Now

$$\sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \exp\left[-\ln\left(l+n'+m'\right)\right]$$

$$-\frac{[s-(n'+m')/a]^2}{[V_0+W_0(n'+m')^2]^2} = \sum_{h=0}^{\infty} (h+l)f_h$$

where h is an integer and

$$f_{n'+m'} = \exp\left[-\ln\left(l+n'+m'\right)\right] - \frac{[s-(n'+m')/a]^2}{[V_0+W_0(n'+m')^2]^2}.$$

However, $(h+1)\exp\left[-\ln\left(l+h\right)\right] = 1$. Hence,

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi Nas}{\sin^2 \pi as} \exp\left(-\frac{4\pi^2}{\beta A_0} s^2\right)$$

$$\times \sum_{h=0}^{\infty} \exp\left[-\frac{(s-h/a)^2}{(V_0+W_0 h^2)^2}\right].$$

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The Significance of Anharmonic Motion in Polymer Crystal Structure Analysis

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Abstract

Nonsystematic absences along certain reciprocal-lattice directions have been observed in the diffraction patterns of the macroscopic single crystals of various materials, both in our laboratory and in the literature. These extinctions are not space-group related nor are they the result of secondary scattering. Incorporation of the lowest-order anharmonic interaction terms, cubic and quartic in displacement, into the Hamiltonian of the molecular lattice, has made it possible to give a complete interpretation of these observations. A general intensity distribution was deduced with the assumption of elastic scattering. The final result provides new insight into the interaction of molecular units within a crystal and reveals new avenues for the solution of some unsolved crystal structures. A general procedure for the application of the required correction term to the intensity distribution is outlined, along with appropriate examples.

Introduction

The functional dependence of the line shape in a diffraction pattern on the nature of the interaction potential among the scattering entities has been established (Thakur, Tripathy & Lando, 1985). It has been shown that the monotonic decrease in the peak intensities is a consequence of the harmonic part of the interaction potential (Debye–Waller effect). The changes in the line shape, on the other hand, were generally interpreted to be a function of the nonharmonic aspect of the interaction potential. The paracrystallinity, finite crystal size and presence of lattice strain were investigated using a very general form of the potential.

It has been observed in our laboratory that certain macroscopic crystalline systems have nonsystematic absences in their diffraction patterns, although intensities calculated from their crystal structures should be observed. Similar observations, not accounted for in detail, were made by various other workers (Akiyama, Tanaka & Iitaka, 1970; Shannon & Katz, 1970; Srivastava & Przybylska, 1970; Mazhar-ul-Haque & Caughlan, 1970; Torii & Iitaka, 1970). In

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this paper is developed a theory dealing with nonsystematic absences in the diffraction pattern of relatively large disorder-free single crystals. These nonsystematic absences are not space-group related, nor are they the results of secondary scattering. These unusual extinctions can be accounted for if certain higher-order terms are included in the interaction potential. Besides these nonsystematic absences, some specific irregularities in the intensity distribution have been observed. Some zones of data may be very weak and diffuse, whereas others may remain relatively sharp. The crystal structure analysis in such cases may become impossible or at least very approximate, based on some *ad hoc* assumption (Comès, Lambert & Guinier, 1970). This problem can be resolved without any such approximation if a general anharmonicity in three dimensions is incorporated into the potential. Consequently, the intensity distribution can be interpreted and the structure analysis may also become much easier if the relevant correction is applied. In other words, this analysis may very well provide a key to the solution of some crystal structures that otherwise may remain unsolved. The required corrections in such cases for both nonsystematic extinctions and anomalous intensity distribution will be discussed in detail along with appropriate examples.

Theory

An effective density of a molecular lattice is generated by convoluting the electron density of the individual molecule $\rho_m(\mathbf{r})$ with the disposition function $A(\mathbf{r})$ (Vainshtein, 1966). The disposition function $A(\mathbf{r})$ for a molecular lattice can be expressed as

$$A(\mathbf{r}) = \sum_{j=1}^{N} a(\mathbf{r} - \mathbf{r}_j), \qquad (1)$$

where $a(\mathbf{r})$ is a function of position and depends only on the interaction potential. The assumption of a Maxwell–Boltzman-type distribution leads to (Thakur, Tripathy & Lando, 1985; Torii & Iitaka, 1970)

$$a(\mathbf{r}) = L \exp[-\beta v(\mathbf{r})], \qquad (2)$$

where L is a normalization constant, $\beta = 1/kT$ and $v(\mathbf{r})$ is the interaction potential. The Fourier transform $b(\mathbf{s})$ of the disposition function $A(\mathbf{r})$ can be expressed as (Thakur, Tripathy & Lando, 1984)

$$b(\mathbf{s}) = L \sum_{j=1}^{N} \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_j) F\{\exp[-\beta v(\mathbf{u})]\},$$
$$\mathbf{u} = \mathbf{r} - \mathbf{r}_j. \qquad (3)$$

