

stoichiometry are obvious (see, for example, Allpress, 1972).

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Temperature Dependence of Integrated Thermal Diffuse Scattering

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The temperature dependence of the integrated thermal diffuse scattering (T.D.S.) surrounding Bragg reflexions is discussed, with particular reference to cryogenic applications. Detailed calculations of the T.D.S. and its ratio to the Bragg intensity are presented for NaCl over the range 0 to 800°K. The T.D.S. includes not only the one-phonon contribution but also multiphonon processes. The temperature dependence of the T.D.S.-to-Bragg ratio is shown to fall off more quickly at low temperatures than the Debye-Waller exponent values. Some insight is gained into the importance of multiphonon processes, and it is concluded that there is much to be gained both in the reduction of T.D.S. and in the increase in intensity of higher-order reflexions by cooling to liquid-nitrogen temperatures.

1. Introduction

There is a growing interest in the application of cryogenic techniques (Coppens, 1972) to cool a single crystal sample which is being studied by X-ray diffraction. Two of the principal reasons for cooling are to increase the intensity of the weaker reflexions and to reduce the thermal diffuse scattering (T.D.S.) corrections which have to be made to all the observed Bragg intensities. These corrections may be large at room temperature but the difficulty of making them for most crystals has led to a lack of confidence in current procedures. In addition, the temperature dependence is considered only in the high-temperature limit (e.g. Warren, 1969, Jen-

nings, 1970) and as a result there are no reliable estimates of the reduction in the T.D.S. to be expected on cooling to cryogenic temperatures. Hence in the following paragraphs this temperature dependence is discussed and accurate figures for the dependence of the (integrated) T.D.S. surrounding Bragg peaks are shown for NaCl. This substance has been widely studied by crystallographers and is used here as a test material because good thermal data are available. Its Debye temperature is almost 300°K.

2. The thermal diffuse scattering

The starting point for the calculation is the numerical technique of Reid & Smith (1970a) used to find the

total phonon scattering at any point in reciprocal space. As a by-product of their calculation, numerical values for the integrated diffuse scattering over a spherical region of radius r surrounding a Bragg peak are obtained. The integrated one-phonon scattering by phonons with a (small) wave vector within this region is obtained and *also* the contribution from all multiphonon processes. Such processes may include any number of these *small* wave vectors (2, 3, 4 . . .) as well as those processes which involve, in a sample over the whole Brillouin zone, two or more larger wave vectors whose sum exactly equals a reciprocal-lattice vector. Strictly speaking this procedure overestimates the multiphonon contribution because the sum of the wave vectors of the small phonons will sometimes be outside the spherical region. However the multiphonon terms increase rapidly when very small wave vectors are involved and this leads to most of the multiphonon scattering coming from processes where the sum of the wave vectors involved lies within the spherical region. An integration shows that over 80% of the two-phonon scattering comes from the region of interest and about half of the three and four-phonon scattering. In practice this introduces no appreciable error since, if multiphonon processes are sufficiently important for the approximation to be poor, it is unlikely that there will be any interest in the Bragg peak. The T.D.S. will be at least as large as the Bragg scattering and the Debye-Waller factor will most probably have reduced the intensity to below the normal observable limit.

In general the best eigendata are used in the numerical calculation of the next section but within the region of the sphere the acoustic branches are assumed linear and isotropic and the optic branches flat. These approximations are almost always made in integrated T.D.S. calculations (Willis, 1969) and should introduce very little error for NaCl.

The important features of the calculation are that multiphonon processes are included and the temperature dependence of the scatter is not approximated. Exact expressions are given by Reid & Smith (1970a) but the results can be understood if one keeps in mind that they lead to a temperature dependence of the observed scatter of the form

$$I \propto |f|^2 \exp[-2W(T)] \exp[K^2\{a + bTr_z\mathcal{J}(T)\}] \quad (1)$$

missing out the sums over different atom types. Equation (1) gives the most important contribution which comes from the small-wave-vector phonons. f is the scattering factor of the atom, $W(T)$ the Debye-Waller term, \mathbf{K} the scattering vector (whose magnitude is $(h^2 + k^2 + l)^{1/2}$ in units of $2\pi/\text{lattice constant}$), T the temperature and a and b known constants determined principally by elastic data. $\mathcal{J}(T)$ is a definite integral given by

