechanical theory of the scattering of radiation by a free atom has been given by Wentzel<sup>1</sup> and independently by Waller and Hartree.<sup>2,3</sup> The latter treatment differs from that of Wentzel in that account is taken of the Pauli exclusion principle; this restricts the number of electron transitions possible and leads to a consequent decrease in the intensity of the incoherent part of the scattered radiation. The coherent part of the

scattering, on both theories, is given by

$$S_1 = I/ZI_e = f^2/Z, \quad (1)$$

where  $S$  is the scattering per electron in terms of the Thomson value  $I_e$ . Wentzel's formula for the incoherent scattering is

$$S_2 = 1 - \left( \sum_{j=1}^Z E_{jj}^2 \right) / Z, \quad (2)$$

where  $E_{jj}$  is the contribution to  $f$  "due to the  $j$ th electron"; i.e.,  $f = \sum_{j=1}^Z E_{jj}$ . The correspond-

ing formula of Waller and Hartree is

$$S_2 = 1 - \left( \sum_{j=1}^Z E_{jj}^2 \right) / Z - \left( \sum_{j \neq k} |E_{jk}|^2 \right) / Z. \quad (3)$$

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<sup>1</sup> G. Wentzel, *Zeits. f. Physik* **43**, 1 and 779 (1927).

<sup>2</sup> I. Waller, *Phil. Mag.* **4**, 1228 (1927); *Nature* **120**, 155 (1927); *Naturwiss.* **15**, 969 (1927); *Zeits. f. Physik* **41**, 213 (1928).

<sup>3</sup> I. Waller and D. R. Hartree, *Proc. Roy. Soc.* **A124**, 119 (1929).

The quantities  $E_{jk}$  are defined by Waller and Hartree (reference 3, Eq. (41)) as

$$E_{jk} = \int \psi_j \psi_k^* e^{i\sigma\mu r} r^2 dr d\mu d\varphi, \quad (4)$$

where  $\sigma = 4\pi(\sin \phi/2)/\lambda$  and  $\psi_j$  is the wave function associated with the  $j$ th electron. The summation is to be taken over all pairs of electrons with the same spin and  $j \neq k$ . Waller and Hartree have compared their calculated values of  $S_1 + S_2$  for argon with the experimental results of Barrett.<sup>4</sup> Now the maximum value of the correction term  $\sum |E_{jk}|^2$  amounts at most to less than ten percent of the *incoherent* scattering for argon and occurs at a value of  $(\sin \phi/2)/\lambda = 0.65$ . But here the *coherent* scattering is by far the largest part of the whole and so the correction term amounts to only a few percent. At larger and smaller values of  $(\sin \phi/2)/\lambda$  its effect rapidly becomes negligible.

The matter is different, however, in the case of the diffuse scattering from crystals. Here the incoherent scattering is always a large part of the whole. It thus seems that this would be the logical place to see whether the inclusion of this term gives better agreement with experiment. The classical theory of the diffuse scattering from a single crystal gives,<sup>5</sup> for a crystal consisting of two kinds of atoms such as NaF,

$$S_{class.} = 1 - \frac{\sum (E_{jj}^2)_1 + \sum (E_{jj}^2)_2}{Z_1 + Z_2} + \frac{f_1^2 + f_2^2 - F_1^2 - F_2^2}{Z_1 + Z_2}, \quad (5)$$

where  $F$  is the atomic structure factor including the effect of thermal agitation and the numerical subscripts refer to the two kinds of atoms. Taking account of the extra term of the Waller-Hartree theory it is seen that we should subtract from Eq. (5) the quantity

$$\left\{ \sum |E_{jk}|_1^2 + \sum |E_{jk}|_2^2 \right\} / (Z_1 + Z_2). \quad (6)$$

We shall now compare the calculated values of

$S_{class.}$  taking account of the expression (6) with the recent results of Williams<sup>6</sup> on the diffuse scattering of monochromatic x-rays from NaF at 295°K. To do this it is necessary to calculate the quantities  $E_{jk}(j \neq k)$ . Since  $\text{Na}^+$  and  $\text{F}^-$  are neon-like and since the  $E_{jk}$  are involved only in a correction term we shall not be appreciably in error if we use  $E_{jk}$  for neon instead of for  $\text{Na}^+$  and  $\text{F}^-$ . We have

$$\psi_{n, l, m} = N_{n, l, m} \chi_{n, l}(r) P_l^m(\mu) e^{im\varphi}, \quad (7)$$

where  $P_l^m$  is the associated Legendre function,  $\chi_{n, l}(r)$  the radial wave function and  $N_{n, l, m}$  a normalizing factor equal to  $[(2l+1)(l-m)!/4\pi(l+m)!]^{1/2}$  if  $\chi_{n, l}(r)$  is taken as already normalized. Analytical approximations to the radial wave functions of neon have been given by Brown.<sup>7</sup> Following Waller and Hartree, we shall neglect values of  $E_{jk}$  which involve a change in the total quantum number  $n$ ; also,  $E_{jk}$  vanishes if  $m$  is not the same in both wave functions. Since the spin must be the same, this leaves as the only possibility  $n=2, l=1, m=0, n'=2, l'=0, m'=0$  and this occurs four times, *viz.*, (210,200) and (200,210) each taken with + and - spin. Inserting these values in Eq. (4) and integrating with respect to  $\mu$  and  $\varphi$ , we obtain

$$E_{210,200} = i(3)^{1/2} \int_0^\infty \left( \frac{\sin \sigma r}{\sigma^2 r^2} - \frac{\cos \sigma r}{\sigma r} \right) \times r^2 \chi_{2,0}(r) \chi_{2,1}(r) dr. \quad (8)$$

TABLE I.

