THE

PHYSICAL REVIEW

A Journal of Experimental and Theoretical Physics

VOL. 44, No. 3 AUGUST 1, 1933 SECOND SERIES

Diffuse Scattering of X-Rays from Sylvine. IV. Scattering at High Temperatures

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(Received June 13, 1933)

Effect of temperature on the diffuse scattering of Mo $K\alpha$ radiation from sylvine.—Intensity measurements have been carried out at 630°K and 1020°K which is about as close to the melting point (1049°K) as it is feasible to work. It is again found that the results are in good agreement with the formula $S=(f^2-F^2)/Z+(1-f^2/Z^2)/(1+\alpha \text{ vers } \phi)^3$ provided experimental values of F are used rather than assuming $F=fe^{-M}$ where M is given by the Debye-Waller formula.

I. INTRODUCTION

THE effect of temperature on the diffuse scattering from crystals has been considered both theoretically and experimentally in a number of papers.[1, 2, 3, 4, 5, 6, 7, 8] Debye, in a paper[1] concerned mainly with the effect of temperature on regular reflection, showed that for a simple cubic crystal consisting of point atoms the intensity of the diffuse scattering should be given by $(1-e^{-M})$ times the scattering from an amorphous substance; M is given by

$$M=\frac{6h^2}{mk\Theta}\left\{\frac{\phi(z)}{z}+\frac{1}{4}\right\}\frac{\sin^2\theta}{\lambda^2} \qquad (1)$$

if the existence of zero-point energy is assumed; if there is no zero-point energy the quantity $\frac{1}{4}$ in Eq. (1) is to be omitted. In this formula h is Planck's constant, k Boltzmann's constant, m the mass of a single atom, Θ the Debye characteristic temperature[9] of the crystal, $z=\Theta/T$ where T is the absolute temperature,

$$\phi(z)=(1/z)\int_0^z ydy/(e^y-1),$$

2θ the angle of scattering and λ the wave-length of the incident radiation. Later work by Waller[10] showed that M should be replaced by $2M$. If we define S as the scattering per electron[11] in terms of the Thomson value[12]

$$I_e=I_0(e^4/2m^2c^4)(1+\cos^2\phi),$$

where I_e is the scattering per unit solid angle in the direction ϕ and I_0 is the intensity of the incident radiation, i.e., if

$$S=I_\phi/ZI_e, \qquad (2)$$

where I_ϕ is the intensity of the scattered radiation and Z the atomic number of the scatterer,

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[1] P. Debye, Ann. d. Physik **43**, 49 (1914).

[2] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

[3] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931).

[4] Y. H. Woo, Phys. Rev. **38**, 6 (1931).

[5] G. E. M. Jauncey, Phys. Rev. **20**, 421 (1922).

[6] W. D. Claus, Phys. Rev. **38**, 604 (1931).

[7] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1925 (1931).

[8] G. G. Harvey, Phys. Rev. **43**, 707 (1933).

[9] P. Debye, Ann. d. Physik **39**, 789 (1912).

[10] I. Waller, *Uppsala Dissertation* 1925; Zeits. f. Physik **17**, 398 (1923).

[11] A. H. Compton, Phys. Rev. **35**, 925 (1930).

[12] J. J. Thomson, *Conduction of Electricity through Gases*, p. 325, 2nd edition.

then according to the Debye theory as modified by Waller the diffuse scattering from a simple cubic crystal consisting of point atoms should be given by

$$S = Z(1 - e^{-2M}). \tag{3}$$

Later work by Jauncey and Harvey[2, 3] showed that the scattering from such a crystal consisting of atoms having spatial extension should, on the classical theory, be given by

$$S = (f^2 - F^2)/Z + 1 - \left(\sum_1^Z E_r^2\right)/Z, \tag{4}$$

where f is the atomic structure factor of the atom at rest, F the atomic structure factor including the effect of thermal agitation and E_r the contribution to f due to the rth electron in an atom. If all the electrons are assumed equivalent then $\sum E_r^2 = f^2/Z$. If the atoms consist of points then $f = Z$ and since $F = fe^{-M}$ Eq. (4) reduces to Eq. (3), as of course it must. Simultaneously and independently Woo[4] showed that on taking account of the fact that part of the radiation is scattered incoherently due to the Compton effect and hence has its intensity diminished by the Breit-Dirac factor[13, 14] the scattering should be given by

$$S = \frac{f^2 - F^2}{Z} + \frac{1 - \left(\sum_1^Z E_r^2\right)/Z}{(1 + \alpha \text{ vers } \phi)^3}, \tag{5}$$

where $\alpha = h/mc\lambda$. The first term gives the coherent and the second the incoherent part of the scattering.

