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The correction of diffuse scattering measurements for thermal effects. By BERNARD BORIE
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Diffuse scattering studies, particularly those intended to measure short range order, are always obscured by temperature diffuse scattering (TDS). It is common practice to minimize the TDS contribution by making measurements as near to the origin in reciprocal space as possible, and then to attempt to eliminate it by extrapolating intensity measurements at two temperatures linearly to absolute zero (Cowley, 1950; Norman & Warren, 1951; Roberts, 1954; Batterman, 1957; Borie, 1957; Suoninen & Warren, 1958). Such an extrapolation is dependent on the assumption that the average energy associated with each normal mode of the lattice is kT . Hence there is always a small amount of TDS which the extrapolation fails to remove. Described here is a method to estimate this residual TDS and thus make the correction for thermal motion more accurate. No knowledge of the Debye temperature or other thermal properties of the crystal is required.

Let $I(T)$, the total diffuse intensity at temperature T at some fixed point in reciprocal space, be

$$I(T) = I_A(T) + I_B.$$

The TDS is given by $I_A(T)$; it is this quantity which we wish to remove from $I(T)$ to obtain I_B , the temperature independent part of $I(T)$ which is of interest. With $I(T)$ measured at T_1 and T_2 (Fig. 1), the linear

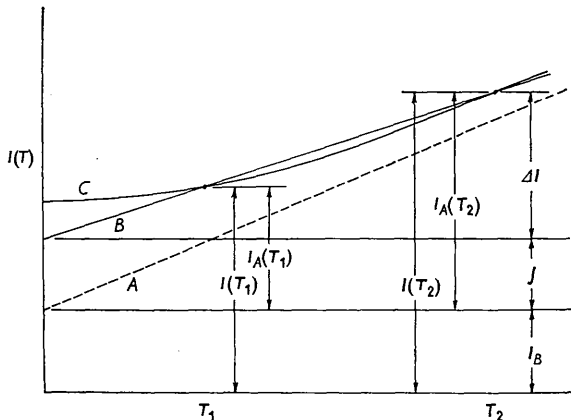


Fig. 1. The total diffuse intensity $I(T)$ plotted schematically as a function of T to illustrate the correction for TDS.

extrapolation to 0 °K yields the straight line B . If the average energy of each mode were really kT , we would have obtained the line A and the TDS correction would have given precisely I_B . But because $I(T)$ follows the curve C rather than A , the extrapolation gives $I_B + J$. It is J , the error resulting from this treatment of the measurements, which we wish to compute.

$$J = I_A(T_2) - \Delta I.$$

* Operated for the U.S. Atomic Energy Commission by the Union Carbide Corporation.

From the line B , ΔI is given by

$$\Delta I = [I_A(T_2) - I_A(T_1)]T_2 / (T_2 - T_1)$$

so that

$$J = I_A(T_1)T_2 / (T_2 - T_1) - I_A(T_2)T_1 / (T_2 - T_1). \quad (1)$$

It is convenient to write $I_A(T)$ in terms of the Debye model for a lattice: All elastic waves are assumed to have the same velocity V . The frequency spectrum is taken to be parabolic with a maximum frequency ν_m related to the Debye temperature Θ by $h\nu_m = k\Theta$. If \mathbf{g} is a vector from the point of measurement in reciprocal space to the nearest reciprocal lattice point, we may write $I_A(T)$ in electron units per atom (James, 1948)

$$I_A(T) = \frac{4h^2 f^2 \sin^2 \theta g_m^2}{mk^2 \Theta^2 \lambda^2 g^2} E_\nu(T).$$

The above expression is valid for a cubic material with one atom of atomic scattering factor f and mass m per unit cell. The average energy associated with a mode of frequency ν ($\nu = Vg$) at temperature T is $E_\nu(T)$; g_m is given by $\nu_m = Vg_m$. Hence equation (1) may be written

$$J = \frac{4h^2 f^2 \sin^2 \theta g_m^2}{mk^2 \Theta^2 \lambda^2 g^2} \frac{1}{T_2 - T_1} [T_2 E_\nu(T_1) - T_1 E_\nu(T_2)]. \quad (2)$$

The energy $E_\nu(T)$ may be written

$$E_\nu(T) = \frac{h\nu}{2} \coth \frac{h\nu}{2kT} \\ = \frac{h\nu}{2} \left[\frac{2kT}{h\nu} + \frac{1}{3} \left(\frac{h\nu}{2kT} \right) - \frac{1}{45} \left(\frac{h\nu}{2kT} \right)^3 + \dots \right].$$

If $h\nu/2kT$ is sufficiently small for all $\nu \leq \nu_m$ that we may safely use only the first two terms of the series expansion,

$$E_\nu(T) \simeq kT + \frac{1}{12} \frac{(h\nu)^2}{kT} = kT + \frac{k\Theta^2 g^2}{12T g_m^2}$$

since $h\nu = k\Theta g/g_m$. Equation (2) becomes

$$J = \frac{h^2 f^2}{3mk} \left(\frac{1}{T_1} + \frac{1}{T_2} \right) \frac{\sin^2 \theta}{\lambda^2}. \quad (3)$$

This very simple intensity expression depends only on known quantities, and varies in reciprocal space only with the square of the distance from the origin. With T_1 and T_2 in degrees Kelvin and λ in Å, it may be written

$$J = 639 \frac{f^2}{A} \left(\frac{1}{T_1} + \frac{1}{T_2} \right) \frac{\sin^2 \theta}{\lambda^2}$$

where A is the atomic weight of the material.

