Extra Negative Term in the Incoherent Part of the Diffuse Scattering of X-Rays from Neon-Like Crystals

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Following the suggestion of Harvey, Williams and Jauncey that experimental evidence for the need of the Waller-Hartree extra negative term which arises from the Pauli exclusion principle can best be obtained in the diffuse scattering of x-rays from crystals, careful measurements of the S_{exp} values for NaF, MgO and SiC have been made at 295°K using the method of Jauncey and Claus. Various precautions are described. Since the theoretical S_{th} values depend somewhat critically upon the characteristic temperature Θ for a given crystal, a discussion of the determination of Θ from specific heat data is given. It is shown that for x-ray purposes the proper value for Θ is that obtained from specific heat data for fairly low temperatures even though the temperature at which x-ray scattering occurs may be fairly high. Tables of quantum-mechanical f and ΣE_r^2 values extend only to $(\sin \phi/2)\lambda = 1.1$. Beyond this the crystals approach neon gas in their scattering and it was found that Brown's analytical formula for neon gives better agreement with experiment than does Froman's extrapolation formula. The experimental results showed excellent agreement with the Waller-Hartree theory and thus give definite evidence for the operation of the Pauli exclusion principle on the outer shell electrons. Some remarks on the classical analog of the extra term are included. A special discussion of the results for SiC is given.

1. INTRODUCTION

THE theory of the diffuse scattering of x-rays from crystals leads to the formula[1]

$$S = S_{coh} + S_{inc}/(1 + \alpha \text{ vers } \phi)^3, \tag{1}$$

in which S_{coh} and S_{inc} refer respectively to the coherent and incoherent parts of the scattered rays. For crystals consisting of two kinds of atoms

$$S_{coh} = \{f_1^2(1 - e^{-M_1}) + f_2^2(1 - e^{-M_2})\}/(Z_1 + Z_2) \tag{2a}$$

and Waller and Hartree's theory of x-ray scattering[2] requires that

$$S_{inc} = 1 - \{\sum (E_{jj}^2)_1 + \sum (E_{jj}^2)_2\}/(Z_1 + Z_2)$$
$$- \{\sum_{j \neq k} |E_{jk}|_1^2 + \sum_{j \neq k} |E_{jk}|_2^2\}/(Z_1 + Z_2), \tag{2b}$$

in which the symbols have previously been defined[3] and the numerical subscripts refer to the two kinds of atoms. Because of its algebraic sign, the term containing the subscripts jk has been called the extra negative term.[4] Harvey, Williams and Jauncey[3] have pointed out that the most favorable situation for showing the

need for the extra negative term is in the diffuse scattering of x-rays from crystals. In addition, they have calculated the values of $\Sigma |E_{jk}|^2$ for neon. Values of f, the atom form factor, and of ΣE_{jj}^2 have been calculated by James and Brindley[5] and by Heisenberg,[6] respectively. Tables of these values are now given by Compton and Allison.[7] We have used the values for Mg^{+2}, Na^+, F^-, O^{-2} in calculating the theoretical values for our crystals of NaF and MgO.

Compton[8] remarks that there seems to be no exact classical analog of the extra negative term, although he suggests that it represents the constraints upon each electron's motion due to the presence of the other electrons in the atom. At a recent symposium on x-ray scattering, Jauncey[9] also suggested this idea of constraints between electrons. In his extension of the Raman-Compton[10, 11] classical theory of x-ray scattering, Jauncey[12] introduced the probability distribution function $p(z_1, z_2, \cdots z_n)dz_1dz_2\cdots dz_n$ for the probability of electrons 1, 2, $\cdots$ n being in $dz_1, dz_2 \cdots dz_n$ at $z_1, z_2, \cdots z_n$, respectively, from the center of the atom. Jauncey then made the simplifying assumption