Including only the third- and fourth-order terms over and above the harmonic term in the interaction potential, the simplest form of the potential can be expressed as

$$V(u) = \tfrac{1}{2}\gamma_0 u^2 + g u^3 + f u^4,$$

where γ_0 is the coefficient of the harmonic term and g and f are parameters related to the specific form of anharmonicity. An estimate of these parameters can be made from the experimentally observed anomalous behavior of the diffraction pattern or, more generally, from the crystal structure refinement.

By substituting back in (2), we obtain

$$a(u) = L_1 \exp[-\tfrac{1}{2}\gamma_0\beta u^2 - \beta(g u^3 + f u^4)].$$

For small u,

$$\exp[-\beta(g u^3 + f u^4)] \simeq 1 - \beta g u^3 - \beta f u^4.$$

Hence,

$$a(u) = L_1 \exp(-\tfrac{1}{2}\gamma_0\beta u^2)[1 - \beta g u^3 - \beta f u^4].$$

Now the Fourier transform of $a(u)$ is given by

$$F[a(u)] = L_1 \frac{2\pi}{\gamma_0\beta}\left[1 - \frac{ig}{(\gamma_0\beta)^{3/2}} H_3 \frac{2\pi}{\gamma_0^{1/2}\beta} s\right.$$
$$\left. - \frac{f}{(\gamma_0\beta)^2} H_4 \frac{2\pi}{\gamma_0^{1/2}\beta} s\right]$$
$$\times \exp[-(2\pi^2/\gamma_0\beta)]_s^2,$$

where $H_n(\xi)$ is the Hermite polynomial of degree n. Thus,

$$b(s) = L_1 \sum_{j=1}^{N} \exp(2\pi i s x_j) \frac{2\pi}{\gamma_0\beta}$$
$$\times \left[1 - \frac{ig}{(\gamma_0\beta)^{3/2}} H_3(\xi)\right.$$
$$\left. - \frac{f}{(\gamma_0\beta)^2} H_4(\xi)\right] \exp(-\xi^2/2),$$

where $\xi = 2\pi s/\gamma_0^{1/2}\beta$, and N is the number of unit cells in the crystal domain. Therefore,

$$|b(s)|^2 = L_1^2 \sum_{j=1}^{N}\sum_{k=1}^{N} \exp[2\pi i s(x_j - x_k)]$$
$$\times \frac{2\pi}{\gamma_0\beta}\left\{\left[1 - \frac{f}{(\gamma_0\beta)^2} H_4(\xi)\right]^2\right.$$
$$\left. + \frac{g^2}{(\gamma_0\beta)^3} H_3^2(\xi)\right\} \exp(-\xi^2).$$

With lattice periodicity $a = x_j - x_{j-1}$

$$\sum_{j=1}^{N}\sum_{k=1}^{N} \exp[2\pi i s(x_j - x_k)] = \frac{\sin^2 \pi N a s}{\sin^2 \pi a s}.$$

Therefore,

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi N a s}{\sin^2 \pi a s} \frac{2\pi}{\gamma_0\beta}$$
$$\times \left[\left(1 - \frac{f}{(\gamma_0\beta)^2} H_4(\xi)\right)^2\right.$$
$$\left. + \frac{g^2}{(\gamma_0\beta)^3} H_3^2(\xi)\right] \exp(-\xi^2).$$

Finally, the intensity distribution can be expressed as

$$I(s) = |F_m(s)|^2 |b(s)|^2$$

$$= |F_m(s)|^2 \frac{\sin^2 \pi Nas}{\sin^2 \pi as} \exp(-\xi^2)$$

$$\times \underset{\text{I}}{\frac{2\pi}{\gamma_0 \beta}} \underset{\text{II}}{L_1^2} \left\{ \left[1 - \underset{\text{III}}{\frac{f}{(\gamma_0 \beta)^2}} H_4(\xi) \right]^2 \right.$$

$$\left. + \underset{\text{IV}}{\frac{g^2}{(\gamma_0 \beta)^3}} H_3^2(\xi) \right\}. \qquad (4)$$

The implications of the first three terms have already been explained (Thakur, Tripathy & Lando, 1984). Specifically, $F_m(s)$ corresponds to the structure factor of the asymmetric units before they are assembled into the crystal lattice. The second term is the Laue interference function, and for large N it has sharp peaks at $s = ha^*$, where a^* is the reciprocal-lattice parameter. $\exp(-\xi^2)$ is the Debye–Waller or temperature factor. Comparing with the commonly used isotropic temperature factor, we have

$$B/2 = 4\pi^2 / \gamma_0 \beta = 4\pi^2 kT / \gamma_0.$$

However, it is the fourth term that contains the intensity information relating to the anharmonic component of the interaction potential. This will be described in greater detail in the next section.

