

Our result indicates that this constraint is physically sensible, resulting in improved values for the parameters we wish to determine. It is crystal clear that analyses of future accurate X-ray data in terms of non-spherical electron density functions will have enhanced success if this joint refinement procedure can be used.

This work was carried out during the tenure of an S.R.C. studentship by one of us (J.A.K.D.), who was

on attachment to Harwell from the University of Oxford.

References

- ANDRESEN, A. F. (1957). *Acta Cryst.* **10**, 107.
 BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc.* **A273**, 435.
 HAMILTON, W. C. & LA PLACA, S. J. (1968). *Acta Cryst.* **B24**, 1147.
 ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1.

Acta Cryst. (1969). **A25**, 484

Contribution of the Thermal Diffuse Scattering to the Integrated Intensities of Cubic Powder Patterns

BY F. R. L. SCHOENING

Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

(Received 21 October 1968)

The contribution of the thermal diffuse scattering to the measured X-ray intensities of cubic powder patterns is calculated without making the approximation that $T \geq \theta$. Correction curves are given which are valid at all temperatures.

When recent measurements of the integrated intensities of diamond powders (Schoening & Vermeulen, 1969) had to be corrected for thermal diffuse scattering (TDS) it appeared that for low temperatures no simple method existed in the literature. The work by Chipman & Paskin (1959*a,b*) which is valid for moderately high temperatures ($T \geq \theta$) was therefore extended to cover low temperatures. The results are of interest because an easy correction procedure has been derived which, within certain limitations, is applicable to cubic powders at all temperatures.

The first-order TDS per cubic unit-cell for a monatomic crystal is (James, 1948)

$$I_2 = F^2 e^{-2M} \frac{4 \sin^2 \theta}{nmg^2 \lambda^2} \sum_j \frac{\bar{E}_{\phi j}}{v_{\phi j}^2} \cos^2 \alpha_{sj}, \quad (1)$$

where n is the number of atoms of mass m in the unit cell and the other symbols are as defined by James (1948). Equation (1) can be applied to f.c.c. or b.c.c. crystals by setting $n=4$ or 2 respectively. For crystals with more than one atom in the primitive cell (e.g. diamond cubic structure for which $n=8$) it remains valid for the acoustic modes. The sum in equation (1) will now be approximated by $\bar{E}_{\phi} v_m^{-2}$ where \bar{E}_{ϕ} and v_m are suitable mean values. Without this approximation it would not be possible to continue without making reference to a specific material.

With $x = hv/KT = g\theta/g_m T$ equation (1) becomes

$$I_2 = F^2 e^{-2M} \frac{4KT \sin^2 \theta}{nmg^2 v_m^2 \lambda^2} \left(\frac{x}{e^x - 1} + \frac{x}{2} \right).$$

Following Warren (1953) the TDS background of the powder patterns is obtained by integrating for constant $2\lambda^{-1} \sin \theta$ over the Brillouin zone which is assumed to be spherical with radius g_m . After summing the contributions of the hkl reflexions, the TDS becomes

$$I_{TD} = F^2 e^{-2M} \frac{2aK\theta \sin \theta}{nmg_m v_m^2 X \lambda^2} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \left\{ \frac{1}{2}(ag_m - |X - X_{hkl}|) - ag_m \frac{T}{\theta} \ln \left[1 - \exp \left(-\frac{\theta}{T} \times |X - X_{hkl}|/ag_m \right) \right] + \frac{T}{\theta} ag_m \ln \left[1 - \exp \left(-\frac{\theta}{T} \right) \right] \right\}, \quad (2)$$

where a is the cubic lattice parameter and j_{hkl} , X and X_{hkl} are as defined by Warren (1953). The result agrees with that by Herbstein & Averbach (1955).

The TDS contribution to the measured integrated intensity can now be obtained by following Chipman & Paskin (1959*b*). They separate the TDS into that part, say B_{TDS} , which is subtracted together with the background, and that part, say P_{TDS} , which remains with the integrated intensity. The sum $A_{TDS} = P_{TDS} + B_{TDS}$ can be obtained by integrating equation (2). B_{TDS} is found by: (1) calculating the TDS from equation (2) at the two positions corresponding to the beginning and end of the measured reflexion, (2) connecting the resulting two intensities by a straight line and (3) cal-

culating the area (which is equivalent to B_{TDS}) under this line. Assuming that only one TDS peak contributes to each hkl reflexion, the above procedure has given results as follows.

