

Conclusion

Nous avons montré que l'erreur systématique apportée par la dérive de la source ne peut être corrigée sans introduire une erreur aléatoire due à la fluctuation quantique du flux moniteur.

Nous constatons une fois de plus l'antagonisme de ces deux types d'erreur. Comme nous l'avions déjà signalé (Tournarie, 1958) comme étant un cas général, l'erreur minimale s'obtient par une correction non pas totale, mais seulement partielle de l'erreur systématique.

Nous pensons donc que les systèmes de comptage doivent comprendre trois éléments:

- { une base de temps ;
- { un compteur de flux diffusé ;
- { un compteur de flux moniteur .

Références

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X-ray and Neutron Diffraction Study of Tetragonal Barium Titanate

BY J. HARADA,* T. PEDERSEN AND Z. BARNEA

School of Physics, University of Melbourne, Australia

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An attempt is made to differentiate between the three previously proposed models of the structure of tetragonal BaTiO₃. In the new model, the serious parameter-interaction problem was avoided by the use of both neutron and X-ray diffraction data collected from *c*-domain single crystals. The result of the refinement gave the displacement of the Ti atom from its cubic position as $0.0135 \pm 0.0004 \text{ \AA}$; the *R* value was 0.027 and 0.024 for the neutron and X-ray data respectively. The analysis also showed that the temperature parameters, B_{33} , along the *c* axis are approximately independent of mass; $B_{33} = 0.32 \pm 0.03 \text{ \AA}^2$ from X-ray and $0.33 \pm 0.04 \text{ \AA}^2$ from neutron diffraction. The average value obtained for the $\overline{B_{11}}$ temperature parameters, $\overline{B_{11}} = 0.50 \text{ \AA}^2$, is considerably higher than the B_{33} value, which thus clearly indicates the existence of low frequency optic modes at room temperature.

Introduction

Below its ferroelectric Curie temperature (120°C) BaTiO₃ has tetragonal symmetry with the space group $P4mm$ (C_{4v}). In this ferroelectric phase, the atoms are shifted from the symmetry positions of the cubic perovskite-type structure along the *c* axis by small amounts Δz . The exact values of these are very difficult to determine because of the large interaction between the position and temperature parameters along the tetragonal axis. This has been shown by Evans (1951, 1961) who in an attempt to solve the structure by X-ray diffraction proposed two models both of which fitted his experimental data equally well with a reliability index *R* of about 0.037. The problem has also been investigated by Frazer, Danner & Pepinsky (1955) and Danner, Frazer & Pepinsky (1960) using neutron diffraction and they obtained a third model, intermediate between the two previous models. Three different models of the structure have thus been proposed.

In the neutron diffraction experiment the crystal was equipped with electrodes to permit unidirectional domain alignment by an electric field. Because of the piezoelectricity of tetragonal BaTiO₃, application of an electric field to the crystal will cause the crystal to become strained. The amount of deformation would be extremely small (Kittel, 1963). The effect of the electric field on the temperature parameters, however, is not yet clear. We have therefore collected both neutron and X-ray diffraction data using free, *c*-domain crystals without electrodes.

In this paper an attempt has been made to differentiate between the three previously proposed models in the light of our data. We also show that it is possible to obtain a model which is in good agreement with both neutron and X-ray data, provided certain initial assumptions are made about the temperature factors.

Experiment

Barium titanate crystals grown at the Matsushita Electric Industry Co. Ltd. by Remeika's method were used in the investigation. Suitable *c*-domain single crystals were chosen with the aid of a polarizing microscope.

* A.I.N.S.E. Research Fellow, on leave from Department of Physics, Tokyo Institute of Technology, Tokyo, Japan. Present address: Physics Department, Brookhaven National Laboratory, N.Y., U.S.A.

