

The Temperature Dependence of X-ray Diffraction Intensities of Crystals

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The correspondence of the thermal movement in crystals and the Bragg-reflexion intensity distributions is treated in terms of a theory developed for describing the effect of static mechanical distortions. The basic functions appearing in that theory are replaced here by the corresponding time averages. The dependence of the temperature factor on the crystal size is discussed. The effect that additional static mechanical distortions have on the temperature factor is also discussed. Moreover it appears from the given expressions that there is a broadening in the Bragg reflexions as a consequence of the crystal distortions due to thermal movement. In the kinematical approximation, the integral intensity of a Bragg reflexion is temperature independent. If the integral intensity decreases as the temperature increases this is either a dynamical effect or a consequence of a measurement that takes only into account the intensity in a limited region around the maximum of the Bragg reflexion. In line profile analysis, the thermal broadening effect can be separated from the mechanical distortion broadening effect by means of Stokes's method if a reference powder, of the same substance (in an undistorted constitution) as the powder subjected to analysis is used.

Introduction

The temperature dependence of X-ray diffraction intensities is usually taken into account by the Debye-Waller factor $\exp(-2W)$, that is derived on the basis of the kinematical theory. However, many authors (see e.g. M. Born, 1942-1943) have noticed that the thermal effect on the diffraction pattern is much more complicated than the factor $\exp(-2W)$ would suggest: in particular the thermal diffuse scattering (TDS) is not completely described by the Debye-Waller factor.

A sharp distinction is generally drawn between Bragg scattering and TDS (in the one, two or more phonon scattering approximation); the Debye-Waller factor is believed to describe the temperature dependence of the Bragg reflexions and it is understood as a general factor of proportionality for the TDS.

It is known that for instance anharmonicity of the crystal causes deviations from the law described by the Debye-Waller factor (Maradudin & Flinn, 1963). Dynamical effects also produce deviations from that law: Parthasarathy (1960) found that the integral intensity of a Bragg reflexion of a thick crystal is proportional to $\exp(-W)$ instead of $\exp(-2W)$.

In this paper we will show that deviations also arise in the region where the kinematical theory describes the diffraction pattern correctly. The theory already developed for the diffraction of small distorted crystals (La Fleur, 1969) is adapted here to the case of thermal movement. Since the distortions due to the thermal movement are time dependent, some quantities defined in the theory mentioned above have to be replaced by their time averages. In this way the broadening of the Bragg reflexions due to the thermal movements in the crystal appears as a special case of a more

general one. The TDS is produced by the tails of those (broadened) Bragg reflexions.

It is found that the integral value of the intensity of a Bragg reflexion, in the kinematical approximation, is temperature independent. The top intensity of a Bragg reflexion is proportional to the Debye-Waller factor $\exp(-2W)$, only if the crystal is sufficiently large (but not so large, that the kinematical theory cannot be used). The value of the temperature factor depends on the crystal size and moreover on additional static mechanical distortions.

Derivation of equations

The distinction between TDS and the Bragg reflexions is based on a series expansion, that is obtained from the exact formula for the intensity distribution $I(\mathbf{s})$:

$$I(\mathbf{s}) = f_0^2 \sum_{l'} \exp \left[2\pi i \mathbf{s} \cdot \{\mathbf{x}_l - \mathbf{x}_{l'}\} - \frac{4\pi^2}{NM} \right. \\ \left. \times \sum_{\mathbf{k}, j} \{\mathbf{s} \cdot \mathbf{e}_j(\mathbf{k})\}^2 E_j(\mathbf{k}) \{1 - \cos(2\pi \mathbf{k} \cdot \mathbf{x}_l - \mathbf{x}_{l'})\} \right]. \quad (1)$$

For the derivation of this formula see, for instance, Maradudin, Montroll & Weiss (1963). The formula holds for a Bravais lattice. The symbols represent the following: \mathbf{s} , reciprocal-space vector; $I(\mathbf{s})$, intensity at the point \mathbf{s} in the reciprocal-space; f_0 , structure factor of an atom; l , set of three integers (l_1, l_2, l_3), indicating \mathbf{x}_l , the l th lattice point of the crystal; N , number of atoms in the crystal; M , mass of an atom; \mathbf{k} , wave-vector of a phonon; j , indication of a branch of the phonon spectrum; $\mathbf{e}_j(\mathbf{k})$, polarisation-vector of a phonon, of the j th branch of the spectrum, with wave-vector \mathbf{k} ; $E_j(\mathbf{k})$ is a shorthand notation for $\{\hbar/2\omega_j(\mathbf{k})\} \coth \{\hbar\omega_j(\mathbf{k})/2kT\}$, where \hbar is Planck's constant divided by 2π , T the temperature,

k the Boltzmann constant and $\omega_j(\mathbf{k})$ is the angular frequency of a phonon, of the j th branch, with wave-vector \mathbf{k} .