$j$	$A_j$	$\alpha_j$	$j$	$A_j$	$\alpha_j$	$j$	$A_j$	$\alpha_j$
1	273.38	12.70	3	295.68	8.17	5	38.59	5.60
2	54.21	10.13	4	95.82	6.63	6	18.97	4.06

TABLE II.

$(\sin \phi/2)/\lambda$	$\sum  E_{jk} ^2$	$(\sin \phi/2)/\lambda$	$\sum  E_{jk} ^2$	$(\sin \phi/2)/\lambda$	$\sum  E_{jk} ^2$
0.05	0.140	0.35	1.210	0.70	0.172
0.10	0.467	0.40	1.027	0.75	0.116
0.15	0.852	0.45	0.849	0.80	0.067
0.20	1.199	0.50	0.643	0.90	0.029
0.25	1.324	0.55	0.482	1.00	0.009
0.275	1.340	0.60	0.351	1.10	0.002
0.30	1.324	0.65	0.248	1.20	0.000

<sup>4</sup> C. S. Barrett, Phys. Rev. **32**, 22 (1928).

<sup>5</sup> G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931); G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931); Y. H. Woo, Phys. Rev. **38**, 6 (1931); and **41**, 21 (1932); G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).

<sup>6</sup> P. S. Williams, Phys. Rev. **46**, 83 (1934).

<sup>7</sup> F. W. Brown, Phys. Rev. **44**, 214 (1933).

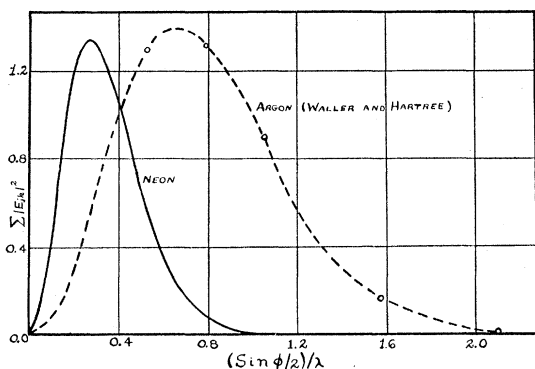


FIG. 1.

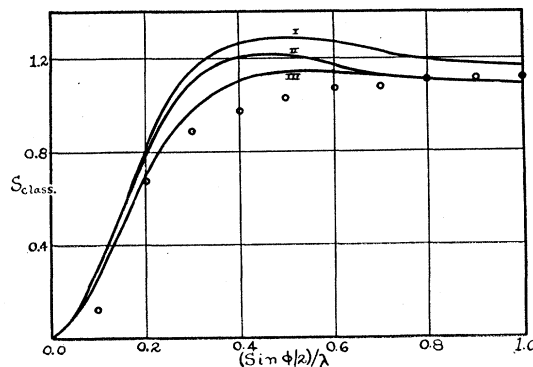


FIG. 2.

But<sup>7</sup>

$$r\chi_{2,0}(r) = 13.60[r e^{-3.22r} - r^2(1.08e^{-3.69r} + 0.35e^{-2.15r})]$$

$$r\chi_{2,1}(r) = 20.13r^2(e^{-4.48r} + 0.198e^{-1.91r}),$$

where  $r$  is expressed in atomic units; performing the integration with respect to  $r$ , we get

$$E_{210,200} = i(3)^{\frac{1}{2}} \left\{ \sum_1^2 \frac{8A_j}{\alpha_j^5} \frac{\sigma}{(1 + \sigma^2/\alpha_j^2)^3} - \sum_3^6 \frac{(40A_j/\alpha_j^6)\sigma - (8A_j/\alpha_j^8)\sigma^3}{(1 + \sigma^2/\alpha_j^2)^4} \right\} \quad (9)$$

and  $\sum |E_{jk}|^2 = 4|E_{210,200}|^2$ . The  $A_j$  and  $\alpha_j$  are given in Table I. The value of  $\sum |E_{jk}|^2$  is given in Table II as a function of  $(\sin \phi/2)/\lambda$  ( $\lambda$  in Å) and is plotted in Fig. 1 together with Waller and Hartree's values of the same quantity for argon. Although only five values are given for argon it is seen that it is possible to draw a curve through these with considerable accuracy. As might be expected, the curve for neon may be approximately obtained from that for argon by multiplying the abscissae of the latter by

$(10-s_1)/(18-s_2)$  where  $s_1$  and  $s_2$  may be considered as average screening constants.

In order to compare the calculated and observed values of  $S$  we have used values of  $E_{ji}$  and  $f$  from the tables of James and Brindley<sup>8</sup> and have obtained  $F$  by multiplying  $f$  by the Debye-Waller<sup>9,10</sup> temperature factors, using Shonka's value,<sup>11</sup> 442°K, for the characteristic temperature of NaF and assuming the existence of zero-point energy. The results are shown in Fig. 2. Curve III takes account of the extra correction term while Curve II neglects it. Curve I is based on the assumption that the probability distribution is the same for all electrons so that  $\sum E_{ji}^2 = f^2/Z$ , i.e.,  $f'' = f$  in the notation used by Jauncey.<sup>12</sup> The points represent the experimental values.<sup>6</sup> We feel that Curve III agrees with the experimental values within the limits of experimental error and that Curve II, and even more so Curve I, differ by more than the experimental error from the observed values.

<sup>8</sup> R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

<sup>9</sup> P. Debye, *Ann. d. Physik* **43**, 49 (1914).

<sup>10</sup> I. Waller, *Diss. Upsala* (1925); *Zeits. f. Physik* **17**, 248 (1923).

<sup>11</sup> J. J. Shonka, *Phys. Rev.* **43**, 948 (1933).

<sup>12</sup> G. E. M. Jauncey, *Phys. Rev.* **42**, 453 (1932).