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Temperature-diffuse scattering for powder patterns from cubic crystals.*

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In the determination of local atomic arrangements and atomic sizes in binary alloys from diffuse-scattering measurements (Warren, Averbach & Roberts, 1951) it is necessary to subtract from the measured diffuse scattering the contribution due to temperature-diffuse scattering. In the past this correction has been estimated on the assumption that the atoms vibrate independently, but it has recently been shown (Warren, 1953) that a better approximation is obtained if it be assumed that the velocities of the elastic waves in the lattice are all equal. Warren's derivation was valid at high temperatures only (i.e. $T > \Theta_M$); however, it is possible in many cases (e.g. Flinn, Averbach & Cohen, 1953) to reduce the correction for temperature-diffuse scattering by making the measurements at low temperatures, and therefore it is desirable to have an expression which is valid at all temperatures.

The temperature-diffuse scattering (by an element) at a point in reciprocal space is given by James (1948) as

$$I_{TD} = I_e f^2 e^{-2M} N^2 \sum_j (G_{\varphi j})_g \,, \quad (5{\cdot}36,\ 5{\cdot}40)$$

where

$$G_{\varphi j} = \frac{2\pi h}{2mN}\frac{1}{\omega_{\varphi j}}(\mathbf{R}\cdot\mathbf{e}_{\varphi j})^2 \coth\left(\frac{h\omega_{\varphi j}}{4\pi kT}\right) . \quad (5{\cdot}22)$$

(The figures in brackets refer to James's equation numbers; some trivial changes have been made in notation.) In the above equations N is the number of atoms, f the atomic scattering factor, $2M$ the usual Debye factor, h is Planck's constant, m is the atomic mass, $\mathbf{R}$ ($= 2\sin\theta/\lambda$) the diffraction vector from the origin of the reciprocal lattice to the point of measurement, $\mathbf{e}_{\varphi j}$ a unit vector in one of the three independent orthogonal directions of vibration of the lattice ($j = 1, 2, 3$) associated with the elastic wave φ, $\omega_{\varphi j}$ is the circular frequency of the elastic wave φj, k the Boltzmann constant and T the absolute temperature.

We now follow Warren and assume that all elastic waves have the same velocity V. Thus $\omega_{\varphi j} = 2\pi V|\mathbf{g}|$ for all φj, where $\mathbf{g}$ is the wave vector of the elastic wave. The temperature-diffuse scattering now becomes

$$I_{TD} = \frac{NI_e h f^2 e^{-2M}}{2mV|\mathbf{g}|}\coth\left[\frac{hV|\mathbf{g}|}{2kT}\right]\sum_j (\mathbf{R}\cdot\mathbf{e}_{\varphi j})^2 . \quad (1)$$

If each Brillouin zone is now replaced by a sphere of equal volume, then (1) becomes (for $2M$ small)

$$I_{TD} = \frac{NI_e f^2(1-e^{-2M})}{6\{\varphi(\chi)/\chi+\frac{1}{4}\}}\frac{g_{\max.}}{g}\coth\left[\frac{\chi}{2}\frac{g}{g_{\max.}}\right] , \quad (2)$$

where $\chi = \Theta/T$ and $\varphi(\chi)$ is the Debye integral.

At high temperatures (χ small) (2) reduces to

$$I_{TD} = NI_e f^2(1-e^{-2M})g^2_{\max.}/3g^2 .$$

This is Warren's equation (3). At low temperatures (χ very large) (2) takes the form

$$I_{TD} = \tfrac{2}{3}NI_e f^2(1-e^{-2M})g_{\max.}/g ,$$

which is applicable when the temperature-diffuse scattering due to the zero-point vibrations of the lattice is required.