The above mentioned series expansion is

$$I(\mathbf{s}) = f_0^2 \exp(-2W) [I_0 + I_1 + I_2 + \dots] \quad (2)$$

with

$$I_0 = \sum_{l,l'} \exp\{2\pi i \mathbf{s} \cdot (\mathbf{x}_l - \mathbf{x}_{l'})\}, \quad (3)$$

$$I_1 = \sum_{l,l'} \frac{4\pi^2}{NM} \sum_{\mathbf{k}j} \{\mathbf{s} \cdot \mathbf{e}_j(\mathbf{k})\}^2 E_j(\mathbf{k}) \times \cos\{2\pi \mathbf{k} \cdot (\mathbf{x}_l - \mathbf{x}_{l'})\} \exp\{2\pi i \mathbf{s} \cdot (\mathbf{x}_l - \mathbf{x}_{l'})\} \quad (4)$$

and so on.

I_0 is interpreted as the Bragg reflexion and I_1, I_2 and further terms as the thermal diffuse scattering. Such an interpretation would be correct if $I_1, I_2 \dots$ would vanish at \mathbf{s}_n , the points in reciprocal space, where Bragg reflexions occur. In reality the TDS peaks at the points \mathbf{s}_n . (See Warren, 1968). It is therefore better to avoid the above series expansion and to write formula (1) in a form equivalent to that indicated in formula (7) of a previous paper (La Fleur, 1969), giving the intensity distribution of a distorted crystal.

We first write down the intensity distribution at a given time t :

$$I(\mathbf{s}, t) = Nf_0^2 \int_{-\infty}^{\infty} \sum_m \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) \delta(\mathbf{x}_m - \mathbf{x}) d\mathbf{x} \times \int_{-\infty}^{\infty} \Phi(\mathbf{x}, \Delta\mathbf{x}, t) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (\mathbf{x}_m = \mathbf{x}_l - \mathbf{x}_{l'}) \quad (5)$$

The function $\Phi(\mathbf{x}, \Delta\mathbf{x}, t)$ is a distribution function for the relative shifts of the atoms (modulo a lattice vector) at time t . For more details of that function we refer to the previous paper (La Fleur, 1969). From equation (5) it follows that the intensity distribution $I_n(\mathbf{s}_0, t)$ around the n th reciprocal lattice point at time t equals:

$$I_n(\mathbf{s}_0, t) = f_0^2 \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) d\mathbf{x} \times \int_{-\infty}^{\infty} \Phi(\mathbf{x}, \Delta\mathbf{x}, t) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (\mathbf{s}_0 = \mathbf{s} - \mathbf{s}_n) \quad (6)$$

When we introduce the time average $\bar{\Phi}(\mathbf{x}, \Delta\mathbf{x})$ of $\Phi(\mathbf{x}, \Delta\mathbf{x}, t)$, we get for the time average $I_n(\mathbf{s}_0)$ of $I_n(\mathbf{s}_0, t)$

$$I_n(\mathbf{s}_0) = f_0^2 \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) d\mathbf{x} \times \int_{-\infty}^{\infty} \bar{\Phi}(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (7)$$

This shows that it is natural to describe the effect of thermal movement in terms of the theory for distorted crystals.

In the same way as in that theory we may write for $\Phi(\mathbf{x}, \Delta\mathbf{x})$:

$$\Phi(\mathbf{x}, \Delta\mathbf{x}) = C(\mathbf{x})\varphi(\mathbf{x}, \Delta\mathbf{x}) + \frac{1}{v} \{1 - C(\mathbf{x})\} \quad (8)$$

where $C(\mathbf{x})$ is the form function of the average coherently scattering region and $\varphi(\mathbf{x}, \Delta\mathbf{x})$ is a new distribution function for the relative shifts (modulo a lattice vector) of the atoms. The function $\varphi(\mathbf{x}, \Delta\mathbf{x})$ fulfils the condition

$$\varphi\{\mathbf{x}, \frac{1}{2}(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)\} = 0 \quad (9)$$

with: $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ primitive basis translation vectors.