The experiments of Jauncey[5] on rocksalt and calcite and of Claus[6] on rocksalt showed that the Debye theory was inadequate to account for the observed effect and although Claus found that the Waller modification seemed to work at low temperatures it did not fit the facts at high temperatures and as he points out, it should not be expected to fit since the atoms are not points. Claus found that Eq. (4), (or Eq. (5)), seemed to account for the observed effect at high temperatures but not at low temperatures. Jauncey and Harvey[7] working with sylvine and using the same apparatus and method as used by Claus (inhomogeneous radiation and photographic measurement of intensity) obtained similar results at low temperatures. Results at high temperature were not published as it was felt that the measurements were not reliable. It may be here stated, however, that an apparent increase of about twenty percent in the intensity of the diffuse scattering was found at large angles whereas Eqs. (4) and (5) predict only a small increase. It is to be noted also that Claus found an apparent trend in the same direction for rocksalt. In view of the success of Eqs. (4) and (5) in correlating the scattering from gases[11, 15] and reflexion from crystals[16, 17] with the diffuse scattering from crystals[18, 19] and in predicting the absolute intensity of the diffuse scattering at room temperature[3, 20, 21, 22, 23] the apparent discrepancy with the results at other than room temperature was regarded with some suspicion. That this suspicion was justified, at low temperatures at least, may be seen from more recent work on sylvine at the temperature of liquid air[8] when homogeneous radiation is used and measurements are made with an ionization chamber and electrometer. The theory was there found to fit very closely. Accordingly the present investigation on the diffuse scattering from sylvine at high temperatures was undertaken.

II. Experimental

The apparatus used has been previously[23] described with the exception of the heating chamber. This consisted of a coil of Nichrome wire wound on a refractory core surrounding the steel crystal mounting. The whole was completely

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[13] G. Breit, Phys. Rev. **27**, 242 (1926).

[14] P. A. M. Dirac, Proc. Roy. Soc. **A111**, 405 (1926).

[15] E. O. Wollan, Phys. Rev. **37**, 862 (1931).

[16] R. W. James and Elsie M. Firth, Proc. Roy. Soc. **A117**, 62 (1927).

[17] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

[18] G. E. M. Jauncey, Phys. Rev. **38**, 1 (1931).

[19] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1071 (1931).

[20] G. G. Harvey, Phys. Rev. **38**, 593 (1931).

[21] G. E. M. Jauncey and P. S. Williams, Phys. Rev. **41**, 127 (1932).

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

[23] G. G. Harvey, Phys. Rev. **43**, 591 (1933).

inclosed in an asbestos container one-half inch thick, thin mica windows being provided for the x-rays. Temperatures were measured by a nickel-iron thermocouple beside the crystal just out of the x-ray beam. As the stray scattering from the furnace and crystal mounting was considerable and as Mo $K\alpha$ radiation is rather strongly absorbed in mica it was not deemed feasible to use the balanced filter method as in the previous work since the necessity of taking the difference of comparable currents, both of which are small, and again taking differences to correct for the stray scattering was considered too unreliable. Instead a rather thick ZrO_2 filter was used. This, however, will not effect the results to any appreciable extent, except possibly at small angles, since the radiation penetrating the filter was predominantly Mo $K\alpha$. The experiment then consisted in measuring the ratio, τ, of the ionization current with the crystal at temperature T to that with the crystal at room temperature (295°K) for a fixed scattering angle ϕ and various values of θ the angle between the primary beam and the normal to the crystal face, both above and below $\theta=\phi/2$ and interpolating to obtain this ratio for $\theta=\phi/2$. The values of this ratio, so measured, are given in Table I for 630°K and 1020°K.

TABLE I.

		$\tau_{630°\text{K}}$			$\tau_{1020°\text{K}}$		
ϕ	$(\sin\phi/2)/\lambda$	D-W	J-B	Exp.	D-W	J-B	Exp.
10°	0.123	1.37	1.43	1.40	1.77	2.10	2.22
20°	0.245	1.50	1.52	1.57	1.99	2.26	2.30
30°	0.365	1.32	1.35	1.35	1.53	1.64	1.64
40°	0.482	1.24	1.26	1.28	1.35	1.38	1.40
50°	0.596	1.17	1.18	1.18	1.22	1.23	1.27
60°	0.708	1.11	1.12	(1.10–1.15)	1.13	1.13	(1.10–1.15)
70°	0.804	1.07		(1.05–1.10)	1.07		(1.05–1.10)
80°	0.905	1.035		(1.00–1.05)	1.035		(1.00–1.05)
90°	0.995	1.015		(1.00–1.02)	1.015		(1.00–1.02)
100°	1.080	1.005		(1.00)	1.005		(1.00)
110°	1.154	1.00		(1.00)	1.00		(1.00)

