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Comments on *The phases of forbidden reflections*, by B. Post & J. Ladell (1987).

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Abstract

The phases derived by Post & Ladell [*Acta Cryst.* (1987), A**43**, 173-179] for forbidden reflections in germanium from asymmetric Renninger profiles are in conflict with crystal symmetry. Anomalous scattering does not explain them. The pattern of asymmetry is that which is predicted by Juretschke [*Acta Cryst.* (1986). A**42**, 405-406] from a detail of the dynamical theory which does not depend on structure-factor phases. It also corresponds to that which would be produced by an asymmmetric spectral distribution of the nearly monochromatic radiation.

Post & Ladell (1987, referred to below as PL) reported observations of three-beam interactions in germanium which involve reflections of the forms {222} and {442} which are approximately forbidden by the special-position rule, and {200} and {420} which are strictly forbidden by the glide-plane rule. The structure-factor phases which were derived for {222} and {442} are in conflict with crystal symmetry. Those derived for the nonexistent {200} and {420} are meaningless. The assertion that anomalous scattering explains the results is in error. Another explanation is needed, and two are proposed below.

In $Fd3m$ (origin at $\bar{3}m$) phases of these reflections are related by the rules (*International Tables for X-ray Crystallography*, 1952)

$$
\begin{aligned}
F(222) &= F(\bar{2}\bar{2}\bar{2}) = F(\bar{2}22) = F(2\bar{2}2) = F(22\bar{2}),\\
F(442) &= F(\bar{4}\bar{4}\bar{2}) = -F(\bar{4}42) = -F(4\bar{4}2) = F(44\bar{2})\\
&= F(424) = F(244).
\end{aligned}
$$

These phase rules are valid regardless of the shape of the atomic electronic distribution, whereas the special-position rule for absent reflections requires that the atomic shape be centrosymmetric. Consistency with these phase rules is a minimal requirement for any method of phase determination. No rule is given for the strictly forbidden reflections because their phases have no meaning in this space group. The phases listed in Table 1 (PL) exhibit three violations of these rules. The rules are also incompatible with the conclusion that the phase is correlated with the parity of $n=(h+k+l+2)/4$. A defect of this conclusion (attributed by PL to anomalous scattering) is that it requires members of a Friedel pair to have phases which differ by π.

The description in PL of the effect of anomalous scattering conflicts with the following analysis. If f_1, f_2 are the scattering factors and T_1, T_2 the temperature factors of the atoms at $\pm(\frac{1}{8},\frac{1}{8},\frac{1}{8})$, the structure factor for any reflection permitted by the face-centered lattice is

$$
\begin{aligned}
F = 4\{&f_1T_1\exp[2\pi i(h+k+l)/8]\\
&+f_2T_2\exp[-2\pi i(h+k+l)/8]\}. \qquad (1)
\end{aligned}
$$

For h, k, l even and $(h+k+l+2)=4n$ (the definition of n used by PL), this reduces to

$$F=4(-1)^n(-if_1T_1+if_2T_2). \qquad (2)$$

The scattering factors include anomalous scattering:

$$f_j=f_{0j}+f'+if'', \qquad (3)$$

where f_{0j} is the Fourier transform of the atomic electron density, and the anomalous-scattering terms f' and f'' are the same for both atoms. For non-centrosymmetric distortions from spherical symmetry f_{01} and f_{02} are complex rather than real, as are T_1 and T_2 for non-centrosymmetric vibration (Dawson, 1967). Because of the center of inversion at the origin, these pairs are complex conjugates: $f_{02}=f_{01}^*$ and $T_2=T_1^*$. Then (2) becomes

$$F=8(-1)^n\{\mathrm{Re}\,(T_1)\,\mathrm{Im}\,(f_{01})+\mathrm{Im}\,(T_1)[\mathrm{Re}\,(f_{01})+f'+if'']\}. \qquad (4)$$

For Ge at 1·54 Å, f' and f'' are small relative to $\mathrm{Re}(f_{01})$; they change the magnitude of the second term only a few percent and its phase only a few degrees. When there is no anharmonic motion, the $\mathrm{Im}(T_1)$ term drops out, and there is no contribution to F from either f' or f''. The $8(a)$ site symmetry includes a twofold axis parallel to each cubic axis; thus if h, k or l is zero, both $\mathrm{Im}\,(f_{01})$ and $\mathrm{Im}\,(T_1)$ are zero, and $F=0$.

This analysis assumes that f' and f'' are scalar quantities. The tensor character of the scattering factor allows forbidden reflections to be observed in special cases (Templeton & Templeton, 1986) but is inapplicable here for two reasons: the high symmetry of the $8(a)$ special positions and the distance of the wavelength from any absorption edge. The analysis also neglects the trivial amount of anomalous scattering which in principle may be associated with the non-spherical part of the bonding-electron density of Ge. According to Cromer's (1983) program, each $3d$ electron contributes 0·003 to f' and 0·0003 to f'' at 1·54 Å, and each valence electron (omitted from the Cromer–Liberman model) will give even less.

