Compton Scattering of X-Rays from Aluminum

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Hartree-Fock self-consistent field wave functions were determined for the aluminum atom and used to calculate the x-ray Compton scattering for aluminum according to the Waller-Hartree theory as extended in a previous paper. The predictions of this theory are compared with experiment and previous theoretical calculations. The theoretical results are in very good agreement with the measurements of Walker but differ from those of Laval at low $\sin\theta/\lambda$.

THERE is at present only very little experimental information on the Compton scattering of x-rays. The most extensive accurate measurements are those of Walker[1] and Curien and Deroche[2] on aluminum. Even though the Waller-Hartree theory is strictly valid only for free atoms, the very existence of the experimental data itself invites comparison with the predictions of this theory. This comparison seems particularly appropriate since the results of Walker and Laval[3] showed that the Compton scattering functions, as calculated by James and Brindley,[4] based on the Compton-Raman-Wentzel equation[5] and currently in constant use, are considerably in error. Furthermore, an approximate calculation of the incoherent scattering that Walker himself carried out, based on the Waller-Hartree expression,[5] also was found unreliable and led Walker to conclude that the known theoretical expressions were incapable of accurately predicting the experimental data. For all these reasons we decided to calculate the Compton scattering intensity for aluminum, using the complete Waller-Hartree theory as developed in the preceding paper[5] (referred to hereafter as I).

METHOD OF CALCULATION

Since the results of the computations depend directly on the choice of one-electron basis functions, it was decided to use Hartree-Fock self-consistent field solutions, as these represent the best free atom wave functions available to date. As no such wave functions had been computed for aluminum, a limited self-consistent field calculation was carried out by the late D. R. Hartree and the writer,[6] using the recently published results for Al^{+}.[7] These wave functions were then used to calculate the scattering matrix elements according to the methods outlined earlier in I.

The numerical integrations were carried out on Whirlwind I, the M.I.T. digital computer; the numerical wave functions were used as direct input data, after being interpolated to a mesh suitable for machine calculation by a routine written by Corbató.[8] The effect of the interpolation procedure on the numerical accuracy was checked by the normalization condition.

RESULTS

The numerical results are given in Table I, as a function of $\sin\theta/\lambda$ in Å^{-1} units. Here $\mathfrak{F}=\sum_i\sum_j|f_{ij}|^2$; and for aluminum in its ^2P ground state, made up out of the $(1s)^2(2s)^2(2p)^6(3s)^2\,3p$ configuration, we have, from the matrix elements derived in I,

$$\mathfrak{F}=2f_{1s}^2+2f_{2s}^2+6f_{2p}^2+2f_{3s}^2+f_{3p}^2$$
$$+4(f_{1s,\,2s}^2+f_{1s,\,3s}^2+f_{2s,\,3s}^2)$$
$$+12(f_{1s,\,2p}^2+f_{2s,\,2p}^2+f_{3s,\,3p}^2)$$
$$+2(f_{1s,\,3p}^2+f_{2s,\,3p}^2+f_{3s,\,3p}^2)+12f_{2p,\,2p}^2$$
$$+2f_{2p,\,3p}^2(0)+4f_{2p,\,3p}^2(2)+\tfrac{1}{5}f_{3p,\,3p}^2,$$

with the definitions[9]

$$f_{ns}=\int P_{ns}^2(r)j_0(kr)dr,$$

$$f_{np}=\int P_{np}^2(r)j_0(kr)dr,$$

$$f_{ns,\,n's}=\int P_{ns}(r)P_{n's}(r)j_0(kr)dr,$$

$$f_{ns,\,n'p}=\int P_{ns}(r)P_{n'p}(r)j_0(kr)dr,$$

$$f_{np,\,np}=\int P_{np}^2(r)j_2(kr)dr,$$

$$f_{np,\,n'p}(m)=\int P_{np}(r)P_{n'p}(r)j_m(kr)dr,\quad m=0,2.$$

[1] C. B. Walker, Phys. Rev. 103, 558 (1956).
[2] H. Curien and C. Deroche, Bull. soc. franç. minéral. et crist. 79, 102 (1956), have results equivalent to those of Walker[1] except for a greater scatter in their measurements.
[3] J. Laval, Compt. rend. 215, 359 (1942).
[4] R. W. James and G. W. Brindley, Phil. Mag. 12, 81 (1931). Their data are conveniently tabulated in A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), p. 782.
[5] See A. J. Freeman [Phys. Rev. 113, 169 (1959), preceding paper], for complete details.
[6] D. R. Hartree and A. J. Freeman (unpublished).
[7] C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).

[8] F. J. Corbató, Ph.D. thesis, Physics Department, Massachusetts Institute of Technology (unpublsihed).
[9] This notation is equivalent to that introduced by D. T. Keating and G. H. Vineyard, Acta. Cryst. 9, 895 (1956).