To illustrate the magnitude of the correction, we compare it with $f^2(2M)$, an approximate average value of the TDS to be expected, in a typical situation. We take $T_2 = 300$ °K and $T_1 = 80$ °K, and we let the sample be copper. Then $2M = 1.25 \sin^2 \theta / \lambda^2$ at room temperature

(Borie, 1956) and $A = 63.5$. Then J is about one-eighth of the average room temperature TDS and nearly half at 80 °K. Near the edges of a Brillouin zone (where in the case of short range order the diffuse scattering of interest is usually concentrated) J is a larger fraction of the TDS, and near the fundamental Bragg maxima it is a smaller part of the total correction. For measurements made in the usual low angle range ($2\theta = 20^\circ - 40^\circ$) with Cu $K\alpha$ radiation, J is roughly an order of magnitude greater than the second order TDS at room temperature.

For most of the diffuse scattering experiments listed in the references, the correction discussed here would be small and perhaps unimportant. It is likely to be useful in future high precision measurements made either

on dilute solid solutions or those with a small difference in the atomic scattering factors of the two components.

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Acta Cryst. (1964). **17**, 213

The influence of impurities on the formation of the Cu_3Au -type structure from the Cr_3Si -type structure. By HENNING VON PHILIPSBORN and F. LAVES, *Institute of Crystallography, Swiss Federal Institute of Technology, Zürich, Switzerland*

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The intermetallic compounds Ti_3Au (Duwez & Jordan, 1952), V_3Au (Wood & Matthias, 1956), and V_3Pt (Greenfield & Beck, 1956), are known to have the Cr_3Si ($A15$)-type structure.* In this investigation stoichiometric amounts of the respective elements were melted or, alternatively, the single-phase compounds were remelted in an argon-arc furnace, a water-cooled copper crucible being used. In the presence of small amounts of oxygen, nitrogen, or carbon, we obtained, along with the Cr_3Si -type structure (hereafter called β phase), a second phase having the ordered Cu_3Au ($L1_2$)-type structure (hereafter called α phase). The amount of α phase formed depends upon the purity of the titanium (99.9% Johnson & Matthey, and less pure from other sources), and vanadium (99.8% Union Carbide, and less pure from other sources) used, and upon the amount of oxygen, nitrogen or carbon picked up during melting. Titanium and vanadium are known to contain oxygen and nitrogen as main impurities.

Melting losses under pure argon (200 Torr, 10^4 cm^3) were about 0.1 wt.% for Ti_3Au (weight of charge 1–4 g). Thus a weight increase by melting in the presence of oxygen or nitrogen indicates the amount picked up during melting. This amount was controlled by variation of the melting time. Remelting $\beta \text{Ti}_3\text{Au}$, e.g. for 10 sec in the presence of oxygen (15 Torr), resulted in the pickup of about 1 wt.% (4.5 at.%) oxygen and the formation of about 40% α phase. Introducing the oxygen by premelting the titanium with TiO yielded the same results. Total conversion of β to $\alpha \text{Ti}_3\text{Au}$ was obtained for 3.4 wt.% (16 at.%) oxygen. Nitrogen and carbon have about the same influence, hydrogen none. V_3Au needs much less oxygen (about 0.7 wt.% or 3 at.%) for complete transformation.

The transformation is irreversible. No β phase was

restored when $\alpha \text{Ti}_3\text{Au}$ created by oxygen was remelted in an electron beam furnace under high vacuum (5×10^{-7} Torr) for 2×10 min. Annealing at 400 °C to 1200 °C for up to 40 days and rapid quenching had no effect. The two phases of Ti_3Au were present within the same range $\text{Ti}_{85}\text{Au}_{15}$ to $\text{Ti}_{85}\text{Au}_{15}$. Melting 50/50 mixtures of V_3Pt with Ti_3Au , Nb_3Au , and Nb_3Pt results in mixtures of the α and β phases with intermediate lattice constants.

Micrographs of Ti_3Au specimens containing 10–20% α phase, according to X-ray determination, revealed regularly oriented dendrites 5–10 μ in diameter. Small dendrite-rich regions of the specimens showed more α phase in X-ray pattern than dendrite-poor regions, indicating that the dendrites are α phase. Dr Kurt F. J. Heinrich kindly examined the specimens by electron microprobe analysis: 'The acicular inclusions have lower electron backscatter and higher target current than the surroundings. Emitted characteristic X-ray lines of both Ti and Au show lower intensities within the inclusions than in the matrix. These results would indicate that an element of low atomic number should be present, at rather low concentrations, in this particular phase' (Heinrich, 1963).

Table 1 shows lattice constants of α phases found. The lattice constants of the β phases agree well with the values given in the literature. The X-ray density of the β phase is from 6–9% larger than that of the α phase. Table 2 shows the good agreement between

Table 1. Lattice constants of α and β phases and ratio of X-ray densities β/α

Compound	α Phase created by	Lattice constant $\pm 0.002 \text{ \AA}$		Ratio of X-ray densities
		α phase	β phase	
Ti_3Au	O, N	4.096	5.096	1.063
Ti_3Au	C	4.147	5.096	1.078
V_3Au	O, N	3.964	4.876	1.074
V_3Pt	?	3.932	4.817	1.088
V_3Pt	O	3.918	4.817	1.076

* Cr_3Si (Borén, 1933) was the first compound definitely shown to have the ($A15$) structure. According to Hägg & Schönberg (1954) W_3O (β tungsten) is completely disordered and according to Kihlberg (1962), the existence of Cr_3O recently used to designate the ($A15$) structure is not confirmed.