X-ray diffraction

The BaTiO₃ crystal used in the X-ray measurements was triangular in shape, of area 27.2 mm² and 0.7 mm thick. The crystal was mounted on an XRD-6 General Electric single-crystal diffractometer in such a way that the *c* axis was always horizontal and parallel to the φ axis. Rotation about the φ axis combined with rotation about the ω axis made it possible to observe up to eight equivalent reflexions of type *hkl* with small *h* and *k* and large *l*. The direct (Mo *K* α) beam was completely intercepted by the crystal. Balanced (Zr-Y₂O₃) filters placed in the diffracted beam were used in conjunction with a scintillation counter and pulse-height analyser. Integrated intensities were obtained using a θ - 2θ scan. The measurements were carried out at $28 \pm 2^\circ\text{C}$.

Fifty-four independent reflexions were observed. Except for the 00*l* reflexions, two to eight equivalent reflexions were measured in each case. Agreement between equivalent reflexions was, with a few exceptions, found to be within about 1%.

Lorentz and polarization corrections were applied to the intensities which were also corrected for absorption by the skew-correction formula (*International Tables for X-ray Crystallography*, 1959). It should be noted that for relative intensities this correction is only geometrical and independent of the absorption coefficient.

Extinction effects were not evident in our data. This is ascribed to the fact that because of the high absorption of BaTiO₃ only a small mosaic surface layer contributed to the diffracted intensity. However, *hk0* data collected by transmission through a very thin crystal exhibited considerable extinction and were therefore not used in the structure analysis.

Neutron diffraction

Two specimens were used. Specimen C4 was a platelet 27 mm² in area and 0.16 mm thick; specimen CJ was a platelet 52.6 mm² in area and 0.16 mm thick.

Integrated intensities were measured on the 4H2 full-circle single-crystal diffractometer at the HIFAR reactor of the Australian Atomic Energy Commission at Lucas Heights. The flux of the incident beam was 10^4 – 10^5 neutrons cm⁻² sec⁻¹ with a mean wavelength of 1.10 Å. The step-by-step θ - 2θ scan was carried out in a range of about 6° (2θ).

Absorption and Lorentz corrections were applied to the intensities by the CDRABS AAEC computer program. Three equivalent reflexions were usually measured in the case of crystal C4 and four for crystal CJ. Agreement between equivalent reflexions was about 4%. Reproducibility of a standard reflexion was better than 2%. The data were obtained at a temperature of $22 \pm 2^\circ\text{C}$.

The agreement between the two sets of intensity data was very good for the weak reflexions but not for the strong. Comparison of structure factors indicated that the disagreement in the case of the strong reflexions was due to extinction. An interesting point to note is

that the two crystals which were grown in different batches exhibited different anisotropy of extinction. Although strong reflexions with extinction were rejected, we could use a total of 78 non-equivalent reflexions from the two crystals for our refinement. Calculations using Zachariasen's (1963) expression for extinction correction showed that the effect of extinction on the weak reflexions was less than the experimental error and could therefore be ignored (average extinction coefficient $C=0.3$).

Computation

The structure analysis was carried out on an IBM 7044 computer using the full-matrix least-squares ORFLS program (Busing, Martin & Levy, 1962).

In all the calculations Dirac-Slater scattering factors (Cromer & Waber, 1965) were used for X-rays and the following neutron scattering lengths:

$$b(\text{Ba}) = 0.528 \times 10^{-12} \text{ cm (Brookhaven National Laboratory, 325, 1966)}$$

$$b(\text{Ti}) = -0.36 \times 10^{-12} \text{ cm}^*$$

$$b(\text{O}) = 0.580 \times 10^{-12} \text{ cm (Brookhaven National Laboratory, 325, 1968)}$$

Weighting scheme

Attempts to arrive at a weighting scheme for the X-ray data on the basis of statistical errors and observed differences between equivalent reflexions indicated that neither of these sources of error could fully account for the discrepancies between the observed and calculated structure factors, and that the discrepancies must be attributed to other sources of error (in the subtraction of background, contribution due to simultaneous reflexions and thermal diffuse scattering (TDS) effects. Unit weights were therefore employed.