III. DISCUSSION

We may write

$$S_1=(f^2-F^2)/Z \tag{6}$$

and

$$S_2=1-\left(\sum_1^Z E_r{}^2\right)/Z, \tag{7}$$

where S_1 is the coherent scattering factor and $S_2/(1+\alpha \text{ vers } \phi)^3$ the incoherent scattering factor. The sum of S_1 and S_2 will be denoted by $S_{\text{class.}}$, as usual, and gives the classical value of the total scattering. The actual scattering, as given by Eq. (5) may be written

$$S=S_1+S_2/(1+\alpha \text{ vers } \phi)^3. \tag{8}$$

However, neither $S_{\text{class.}}$ nor S is measured directly. What is actually measured is the ionization current produced by the scattered radiation or, in the case of the temperature effect, the ratio of the ionization currents at the two temperatures in question. If this ratio is denoted by τ then

$$\tau=\frac{S_{1,\,(1)}+TS_2(K_\phi/K_0)/(1+\alpha \text{ vers } \phi)^3}{S_{1,\,(2)}+TS_2(K_\phi/K_0)/(1+\alpha \text{ vers } \phi)^3}, \tag{9}$$

wherein it is assumed that F is the only quantity affected by temperature. $S_{1,\,(1)}$ is the value of S_1 at temperature T_1 and $S_{1,\,(2)}$ the value at T_2; the factor T is due to the fact that the incoherent radiation is more completely absorbed in the crystal itself.[24] K_ϕ is the percentage absorption of the incoherent radiation in the ionization chamber and K_0 the same quantity for the coherent radiation. Values of τ were calculated for the two temperatures 630°K and 1020°K with respect to 295°K. In these calculations f values of James and Brindley[25] were used and $\sum E_r{}^2$ was taken as f^2/Z. However, the values of τ are practically unaltered by making this assumption. In order to obtain values of F at high temperatures the following procedure was used. James and Brindley have measured[17] the integrated reflection from sylvine for a number of spectra at various temperatures and although it was found that the Debye-Waller theory breaks down at high temperatures the values of $(\lambda^2/\sin^2\theta)\log(\rho_T/\rho_{290})$ when plotted against temperature fall on a smooth curve which is approximately a parabola; ρ denotes the integrated reflexion and is given by

$$\rho=\frac{N^2\lambda^3}{2\mu}\frac{e^4}{m^2c^4}\left(\sum fe^{-M}\right)^2\frac{1+\cos^2 2\theta}{2\sin 2\theta}. \tag{10}$$

Hence from this empirical curve it is possible to obtain experimental values of ΔM, the change in the temperature factor M from 290°K to T°K,

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[24] G. E. M. Jauncey and O. K. Defoe, Phil. Mag. **1**, 711 (1926).

[25] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

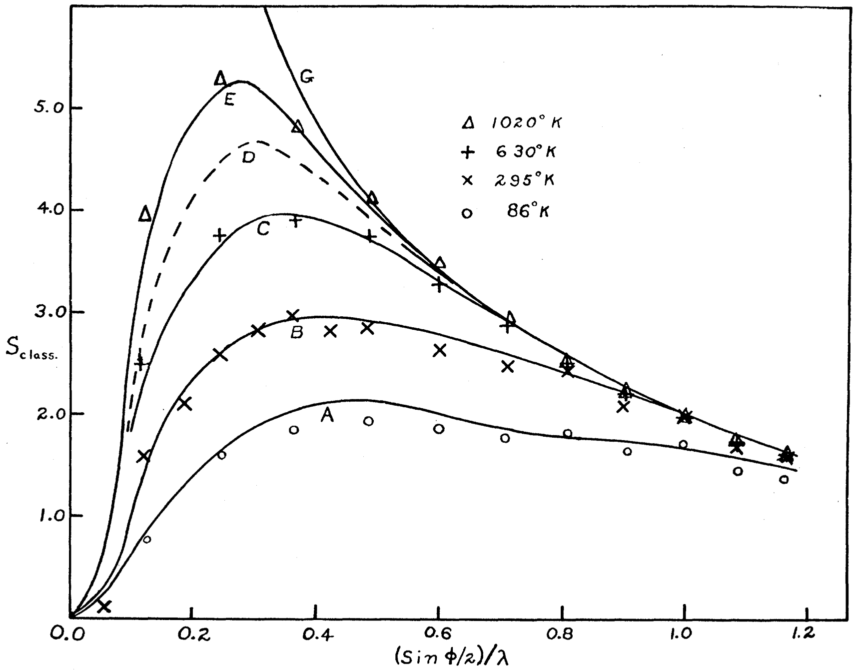

FIG. 1.