TABLE I. X-ray incoherent scattering function for aluminum.

sinθ/λ	f_{1s}	f_{2s}	f_{2p}	f_{3s}	f_{3p}	$f_{1s,2s}$	$f_{1s,3s}$	$f_{2s,3s}$	$f_{1s,2p}$	$f_{2s,2p}$	$f_{3s,2p}$
0	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.9985	0.9669	0.9678	0.6023	0.2650	0.0014	0.0002	0.0189	0.0172	−0.1288	0.0334
0.2	0.9942	0.8745	0.8788	0.1041	−0.0136	0.0051	0.0009	0.0590	0.0399	−0.2364	0.0387
0.3	0.9871	0.7411	0.7527	−0.0354	0.0063	0.0112	0.0022	0.0953	0.0499	−0.3082	0.0151
0.4	0.9773	0.5895	0.6128	−0.0185	0.0219	0.0191	0.0039	0.1107	0.0642	−0.3419	−0.0183
0.5	0.9649	0.4406	0.4778	0.0088	0.0222	0.0286	0.0060	0.1048	0.0770	−0.3407	−0.0449
0.6	0.9500	0.3089	0.3595	0.0192	0.0172	0.0392	0.0083	0.0856	0.0878	−0.3150	−0.0584
0.7	0.9330	0.2017	0.2624	0.0187	0.0126	0.0502	0.0109	0.0624	0.0969	−0.2751	−0.0609
0.9	0.8929	0.0626	0.1292	0.0088	0.0056	0.0726	0.0162	0.0238	0.1087	−0.1842	−0.0482
1.1	0.8465	0.0009	0.0567	0.0020	0.0020	0.0928	0.0212	0.0035	0.1133	−0.1069	−0.0301

sinθ/λ	$f_{1s,3p}$	$f_{2s,3p}$	$f_{3s,3p}$	$f_{2p,2p}$	$f_{3p,3p}$	$f_{2p,3p}^{(0)}$	$f_{2p,3p}^{(2)}$	$\Sigma|f_{ii}|^2$	$\mathfrak{F}$	$13-\mathfrak{F}$
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	13.00	13.00	0.00
0.1	0.0035	−0.0059	−0.3000	0.0128	0.2125	0.1226	−0.0029	10.29	10.72	2.28
0.2	0.0069	−0.0192	−0.1215	0.0463	0.1100	0.1356	−0.0060	8.19	8.97	4.03
0.3	0.0100	−0.0375	−0.0052	0.0918	0.0186	0.1371	−0.0018	6.55	7.80	5.20
0.4	0.0130	−0.0532	+0.0098	0.1345	−0.0019	0.1232	+0.0094	5.08	6.62	6.38
0.5	0.0156	−0.0613	−0.0003	0.1679	−0.0007	0.1008	0.0217	3.96	5.52	7.48
0.6	0.0177	−0.0614	−0.0083	0.1884	0.0035	0.0770	0.0307	3.20	4.58	8.42
0.7	0.0196	−0.0560	−0.0116	0.1962	0.0057	0.0563	0.0359	2.70	3.81	9.19
0.9	0.0220	−0.0387	−0.0100	0.1842	0.0076	0.0272	0.0368	2.11	2.72	10.28
1.1	0.0230	−0.0226	−0.0063	0.1543	0.0070	0.0117	0.0317	1.74	2.08	10.92

From Table I we see that the exchange contribution, i.e., the $\sum_i \sum_{j \neq i} |f_{ij}|^2$ terms in Eq. (2) of I, are by no means negligible.

Even though individually the exchange terms are small, there are so many of them that their total contribution is considerable. With increasing atomic number, the number of such exchange integrals rises rapidly and hence so does their sum. In fact, for aluminum, for sinθ/λ equal to 0.3 and 0.4, the exchange integrals amount to 25% of the total scattering intensity.

For aluminum, with only a single $3p$ electron outside a closed shell, the contribution to the total scattering due to the nonsphericity of the charge distribution is small since this nonspherical charge density is quite small. Furthermore, these terms contribute mainly at small sinθ/λ, the region in which the outer electronic scattering is most effective.

COMPARISON WITH EXPERIMENT

In Fig. 1, we show a comparison of our results, Curve C, with the experimental results of Walker (open circles) and some earlier measurements of Laval (closed squares) on aluminum. The dotted curve represents Walker's estimate of the best experimental curve. Also included are the results of several other theoretical calculations (referred to briefly above).

Curve A is a plot of the James and Brindley[4] values calculated from Eq. (1) of I. Self-consistent field wave functions without exchange were used in this calculation and only the $\langle j_0 \rangle$ terms in Table I of I were included. These values differ very markedly from the experimental data over the entire range in sinθ/λ, due in part to the many approximations that were made in the calculation.