We denote the volume of a unit cell by v and that of the crystal by V . For a more detailed description of the quantities $\varphi(\mathbf{x}, \Delta\mathbf{x})$ and $C(\mathbf{x})$ we refer to the previous paper (La Fleur, 1969).

The effect of the finiteness of the crystal is taken into account by the form function of the crystal $V \cdot V(\mathbf{x})$. Including this effect also in equation (6) and using equation (7) one obtains

$$I_n(\mathbf{s}_0) = f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) C(\mathbf{x}) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) d\mathbf{x} \times \int_{-\infty}^{\infty} \varphi(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (10)$$

We try now to write formula (1) in the form of equation (10). Writing \mathbf{x}_m for $\mathbf{x}_l - \mathbf{x}_{l'}$ and using the fact that $\mathbf{s}_n \cdot \mathbf{x}_m$ are integers, we get

$$I(\mathbf{s}_0) = f_0^2 \sum_m V \cdot V(\mathbf{x}_m) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}_m) \times \exp\left[-\frac{4\pi^2}{NM} \sum_{\mathbf{k}j} \{\mathbf{s} \cdot \mathbf{e}_j(\mathbf{k})\}^2 E_j(\mathbf{k}) \{1 - \cos(2\pi \mathbf{k} \cdot \mathbf{x}_m)\}\right] \quad (11)$$

Replacing summation by integration formula (10) becomes

$$I_n(\mathbf{s}_0) = f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) \times \exp\{-U(\mathbf{s}, \mathbf{x})\} d\mathbf{x} \quad (12)$$

where

$$U(\mathbf{s}, \mathbf{x}) = \frac{4\pi^2}{NM} \sum_{\mathbf{k}j} \{\mathbf{s} \cdot \mathbf{e}_j(\mathbf{k})\}^2 E_j(\mathbf{k}) \times \{1 - \cos(2\pi \mathbf{k} \cdot \mathbf{x})\} \quad (13)$$

Comparison of equations (10) and (12) shows that

$$C(\mathbf{x}) \int_{-\infty}^{\infty} \varphi(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) = \exp\{-U(\mathbf{s}, \mathbf{x})\} \quad (14)$$

We now show that in equations (10) and (12) \mathbf{s} can be replaced by \mathbf{s}_n within a very good approximation. Take the Fourier transform of $I_n(\mathbf{s}_0)$. According to equation (10) one finds

$$\begin{aligned}
& \int_{-\infty}^{\infty} I_n(\mathbf{s}_0) \exp(-2\pi i \mathbf{s}_0 \cdot \mathbf{x}') d\mathbf{s}_0 \\
&= f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) C(\mathbf{x}) \exp\{2\pi i \mathbf{s}_0 \cdot (\mathbf{x} - \mathbf{x}')\} dx d\mathbf{s}_0 \\
&\times \int_{-\infty}^{\infty} \varphi(\mathbf{x}, \Delta \mathbf{x}) \exp\{2\pi i (\mathbf{s}_n + \mathbf{s}_0) \cdot \Delta \mathbf{x}\} d(\Delta \mathbf{x}) \\
&= f_0^2 V \int_{-\infty}^{\infty} \delta(\mathbf{x}' - \mathbf{x} + \Delta \mathbf{x}) V(\mathbf{x}) C(\mathbf{x}) dx \\
&\times \int_{-\infty}^{\infty} \varphi(\mathbf{x}, \Delta \mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta \mathbf{x}) d(\Delta \mathbf{x}) \\
&= f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}' + \Delta \mathbf{x}) C(\mathbf{x}' + \Delta \mathbf{x}) \varphi(\mathbf{x}' + \Delta \mathbf{x}, \Delta \mathbf{x}) \\
&\times \exp(2\pi i \mathbf{s}_n \cdot \Delta \mathbf{x}) d(\Delta \mathbf{x}). \quad (15)
\end{aligned}$$