Integrating equation (2) from $X = -\delta$ to $+\delta$, where $\delta = (a\Delta \cos \theta)/2g_m\lambda \ll X_{hkl}$ is related to the total spread of the reflexion Δ , gives

$$A_{TDS} = F^2 e^{-2M} \frac{2a^2 K \Theta \sin^2 \theta}{nmv_m^2 \lambda^2} \frac{j_{hkl}}{X_{hkl}} \left\{ \frac{\delta}{X_{hkl}} + 2 \frac{T}{\Theta} \frac{\delta}{X_{hkl}} \ln \left[1 - \exp \left(-\frac{\Theta}{T} \right) \right] + 2 \frac{T^2}{\Theta^2} \frac{ag_m}{X_{hkl}} \times [1.642 - C\varphi(C)] \right\},$$

where

$$\varphi(y) = \frac{1}{y} \int_0^y \frac{\xi d\xi}{e^\xi - 1}$$

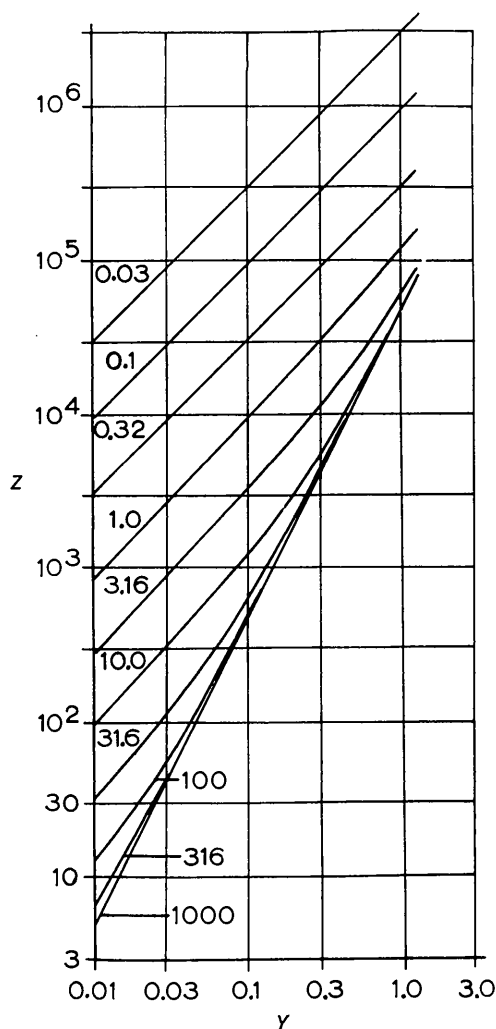


Fig. 1. Curves for finding the ratio σ of the integrated TDS to the integrated Laue-Bragg intensity. The curves are labelled with their respective Θ/T parameters.

$$C = -\ln \left[1 - \exp \left(-\frac{\Theta}{T} \frac{\delta}{ag_m} \right) \right].$$

From equation (2) the integrated intensity under the straight line becomes

$$B_{TDS} = F^2 e^{-2M} \frac{2a^2 K \Theta \sin^2 \theta}{nmv_m^2 \lambda^2} \frac{j_{hkl}}{X_{hkl}} \delta \left\{ 1 - \frac{\delta}{ag_m} - 2 \frac{T}{\Theta} \ln \left[1 - \exp \left(-\frac{\Theta}{T} \frac{\delta}{ag_m} \right) \right] + 2 \frac{T}{\Theta} \ln \left[1 - \exp \left(-\frac{\Theta}{T} \right) \right] \right\}.$$

Transforming the difference $A_{TDS} - B_{TDS}$ to the diffractometer coordinates and dividing by the Laue-Bragg intensity (Warren, 1955), the ratio of the integrated TDS intensity to the integrated Laue-Bragg intensity becomes

$$\sigma = \frac{8\pi a^2 K \Theta \sin^2 \theta}{nmv_m^2 \lambda^2} \delta \left\{ \frac{\delta}{ag_m} - 2 \frac{T}{\Theta} \times \left(C - \frac{T}{\Theta} \frac{ag_m}{\delta} [1.642 - C\varphi(C)] \right) \right\}.$$

The intensity corrected for TDS is $1/(1 + \sigma)$ times the measured intensity. The expression for σ can be rewritten in the form

$$Z = 4.810 \times 10^4 Y \left\{ Y - 2 \frac{T}{\Theta} \left(C - \frac{T}{\Theta} \frac{1}{Y} \times [1.642 - C\varphi(C)] \right) \right\}, \quad (3)$$

where

$$Z = \sigma nm_a \Theta / a^3 g_m^3 \lambda^{-2} \sin^2 \theta, \\ Y = (a\Delta \cos \theta) / 2ag_m \lambda,$$

and m_a is the atomic weight, Θ a mean characteristic temperature in $^\circ\text{K}$, a the cubic lattice parameter in \AA , λ the X-ray wavelength in \AA and Δ the spread of the reflexion in rad 2θ . For b.c.c. crystals $n=2$ and $ag_m = (3/2\pi)^{1/3}$, for a f.c.c. crystal $n=4$ and $ag_m = (3/\pi)^{1/3}$ and for a diamond cubic crystal $n=8$ and $ag_m = (6/\pi)^{1/3}$. Equation (3) is suitable for numerical calculations at low temperatures, *i.e.* for $\Theta/T > 1$. In the range $\Theta/T \leq 1$ the approximate expression

$$Z = 9.720 \times 10^4 Y \frac{T}{\Theta}$$

is better suited for numerical work.