Implication of the anharmonic term

The anharmonic term in the intensity expression (subsequently referred to as I_{anh}) for the special case of $f = g = 0$ reduces to a constant as expected, and results relevant to the harmonic crystal lattice are obtained. If the potential is chosen to be symmetric, $V(u) = V(-u)$, then $g = 0$ and hence I_{anh} assumes the form

$$I_{anh} = \frac{2\pi}{\gamma_0 \beta} L_1^2 \left\{ 1 - \frac{f}{(\gamma_0 \beta)^2} H_4(\xi) \right\}^2.$$

In the special case where

$$H_4(\xi) = (\gamma_0 \beta)^2 / f, \qquad (a)$$

$$I_{anh} = 0.$$

Thus, for the reciprocal-lattice vector a^* (for which $\xi = \xi_0$) given by

$$\xi_0 = \frac{2\pi}{\gamma_0^{1/2} \beta} h_0 a^*, \qquad (b)$$

satisfying condition (a), there will be complete extinction of intensity. The Miller index of the vanishing peak is h_0. We infer from condition (a) that two independent peaks will be extinct along a reciprocal-lattice direction. This result can be easily generalized

to three dimensions. When the extinction condition is not exactly satisfied, skewing of the diffraction maxima and other anomalous intensity modulations can be expected.

Another interesting consequence of I_{anh} results at very high ξ values. For $\xi \to \infty$, $H_4(\xi)$ also approaches ∞. Thus, even though the combination of form and temperature factors cuts off the intensity at higher values of ξ (higher-order reflections), $H_4(\xi)$ may be large enough to result in enhanced intensity.

In polymeric single crystals with bulky side groups (certain polydiacetylenes) and in molecular crystals with highly flexible or constrained side groups (non-optimally packed), the interaction potential is expected to be strongly anharmonic. These anharmonicities are anisotropic and the anomalies in the diffraction pattern are expected to be anistropic as well. In crystals of these types, even the use of suitable anisotropic temperature factors does not lead to a proper refinement of the crystal structure against the intensity data. The structure refinement in these cases will be impossible if one is not aware of the anharmonic terms and their consequences.

One approach to solving the crystal structure in systems with strong anharmonicity will be to eliminate the anharmonic contribution from the observed data and to apply subsequently the usual ideal harmonic approximation to arrive at the solution. Thus, the corrected intensities $I_{corrected}$ are given by I_{obs}/I_{anh}. However, to begin with, I_{anh} is not known (since g's and f's are not known). One should use the general expression of intensity $I(s)$ of the form given in (4) and use g's and f's along with other parameters as variables in the structure refinement process. In the following section such a procedure is outlined for a specific example.

Before we begin to discuss an example, let us deduce the general intensity distribution in three dimensions [generalization of (4)] to look at some other specifically important implications of the anharmonic interaction. The general potential in three dimensions can be expressed as

$$V(u) = \frac{1}{2} \sum_i \sum_j u_i u_j \gamma_{ij} + \frac{1}{6} \sum_i \sum_j \sum_k u_i u_j u_k g_{ijk}$$

$$+ \frac{1}{24} \sum_i \sum_j \sum_k \sum_l u_i u_j u_k u_l f_{ijkl}.$$

After a Fourier transform, the tensorial force constant (γ_{ij}) leads to an anisotropic temperature factor. The anharmonic coefficients g_{ijk} and f_{ijkl}, being respectively the third- and fourth-rank tensors, lead to a very complicated general expression of the intensity distribution. It becomes fairly difficult to extract any useful information. A simple way to get around this difficulty without losing any generality is to modify the scanning system so that a three-dimensional problem reduces to a one-dimensional one. If we scan

through each parallel set of planes $n(hkl)$ ($n = 1, 2, 3, \ldots$) separately, then we can consider vibrations only along a direction perpendicular to this set of planes. As a result we will be left with a one-dimensional problem in which the different planes are separated by their corresponding d spacings. In the diffraction or the reciprocal space this will be performed by considering each set of reflections lying along a line passing through the origin separately. The resulting intensity distribution subsequently takes the following form, obtained by some minor modifications of (4) (replacement of a by d_{hkl} etc.).