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[1] G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).
[2] I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1929).
[3] G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).
[4] E. O. Wollan, Phys. Rev. **43**, 955 (1933).
[5] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).
[6] W. Heisenberg, Physik. Zeits. **32**, 737 (1931).
[7] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, pp. 781, 782.
[8] A. H. Compton, Phys. Rev. **47**, 367 (1935).
[9] G. E. M. Jauncey, Phys. Rev. **47**, 196 (1935).
[10] C. V. Raman, Ind. J. Phys. **3**, 357 (1928).
[11] A. H. Compton, Phys. Rev. **35**, 925 (1930).
[12] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

$$p(z_1, z_2, \cdots z_n) = p_1(z_1) \cdot p_2(z_2) \cdots p_n(z_n). \quad (3)$$

This means that the probability distribution function for any one electron is independent of the position of any other electron in the atom. This assumption leads in the case of crystals consisting of atoms of one kind or of monatomic gases to

$$S_{\text{inc}} = 1 - (\sum_{r=1}^{Z} E_r{}^2)/Z, \quad (4)$$

where for the rth electron

$$E_r = \int p_r \cos kz_r dz_r \quad (5)$$

and $k = 4\pi(\sin \phi/2)/\lambda$. If, however, the probability distribution function for one electron is not independent of the positions of the other electrons in the atom, the relation (3) no longer holds and S_{inc} is no longer given by (4). As an example of the change in S_{inc} caused by introducing constraints, let us consider the two models of the helium gas atom discussed by Compton.[11] In the first model each electron is at random on a sphere of radius b. In this case

$$p(z_1, z_2) = p_1(z_1) \cdot p_2(z_2), \quad (6)$$

where

$$\begin{aligned} p_1(z_1) = p_2(z_2) = 1/2b, \quad &-b < z < b \\ = 0, \quad &|z| > b \end{aligned} \quad (7)$$

and we arrive at

$$f = \sum_{r=1}^{Z} E_r = 2(\sin kb)/kb, \quad (8)$$

$$S_{\text{coh}} = f^2/Z = 2(\sin^2 kb)/k^2 b^2 \quad (9a)$$

and

$$S_{\text{inc}} = 1 - (\sin^2 kb)/k^2 b^2. \quad (9b)$$

In the second model, each electron is again on a sphere of radius b but the two electrons are always at opposite ends of a diameter. Now, although (7) is true, the relation (6) is not true. For the second model, Debye[13] gives

$$S = 1 + (\sin 2kb)/2kb. \quad (10)$$

According to the classical theory the coherent part of the rays scattered from an atom can be eliminated in all directions, except the Laue directions, by assembling many like atoms into a perfect lattice.[14] The scattering which does occur in the non-Laue directions is then incoherent. Using this criterion, we find that

$$S_{\text{inc}} = 1 + (\sin 2kb)/2kb - 2(\sin^2 kb)/k^2 b^2. \quad (11)$$

This expression differs from (9b) because of the electrons being constrained to move at the opposite ends of a diameter. Each model has the same atom form factor (8) and so for either model of helium gas S_{coh} is given by (9a).

A comparison of Williams' experimental S values[15] for NaF with theory indicates a better agreement when the extra negative term is included than when not.[3] However, the discrepancy between theory and experiment is too great for comfort; and, in view of the importance of the theory, a more accurate test of the formula was considered necessary, and so this present research was undertaken.

2. EXPERIMENTAL METHOD

Following the method described by Jauncey and Claus,[16] we used the continuous spectrum from a tungsten target tube operated at 34.3 kv peak and 8 ma. As always, great care was taken in evading Laue spots. The distribution of intensity in the continuous spectrum was obtained by reflection from calcite and is shown in Fig. 1. This curve is uncorrected for change in the reflecting power of the calcite for different wavelengths. Thicknesses of aluminum sufficient to reduce the intensity of the primary rays from 1.00 to 0.86, 0.61, 0.42, and 0.22, respectively, were determined experimentally. The reduction of total intensity in the continuous spectrum due to each of these thicknesses was calculated as previously described[16] and found to agree very well with each of the respective values just

13 P. Debye, Ann. d. Physik 46, 809 (1915).

14 This is evident from the fact that the double summation in Jauncey and Harvey's paper (Phys. Rev. 37, 1203 (1931)) becomes zero when the atom centers are always exactly at lattice points and there is thus no thermal motion.
15 P. S. Williams, Phys. Rev. 46, 83 (1934).
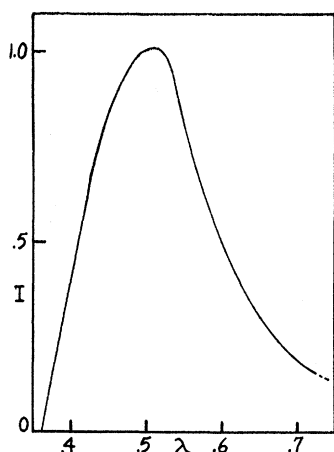16 G. E. M. Jauncey and W. D. Claus, Phys. Rev. 46, 941 (1934).