For the neutron diffraction data, the weighting scheme was based on the discrepancies between equivalent reflexions, these being larger than the statistical errors.

Previous models

The unit cell of tetragonal BaTiO₃ has dimensions $a=3.9945$ and $c=4.0335$ Å (Rhodes, 1949) and contains one formula unit of BaTiO₃ with atoms in the following locations:

Ba in (*a*): 0, 0, 0 selected origin

Ti in (*b*): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \Delta z_{\text{Ti}}$

O(1) in (*b*): $\frac{1}{2}, \frac{1}{2}, \Delta z_{\text{O}(1)}$

O(2) in (*c*): $\frac{1}{2}, 0, \frac{1}{2} + \Delta z_{\text{O}(2)}$; $0, \frac{1}{2}, \frac{1}{2} + \Delta z_{\text{O}(2)}$.

It is assumed that the structure can be completely described in terms of 12 parameters – three position

* A suitable average of the two values currently accepted $b(\text{Ti}) = -0.34 \pm 0.02 \times 10^{-12}$ cm (Shull, Wilkinson & Mueller, 1960), $b(\text{Ti}) = -0.37 \pm 0.01 \times 10^{-12}$ cm (Brookhaven National Laboratory, 325, 1968).

parameters z_{Ti} , $z_{O(1)}$, $z_{O(2)}$ and nine temperature parameters, two for each of Ba, Ti, and O(1), and three for O(2).

Table 1 shows the reliability indices of Evans's two 12-parameter models (E_1, E_2) (Evans, 1961) and the 12-parameter model of Danner *et al.* (1960) calculated with the present X-ray and neutron data. From this Table it appears that the model of Frazer *et al.* is the most reliable of the three.

Table 1. R values for Evans's two models (E_1, E_2) and the model of Frazer *et al.* (F)

	X-rays	Neutrons
E_1	0.037	0.087
E_2	0.030	0.089
F	0.039	0.052

In the case of the X-ray data, the reliability indices of the three models are almost the same. This indicates that it is not possible to distinguish between them by using only X-ray diffraction techniques (Shirane, Jona & Pepinsky, 1955; Shirane & Jona, 1962). A closer look at the models, however, shows that the differences are mainly in the oxygen parameters, the accurate values of which cannot be determined from the X-ray data, because the oxygen contribution to the X-ray structure factors is almost negligible, especially at high scattering angles.

In the case of neutron diffraction there is no such problem with the oxygen parameters, since in this case the scattering lengths of the three atoms are approximately equal. The different circumstances of scattering power and form factors do not, however, as may be

expected, prevent the coupling of the parameters. Calculation of the correlation matrix for the 12-parameter model of Frazer *et al.* using the present neutron data indicated strong correlation between z_{Ti} and all β_{33} parameters including $\beta_{33}(\text{Ba})$ (Danner *et al.*, 1960) as well as correlation between the three position parameters z_{Ti} , $z_{O(1)}$, and $z_{O(2)}$. The coupling of the parameters cannot be eliminated or avoided simply by changing the structure analysis technique (Evans, 1961) but it may be reduced by using two different types of diffraction data: X-ray data from which the Ba and Ti parameters can be determined fairly accurately in combination with neutron data which is very sensitive to the oxygen position parameters.

Analysis of the experimental data

Assumption

Because of the parameter-interaction problem, before any refinement of the experimental data is attempted, it is essential that some limiting assumptions concerning the temperature parameters be made. From a study of the X-ray thermal diffuse scattering of BaTiO_3 (Harada & Honjo, 1967) it was noted that contributions to the temperature parameter of the k th atom along the c axis, $\beta_{33}(k)$, come mainly from the acoustic vibrations ($\beta_{xx} = B_{xx} \times \frac{1}{4}d^2$ where d is the lattice spacing). For these vibrations, the actual frequency distribution may, to a first approximation, be replaced by a Debye continuous model in which the temperature parameters are independent of mass. We therefore felt justified in assuming that the $\beta_{33}(k)$ temperature parameters were approximately the same for all the atoms, an assumption warranted by reference