$$\mathcal{J}(T) = \frac{1}{y} \int_0^y \frac{xdx}{(e^x - 1)}, \quad y \propto \frac{r_z}{k_B T}, \quad (2)$$

and whose value increases monotonically from 0 to 1 as T goes from 0°K to high-temperature limit (Abramovitz & Stegun, 1965). If the exponential of equation (1) is expanded, the first term gives the Bragg scatter and the next term the one-phonon scatter. Therefore the one-phonon contribution will be

$$I_1 \propto |f|^2 \exp[-2W(T)] K^2 \{a + bTr_z\mathcal{J}(T)\} \quad (3)$$

$$\xrightarrow[\text{temp.}]{\text{high}} |f|^2 \exp[-2W(T)] K^2 b r_z T. \quad (4)$$

The usual form quoted in the high-temperature limit is given by equation (4).

Although the temperature dependence of equation (1) is determined by the term $T\mathcal{J}(T)$, the crucial parameter which governs whether there will be a departure from the high-temperature limit is the radius of the sphere, r_z . In this sense it is the modes at the boundary of the sphere which determine the temperature dependence and not those near the centre. For the calculations, temperature-dependent Debye-Waller factors (Reid & Smith, 1970b) and lattice constants were used at all temperatures. Below room temperature, the temperature dependence of the elastic constants and optic frequencies was also taken into account.

3. Numerical results

Choosing the volume of the sphere to occupy 1/500th of the Brillouin zone gives the ratio of ($I_{T.D.S.}/I_{\text{Bragg}}$) shown in Fig. 1 for a range of lengths of scattering vector and for three temperatures. At room temperature, the variation with K for the smaller K values (less than $8 \times 2\pi/d$, where d is the lattice constant) nearly follows the square law showing that one-phonon processes are dominant for this volume. For higher-index reflexions, multiphonon effects are important even at room temperature. However by the time the temperature has been reduced to near that of liquid nitrogen, multiphonon effects have been virtually frozen out over the whole range of K values. Nevertheless, there is still a substantial reduction in the T.D.S.-to-Bragg ratio to be gained by reducing the temperature to the liquid-helium level. This is emphasized in more detail in Fig. 2 which shows the temperature dependence of three typical peaks covering the K range over temperatures from 0–800°K. At higher temperatures, the upward curvature which destroys the linearity is again due to multiphonon effects. As a rough guide, ignoring the multiphonon contribution is likely to lead to an underestimate of the integrated T.D.S. intensity by at least 20% if the one-phonon scatter is 40% of the Bragg intensity. It has sometimes been suggested that the ratio of T.D.S. to Bragg intensity involves similar temperature factors to the Debye-Waller B terms which occur in the Debye-Waller exponent,

$$W(T) = B \sin^2 \theta / \lambda^2.$$

Equation (3) shows that the T.D.S.-to-Bragg ratio falls away considerably faster than the B terms at low temperatures because of the reduction of the integral $\mathcal{J}(T)$, and this is borne out in Fig. 2.

It is also of interest to look individually at the variation of the Bragg intensity and the quite complicated variation of the T.D.S. as a function of temperature. These are shown in Fig. 3(a) and (b) each expressed as a percentage of their values at 295°K for a range of Bragg reflexions along the [100] axis. For the low-index reflexions there is a continuous increase with temperature of the integrated T.D.S. owing to the increasing occupation numbers of the lattice modes. For the high-index peaks the occupation numbers initially increase the scattering below liquid-nitrogen temperatures but then the large Debye-Waller term takes over, giving rise to a maximum in the scattering. Nearer the melting point the multiphonon terms start to overcome even the Debye-Waller term and the intensity begins to rise again. If one goes to many times the Debye temperature, by which time NaCl has melted but many materials are still solid, the multiphonon terms dominate for all peaks and the diffuse scattering rapidly increases non-linearly with temperature. The same trends are found with Bragg reflexions in other directions. Fig. 3(b) shows the remarkable gain in the Bragg intensity of higher-order reflexions at low temperature.

