

the layer displacements at some definite regular intervals, which may not always be possible, as in the case of CdBr_2 crystals. It is seen that these crystals always display large arcing and heavy streaking on their X-ray photographs (Agrawal & Trigunayat, 1970), indicating that the edge dislocations and the stacking faults occur more frequently in them than in CdI_2 or PbI_2 crystals. The frequency of layer displacements may be too high to render the chances of their stabilization a remote possibility. Hence, the observed low incidence of polytypism in CdBr_2 crystals is accounted for.

These observations lead to the conclusion that various polytypes are formed by the creation of stacking faults at different regular intervals. The formation of several polytypes of CdI_2 , e.g. $30R$, $42R$, $8H_b$, $24H_g$ (Chadha & Trigunayat, 1967*a,b*), $12R$ (Agrawal & Trigunayat, 1968), $20H_p$, $20H_q$ (Agrawal, Chadha & Trigunayat, 1970*b*), $18H_g$, $30H_f$, $24R$ and $36R$ (Jain, Chadha & Trigunayat, 1970) and of PbI_2 (Agrawal *et al.*, 1970*a*) have already been explained in similar terms. Recently Mardix, Kálmán & Steinberger (1968) have also explained the formation of various polytypes of ZnS in terms of periodic slip at regular intervals. The formation of various structural series, viz. $(22)_n1111$ in CdI_2 (Agrawal *et al.*, 1970*b*) and $(11)_n22$ in PbI_2 (Agrawal *et al.*, 1970*a*) can be easily explained by considering a double stacking fault occurring in their common polytypes at regular intervals of $4(n+1)$ layers and $2(n+2)$ layers, respectively [Fig. 1(*a*), (*b*)]. The common polytypes of CdI_2 and PbI_2 are the types $4H$ and $2H$, respectively. A double fault is formed when a single fault is immediately followed by another single fault [Fig. 1(*a*), (*b*)]. The formation of rhombohedral polytypes of CdI_2 belonging to the $[(22)_n13]_3$ series, viz. $12R$ (Agrawal & Trigunayat, 1968) and $24R$ (Jain *et al.*, 1970), can be easily explained in terms of a single stacking fault occurring at an interval of $4(n+1)$ layers in the common type $4H$ [Fig. 1(*c*)]. CdI_2 polytypes belonging to $(22)_n11$ series (Chadha & Trigunayat, 1968) can be explained by considering an intrinsic fault (a low energy type fault which does not disturb nearest-

neighbour packing), produced by shearing operations on the $\{0001\}$ planes about the B layer, in the common type $4H$ with layer sequence $(A\gamma B)(C\alpha B)$ after every $(4n+2)$ layers.

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A comment on the paper *Coherent crystal radiation affects the measurement of the X-ray linewidths* (Das Gupta & Welch, 1968) By A. FINGERLAND* and J. DRAHOKOUPIL, *Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia*

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Das Gupta & Welch have introduced the concept of 'coherent crystal radiation' to explain their experiments. As a consequence of their interpretation the fundamental X-ray line widths taken with the double-crystal spectrometer are in error. As shown in the present paper, the results of Das Gupta & Welch can be explained by means of the existing theories of the double-crystal spectrometer and triple-crystal diffractometer.

In their recent paper Das Gupta & Welch (1968) have made essentially two statements:

(I) In the double crystal spectrometer arrangement (DCS) the second crystal is the source of a 'coherent crystal radiation' (CCR) (which results in the appearance of extra

peaks in the triple-crystal diffractometer (TCD) rocking curves).

(II) As a consequence of (I) DCS is 'obviously unsuitable to determine the fundamental widths of X-ray emission lines'.

The aim of the present paper is to show that one can explain both the extra peaks and the line-widths by means of the existing theories of DCS (Compton & Allison,

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1935) and the triple-crystal diffractometer (TCD) (Bubáková, Drahoukoupil & Fingerland, 1961) without introducing new concepts.

We start with the equation for TCD [Bubáková *et al.*, 1961, equation (1)] written for the (1,1,*n*) position (neglecting the vertical divergence,* extending the integration limits to $(-\infty, \infty)$ and including the angular shift β of the second crystal from the maximum of the spectral line)

$$P_{\beta}(\gamma) \propto \iint I(\lambda - \lambda_0) C_1[\alpha - (\lambda - \lambda_0) D_1] C_1[-\alpha - (\lambda - \lambda_0) \times D_1 - \beta] C_n[\gamma + \alpha + 2\beta - (\lambda - \lambda_0) D_n] d\alpha d\lambda. \quad (1)$$

Here I is the spectral distribution of the measured emission line, λ_0 the wavelength at its maximum intensity, C_1 and C_n the diffraction patterns for the 1st and *n*th order respectively; $D_i = \tan\theta_i/\lambda_0$ are the corresponding dispersions and γ the angular setting of the third crystal.