Curve B was obtained by Walker from a modified Waller-Hartree calculation. For the core electrons he used the $\sum |f_{ii}|^2$ values of James and Brindley for a free aluminum atom, and the exchange contribution calculated for neon by Harvey et al.[10] To this was added the contribution of three conduction electrons, calculated for a free electron gas. For neon, Harvey et al.[10] only included the exchange contribution between the $2s$ and $2p$ electrons. All other exchange terms were totally neglected. This calculation shows better agreement with experiment than Curve A, but still shows substantial disagreement for high sinθ/λ. Again, by comparison with the earlier results of the preceding paper we recognize the many approximations made in this calculation as well.

The agreement between our results, Curve C, and experiment is quite good, within the estimated experimental error quoted by Walker, over the whole region of Walker's results. For low sinθ/λ the agreement with Laval's data is not as good, but since Laval made no estimate of the accuracy of his measurements it is difficult to state how large these deviations really are. (It is at low sinθ/λ that the experimental error is largest since there are many experimental difficulties connected with measurements at small scattering angles.)

Actually though, this deviation between theory and experiment at low sinθ/λ is to be expected since we have used a free-atom theory to predict the scattering from a crystal. In the crystalline environment it is the electronic distribution of the outer electrons which are most disturbed from their free-atom form. Since these outer electrons contribute mostly in the region of small sinθ/λ, it is in this region that we should expect the largest deviations with experiment to occur.

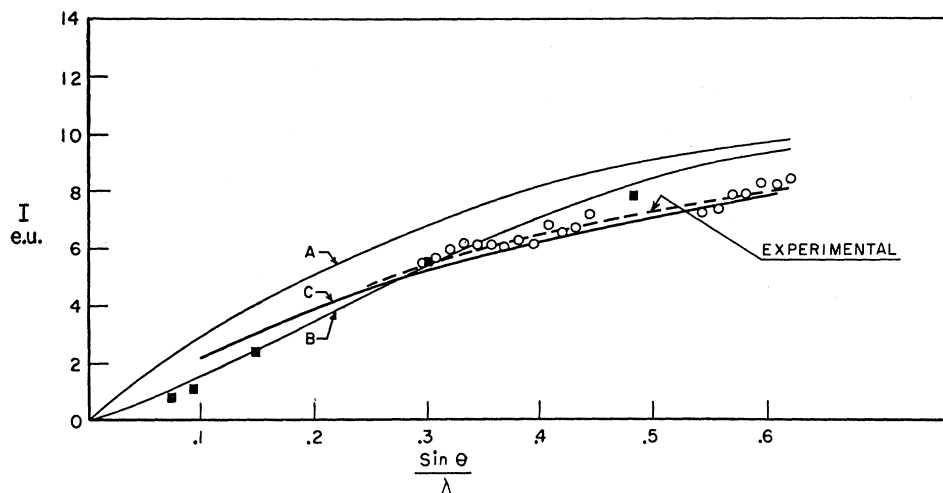[10] Harvey, Williams, and Jauncey, Phys. Rev. 46, 365 (1934).

FIG. 1. Compton scattering intensity for aluminum in electron units (e.u.). The open circles are the measurements of Walker, the closed squares those of Laval. Curve *A* is calculated from the Compton-Raman-Wentzel equation, Curve *B* is Walker's modified Waller-Hartree calculation and Curve *C* is the present result obtained from the complete Waller-Hartree theory.

There are of course other reasons for expecting the scattered intensities to be weaker than that predicted by the Waller-Hartree theory. As Curien[11] and Laval[3] have pointed out, the ejected electrons are not free electrons but must travel through the crystal. Therefore the number of allowed energy states for these electrons is not the continuum of states which exist for the free atom, but rather consists of a series of allowed and forbidden energy bands. Since the recoil electron may not occupy any of these forbidden states, this leads to a reduction of the Compton scattering for the crystal. This effect, however, is probably of greater importance for insulators and semiconductors than for metals.

CONCLUSION

Even though based on a free-atom theory, the Waller-Hartree equation has been found to predict, with good accuracy, the intensity of Compton scattering for crystalline aluminum for all but small values of $\sin\theta/\lambda$. The exchange terms in the scattering ex-

pression, Eq. (2) of I, are of great importance for obtaining these good results.

It is too soon to say whether this free-atom theory will yield the same good agreement with experiment for crystals other than aluminum. More experimental work, along the lines suggested by Curien, Walker, and Laval, is required, together with more new calculations (such as the one described here for aluminum), before the general validity and applicability of the theory is established. In the absence of a theory for crystalline scattering, the best theoretical calculation of the Compton scattering intensity is found from the Waller-Hartree equation using self-consistent field wave functions with exchange.

ACKNOWLEDGMENTS

[11] H. Curien, Revs. Modern Phys. 30, 232 (1958).