$$I(s) = L^2 |F_m(s)|^2 \frac{\sin^2 \pi N d_{hkl} s}{\sin^2 \pi d_{hkl} s} \exp\left[-(4\pi^2/\gamma\beta)^2_s\right]$$

$$\times \underbrace{\left\{ \left[1 - \frac{f}{\gamma\beta} H_4(\xi)\right]^2 + \frac{g^2}{(\gamma\beta)^3} H_3^2(\xi) \right\}}_{I_{anh}}$$

$$= L^2 |F_m(s)|^2 \frac{\sin^2 \pi N d_{hkl} s}{\sin^2 d_{hkl} s}$$

$$\times \exp\left[-(4\pi^2/\gamma\beta)s^2\right] I_{anh}(s). \qquad (5)$$

In this equation the term $I_{anh}(s)$ contains all the contributions from the anharmonic vibrations. It is equal to one (as it should be) when the anharmonic coefficients (g, f) are zero or negligible. The constant factor L^2 should be chosen properly so that the relation

$$\int_{\text{all space}} I(s) \, ds = \int_{\text{all space}} \rho(r) \, dr$$

(Parseval's theorem) is satisfied. In other words, the total scattered or diffracted intensity should be a constant quantity.

This is true for any elastic scattering. Now let us consider the general case when $g, f \neq 0$; therefore $I_{anh} \neq 1$ but a function of the reciprocal-lattice vector s. Since the effective intensity $I(s)$ is proportional to $I_{anh}(s)$ [(5)], the variation of $I_{anh}(s)$ with s will lead to a modification of the distribution of the effective intensity $I(s)$. Thus some of the reflections may be anomalously intense or weak, depending on the value of $I_{anh}(s)$ at that point in reciprocal space. However, to maintain the conservation of the total intensity, the loss (gain) of certain reflections will exactly equal the gain (loss) at certain other points. Consequently a considerable amount of diffuse background around some reflections may be inevitable. In summary, it will result in a very irregular intensity distribution in diffraction space. An example of such a diffraction pattern [single crystal poly(5,7-dodecadiyne-1,12-bisphenylurethane)] is given in Fig. 1, where the $0k0$ reflections are reasonably sharp and strong but the $00l$ reflections are weak and highly diffuse. The corresponding crystal structure has been solved only in two dimensions (ab projection) but because of these

Table 1. *Comparison of the calculated, observed and corrected intensities of some of the $0k0$ reflections for poly-TCDU (phase II)*

h	k	l	I_{calc}	I_{obs}		$I_{corrected}$
0	9	0	18243	17937		17937
→0	10	0	8040	165	↔	8250
0	11	0	3250	1047		3490
→0	12	0	1205	150	↔	1666
0	13	0	410	1993		333
0	14	0	128	3186		80

The 090 reflection has been used for scaling.

anomalies in the upper-level ($L \neq 0$) data the three-dimensional structure is not yet solved. A novel attempt at its solution is presently being made in the light of the anharmonic interaction and the results so far are quite promising. In the following section this will be discussed in greater detail.

Corrections for anharmonic effects

1. Nonsystematic extinctions

Table 1 shows the calculated, observed and corrected intensities of some reflections along the $[0k0]$ direction of a phase II poly(TCDU) crystal. The intensity data were collected using a Picker FACS 1 four-circle diffractometer. The unit cell is monoclinic and the space group is $P2/a$ (unique axis c). The calculated intensities are obtained from a two-dimensional (ab projection) crystal structure analysis, as previously stated. A three-dimensional refinement could not be done because of the disorder along the c axis of the crystal.
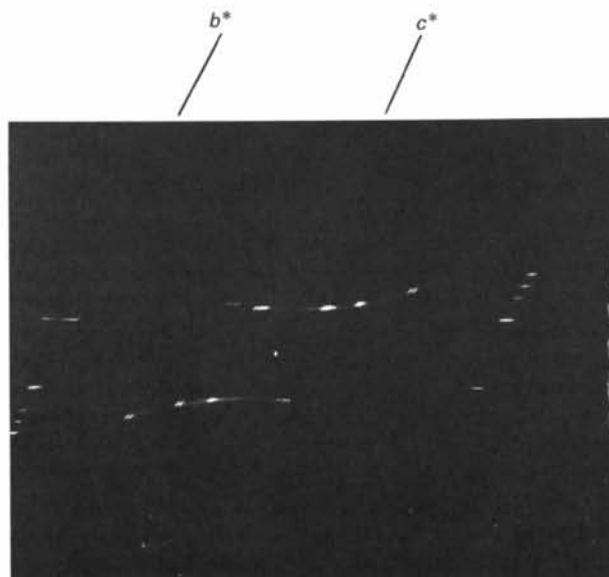

Fig. 1. Weissenberg photograph of poly-TCDU (phase II), showing $0kl$ reflections. The $0k0$ reflections are sharp, whereas the $00l$ reflections are weak and diffuse.