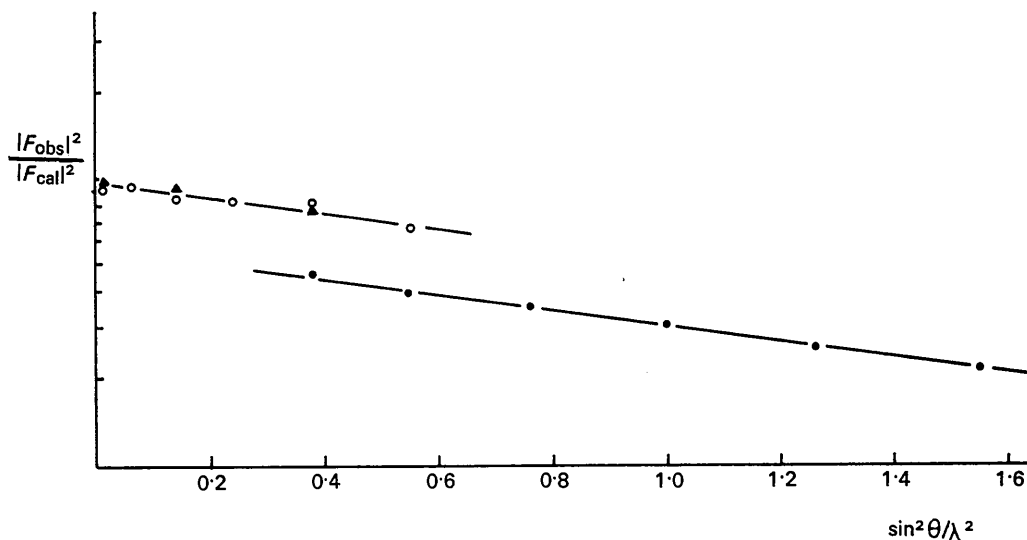


Fig. 1. Graph of $\log_e \frac{|F_{\text{obs}}|^2}{|F_{\text{cal}}|^2}$ vs. $(\sin^2 \theta) / \lambda^2$, where F_{cal} is based on the present model not corrected for thermal motion.

○ Neutron intensities from crystal C4, ▲ neutron intensities from crystal CJ, ● X-ray intensities. For clarity, the two plots have been displaced with respect to one another along the ordinate axis.

to the individual temperature parameters of other substances (*e.g.* KCl, RbCl, CsCl, CsI) for which the frequencies of the acoustic vibrations are very much less than those of the optic vibrations.

The particularly large contribution from the low-frequency transverse optic vibrations as well as the acoustic vibrations in the case of the $\beta_{11}(k)$ temperature parameters (Harada & Pedersen, 1968) indicates that in general $\beta_{11}(k) \neq \beta_{33}(k)$. The use of isotropic temperature parameters may therefore not be satisfactory even in the initial stages of the refinement.

Analysis

As very little is known about the individual $\beta_{11}(k)$ temperature parameters, attention was first focused on the $00l$ type reflexions. With the assumption that $\beta_{33}(k) = \text{constant}$, the number of parameters to be determined from these reflexions is reduced to five.

A reasonable value of z_{Ti} was first obtained from the $00l$ X-ray data, as for these data the contribution of the oxygen atoms to the intensity is very small, particularly in the case of the weak reflexions which are of the form $f(\text{Ba}) - f(\text{Ti}) + f[\text{O}(1)] - 2f[\text{O}(2)]$. Keeping z_{Ti} fixed at the X-ray value, refinement of the neutron $00l$ data yielded the oxygen parameters. These were then used in the X-ray data to obtain a more accurate value of z_{Ti} which was in turn used to obtain more accurate oxygen parameters from the neutron data.

