# letters to the editor

# X-ray structure of barium titanate – missed opportunities

K. S. Chandrasekaran, S. K. Mohanlal,* R. Saravanan† and S. Israel

School of Physics, Madurai Kamaraj University, Madurai 625021, India

† Present address: The Madura College, Madurai 615011, Tamil Nadu, India.

Correspondence e-mail: saravana@pronet.net.in

Anomalous X-ray scattering effects are quite extensive in the noncentrosymmetric ferroelectric structure of barium titanate, and typical estimates for three published X-ray diffraction experiments are computed. These data show that the Bijvoet pairs should not be averaged before least-squares refinement for this polar crystal with small atomic displacements from a higher symmetric space group.

In the tetragonal ferroelectric structure of barium titanate, the heavy atoms have the dispersive components $f'_{Ba} = -0.613$, $f''_{Ba} = 2.28$, $f'_{Ti} = 0.28$ and $f''_{Ti} = 0.446$ (*International Tables for X-ray Crystallography*, 1974) for Mo $K\alpha$ X-rays used in three extensive structure analyses, namely Evans (1961), Harada *et al.* (1970; HPB) and recently Buttner & Maslen (1992; BM). For the point group $4mm$, any reflection with $l \neq 0$ can exhibit a Bijvoet difference $\Delta = 0.5(I - \bar{I})/(I + \bar{I})$ between the intensities of inverse reflections.

In Table 1, our estimated dispersive effects for a few reflections are displayed for the above three reported structures. The structure magnitudes $|F_+|$, $|F_-|$, the phase angles $\alpha_+$, $\alpha_-$ and the $\Delta$ values are listed along with $|F_c|$ and $\sigma(F_o)$, as reported by the above three authors. $\sigma(\Delta)$ can be up to four times larger than $\sigma(F_o)$ and therefore such dispersive scattering estimates should have been measurable.

We have in fact computed the $|F_+|$, $|F_-|$ and $\Delta$ values at ambient temperature for all reflections up to $\sin\theta/\lambda \simeq 1.4$ Å$^{-1}$ for the BM (1992) structure. The trends are summarized in Table 2.

Evans (1961) measured approximately 350 $h0l$ reflections using a Geiger counter fitted to a Weissenberg instrument and Mo $K\alpha$ X-rays up to $\sin\theta/\lambda \simeq 1.4$ Å$^{-1}$. He reported an 'impasse' in the structure determination, even with residuals as low as 0.03, owing to parameter interaction in the least-squares refinements with such a polar space group deviating by small atomic displacements from a higher symmetric space group. In a discussion we pointed out (Chandrasekaran & Mohanlal, 1965) our estimates of the very appreciable $\Delta$ values for a large number of reflections. In a rejoinder Evans (1966) stated that his raw

experimental data for $h0l$, $\bar{h}0l$ and $h0\bar{l}$, $\bar{h}0\bar{l}$ had not shown any such differences, which he attributed to 'antiparallel twinning', with $l_+$ and $l_-$ intensities tending to average out. In HPB (1970) a single C domain crystal was used for the X-ray studies; dispersive scattering effects were noticed in that only the refinements using an $l$ index of positive sign yielded the best standard errors for the parameters with low residuals.

BM (1992) recorded two independent sets of measurements on the same sample with ∼3500 data in each set, up to 1.08 Å$^{-1}$ for Mo $K\alpha$. They stated that 'Friedel pairs were averaged and merged even in case 3 (the correct noncentrosymmetric $P4mm$ structure), because the effects of anomalous dispersion are very small (Buerger, 1960)'. It is not clear to us from this quote whether they had sought to measure Bijvoet differences at all in their experiment or merely cited the text (Buerger, 1960) to justify their merging and averaging of the Friedel pairs. Also, BM (1992) had probably taken the magnitudes $|f + f' + if''|$ for the atomic scattering factors, which procedure would eliminate any $\Delta$ values in the structure-factor calculations and, in addition, lead to large errors in the structure-factor magnitudes and phases. Furthermore, Buerger (1960) devotes four pages to anomalous scattering, with Argand diagrams for $F_+$ and $F_-$, a table for $f'$ and $f''$ for different targets and several examples of the actual experimental measurement of Bijvoet differences.