No systematic absences are observed in the diffraction pattern along the [0k0] direction. Yet the observed intensities of the 0,10,0 and 0,12,0 reflections are extremely low and may be approximated as zero with respect to the others (for the sake of simplicity). Moreover, the higher-order reflection 0,14,0 is considerably higher in observed intensity than in the calculated intensity. Thus the observed data are very clearly indicative of the existence of anharmonicity. Since there are two observable extinctions along the same reciprocal-lattice line, it is possible to calculate the anharmonic parameter uniquely. Specifically:

$$H_4(\xi_0) = 1/\sigma \text{ (condition } a)$$

with the explicit representation of $H_4(\xi_0)$

$$16\xi_0^4 - 48\xi_0^2 + 12 = 1/\sigma$$

$$\Rightarrow \xi_0 = \tfrac{1}{2}[3 \pm (6 + 1/4\sigma)^{1/2}]^{1/2}.$$

The two vanishing peaks are at

$$\xi_{01} = 10b^*, \ \xi_{02} = 12b^*.$$

Thus,

$$\frac{[3 + (6 + 1/4\sigma)^{1/2}]^{1/2}}{[3 - (6 + 1/4\sigma)^{1/2}]^{1/2}} = \frac{12}{10},$$

Hence,

$$\sigma = -0.0438.$$

$$I_{anh} = [\text{front factor}][1 + 0 \cdot 0438(16\xi^4 - 48\xi^2 + 12)]^2$$

$$\xi = 0 \cdot 113k.$$

This expression can now be used to calculate the corrected intensities listed in the last column of Table 1. The excellent agreement between the calculated and corrected intensities is obvious. It should be pointed out, however, that if the refinement were carried out in an iterative fashion the agreement would improve even further.

2. Irregular distribution of intensity

The general expression for the intensity of a reflection hkl is given by

$$I(hkl) = N^2 L^2 |F_m(hkl)|^2 \exp[-(4\pi^2/\gamma\beta)$$

$$\times (1/d_{hkl}^2)]I_{anh}(hkl).$$

The term $I_{anh}(hkl)$ leads to a diffuse background associated with a modification of the peak intensities as discussed in the earlier section with an experimental example of the diffraction pattern of poly(TCDU). As indicated by the diffraction pattern, the upper-level reflections $(00L, L > 0)$ were much disordered in their intensities. This irregularity was more clearly observed when a complete set of data for the intensities was collected using a Picker FACS 1 four-circle diffractometer. Initially, a structure calculation was tried ignoring these irregularities. Although

a reasonable solution in two dimensions was obtainable using only the hk0 data, a complete solution in three dimensions was found to be impossible. The minimum residual at this point converged at 0·35 and no appreciable change was observed on further variation of the structural parameters. It was quite clear that the existing irregularities in the upper-level intensities were responsible for this failure of structural refinement. The irregularities were subsequently found to be a consequence of the anisotropic nature of the anharmonic term $I_{anh}(hkl)$. Polymer molecules in general have higher mobility along the chain direction because it is easier for a long chain to slide lengthwise than in the transverse direction. Thus the anharmonic content along the chain direction is higher than in the other directions. As a result $I_{anh}(h\bar{k}l)$ to a good approximation becomes dependent on L only. Therefore, in the subsequent calculation of the structure of poly(TCDU) two additional variable parameters (g, f) were refined and a sharp drop of the residual from 0.35 to 0.23 was observed. The agreement improved by 12%, indicating the importance of the anharmonic correction. A reasonable solution in three dimensions was approached. To arrive at a more complete solution two additional factors need to be considered: (1) the monomer-polymer conversion in poly(TCDU) may not be complete (100%); therefore a monomer contribution should also be incorporated in the structure-factor calculation. (2) The monomer mobility should be different from the polymer chain mobility; therefore two additional anharmonic parameters (g, f) need to be refined. Once these factors are properly taken care of, the refinement should be complete. This work is now under way and the results will be reported shortly. In conclusion, anharmonic interaction has quite a significant consequence on the intensity distribution and an appropriate correction is indispensable to arrive at the solution of some structures.

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