FIG. 1. Spectral distribution curve for the x-rays falling upon, but not penetrating through, the crystals.

given. It seemed better not to attempt any correction of the curve of Fig. 1.

Instead of comparing the intensity of the rays scattered from the crystal under observation with that of the rays scattered from paraffin as was usually done by Jauncey and Claus,[16] we always compared the intensity of the diffusely scattered rays with that of the primary rays penetrating the crystal. To do this we cut off a flash of primary rays of duration 1/60 sec. by means of a pendulum. We then calculated

$$S_{exp} = (R^2 W/ANZ\rho t) \cdot (2 \cos \phi/2)/(1+\cos^2 \phi)$$

$$\cdot (m^2 c^4/e^4) \cdot D_\phi/D, \quad (12)$$

where D_ϕ is the ion current due to the rays scattered in a direction ϕ, D is that due to the primary rays transmitted through the crystal slab, and the remaining quantities have previously been defined.[17] It is to be noted that the ratio D_ϕ/D is of the order 1/10,000. The disparity in the concentration of the ions in the ionization chamber is even greater than this because of the fact that the primary beam is fairly narrow. It was feared that there might be some unsuspected ion-recombination effect. We therefore reduced D from 1.00 to 0.66, 0.25, and 0.11 and obtained no certain change in the ratio D_ϕ/D, as compared with the corresponding theoretical value of D_ϕ/D, for a scattering angle of 30°. Since D_ϕ/D is not a function of D, we

[17] G. E. M. Jauncey and Ford Pennell, Phys. Rev. **43**, 505 (1933).
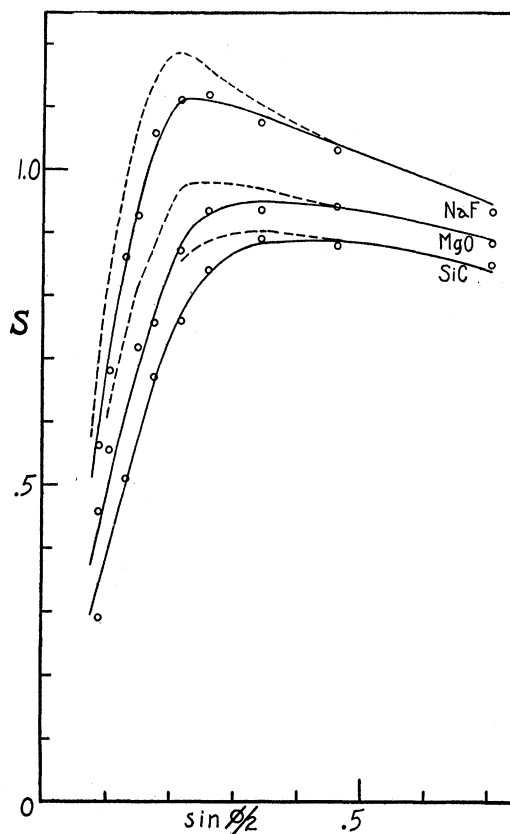

FIG. 2. Comparison of theory and experiment. Full curves include the Waller-Hartree extra negative term; broken curves do not.

conclude that the experimental D_ϕ and D are saturation values. Of course, we had, in addition, applied the usual test for saturation by varying the voltage across the ionization chamber. We estimate our experimental error at about 0.02 in the S_{exp} values.

The values of S_{exp} for single crystal slabs of NaF, MgO and SiC (carborundum) are given in Table I and are shown as circles in Fig. 2. The

TABLE I. S_{exp} values.

sin $\phi/2$	NaF	MgO	SiC
0.087	0.56	0.46	0.29
.104	0.68	0.55	—
.130	0.86	—	.51
.148	0.93	.72	—
.174	1.06	.76	.67
.216	1.11	.87	.76
.259	1.12	.93	.84
.342	1.08	.93	.89
.462	1.03	.94	.88
.707	0.93	.88	.85

values of ρt for the crystal slabs were: NaF, 0.349; MgO, 0.681; SiC, 0.326 g/cm². It is to be noted that our S_{exp} values are all absolute and that there has been no fitting of the experimental and theoretical values at any point.