and thus values of $F_T = F_{290}e^{-\Delta M}$. James and Brindley's measurements extend only to 936°K and it was necessary to extrapolate to 1020°K. This may introduce considerable uncertainty, especially since the measurements of ρ at high temperature are subject to considerable error due to the extremely weak intensity. Further, sylvine melts at 1049°K and it is doubtful whether an extrapolation up to a temperature so near the melting point is justifiable. The values of the temperature factor τ so calculated are denoted by J–B in Table I. τ was also calculated assuming the Debye-Waller theory to be valid, i.e., by taking M from Eq. (1) and putting $F = fe^{-M}$. These values are also given in Table I, (D–W), together with the experimental ratios. At 630°K it does not make much difference whether M is taken from Eq. (1) or from James and Brindley's data and the experimental ratios cannot be said to distinguish between the two. At 1020°K, however, the difference is quite marked at small angles and here the experimental ratios definitely favor the results of James and Brindley. Fig. 1 shows the results plotted in the form of $S_{\text{class.}}$; the curves[8, 23] for 86°K and 295°K are also included for completeness. In obtaining these curves $S_{\text{class.}}$ for 295°K has been multiplied by τ_T to obtain $S_{\text{class.}}$ at T°K since, as pointed out for the low temperature work,[8] for radiation as soft as Mo $K\alpha$ and with almost complete absorption in the ionization chamber the ratio of the ionization currents is practically identical with the ratio of the $S_{\text{class.}}$ values. This fact enables experimental values of $S_{\text{class.}}$ to be obtained without making any assumption as to what quantities are affected by temperature. In general, for hard radiation and small absorption in the ionization chamber both TK_ϕ/K_0 and $TK_\phi/K_0(1+\alpha \text{ vers } \phi)^3$ may differ considerably from unity and the only way to obtain the *experimental* ratio of $S_{\text{class.}}$ or S values at two temperatures, without assuming that the entire change is due to a change in F, would be to carry out another experiment in which S_1/S_2 or $S_1/(S_1+S_2)$ was determined at the two temperatures, and this is a difficult thing to do with any accuracy.[26] In such a case it would be better merely to compare measured and calcu-

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[26] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **40**, 329 (1932).

lated values of τ as measurement of the diffuse scattering is probably not an accurate method for determining F.

Curve D in Fig. 1 is based on the Debye-Waller value of M at 1020°K while E is based on the results of James and Brindley. At 630°K the Debye-Waller curve is only slightly below the James and Brindley curve C and is omitted. At first sight it would appear that the results are in very close agreement with James and Brindley's values of F. Too much significance should not be attached to this close agreement since, as pointed out above, the F values at 1020°K are rather uncertain and the absolute value of $S_{\text{class.}}$ at small angles might thus be considerably different from that shown in curve E. This, however, can hardly be the case at large angles where any reasonable assumption concerning M leads to insignificant values of F. It is thus satisfactory to find that the large angle points closely follow curve G which is calculated on the assumption $F=0$ and gives the scattering from a monatomic gas[11] consisting of K^+ and Cl^-. At small angles, where the temperature effect is most marked, any reflected radiation present would tend to make the experimental values of τ too near unity so that the experimental points may be too low. The presence of radiation of shorter wave-length would also have the same effect since $\tau \rightarrow 1$ for large values of $(\sin \phi/2)/\lambda$. On the whole, however, it is felt that the experimental results are reasonably accurate and that there is no large discrepancy between the measured values of S and those calculated from Eq. (5).

To what extent the relation[19]

$$S_{\text{gas}} = (S + F^2/Z)_{\text{crystal}} \tag{11}$$

is verified at various temperatures, S_{gas} being taken as independent of temperature, may be approximately judged from the departure of the experimental points from the theoretical curves in Fig. 1. Jauncey and Pennell[22] have measured a quantity S_{th}, which is related to $S+F^2/Z$ for a powdered crystal, and have found good agreement between calculated and measured values. More recently[27] they have measured this quantity at low temperature and have found a slight decrease of one or two percent at small angles. They have suggested that this may indicate a change in f with temperature. However, as may be seen from their paper[22] S_{th} is equal to S_g plus a correction term involving F, this term being most important at small angles. Thus S_{th} should vary slightly irrespective of a change in f. That $S+F^2/Z$ decreases with decreasing temperature (or increases with increasing temperature) is not inconsistent with the results shown in Fig. 1 but the author would be unwilling to assert that his results are inconsistent with even the opposite conclusion. It would be an extremely difficult matter to measure the diffuse scattering from a single crystal to an accuracy of one percent due to the necessity of using as wide slits as possible in order to obtain a measurable intensity and yet narrow enough so as to be sure that only diffuse scattering is measured.

The author wishes to take this opportunity to express his appreciation to Professor Arthur H. Compton for his interest in the work and the use of the Ryerson Physical Laboratory.

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[27] Ford Pennell and G. E. M. Jauncey, Bull. Am. Phys. Soc. **8**, No. 4, p. 25 (1933). Paper presented at Chicago meeting, June, 1933.