The restriction of the foregoing discussion to one particular size of sphere has no special significance. The larger the sphere, the more important are multiphonon effects at a given temperature but equation (1) suggests how this can be taken into account. Since a is small and $\mathcal{J}(T)$ is not strongly dependent on r_z for the range of interest,

$$\ln \left(1 + \frac{\text{T.D.S.}}{\text{Bragg}} \right) \propto r_z \quad (5)$$

giving the scaling to different sphere sizes within the limits of the approximations used. In practice, equation (5) was tested up to a sphere occupying 1/100th of the zone and was found to be accurate to a few percent, even for the highest-index reflexions at room temperature where the T.D.S. intensity exceeded the Bragg intensity.

In actual practice, T.D.S. corrections to observed intensities are made by first subtracting a background obtained from the experimentally measured T.D.S. outside the Bragg peak and then subtracting the calculated value of the T.D.S. that lies above the background under the Bragg peak. This procedure saves having to estimate the scattering from optic modes, of which there may be up to several thousand in crystals with large unit cells, and other slowly varying quantities such as the Compton scattering. As a result the usual T.D.S. correction factor α (Willis, 1969) is smaller than the T.D.S.-to-Bragg ratio discussed so far by the amount of the background scattering. Taking the average background to be represented by the scattering at

the edge of the spherical region, Willis (1969) considers the one-phonon scattering and obtains

$$\alpha = 0.67 \left(\frac{\text{T.D.S.}}{\text{Bragg}} \right). \quad (6)$$

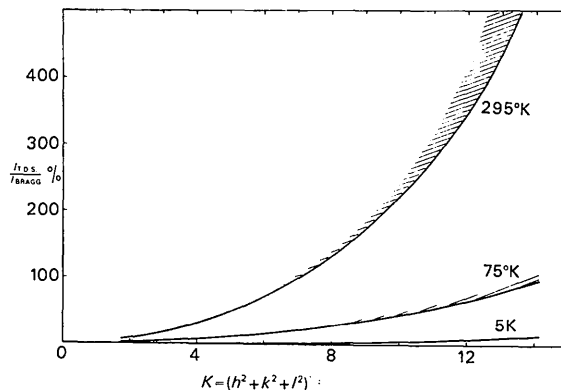


Fig. 1. NaCl. The ratio of $(I_{\text{T.D.S.}}/I_{\text{Bragg}})$ expressed as a percentage for a range of scattering lengths K (in units of $2\pi/d$) and for the temperatures 295, 75 and 5°K. The T.D.S. is integrated over a sphere in reciprocal space whose radius extends 0.124 to the (100) zone boundary. The shaded region represents the anisotropy that arises from true multiphonon processes which exactly sum to a reciprocal-lattice vector.

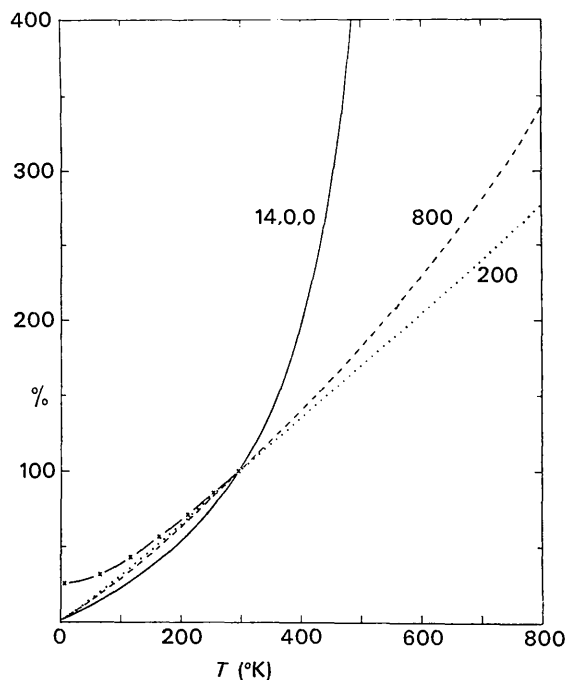
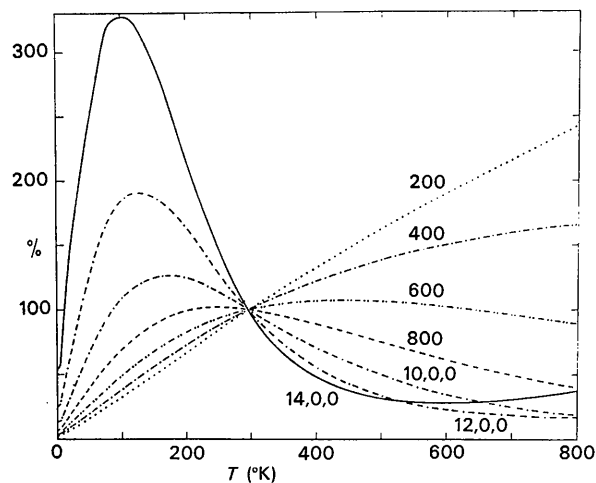