3. COMPARISON WITH THEORY

The theoretical quantity S_{th} is defined by[17]

$$S_{\mathrm{th}}=\int\left\{S_{\mathrm{coh}}+\frac{S_{\mathrm{inc}}K_\phi T_\phi}{K_0(1+\alpha \text{ vers } \phi)^3}\right\}I d\lambda\Big/\int I d\lambda, \quad (13)$$

where I is a function of λ representing the distribution of intensity in the spectrum of the x-rays penetrating the crystal slab, so set that the normal to the slab bisects the angle of scattering. The spectral distribution curve shown in Fig. 1 is not the curve of I vs. λ used in (13) but is the distribution curve for the x-rays falling on the slab. Knowing the absorption coefficients for various wave-lengths in a given crystal slab and knowing its effective thickness $t/(\cos \phi/2)$, the curve of I vs. λ for the rays penetrating the crystal can easily be calculated from Fig. 1. There is a separate curve for each angle of scattering and for each crystal.

From (2a) we see that it is necessary to know the Debye-Waller exponents M_1 and M_2. In the case of cubic crystals consisting of atoms of nearly equal mass, M_1 may be taken as equal to M_2. This is the case for NaF. Also $M_1 \sim M_2$ when the experimental temperature, which for our experiments was 295°K, is considerably lower than the characteristic temperature of the crystal. This is the case for MgO and SiC. Waller's theory[18] shows that at temperatures below the characteristic temperature it is the mass per unit volume[19] which is involved in the formula for M, and so we have used the average atomic weight in this formula. But, before M can be calculated, the characteristic temperature Θ must be known. Shonka[20] has obtained $\Theta=442$°K for NaF by comparing the intensities of the various Debye-Scherrer circles for the powdered crystal at 295°K with the intensities of the corresponding circles for 86°K.

Unfortunately, we are unaware of any x-ray determination of Θ for MgO or SiC. We find that the uncertainties in the values of Θ as calculated from specific heat data lead to variations in S_{th} which are greater than our experimental error in S_{exp} and are a considerable fraction of the change in S_{th} expected as the result of the inclusion or otherwise of the Waller-Hartree extra negative term.

In order to obtain a method of calculating Θ from specific heat data which will be valid for x-ray purposes, we have taken the tabulated specific heat values for NaCl and KCl[21] and for NaF.[22] We have changed these values from C_p to C_v by means of the formulas[23]

$$C_p-C_v=C_p{}^2T\times .0214/T_m, \quad (14)$$

where T_m is the melting point, and

$$C_p-C_v=\beta^2 MT/K\rho, \quad (15)$$

where β is the coefficient of volume expansion, M the molecular weight, K the compressibility and ρ the density of the crystal. The values of C_v for our crystals determined by either formula are in good agreement, but lack of extensive thermal data makes (14) the more useful. We then compared the C_v values with a table of Debye's specific heat function[24] and found the corresponding Θ/T values. Knowing the temperature for each of these values, we have calculated values of Θ and have then plotted curves of Θ vs. Θ/T as shown in Fig. 3. It is seen that the points give evidence of falling on curves which approach a constant value. The dotted lines show the values of Θ which are satisfactory for x-ray purposes as found by Shonka for NaF, by James and Brindley[25] for KCl, and by James and Firth[26] for NaCl. It is seen that the x-ray value of Θ for each of these crystals corresponds to the constant value which is obtained from specific heat data at fairly low temperatures. The specific heat values of Θ for MgO[21] are also shown

[18] I. Waller, Diss. Uppsala (1925).
[19] Dr. C. Zener of this laboratory has informed us of this interesting theoretical fact.
[20] J. J. Shonka, Phys. Rev. 43, 947 (1933).