The powder pattern corresponding to equation (2) can now be calculated in the manner outlined by Warren. For a face-centered cubic element this gives the ratio of I_{TD} to that for independent vibrations as:

$$G(X) = \frac{I_{TD}}{NI_e f^2(1-e^{-2M})} = \frac{(3/\pi)^{\frac{2}{3}}}{6\{\varphi(\chi)+\frac{1}{4}\chi\}}\frac{1}{X}\sum_{hkl}\frac{j_{hkl}}{X_{hkl}}\ln\left\{\frac{\sinh\frac{1}{2}\chi}{\sinh[\frac{1}{2}\chi(\frac{1}{3}\pi)^{\frac{1}{3}}|X-X_{hkl}|]}\right\},$$

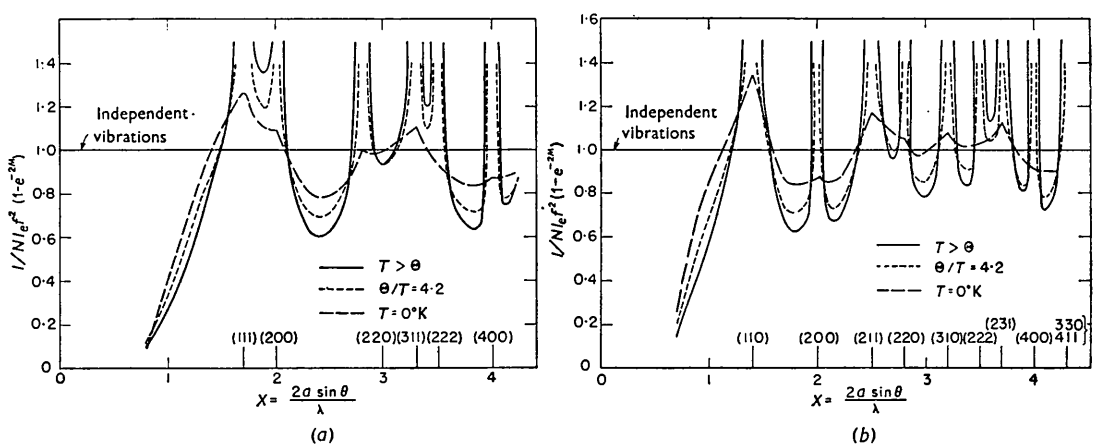

Fig. 1. The temperature-diffuse scattering in the powder pattern of (*a*) a face-centered cubic element, (*b*) a body-centered cubic element, at high, intermediate and low temperatures, calculated on the assumption that the velocities of all the elastic waves are equal.

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where

$$X = 2a \sin\theta/\lambda,\ X_{hkl} = 2a \sin\theta_{hkl}/\lambda,\ g_{\max.} = (3/\pi)^{\frac{1}{2}}/a;$$

a = cell edge, j_{hkl} = multiplicity of hkl reflection.

In Fig. 1(*a*) $G(X)$ is drawn (i) for $T > \Theta$, (ii) for $\Theta/T = 4{\cdot}2$ (this curve applies approximately to Al at liquid-nitrogen temperature), (iii) for $T = 0°$ K. Curves (i) and (ii) are similar, although the modulations in the curve (ii) are not as pronounced as those in curve (i). The curve for the temperature-diffuse scattering due to the zero-point vibrations differs from the others in that it does not have infinite singularities (of finite area) at the reciprocal-lattice points. The corresponding curves for a body-centered cubic element are shown in Fig. 1(*b*).

It should be emphasized that the assumption that the velocities of all the elastic waves in the lattice are equal is not a valid one for real crystals, for it would imply (Jahn & Lonsdale, 1942) that either the shear constant, C_{44}, or the compressibility $(C_{11}+2C_{12})$, was negative. It appears, however, that the deficiencies in the initial assumptions are largely compensated by the averaging process inherent in the powder pattern.

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Precision measurement of dimensional changes in beryllia on neutron irradiation.