We introduce $D_n/D_1 = k_n$, $(\lambda - \lambda_0)D_1 = l$ and $J(l) = I(l/D_1)$, and get

$$P_{\beta}(\gamma) \propto \iint J(l) C_1(\alpha - l) C_1(-\alpha - l - \beta) \times C_n(\gamma + \alpha + 2\beta - k_n l) d\alpha dl. \quad (2)$$

This is the expression for the TCD rocking curve, and by substituting $\alpha + 2\beta - k_n l = x$ we get

$$P_{\beta}(\gamma) \propto \int S_{\beta}(x) C_n(\gamma + x) dx, \quad (3)$$

with

$$S_{\beta}(x) \propto \int J(l) C_1[x - 2\beta + (k_n - 1)l] C_1[-x + \beta - (k_n + 1)l] dl. \quad (4)$$

Thus $P_{\beta}(\gamma)$ results from $S_{\beta}(x)$ by smearing with C_n . The 'smearing' is a known effect, and therefore we shall discuss only $S_{\beta}(x)$. It is a rather complicated function. However, to a good approximation all functions on the right hand side of equation (4) are bell shaped and reach their maxima at zero value of their argument. Thus we may estimate, at least qualitatively, the positions of the maxima of $S_{\beta}(x)$ by looking for the conditions of the maximum overlap of the functions behind the integration sign. This gives the following values:

$$x_1 = \beta \quad x_2 = 2\beta \quad x_3 = (k_n + 3)\beta/2.$$

According to the experimental conditions of Das Gupta & Welch (1968) we have $x_3 \simeq 2\beta$, $\frac{3}{2}\beta$, 3β for the first, second and third order respectively. In Fig. 1 of Das Gupta & Welch (1968) we may see only maxima x_1 (denoted by *A*) and not resolved maxima x_2 x_3 (denoted by *B*). Our own measurements show all three peaks in corresponding points (Fig. 1).

Hence we conclude, that the 'CCR' is in fact a consequence of the overlap of the long-tailed functions J and C 's.

The spectral measurements according Das Gupta & Welch (1968) are made by plotting the peak intensity at the point $B(\simeq x_3)$ * as a function of β .

If we put $\gamma = -x_3$ in (2) and make the substitutions $\alpha + \beta/2 = x$, $l + \beta/2 = y$, we get

$$P(\beta) \propto \int J(y - \beta/2) V(y) dy, \quad (5)$$

with

$$V(y) = \int C_1(x - y) C_1(-x - y) C_n(x - k_n y) dx. \quad (6)$$

Equation (5) shows that we get the spectral distribution J 'smeared' by $V(y)$ from equation (6).

This smearing function is the clue to the explanation of the extremely narrow spectral line widths, obtained by Das Gupta & Welch, namely, the correction used in their paper is the subtraction of the width of the smearing function w_R from the width of the observed curve, *i.e.*

$$w_T = w_O - w_R.$$

This is by no means exact, but may still be a reasonable estimate, if we take for w_R the width of $V(y)$. But in the paper cited, w_R was taken constantly equal to the width of the parallel position rocking curve of DCS, which in our notation reads

$$V_x(y) = \int C_1(x - y) C_1(x + y) dx. \quad (7)$$

By comparing (6) and (7) we may see, that even in the first order the correction made by Das Gupta & Welch is not correct.

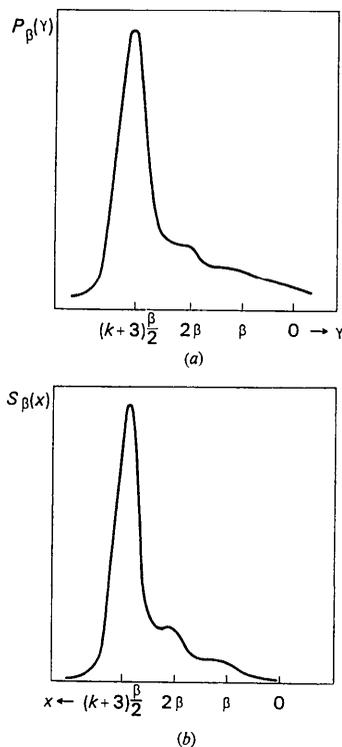


Fig. 1. (a) TCD rocking curve $P_{\beta}(\gamma)$ in the (1,1,3) position, using three germanium crystals cut parallel to the (111) planes. Mo $K\alpha_1$ radiation; $\beta = 32.5$ seconds of arc; $k = 3.15$. (b) The corresponding $S_{\beta}(x)$ resulting from a (rather crude) calculation according to equation (4). $\beta = 33$ seconds of arc; $k = 3$.