[21] Int. Crit. Tables, V, 91.
[22] Int. Crit. Tables, V, 100.
[23] See F. K. Richtmyer, Introduction to Modern Physics, (first edition) pp. 244, 245.
[24] See J. K. Roberts, Heat and Thermodynamics, p. 404.
[25] R. W. James and G. W. Brindley, Proc. Roy. Soc. A121, 155 (1928).
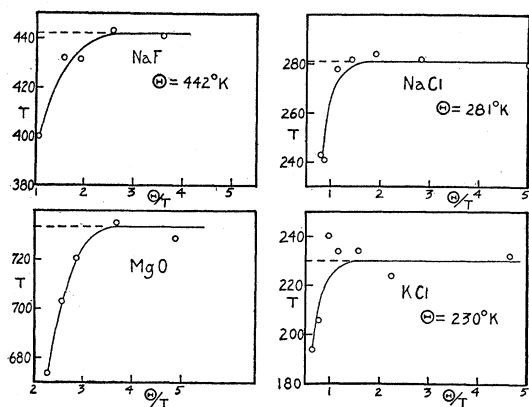[26] R. W. James and E. Firth, Proc. Roy. Soc. A117, 62 (1927).

FIG. 3. Characteristic temperature curves obtained from specific heat data. The value of Θ shown in the body of each graph is that most suitable for x-ray purposes. Errata: The ordinates should be labeled Θ instead of T.

in Fig. 3. It seems, therefore, that the x-ray value of Θ for MgO should be 734°K.

The rest of the calculation of the S_{th} values was done as described by Jauncey and Claus,[16] these values being averaged for ionization chamber window width and height and for cross-sectional area of the primary beam of x-rays at small angles of scattering. The full curves of Fig. 2 show the S_{th} values in which the Waller-Hartree extra negative term has been included, while the broken curves are for the omission of this term. The agreement of experiment with the Waller-Hartree theory is remarkably good. It should be noted that it is necessary in the case of MgO to use $\Theta = 734°K$ and not 674°K (shown as the lowest value in Fig. 3) in order to get an agreement between theory and experiment. If one assumes the Waller-Hartree theory to be correct, this means that the x-ray value of Θ for MgO is about 734°K. Our results also imply the excellence of the quantum-mechanical f and ΣE_r^2 values as calculated approximately by James and Brindley and by Heisenberg.[27]

The experimental points and theoretical curves for SiC are worthy of comment. The ions in NaF and MgO are neon-like, but there is no certainty that the Si and C atoms become quadruply ionized and therefore neon-like. Also we were hard put to it to determine Θ for SiC. The structure of this crystal is more complicated than that of NaF or MgO. Perhaps for this reason, when we tried to determine Θ by the method of Fig. 3, we found no tendency for the points to fall on a curve similar to those of Fig. 3. We therefore resorted to an average value which we took as 1023°K. Using this value and assuming the ions C^{-4} and Si^{+4}, we obtained the theoretical curves shown.[28] The numerical values of the Waller-Hartree extra negative term as worked out by Harvey, Williams and Jauncey[3] are for neon, and in this paper we have assumed these neon values to be valid for neon-like ions. The formulas given by Waller and Hartree only apply to cases where the outer shell of electrons is complete. We do not know how to correct for the operation of the Pauli exclusion principle in other cases, and so we have made no attempt to calculate values of S_{th} for SiC for possibilities other than Si^{+4} and C^{-4}. It is probably a coincidence, but it is possibly of interest, that the experimental points for SiC fall so well on the Waller-Hartree curve for the quadruply ionized atoms.

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[27] These values do not extend beyond $(\sin \phi/2)/\lambda = 1.1$ and some kind of extrapolation becomes necessary at the larger angles of scattering. We have found that Brown's (Phys. Rev. **44**, 214 (1933)) analytical formula for neon gives much better agreement with experiment for all three crystals than does Froman's extrapolation formula (Phys. Rev. **36**, 1339 (1930)).

[28] The following f and ΣE_r^2 values were necessary for our calculation of S_{th} values but were not available in the literature. Using the information contained in James and Brindley's paper[5] we have obtained

$(\sin \phi/2)/\lambda$												
0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
$f(C^{-4})$												
10.0	6.2	3.7	2.6	1.9	1.7	1.6	1.4	1.3	1.2	1.0	0.9
$\Sigma E_r^2(C^{-4})$												
10.0	5.8	3.1	1.65	1.4	1.3	1.0	0.8	0.7	0.6	0.5	0.4
$\Sigma E_r^2(Si^{+4})$												
10.0	9.4	8.3	6.8	5.2	4.0	3.1	2.5	2.0	1.8	1.65	1.5

These values should be useful to other workers in this field.