taken from Brewer, Bromley, Gilles & Lofgren (1950). The heat of atomization D of sulphur at 298·16° K. is the value listed by Rossini *et al.* (1952), and the heats of atomization of the metals L_0 at 0° K. are the quantities adopted by Baughan (1954). The ionization potentials I of the elements at 0° K. have been taken from Moore (1949).

The $E(\mathrm{S} \rightarrow \mathrm{S}^{2-})$ values refer to 0° K. and are equal to the sum of the thermodynamic terms, corrected to 0° K. where necessary. The small energy changes between 0 and 298·16° K. have been estimated, and have been included in the calculation of the electron affinity, although they are not given explicitly in the table.

The good agreement between the values for the double electron affinity of sulphur obtained from the three sulphides supports the thesis that the forces operative in the crystals are those described above, which underlie the equation for lattice energy.

It appears that the probable error in the arithmetical mean for $E(\mathrm{S} \rightarrow \mathrm{S}^{2-})$ given in Table 2 as ±0·9 kcal., may be outweighed by unknown systematic errors. This error is therefore multiplied by a factor of 3 to denote the reasonable limit of the arithmetical mean. It is concluded that

$$E(\mathrm{S} \rightarrow \mathrm{S}^{2-}) \\ = -94{\cdot}5 \pm 2{\cdot}7 \text{ kcal. or } -4{\cdot}10 \pm 0{\cdot}1 \text{ e.V. } (0^\circ \text{ K.}).$$

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Contributions of One- and Two-Phonon Scattering to Temperature Diffuse Scattering

By Arthur Paskin

Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, U.S.A.

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Borie has recently given a procedure for obtaining the atomic scattering factor and the Debye–Waller factor independently from a set of X-ray measurements taken at one temperature. In analyzing the temperature diffuse scattering, use was made of Warren's formula derived for the case that the Debye–Waller factor is much less than unity and based on single-phonon scattering. Borie has extended Warren's formula into a region where the Debye–Waller factor is of the order of unity and where two-phonon processes are as important as one-phonon contributions. It is here shown why the Warren formula is a better approximation than the usual single-phonon temperature diffuse scattering term. A formula for two-phonon temperature diffuse scattering in powders is derived and compared with experiment. The importance of two-phonon scattering effects is also clearly demonstrated using Borie's temperature diffuse scattering data taken on copper powders.

Introduction

Borie (1956) has recently published a procedure for obtaining the atomic scattering factor f_0 and the Debye–Waller factor $2M$ independently from a set of measurements made at one temperature. The method makes use of the fact that the temperature diffuse scattering (TDS) and the intensity of a Bragg peak depend differently on f_0 and $2M$. Thus, the experimental data when combined with appropriate theoretical relationships yield two independent equations for f_0 and $2M$. These equations may, in turn, be solved for the appropriate values of f_0 and $2M$ at the given temperature. In applying this technique to copper powder, Borie made use of Warren's TDS formula (1953), which was derived for cubic powders when $2M$ is much less than unity and considering *in detail* only the effect of single-phonon scattering. It would *a priori* be expected that the extension of the Warren formula into the region where $2M$ is of the order of unity would evidence itself in appreciable departures between the expected and observed behavior of $2M$. The fact that this does not seem to be so suggests that the Warren formula is more valid than justified on the basis of the original approximations made in the derivation. In order to examine this point we shall here compare the effects of inclusion of two-phonon scattering on TDS with the relationship derived neglecting two-phonon scattering. It will further be shown in what way the Warren formula does contain some compensation for the higher-order phonon scattering effects. The data of Borie will also be re-examined in terms of the present results and evidence obtained for the importance of two-phonon scattering when $2M$ becomes of the order of unity.

General temperature diffuse scattering relationships

Before considering the effects on the TDS arising directly from two-phonon scattering processes, we shall first give the general TDS intensity relationship and see how Warren's formula approximates the general result. Using the notation of James (1948), I, the total intensity, is given by

$$I = |f_0|^2 \exp\,[-2M] \sum_n \sum_{n'} \exp\left[\frac{i2\pi}{\lambda}\mathbf{S}\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})\right] \times \exp\,[\sum_{\varphi j} G_{\varphi j} \cos 2\pi\mathbf{g}\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})]\,, \quad (1)$$

where $2M = \sum_{\varphi j} G_{\varphi j}$ is the Debye–Waller factor, f_0 the atomic scattering factor and $\mathbf{g}$ a vector in the direction of the wave normal of the lattice wave φj whose magnitude is the reciprocal wave length. Expanding the final exp [ ] term in (1) we arrive at the intensity in terms of the lth-order phonon process as follows:

$$\begin{aligned} I = |f_0|^2 \exp\,[-2M] \sum_n \sum_{n'} \exp\left[\frac{i2\pi}{\lambda}\mathbf{S}\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})\right] \\ \times \left\{1+\frac{1}{1!}\sum_{(\varphi j)} G_{(\varphi j)_1} \cos 2\pi\mathbf{g}_1\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})\right. \\ +\frac{1}{2!}\sum_{(\varphi j)_1}\sum_{(\varphi j)_2} G_{(\varphi j)_1} \cos 2\pi\mathbf{g}_1\,.\,(\mathbf{r}_n-\mathbf{r}_{n'}) \\ G_{(\varphi j)_2} \cos 2\pi\mathbf{g}_2\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})+\ldots \\ +\frac{1}{l!}\sum_{(\varphi j)_1}\sum_{(\varphi j)_2}\ldots\sum_{(\varphi j)_l} G_{(\varphi j)_1} \cos 2\pi\mathbf{g}_1\,.\,(\mathbf{r}_n-\mathbf{r}_{n'}) \\ \times G_{(\varphi j)_2} \cos 2\pi\mathbf{g}_2\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})\ldots G_{(\varphi j)_l} \cos 2\pi\mathbf{g}_l\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})\,, \\ (2) \end{aligned}$$

where the first term in (2) is the Bragg reflection term (zero-phonon process), the second term arises from a one-phonon process, the third term from a two-phonon process and the $(l+1)$th term from a l-phonon process. Converting the cosine terms to appropriate sums of exponentials, the sum over n and n' can be performed and the resultant expression is

$$\begin{aligned} I = |f_0|^2 \exp\,[-2M]\left\{I_0(\mathbf{S}/\lambda)+\frac{1}{1!}\sum_{(\varphi j)_1} G_{(\varphi j)_1} I_0(\mathbf{S}/\lambda+\mathbf{g}_1)\right. \\ +\frac{1}{2!}\sum_{(\varphi j)_1}\sum_{(\varphi j)_2} G_{(\varphi j)_1} G_{(\varphi j)_2} I_0(\mathbf{S}/\lambda+\mathbf{g}_1+\mathbf{g}_2)+\ldots \\ +\frac{1}{l!}\sum_{(\varphi j)_1}\sum_{(\varphi j)_2}\ldots\sum_{(\varphi j)_l} G_{(\varphi j)_1} G_{(\varphi j)_2}\ldots G_{(\varphi j)_l} \\ \times I_0(\mathbf{S}/\lambda+\mathbf{g}_1+\mathbf{g}_2+\ldots+\mathbf{g}_l)\,, \quad (3) \end{aligned}$$

where $I_0(\mathbf{X}) = \sum_n \sum_{n'} \exp\,[i2\pi\mathbf{X}\,.\,(\mathbf{r}_n-\mathbf{r}_{n'})]$. Denoting all the terms excluding the Bragg term as $I_{TD} = I_{TD1}+I_{TD2}+\ldots+I_{TDl}$, where the numerical subscript refers to the lth-phonon process, we are now in a position to examine the Warren formulation. Excluding for the moment the simplifications that Warren makes about the form of $G_{\varphi j}$, the major approximation consists of limiting himself to the case $2M$ much less than unity and therefore in assuming that $I = I_{TD1}$. While this is a good approximation for $2M$ less than unity it is a poor approximation as $2M$ becomes greater than unity—a region where Borie applied Warren's formulation. Nevertheless, the Warren formula appeared to be more successful than might have been supposed and the reason for this becomes evident as we examine the final form of I_{TD1} chosen by Warren. Instead of directly using the equation for I_{TD1} Warren manipulated the form as follows:

$$I_{TD1} = |f_0|^2 \exp\,[-2M] \sum_{(\varphi j)_1} G_{(\varphi j)_1} I_0(\mathbf{S}/\lambda+\mathbf{g}_1)\,, \quad (4)$$

$$\cong [|f_0|^2(1-\exp\,[-2M])] \sum_{(\varphi j)_1} G_{(\varphi j)_1} I_0(\mathbf{S}/\lambda+\mathbf{g}_1)/[\sum_{\varphi j} G_{\varphi j}] \quad (5)$$