For $V(\mathbf{x})$, $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta \mathbf{x})$ sufficiently slowly varying functions of \mathbf{x} , since $\Delta \mathbf{x} \ll \mathbf{x}$, one may also write instead of equation (15):

$$\begin{aligned}
& \int_{-\infty}^{\infty} I_n(\mathbf{s}_0) \exp(-2\pi i \mathbf{s}_0 \cdot \mathbf{x}) d\mathbf{s}_0 \\
&\simeq f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) C(\mathbf{x}) \varphi(\mathbf{x}, \Delta \mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta \mathbf{x}) d(\Delta \mathbf{x}). \quad (16)
\end{aligned}$$

This is the same as replacing \mathbf{s} by \mathbf{s}_n in equation (10).

For justifying this approximation in the case of the thermal movement, we only need to show that $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta \mathbf{x})$ vary slowly with \mathbf{x} . According to equation (14) $\varphi(\mathbf{x}, \Delta \mathbf{x})$ has the following Fourier expansion:

$$\begin{aligned}
\varphi(\mathbf{x}, \Delta \mathbf{x}) = \frac{1}{v} + \frac{2}{vC(\mathbf{x})} \sum_{n \neq 0} \cos(2\pi \mathbf{s}_n \cdot \Delta \mathbf{x}) \\
\times \exp\{-U(\mathbf{s}_n, \mathbf{x})\}, \quad (17)
\end{aligned}$$

where $\mathbf{x} \neq \mathbf{0}$ and $n \neq 0$ means $n = (n_1, n_2, n_3) \neq (0, 0, 0)$; $\mathbf{0}$ is the zero vector.

We also have

$$\begin{aligned}
\varphi(\mathbf{x} + \Delta \mathbf{x}, \Delta \mathbf{x}) = \frac{1}{v} + \frac{2}{vC(\mathbf{x} + \Delta \mathbf{x})} \sum_{n \neq 0} \cos(2\pi \mathbf{s}_n \cdot \Delta \mathbf{x}) \\
\times \exp\{U - (\mathbf{s}_n \cdot \mathbf{x} + \Delta \mathbf{x})\}. \quad (18)
\end{aligned}$$

It is now always possible to find a $\Delta \mathbf{k} \ll \mathbf{k}$, such that

$$\cos\{2\pi(\mathbf{k} + \Delta \mathbf{k}) \cdot \mathbf{x}\} = \cos\{2\pi \mathbf{k} \cdot (\mathbf{x} + \Delta \mathbf{x})\} \quad (19)$$

so equation (18) is equivalent to:

$$\begin{aligned}
\varphi(\mathbf{x} + \Delta \mathbf{x}, \Delta \mathbf{x}) = \frac{1}{v} + \frac{2}{vC(\mathbf{x} + \Delta \mathbf{x})} \sum_{n \neq 0} \cos(2\pi \mathbf{s}_n \cdot \Delta \mathbf{x}) \\
\times \exp\left[-\frac{4\pi^2}{NM} \sum_{kj} \{\mathbf{s}_n \cdot \mathbf{e}_j(\mathbf{k} - \Delta \mathbf{k})\}^2 E_j(\mathbf{k} - \Delta \mathbf{k})\right. \\
\left. \times \{1 - \cos(2\pi \mathbf{k} \cdot \mathbf{x})\}\right]. \quad (20)
\end{aligned}$$

Since $\mathbf{e}_j(\mathbf{k})$ and $\omega_j(\mathbf{k})$ vary slowly for most values of \mathbf{k} instead of equation (20) we can set

$$\begin{aligned}
\varphi(\mathbf{x} + \Delta \mathbf{x}, \Delta \mathbf{x}) \simeq \frac{1}{v} + \frac{2}{vC(\mathbf{x} + \Delta \mathbf{x})} \\
\times \sum_{n \neq 0} \cos(2\pi \mathbf{s}_n \cdot \Delta \mathbf{x}) \exp\{-U(\mathbf{s}_n, \mathbf{x})\}. \quad (21)
\end{aligned}$$

Comparison of equations (21) and (17) shows that $\varphi(\mathbf{x} + \Delta \mathbf{x}, \Delta \mathbf{x})$ and $C(\mathbf{x} + \Delta \mathbf{x})$ can be replaced by $\varphi(\mathbf{x}, \Delta \mathbf{x})$ and $C(\mathbf{x})$ respectively within a good approximation, so they can be considered as slowly varying functions of \mathbf{x} .