One possible explanation of this experiment is that the nearly monochromatic radiation has an asymmetric distribution of intensity with wavelength. The azimuthal setting for the Renninger effect is sensitive to wavelength. Calculations for each of the 24 cases in Table 1 (PL) verified that the side for gradual fall-off is that for which the third reciprocal-lattice point for three-beam interaction is inside the Ewald sphere; this is the same as the side for exact three-beam interaction at a slightly longer wavelength. A change of wavelength of 0·00025 Å (photon energy change 1·3 eV) will shift the azimuth an amount in the range 0·002–0·02°. More radiation on one side than the other this far from the peak would be about enough to cause the observed asymmetry of line shape. The natural width of the Cu $K\alpha_1$

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line is 2·11 eV (Krause & Oliver, 1979). It is apparent from the widths of the Renninger peaks that the monochromator has reduced this spectral width, with an opportunity to introduce asymmetry.

Juretschke (1986) provided another possible explanation of this experiment in advance of its publication: asymmetry of peak profiles can come from changes of absorption which are correlated with whether the third reciprocal-lattice point is inside or outside the Ewald sphere, regardless of the phase of the structure-factor triplet. For both explanations the predicted pattern of asymmetry is that reported by PL, and not that which corresponds to the rules for phases of equivalent reflections. Neither explanation involves any distinction between the very weak and the strictly absent reflections. Perhaps both effects occur in the experiment.

I thank Professor Juretschke for helpful discussions.

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Reply to *Comments on The phases of forbidden reflections, by B. Post & J. Ladell* (1987), by David H. Templeton.

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Abstract

Some general remarks regarding the experimental determination of X-ray reflection phases may help the reader assess the validity of Templeton's [*Acta Cryst.* (1988). A44, 394-395] comments on a paper by Post & Ladell [*Acta Cryst.* (1987). A43, 173-179].

The reality of the intensities of 'forbidden' reflections, such as {222} and {442} of germanium, is no longer in question. Nevertheless, substitution of the positions of the germanium atoms in the expressions cited by Templeton (1988) yields structure factors equal to zero. It is evident that the use of those expressions for the calculation of the phases of forbidden reflections may yield incorrect results.

The experimental phases listed by Post & Ladell (1987) are based on data which necessarily include effects due to anharmonic thermal vibrations, static distortions of electron density distributions and anomalous scattering of the incident X-ray beam. Those are not taken into account in the *International Tables for X-ray Crystallography* (1952) expressions. They play minor roles in the determination of the phases of moderately strong reflections but can be of decisive importance when ultra-weak forbidden reflections are considered. It would therefore have been surprising if the phases reported by Post & Ladell were in perfect agreement with those listed in *International Tables for X-ray Crystallography* (1952).

Willis & Pryor (1975) have drawn attention to the fact that the *International Tables* rules for special positions, such as those of germanium atoms in the diamond structure, are valid only for spherically symmetric atoms. Atoms in crystals are not spherically symmetric and may generate effects which differ from those calculated for spherical atoms.

Simple procedures were used by Post & Ladell (1987) for the determination of the phases of individual reflections. Invariant triplet phases are displayed in *n*-beam patterns in the form of asymmetric intensity profiles. The phases of two of the reflections in each triplet are well known; the third is the unknown phase of the forbidden reflection. Subtraction of the sum of the two known phases from the invariant experimental triplet phase yields the phase of the forbidden reflection.

Our replies to specific comments by Templeton (1988) are listed below.

(1) Templeton notes that relations among the phases of reflections of the forms {222} and {442}, listed in Post & Ladell (1987), do not correspond to those calculated on the basis of expressions given in *International Tables*. The experimentally determined phases of {222} were found to alternate in sign for the sequence $222, 22\bar{2}, 2\bar{2}\bar{2}, \bar{2}\bar{2}\bar{2}$. Templeton's calculations indicate that all four reflections have identical signs. Possible causes of the differences between the two sets of results have been outlined above. In addition, it is not clear whether Templeton's calculations, presumably based on expressions given in *International Tables*, are applicable to forbidden reflections. On p. 341 of *International Tables*, we are informed that only those reflections whose indices sum to $4n$ or $2n+1$ satisfy the conditions for possible reflection for eightfold positions in space group $Fd3m$. It is therefore difficult to understand why the Editors of *International Tables* would wish to list relations among the phases of structure factors to which they have assigned zero values. More likely, those expressions were intended to apply only to structure factors calculated for atoms in positions other than those of eightfold multiplicity in space group $Fd3m$.

(2) Templeton states that the *International Tables* rules 'are incompatible with the conclusion that the phase is correlated with the parity of n' in $4n-2$ (the sums of the indices of forbidden reflections equal $4n-2$). Templeton's

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