by replacing $2M$ by $(\exp\,[2M]-1)$, a reasonable approximation for $2M$ much less than unity. The choice of (5) over (4) seems to have been motivated by the desire to obtain a form readily comparable with $I_D(\text{Debye}) = N|f_0|^2(1-\exp\,[-2M])$ derived with the assumption of independent vibrations. For $2M \ll 1$, (4) and (5) are of course almost identical; however, for $2M \gtrsim 1$, (5) contains additional terms proportional to $(2M)^2$, $(2M)^4$, etc. which are somewhat similar to terms appearing in the more general formula for I_{TD} as given by (3). Comparing (3) and (5) we find that the degree to which (5) approximates the general relationship in the region $2M \gtrsim 1$ depends on the degree to which

$$\begin{aligned} \mathscr{R} &= \sum_{(\varphi j)_1} G_{(\varphi j)_1} I_0(\mathbf{S}/\lambda+\mathbf{g}_1)/[\sum_{\varphi j} G_{\varphi j}] \\ &= \sum_{(\varphi j)_1}\sum_{(\varphi j)_2} G_{(\varphi j)_1} G_{(\varphi j)_2} I_0(\mathbf{S}/\lambda+\mathbf{g}_1+\mathbf{g}_2)/[\sum_{\varphi j} G_{\varphi j}]^2 \\ &= \sum_{(\varphi j)_1}\sum_{(\varphi j)_2}\ldots\sum_{(\varphi j)_l} G_{(\varphi j)_1} G_{(\varphi j)_2}\ldots G_{(\varphi j)_l} \\ &\quad \times I_0(\mathbf{S}/\lambda+\mathbf{g}_1+\mathbf{g}_2+\ldots+\mathbf{g}_l)/[\sum_{\varphi j} G_{\varphi j}]^l\,. \quad (6) \end{aligned}$$

That these terms are in general not equal becomes apparent in examining the details of the numerators of (6). Nevertheless, the use of I_{TD1} (Warren) rather than I_{TD1} is a better approximation for the case examined by Borie. It will be shown that whereas the use of (4), which includes in detail only single-phonon contributions, leads to wide divergences, the use of (5) gives better results. A further analysis which separates the data into one- and two-phonon contributions also shows the importance of the two-phonon scattering process.

One- and two-phonon contributions to TDS

We shall now examine in detail I_{TD1}, I_{TD1} (Warren) and I_{TD2}. Considering first I_{TD1}, we can perform the sum over φj as described in James and we find that at room temperature

$$I_{TD1} = N^2|f_0|^2 \exp[-2M] \times \left(\frac{kT}{4\pi^2 mN|\mathbf{g}|^2}\right) \sum_j \frac{1}{v_{\varphi j}^2} (\varkappa \mathbf{S}.\mathbf{e}_{\varphi j})^2 , \quad (7)$$

where T is the temperature, m the mass of the atom, and $v_{\varphi j}$ the velocity of the lattice wave. By assuming all lattice waves have the same average velocity V, the sum over the j independent waves can be performed and we find

$$I_{TD1} = N|f_0|^2 \exp[-2M] \left(\frac{kT}{mV^2}\right)\left(\frac{\sin\theta}{\lambda}\right)^2 \frac{1}{|\mathbf{g}|^2}, \quad (8)$$

$$\cong N|f_0|^2 \exp[-2M](2M_D) g_{\text{max.}}^2 / 3|\mathbf{g}|^2 . \quad (9)$$

Here $g_{\text{max.}}$ is the radius of a sphere of volume equal to each Brillouin zone and we have also been careful to differentiate between $2M$, as earlier defined, and $2M_D$, which uses the Debye model of a lattice to relate V to the Debye characteristic temperature, which in turn can be related to the Debye–Waller *calculation* of $2M$. Carrying out the appropriate integrations within a Brillouin zone as described by Warren for powders, we obtain the appropriate average intensity $\bar{I}$, thus,

$$\bar{I}_{TD1} = (N|f_0|^2 \exp[-2M] 2M_D) \times \left[\frac{a^2 g_{\text{max.}}^2}{6X} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \ln \frac{a g_{\text{max.}}}{|X - X_{hkl}|}\right]. \quad (10)$$

Here a is the edge of a cubic cell, $X = 2a \sin\theta/\lambda$, $X_{hkl} = 2a \sin\theta_{hkl}/\lambda$ and j_{hkl} is the multiplicity factor. $\bar{I}_{TD1}$(Warren), the Warren formula for $\bar{I}_{TD1}$, is obtained by setting $\exp[-2M](2M_D) = (1 - \exp[-2M])$ and replacing $g_{\text{max.}}$ for a face centered cubic by $(3/\pi)^{\frac{1}{3}}/a$.