The least-squares and Fourier procedures for noncentrosymmetric structures with appreciable dispersive scattering have been extensively discussed in a previous review (Srinivasan, 1972) and an International Conference Report (Ramaseshan & Abra-

**Table 1**
Our dispersion estimates for the three experiments.

[a]Our dispersion estimates (Chandrasekaran & Mohanlal, 1965) applying an average isotropic Debye–Waller term, $\exp(-2B\sin^2\theta/\lambda^2)$ for the intensities. See text. [b]Estimates for ambient room temperature.

| hkl | Evans (1961) $|Fc|;\sigma(Fo)$ | Our dispersion estimates (1965)[a] Δ% | HPB (1970) $|Fc|$ | Our dispersion estimates for HPB[b] | | | BM (1992) $|Fc|;\sigma(Fo)$ | Our dispersion estimates[b] for BM (1992) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $|F+|$ | $|F-|$ | Δ% | | $|F+|$ | $|F-|$ | Δ% | α+ | α− |
| 000 | 102 | – | 101.6 | 101.6 | 101.6 | – | 102 | 101.6 | 101.6 | – | | |
| 003 | 21;0.32 | 8.4 | N.M. | 19.2 | 18.5 | −7.4 | 19.1;0.06 | 17.6 | 18.4 | 8.9 | 13.9 | −3.3 |
| 005 | 15.5;0.26 | 10.3 | 14.8 | 14.7 | 13.7 | −13.8 | 13.8;0.1 | 11.9 | 13 | 17.6 | 18.9 | −5.9 |
| 007 | 11.2;0.1 | 16 | 10.3 | 10.5 | 9.2 | −25.9 | 9.2;0.13 | 7 | 8.3 | 34.5 | 25.7 | −9.2 |
| 009 | 8.1;0.11 | 21.7 | 7.9 | 8.1 | 6.7 | −36.8 | N.M. | 4.3 | 5.6 | 50 | 29.4 | −10.2 |
| 207 | 10.4;0.07 | 15.1 | 9.9 | 9.9 | 8.6 | −27.7 | 9;0.08 | 6.6 | 7.9 | 26.2 | 25.8 | −8.8 |
| 307 | 18;0.05 | 16.7 | 17.9 | 16.7 | 18 | 15.4 | 14.8;0.27 | 13 | 11.6 | −22.4 | −7.2 | 20.3 |
| 407 | 9.3;0.09 | 17 | 8.2 | 8.4 | 7.1 | −32.7 | 7.7;0.09 | 5.7 | 6.8 | 36.4 | 25.8 | 1.3 |
| 507 | 15;0.09 | 18.6 | N.M.† | 13.7 | 15 | 17.6 | 11.9;0.27 | 10 | 8.9 | −25.3 | −6.1 | 20.4 |
| 108 | 18.2;0.06 | 0.55 | 9.7 | 9.9 | 8.8 | −22.9 | 7.7;0.09 | 5.5 | 6.8 | 42 | 33.3 | −16.2 |
| 208 | 17.4;0.1 | 1.08 | 17.3 | 18.1 | 18.7 | 5.7 | 14.8;0.2 | 14 | 13.3 | −9.7 | −1.4 | 13.6 |
| 308 | 9;0.08 | 0.66 | 8.2 | 8.9 | 7.9 | −25.1 | 7.1;0.09 | 5.1 | 6.3 | 42 | 32.5 | −14.7 |
| 408 | 15.2;0.08 | 1.28 | 15 | 15.9 | 16.4 | 6.5 | N.M. | 12.1 | 11.5 | −10 | −0.4 | 13.5 |

† N.M. – Not measured.

**Table 2**
Summary of compound dispersion values for reflections with $\sin\theta/\lambda \leq 1.4$ Å$^{-1}$.

| Description | No. of reflections |
|---|---|
| Total up to 1.5 Å$^{-1}$ for Mo K$\alpha$ | 912 |
| With $l = 0$ index | 112 |
| With $l \neq 0$ and $|F| > 4$ electrons | 735 |
| $|\Delta| > 20\%$ | 268 (+ve = 181, −ve = 87) |
| $|\Delta| > 10\%$ | 187 (+ve = 94, −ve = 93) |
| $|\Delta| > 5\%$ | 145 (+ve = 68, −ve = 77) |
| $|\Delta| < 5\%$ | 312 (+ve = 108, −ve = 204) |

Thus, the dispersive scattering effects are quite appreciable for a large number of reflections, with both positive and negative signs for $\Delta$ (negative, −ve for $I < \bar{I}$).

hams, 1974). Here, therefore, we only cite Ibers & Hamilton (1964), who recommend that Friedel pairs should be treated independently in the least squares, using the actual observed values and corresponding calculated values $|F_+(H)|$ and $|F_-(H)|$. For the effects of domains in BaTiO$_3$, tending to average out $l_+$ and $l_-$ intensities, the Flack enantiopole parameter (Flack, 1983), namely $|F(\bar{h})|^2 = (1 - x)\,|F(h)|^2 + x|F(-h)|^2$, is called for to account for the intensities, with $x$ as a parameter for refinement.

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