* See note at the end of this paper.

We measured the Mo $K\alpha_1$ spectral line by TCD in the position (1,1,1) and (1,1,3) and by DCS in position (1,1). The DCS width is larger than the widths taken with TCD. This is in agreement with smaller widths of the smearing functions shown in Table 1.

Table 1 *Widths (w_R) of the smearing functions*

Experimental arrangement with germanium crystals cut parallel to the (111) planes; Mo $K\alpha_1$ radiation.

Position	w_R
(1, -1)	0.17 mÅ
(1, 1, 1)	0.15
(1, 1, 3)	0.05

Conclusions

The paper of Das Gupta & Welch seemed to support their statement that the fundamental widths of the X-ray emis-

sion lines taken with DCS are in error. In view of our own analysis and experiments this statement is not convincing.

Note:—The role of the vertical divergence, the use of x_3 instead of the (unsuitable) position of the maximum B , and perhaps other questions should be treated in detail, but were omitted here because of their complexity.

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Role of the dispersion correction in analysis of X-ray diffraction data. By M. LINKOAHO, *Laboratory of Physics, Helsinki University of Technology, Otaniemi, Finland*, and M. MERISALO, *Department of Physics, University of Helsinki Helsinki 17, Finland*

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The role of the dispersion correction in the analysis of X-ray diffraction data of lithium fluoride has been considered by applying the recent theoretical and experimental values of the dispersion corrections.

In applying modern methods in the analysis of X-ray diffraction data the dispersion corrections are introduced as parameters. Their contributions are commonly taken into account by assuming the theoretical values. Of these, the most often used and probably the most reliable are those of Cromer (1965) and Cromer & Liberman (1968). Recently, Bonse & Hellkötter (1969) have determined the real part of the dispersion corrections from measurements of the refractive index for Cu $K\alpha$ radiation. Their result for fluorine in lithium fluoride, $\Delta f' = 0.18 \pm 0.02$, is in indisputable disagreement with the theoretical value $\Delta f' = 0.081$ (Cromer & Liberman, 1968).[†] In this note we consider the effects of this difference on conclusions arrived at in the analysis of the recent X-ray diffraction study for lithium fluoride (Merisalo & Inkinen, 1966).

First, the Debye-Waller coefficients B [in $\exp \{-B(\sin\theta/\lambda)^2\}$] have been determined by employing the difference Fourier method (see *e.g.* Kurki-Suonio & Fontell, 1964; Järvinen & Inkinen, 1967). The resulting values are listed in Table 1 along with the values calculated by Merisalo (1968) from the eigenfrequency-eigenvector data reported by Karo & Hardy (1963). It is obvious from Table 1 that the adoption of the experimentally determined result for the dispersion correction of fluorine gives particularly close agreement of the experimental and theoretical B and B_+/B_- values. Further, the experimental Debye-Waller coefficients and their ratio are found to be strongly dependent on the values of the dispersion correction applied. Thus any comparison between a theoretical vibration model and experimental results is of little value unless the dispersion correc-

tions are known reliable enough. It should be realized that the ratio of the Debye-Waller coefficients is probably the best test of the various theoretical vibration models (Karo & Hardy, 1969).

Table 1. *The experimental and theoretical Debye-Waller coefficients of lithium fluoride at 300°K in (Å)² for the cation (B_+) and anion (B_-) together with their ratio (B_+/B_-)*

	C & L	B & H	K & H
B_+	1.04	1.02	1.01
B_-	0.67	0.82	0.83
B_+/B_-	1.55	1.24	1.22

L: with the dispersion corrections calculated by Cromer & Liberman (1968).

H: with the dispersion corrections measured by Bonse & Hellkötter (1969).

H: calculated from the normal mode data of Karo & Hardy (1963).

Secondly, the electron distributions of the atoms in lithium fluoride were studied in terms of cubic harmonics, (Kurki-Suonio & Merisalo, 1967; Kurki-Suonio, 1967, 1968). Again, the analysis was carried out by applying both the theoretical and experimental values for the dispersion correction of fluorine. As an example, the differences between experimental and theoretical radial scattering amplitudes of fluorine, Δf_0 (the spherical component) and Δf_4 (the first non-spherical component), are illustrated in Fig. 1. It is found that the Δf_0 component is sensitive to the choice of the dispersion correction while the non-spherical component Δf_4 is, to first order, independent of the

[†] *Note added in proof:* Creagh & Hart (1970) give an experimental value $\Delta f' = 0.099 \pm 0.009$