Making the same sort of approximations described above (see the Appendix for details), we find that $\bar{I}_{TD2}$ is given by

$$\bar{I}_{TD2} = [N|f_0|^2 \exp[-2M](2M_D)^2/2] \times \left\{\frac{\pi^3 a^4 g_{\text{max.}}^4}{18X} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} [a g_{\text{max.}} - |X - X_{hkl}|]\right\}. \quad (11)$$

Comparison of theory and experiment

In this section we shall examine Borie's TDS data on copper powders in terms of $\bar{I}_{TD1}$, $\bar{I}_{TD1}$ (Warren) and $\bar{I}_{TD1} + \bar{I}_{TD2}$. That is we shall see to what degree the experimental data I_{TD} (exp.) can be approximated over a wide range of $(\sin\theta/\lambda)$ by formulae considering only one-phonon processes and the formula that takes both one- and two-phonon effects into account. Denoting $I_{TD}(\text{exp.})/(N|f_0|^2 \exp[-2M][\,])$ by $\mathscr{I}$ (the $[\,]$ refers to the bracketed term in (10)) we observe that if only the single-phonon process is important $\mathscr{I}$ must be proportional to $2M_D$, which in turn is proportional to $(\sin\theta/\lambda)^2$. Thus, the plot of $\mathscr{I}$ against $(\sin\theta/\lambda)^2$ shown in Fig. 1 should be a straight line for the one-phonon process. The fact that it is not shows that higher-phonon processes are contributing. If only one- and two-phonon processes are important, then a plot of $\mathscr{I}/(\sin\theta/\lambda)^2$ against $(\sin\theta/\lambda)^2$ should be a straight line provided on the average, R, the ratio of the braced term of (11) to the bracketed term of (10), is independent of $(\sin\theta/\lambda)^2$. That this is so is readily seen in Fig. 1. In Fig. 1 we also give a plot of $\ln(\mathscr{I}+1)$ against $(\sin\theta/\lambda)^2$, which should be a straight line if $\bar{I}_{TD1}$ (Warren) somehow approximates $\bar{I}_{TD1} + \bar{I}_{TD2}$. This is also found to be the case; however, the values of $2M_D$ obtained using the one- and two-phonon formula and the Warren formula differ considerably. Thus, at $(\sin\theta/\lambda) = 1$, we find that $2M_D$ is 1·3 using the Warren approximation and 0·76 using the one- and two-phonon approximation. In the light of the

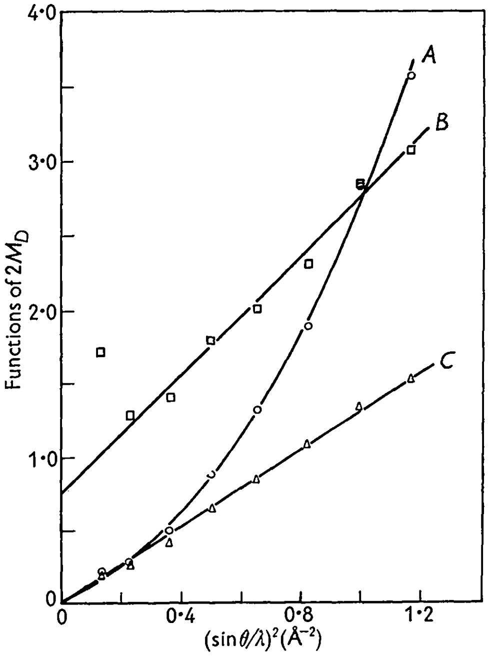

Fig. 1. Curve A: values of $\mathscr{I}$; curve B: values of $\mathscr{I}/(\sin\theta/\lambda)^2$ and curve C: values of $\ln(\mathscr{I}+1)$. At $(\sin\theta/\lambda) = 0$, $2M/(\sin\theta/\lambda)^2$ is given by the slopes of curves A and C and the ordinate of curve B.

marked difference in the two values, we further checked the reasonableness of the one- and two-phonon approximation by comparing calculated and observed values of R. We find that in the region between the 600 and the 620 peak, the theoretical ratio is $R = 6{\cdot}9$, whereas the observed ratio is 7·3. This agreement certainly supports the reasonableness of the separation of I_{TD} into its I_{TD1} and I_{TD2} components, albeit the agreement between the theoretical and experimental values of R is better than might be expected.