Except for σ , all quantities in equation (3) are either experimental or material constants. The plot of Z vs. Y , shown in Fig. 1, is therefore applicable to all cubic materials with one atom in the primitive cell and to the acoustic branches of cubic materials with more than one atom in the primitive cell. At high temperatures the curves become straight lines which agree with the results of Chipman & Paskin (1959b).

One aspect of selecting the proper value for Θ in equation (3) is related to finding the average \bar{E}_φ and

v_m . In the high temperature approximation, for which $\bar{E}_\phi = KT$, Chipman & Paskin (1959*a*) have considered the averaging of the wave velocities, reaching the conclusions that Θ_D is usually adequate (Chipman & Paskin, 1959*b*). At intermediate temperatures the calculation becomes very involved. For very low temperatures it is seen from Fig. 1 that, except for very narrow peaks, the zero point energy terms dominate the correction factor σ , e.g. for $Y > 0.03$ the difference between Z for $\Theta/T = 1000$ and Z for $\Theta/T = 100$ becomes small. Therefore, in order to obtain a low temperature estimate for v_m , the TDS at 0°K was calculated for the general case that $v_l = pv_t$. The mean velocities which would give the same TDS, are as follows, (1) in the immediate vicinity of the centre of the Brillouin zone the mean velocity is given by $v_m^{-1} \simeq pv_l^{-1}$, (2) a quarter of the way towards the zone boundary $v_m^{-1} \simeq [1 + 0.838(p-1)]v_l^{-1}$, (3) half way towards the zone boundary $v_m^{-1} \simeq [1 + 0.666(p-1)]v_l^{-1}$ and (4) near the zone boundary $v_m^{-1} \simeq v_l^{-1}$. Because measurements of the integrated intensities are usually confined to the vicinity of the peak, Θ_D which for $p=2$ is equivalent to $v_m^{-1} = 1.78v_l^{-1}$, or Θ_M which for $p=2$ is equivalent to $v_m^{-1} = 1.67v_e^{-1}$ could both be approximately applicable.

A more important aspect of selecting a Θ value is the inapplicability of the Debye frequency distribution

which has been assumed throughout. A real frequency distribution can only give equivalent Θ_M 's and Θ_D 's which can differ considerably at low temperatures, Θ_M , in general, varying less with temperature than Θ_D . It can be expected that Θ_M is the better estimate to be used in equation (3) because the averaging over the Brillouin zone for TDS is more like that used for the Debye-Waller factor than that for the specific heat. Therefore, Θ_M should be preferred when both Θ_M and Θ_D are known.

The author wishes to thank Dr L. A. Vermeulen and Mr D. C. MacMurray for participating in the work.

References

- CHIPMAN, D. R. & PASKIN, A. (1959*a*). *J. Appl. Phys.* **30**, 1992.
 CHIPMAN, D. R. & PASKIN, A. (1959*b*). *J. Appl. Phys.* **30**, 1998.
 HERBSTSTEIN, F. H. & AVERBACH, B. L. (1955). *Acta Cryst.* **8**, 843.
 JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
 SCHOENING, F. R. L. & VERMEULEN, L. A. (1969). *Solid State Comm.* **7**, 15.
 WARREN, B. E. (1953). *Acta Cryst.* **6**, 803.
 WARREN, B. E. (1955). *Norelco Repr.* **2**, 63.

Acta Cryst. (1969). **A25**, 486

Bond Type in the Dioxides of Titanium, Germanium and Tin

BY M. F. C. LADD

Department of Chemical Physics, University of Surrey, Guildford, Surrey, England

(Received 7 October 1968)

The crystal energies of TiO_2 , GeO_2 and SnO_2 have been calculated by both the Born-Haber cycle and Born-Mayer equations. The agreement between the results suggests strongly ionic character in the M-O bonds.

Calculations by Baur (1961) and by Kingsbury (1968) have led to the suggestion of appreciable covalent character of the M-O bond in the dioxides of Ti, Ge and Sn, because the calculated crystal energies have been found to be about 25% larger (more positive) than the corresponding Born-Haber (thermodynamic) values. The following calculations, however, based upon the Born-Mayer electrostatic model, lead to results in good agreement with the thermodynamic values.

For present purposes, the Born-Haber cycle may be cast into the equation:

$$\Delta U = \Delta H_f(\text{MO}_2, \text{cryst}) - I_M - S_M - D(\text{O}_2) - 2E(\text{O}^{2-}) + 3RT. \quad (1)$$

The enthalpies of formation and of sublimation have been taken from Kubaschewski, Evans & Alcock (1967), the ionization potentials from Moore (1949, 1952, 1958), the dissociation energy from Rossini, Wagman, Evans, Levine & Jaffe (1952) and the electron affinity from Ladd & Lee (1960). The results are listed in Table 1.

The simple Born-Mayer ionic model leads to the equation

$$U(r) = \frac{-NAe^2}{10^3 J r} (1 - q/r) \text{ kcal.mole}^{-1}, \quad (2)$$

where q/r is given by

$$q/r = \frac{Ae^2/r}{9\sqrt{\beta + 2Ae^2/r}}. \quad (3)$$