In the case of the thermal movement explicit expressions can be given for $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta \mathbf{x})$. So $C(\mathbf{x})$ can be found by substituting equation (11) into equation (17). One obtains

$$C(\mathbf{x}) = 2 \sum_{n \neq 0} (-1)^{n_1 + n_2 + n_3 + 1} \exp\{-U(\mathbf{s}_n, \mathbf{x})\}. \quad (22)$$

Substituting equation (20) into equation (17) one gets an expression for $\varphi(\mathbf{x}, \Delta \mathbf{x})$. Note that by definition $C(\mathbf{0}) = 1$ and $\varphi(\mathbf{0}, \Delta \mathbf{x}) = \delta(\Delta \mathbf{x})$.

The general behaviour of the functions $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta \mathbf{x})$ is the same in the case of thermal movement and of static mechanical deformation: $C(\mathbf{x})$ decreases when \mathbf{x} increases and the spread of $\varphi(\mathbf{x}, \Delta \mathbf{x})$ as a function of \mathbf{x} increases with increasing \mathbf{x} . Therefore the thermal movement also produces Bragg reflexions exhibiting a 'particle-size broadening' and a 'distortion broadening'. The former one is order independent whereas the latter one is order dependent.

Nevertheless in the case of thermal movement the functions $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta \mathbf{x})$ have an additional interesting property. The factor $\cos(2\pi \mathbf{k} \cdot \mathbf{x})$ oscillates very rapidly as a function of \mathbf{k} for large $|\mathbf{x}|$. Therefore in this case the contribution of the term containing $\cos(2\pi \mathbf{k} \cdot \mathbf{x})$ in the exponentials of equations (17) and (22) vanishes by the summation over \mathbf{k} , and $C(\mathbf{x})$ becomes independent of \mathbf{x} :

$$\begin{aligned}
\lim_{\mathbf{x} \rightarrow \infty} C(\mathbf{x}) = 2 \sum_{n \neq 0} (-1)^{n_1 + n_2 + n_3 + 1} \\
\times \exp\left[-\frac{4\pi^2}{NM} \sum_{kj} E_j(\mathbf{k}) \{\mathbf{s}_n \cdot \mathbf{e}_j(\mathbf{k})\}^2\right] \\
= 2 \sum_{n \neq 0} (-1)^{n_1 + n_2 + n_3 + 1} \exp(-2W) \quad (23)
\end{aligned}$$

where W is a function of (n_1, n_2, n_3) . The same can be proved for $\varphi(\mathbf{x}, \Delta \mathbf{x})$.

Let us consider now the effect of thermal movement on the diffraction intensity distribution when static mechanical distortions are present in the crystal. We assume that the dynamics of the thermal movement is not affected in first approximation by the static distortions. We introduce the function $\Phi_{me}(\mathbf{x}, \Delta \mathbf{x})$, being the distribution function for the relative shifts of the atoms (to within a lattice vector) in the absence of thermal movement. When we take into account the thermal movement, we get for the intensity distribu-

$$I_n(\mathbf{s}_0) = f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) \exp\{-U(\mathbf{s}_n, \mathbf{x})\} d\mathbf{x} \\ \times \int_{-\infty}^{\infty} \Phi_{me}(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}). \quad (24)$$

The thermal effect is described by $\exp\{-U(\mathbf{s}_n, \mathbf{x})\}$; this exponential can be written as the Fourier transform of a function $\Phi_{th}(\mathbf{x}, \Delta\mathbf{x})$:

$$\exp\{-U(\mathbf{s}_n, \mathbf{x})\} = \int_{-\infty}^{\infty} \Phi_{th}(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}). \quad (25)$$

Combining equations (24) and (25) we find that the intensity distribution is given again by equation (7) if we put

$$\Phi(\mathbf{x}, \Delta\mathbf{x}) = \Phi_t(\mathbf{x}, \Delta\mathbf{x}) = \Phi_{me}(\mathbf{x}, \Delta\mathbf{x}) * \Phi_{th}(\mathbf{x}, \Delta\mathbf{x}). \quad (26)$$

Of course the convolution integral is taken with respect to the variable $\Delta\mathbf{x}$.