Fig. 2. The temperature dependence of the ratio $(I_{\text{T.D.S.}}/I_{\text{Bragg}})$ for the reflexions 14,0,0, 800 and 200 calculated under the conditions given in Fig. 1. Each ratio is expressed as a percentage of its value at 295°K. The line of crosses shows in a similar way the low-temperature variation of the Debye-Waller B terms.

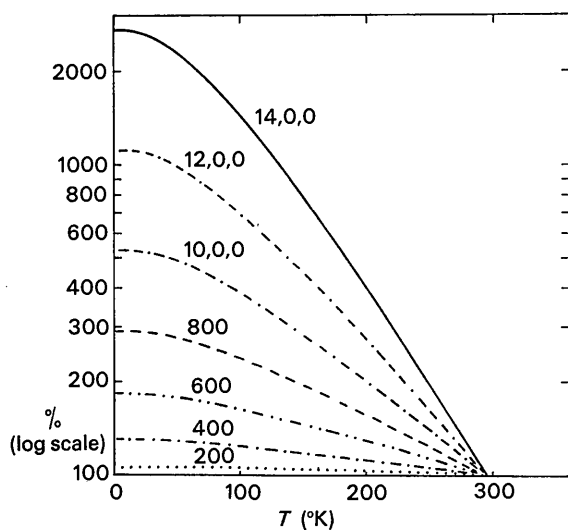
By taking the average scattering vector to go to a spherical shell surrounding the region of integration, equation (5) can be used to include multiphonon con-

tributions to the background. In this case

$$\alpha = 0.74 \left(\frac{\text{T.D.S.}}{\text{Bragg}} \right) - 0.16 \left(\frac{\text{T.D.S.}}{\text{Bragg}} \right)^2 + 0.04 \left(\frac{\text{T.D.S.}}{\text{Bragg}} \right)^3 + \dots \quad (7)$$



(a)



(b)

Fig. 3. The temperature dependence of (a) the T.D.S. and (b) the Bragg reflexions for the $h00$ reflexions of NaCl from 200 to 14,0,0. Each is expressed as a percentage of its value at 295°K. Very similar results are obtained for reflexions lying in other directions.

The first term is larger than that of equation (6) because the region over which the background is averaged is slightly further from the Bragg peak. The other terms subtract off some of the multiphonon contributions to the calculated T.D.S.-to-Bragg ratio and hence help to reduce the multiphonon effects in the integrated intensity. The important point as far as the temperature dependence is concerned is that to a good approximation, especially at lower temperatures, the temperature dependence of the usual T.D.S. correction factor (α) is the same as the temperature dependence of the T.D.S.-to-Bragg ratio.

In conclusion it can be seen that there is much to be gained by cooling to liquid-nitrogen temperatures where the ratio of the T.D.S. to Bragg scattering is generally reduced by a factor of 5 and also the higher-index reflexions are increased in intensity by at least this amount. Multiphonon effects are effectively frozen out. The main advantage of further cooling to liquid helium is another reduction by at least a factor of 5 in the T.D.S. although there is not much gain in Bragg intensity. An appropriate scaling of these results can be made to other materials whose Debye temperatures are not near the NaCl value of approximately room temperature.

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