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At the time of the recent International Conference at Geneva on the Peaceful Uses of Atomic Energy a good deal of previously classified information on the effect of neutron irradiation on the properties of solids was released for publication. Mention was made in several papers of X-ray investigations in various laboratories of the change in the crystal structure of graphite after irradiation. Some account of the X-ray work in this country is being prepared for publication. At the same time as the main studies of graphite have proceeded, a search has been made for changes in other materials which were of interest as moderators in nuclear piles. The purpose of the present note is to record some observations of a small effect in beryllia which was noted in 1952.

It was established that after a total irradiation by 7×10^{20} neutrons/cm.^{2} the c axis of BeO had increased by $0{\cdot}088\pm0{\cdot}003$% and the a axis had increased by $0{\cdot}033\pm0{\cdot}002$%. Previous measurements after irradiations by approximately 1×10^{20} neutrons/cm.^{2} had shown no conclusive change. For comparison it is to be noted that the irradiation of graphite by 7×10^{20} neutrons/cm.^{2} produces an increase of about 8% in the c dimension and a decrease of 1% in the a dimension.

In the case of beryllia the small changes were first detected by noticing a relative movement of the lines $10\bar{1}5$ and $21\bar{3}2$ on X-ray diffraction photographs with Cu $K\alpha$ radiation in a 19 cm. powder camera. These are closely spaced lines at Bragg angles of 70·0°, 70·2° respectively for the α_1 components, and their separation is very sensitive to any differential changes in a and c. The experimental accuracies quoted above amount to $\pm0{\cdot}0001$ Å for c and $\pm0{\cdot}00005$ Å for a. In order to obtain these accuracies, bearing in mind that the simple extrapolation procedure available for cubic materials cannot be employed, three different measurements were made, all involving high-angle lines.

(i) With unfiltered Cu K radiation a was determined directly from the $30\bar{3}0\alpha_1$ line at $\theta = 81{\cdot}5°$. The $20\bar{2}5\beta$ line at $\theta = 83{\cdot}6°$ was then used for obtaining c with the aid of the a value obtained from $30\bar{3}0$. The spacing change Δd for $20\bar{2}5$ is proportional to $(\Delta a+1{\cdot}1\Delta c)$ and, since Δc is about four times as great as Δa, provides a good measure of Δc.

(ii) With unfiltered Co K radiation direct measurements were made of the $10\bar{1}5\beta$ line at $\theta = 81{\cdot}5°$, for which Δd is proportional to $(\Delta a+4{\cdot}3\Delta c)$ and which is therefore very sensitive to changes in c, and of the $21\bar{3}2\beta$ line at $\theta = 81{\cdot}8°$, for which Δd is proportional to $(10\Delta a+\Delta c)$ and is therefore sensitive to changes in a.

(iii) Mixtures of beryllia and sodium chloride were examined with filtered Cu $K\alpha$ radiation and the spacings of individual lines were corrected with the aid of the NaCl extrapolation curve (Bacon, 1948). Subsequently a was deduced from the spacings of $21\bar{3}0$ and $30\bar{3}0$, particularly the latter which is at $\theta = 81{\cdot}5°$, and c from $20\bar{2}3$ and $10\bar{1}5$, the latter being very sensitive to changes in c, as already mentioned above.

The values of Δc found by the three methods were 0·0039, 0·0039, 0·0038 Å respectively, and of Δa 0·00085, 0·0009, 0·0009 Å respectively.

The observed anisotropy, whereby the linear expansion along the c axis under neutron irradiation is more than twice as great as that along the a axis, is to be contrasted with the thermal expansion, which is almost isotropic. Approximate values of the thermal expansion coefficients between −195° C. and 20° C. were found by X-ray measurements to be ${}^{\alpha}c = 4{\cdot}3\times10^{-6}$ and ${}^{\alpha}a = 4{\cdot}0\times10^{-6}$/°C. The dimensional changes produced by irradiation can be reversed by subsequent annealing. After heating for 8 hr. at 500° C. about 20% recovery has taken place, and at 1100° C. the recovery is 95% or more.

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