Now equation (24) can be put into the form of equation (10), the functions $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta\mathbf{x})$ determining completely the autocorrelation function $\mathcal{P}(\mathbf{x})$, given by

$$\mathcal{P}(\mathbf{x}) = \sum_m \Phi_t(\mathbf{x}_m, \Delta\mathbf{x}) \quad (27)$$

and describing the time averaged probability density of finding an atom at a distance \mathbf{x} from another arbitrary atom in the crystal.

Discussion

An expression for the integral intensity of a Bragg reflexion can be derived directly from equations (24) and (26)

$$\int_{-\infty}^{\infty} I_n(\mathbf{s}_0) d\mathbf{s}_0 = Vf_0^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) \\ \times \exp\{-U(\mathbf{s}_n, \mathbf{x})\} d\mathbf{x} d\mathbf{s}_0 \\ \times \int_{-\infty}^{\infty} \Phi_{me}(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \\ = Vf_0^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(2\pi i \mathbf{s}_0 \cdot \mathbf{x}) d\mathbf{x} d\mathbf{s}_0 \\ \times \int_{-\infty}^{\infty} \Phi_t(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \\ = Vf_0^2 \int_{-\infty}^{\infty} \delta(\mathbf{x}) V(\mathbf{x}) d\mathbf{x} \\ \times \int_{-\infty}^{\infty} \Phi_t(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \\ = Vf_0^2 \int_{-\infty}^{\infty} \delta(\Delta\mathbf{x}) \exp(2\pi i \mathbf{s}_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) = Vf_0^2. \quad (28)$$

The value obtained is temperature independent, a conclusion that seems to contradict experiment. Note however, that here the contribution due to the TDS is also included. According to us this is more correct than separating the TDS from the Bragg reflexions since they are always observed together.

It follows that the kinematical theory cannot explain an exponential decrease of the integral intensity with the temperature. Nevertheless, when a decrease of that intensity is experimentally observed there may be (at least) two reasons for it. Either it may be a dynamical effect (we refer here to the work of Parthasarathy (1960) for more details) or the decrease is found since the intensity is measured in a limited region around \mathbf{s}_n only. Since for higher temperatures $C(\mathbf{x})$ decreases faster with \mathbf{x} and $\varphi(\mathbf{x}, \Delta\mathbf{x})$ is a broader function of $\Delta\mathbf{x}$, at constant \mathbf{x} , than for lower temperatures, the Bragg reflexions broaden more and more by increasing temperature and the corresponding fraction of the total amount of radiation that enters the ionization chamber decreases. In this sense we agree with Owen & Williams (1947), when they suppose that the increase of the slope

of the $\ln \int_{\Delta\mathbf{s}_0} I_n(\mathbf{s}_0) d\mathbf{s}_0$ versus T curve is connected with

an increase of the TDS. ($\Delta\mathbf{s}_0$ indicates a limited region of integration around \mathbf{s}_n .)

Let us consider now the top intensity of a Bragg reflexion. Assuming that the top intensity is found at the point $\mathbf{s}_0 = \mathbf{0}$, we get from formula (12)

$$I_n(\mathbf{0}) = Vf_0^2 \int_{-\infty}^{\infty} V(\mathbf{x}) \exp\{-U(\mathbf{s}_n, \mathbf{x})\} d\mathbf{x}. \quad (29)$$

$I_n(\mathbf{0})$ depends implicitly on the form of the crystal. The Debye-Waller factor follows from equation (29) if one assumes that the crystal is very large (but not so large that the kinematical approximation cannot be used). To show this we choose a distance r , such that the contribution of the term with $\cos(2\pi \mathbf{k} \cdot \mathbf{x})$ in the exponential of equation (29) vanishes for all \mathbf{x} with $|\mathbf{x}| \geq r$. The right-hand side of equation (29) can be split into two parts:

$$I_n(\mathbf{0}) = Vf_0^2 \int_{|\mathbf{x}| \leq r} V(\mathbf{x}) \exp\{-U(\mathbf{s}_n, \mathbf{x})\} d\mathbf{x} \\ + V \exp(-2W) \int_{|\mathbf{x}| \geq r} V(\mathbf{x}) d\mathbf{x}. \quad (30)$$

If the crystal is large the first right-hand term of equation (30) is much smaller than the second one and can be neglected. One finds

$$I_n(\mathbf{0}) \simeq V^2 f_0^2 \exp(-2W), \quad (31)$$

i.e. the well known Debye-Waller factor. Note that the top intensity is also proportional to the square of the volume of the crystal.