APPENDIX

The two calculations of I_{TD2} (Olmer, 1948; Walker, 1956) in the literature differ somewhat in their physical assumptions but are alike in that their results are given in numerical, tabular form. We shall here give a third derivation that does give a closed-form expression, which is useful for powder work. At room temperature in accord with previous assumptions in deriving $\bar{I}_{TD1}$, I_{TD2} may be written as

$$I_{TD2} = \frac{|f_0|^2}{2}\exp\left[-2M\right]\left(\frac{2M_D}{3}\right)^2 a^6 g^4_{\mathrm{max.}} \times \int\frac{d\mathbf{g}_1}{|\mathbf{g}_1|^2}\int\frac{d\mathbf{g}_2}{|\mathbf{g}_2|^2} I_0(\mathbf{S}/\lambda+\mathbf{g}_1+\mathbf{g}_2)\,. \quad \text{(A-1)}$$

Here the sums over g_1 and g_2 of (3) have been replaced by integrals over the appropriate phase-cells. The integral over $d\mathbf{g}_2$ is readily performed (see James for the procedure used in calculating I_{TD1}) and we obtain

$$I_{TD2} = N\frac{|f_0|^2}{2}\exp\left[-2M\right]\left(\frac{2M_D}{3}\right)^2 a^3 g^4_{\mathrm{max.}}\int\frac{d\mathbf{g}_1}{|\mathbf{g}_1|^2|\mathbf{Y}-\mathbf{g}_1|^2}\,,$$
$$= \xi\int d\mathbf{g}_1/[|\mathbf{g}_1|^2|\mathbf{Y}-\mathbf{g}_1|^2]\,, \quad \text{(A-2)}$$

where $\mathbf{g}_1+\mathbf{g}_2 = \mathbf{Y}$ is the vector in reciprocal-lattice space joining $\mathbf{S}/\lambda$ and the appropriate reciprocal-lattice point. By choosing a coordinate system such that z is along $\mathbf{Y}$ and the y–z plane contains $\mathbf{g}_1+\mathbf{g}_2$, (A-2) becomes

$$I_{TD2} = \xi\int_0^{2\pi} d\varphi\int_{\theta_{\mathrm{min.}}}^{\theta_{\mathrm{max.}}} d\theta\,\sin\theta/(Y^2+g^2-2Yg\cos\theta)\,, \quad \text{(A-3)}$$

where θ and φ are the usual polar angles in the rotated coordinate system, and, for a particular $|\mathbf{Y}|$, the minimum and maximum values are obtained by the conditions that $\mathbf{Y} = \mathbf{g}_1+\mathbf{g}_2$ and $|\mathbf{g}_1| \leq g_{\mathrm{max}}$ and $|\mathbf{g}_2| \leq g_{\mathrm{max.}}$. Equation (A-3) can now be integrated and the results given in series form for all values of $|\mathbf{Y}|$. However, in powder work it is preferable to have a simple, closed-form approximate relationship to an exact complicated expression for (A-3). We have found that the solution of I_{TD2} for $|\mathbf{Y}|/g_{\mathrm{max.}} \ll 1$ may be extended over the whole range of $|\mathbf{Y}|/g_{\mathrm{max.}} \leq 1$ without serious error. Thus, we find

$$I_{TD2} \cong \xi\pi^3/|\mathbf{Y}| = Zg_{\mathrm{max.}}/|\mathbf{Y}|\,, \quad \text{(A-4)}$$

a useful approximation. It is interesting to note that if for comparison purposes we assume that the longitudinal and transverse velocities in Walker's calculation are equal (in accord with a similar assumption made here), then (A-4) is a reasonable approximation to his results despite the more complicated dispersion relationship used by Walker. In Table 1 we compare values of I_{TD2}/Z as calculated from (A-4) and as taken from Walker's results.

Table 1. *Comparison of I_{TD2}/Z from Walker with present calculation*

$\frac{I_{TD2}}{Z}$	Walker	∞	5·4	2·5	1·9	1·4	0·76
	(A-4)	∞	5·0	2·5	1·7	1·3	1·0
$\lvert\mathbf{Y}\rvert/g_{\mathrm{max.}}$		0	0·2	0·4	0·6	0·8	1·0

In order to obtain a useful formula for powder work we must average I_{TD2} over the appropriate Brillouin zones. Although a more exact calculation would require the averaging over two Brillouin zones, we have made use of the fact that our exact calculation of I_{TD2} shows that it drops off quite rapidly when $|\mathbf{Y}|/g_{\mathrm{max.}} > 1$ and hence we neglect the contribution from other than the first Brillouin zone. Taking the average of I_{TD2} over a single Brillouin zone, we find

$$\bar{I}_{TD2} = \frac{\xi\pi^3 a}{2X}\sum_{hkl}\frac{j_{hkl}}{X_{hkl}}\left[ag_{\mathrm{max.}}-|X-X_{hkl}|\right]\,, \quad \text{(A-5)}$$

where $X = 2a\sin\theta/\lambda$, $X_{hkl} = 2a\sin\theta_{hkl}/\lambda$ and j_{hkl} is the multiplicity factor.

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