For a very small crystal $V(\mathbf{x})$ tends very rapidly to zero for increasing \mathbf{x} . In the limit, of an infinitely small

crystal, we can approximate in formula (29) $\cos(2\pi\mathbf{k} \cdot \mathbf{x})$ by 1 and in this case one obtains

$$I_n(\mathbf{0}) \simeq Vf_0^2 \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(\mathbf{0}) d\mathbf{x} = Vf_0^2. \quad (32)$$

The value of the top intensity therefore can vary between $V^2f_0^2 \exp(-2W)$ and $V^2f_0^2$ depending upon the crystal size. In the intermediate region between both limits the top intensity will show a more involved temperature dependence than the exponential one.

The temperature factor of the Bragg reflexion intensity also depends on mechanical distortions. This appears from equation (24). At low temperatures $I_n(\mathbf{0})$ will tend to the temperature independent value

$$I_n(\mathbf{0}) = Vf_0^2 \int_{-\infty}^{\infty} V(\mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} \Phi_{me}(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i s_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}). \quad (33)$$

If the crystal is sufficiently large and at high temperatures $I_n(\mathbf{0})$ will tend to

$$I_n(\mathbf{0}) = f^2 V^2 \exp(-2W). \quad (34)$$

In the presence of static mechanical distortions the slope of the $\ln I_n(\mathbf{0})$ versus T curve increases with the temperature. Anharmonicity also causes an increase of that slope. Anharmonicity studies based on this last effect (following the proposal of Maradudin & Flinn, 1963) have to take into account the former effect also.

In the study of the mechanical distortions by harmonic analysis of the Debye-Scherrer line intensity distributions we have to account apparently for the broadening due to the thermal movement. For the separation of the instrumental broadening from the particle size and the distortion broadening effects one generally uses Stokes's (1948) method. Here the ex-

perimental intensity distribution is considered as the convolution of $I_n(\mathbf{s}_0)$ given by equation (24) and that of a reference powder: $I_{n,ref}(\mathbf{s}_0)$.

The thermal broadening effect is separated automatically from the static mechanical distortion broadening effect, if a mechanical undistorted reference powder is used of the same substance as that subjected to the analysis. Indeed, according to equations (24), (25) and (26) we can write

$$I_n(\mathbf{s}_0) = I_{n,th}(\mathbf{s}_0) * I_{n,me}(\mathbf{s}_0), \quad (35)$$

with

$$I_{n,th}(\mathbf{s}_0) = f_0^2 V \int_{-\infty}^{\infty} V(\mathbf{x}) \exp(2\pi i s_0 \cdot \mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} \Phi_{th}(\mathbf{x}, \Delta\mathbf{x}) \times \exp(2\pi i s_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (36)$$

and

$$I_{n,me}(\mathbf{s}_0) = \int_{-\infty}^{\infty} \exp(2\pi i s_0 \cdot \mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} \Phi_{th}(\mathbf{x}, \Delta\mathbf{x}) \times \exp(2\pi i s_n \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}). \quad (37)$$

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Interpretation of Anomalous Streaks in Crystals of Anthrone

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Streaks on $\{h1l\}$ Weissenberg photographs of some anthrone crystals have been explained as being due to disorder in the stacking sequence of a layer structure or to multiple twinning on (201). The two views are geometrically identical. With such a model no streaks are either expected or observed on $\{h0l\}$ Weissenberg photographs.

Introduction

Flack (1968, 1970) and Glazer (1968, 1970) have recently made an extensive study of short-range order,

thermal vibration and expansion of pseudosymmetric and mixed crystals of some small organic molecules. For example, stationary-crystal photographs of anthrone (I) taken with white plus characteristic X-radiation show layers of diffuse scattering corresponding to $k = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. This diffuse scattering has been interpreted in terms of domains of short-range order ori-

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