Initially β_{33} was kept constant at 0.0044 corre-

sponding to $B_{33} = 0.29 \text{ \AA}^2$ (Harada & Pedersen, 1968), but the whole procedure was repeated with values of β_{33} varying from 0.0031 to 0.0054, until a model was found which gave satisfactory agreement between the neutron and X-ray results. Figs. 1 and 2 show a plot of $\log_e |F_{\text{obs}}|^2 / |F_{\text{calc}}|^2$ vs. $(\sin^2 \theta) / \lambda^2$ for the present model and also for the models of Frazer *et al.* and Evans for comparison.

Having obtained scale factors, z parameters and β_{33} from the $00l$ reflexions, the full data were used to determine the $\beta_{33}(k)$ parameters. Approximate values of these were obtained from trial calculations of the $hk0$ neutron data which were followed by least-squares refinement, keeping the scale factor constant at all times, as this constitutes the major interaction problem. (It was impossible to obtain oxygen β_{11} parameters from the X-ray data because of the limited number and type of the X-ray reflexions - mainly $h0l$ with small h .)

Refining the X-ray and neutron data independently, the z parameters, scale factors and β_{33} were redetermined using the full set of data. This was done by first varying the z parameters and keeping β_{33} constant, then varying all β_{33} keeping the z parameters constant. The whole process was then repeated from the determination of the $\beta_{11}(k)$ to the z parameters and β_{33} . Finally all parameters were varied to obtain the correlation matrices (see Appendix). The result of the analysis is shown in Table 2.

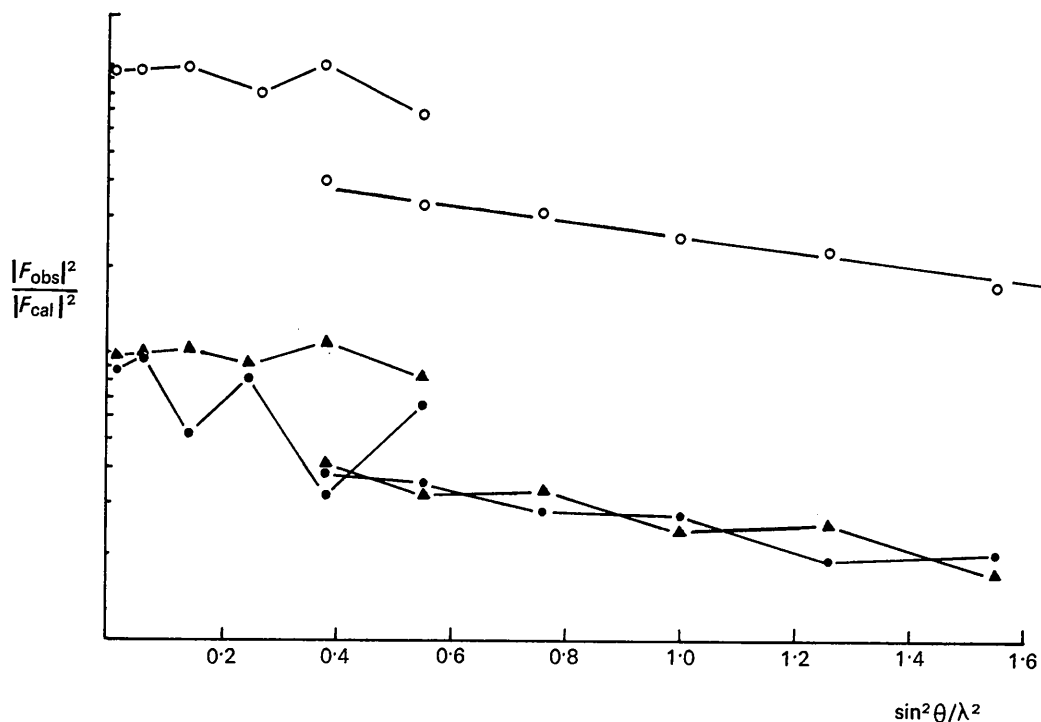


Fig. 2. The same as Fig. 1 for Evans's two models and the model of Frazer *et al.* ● Evans's model 1, ▲ Evans's model 2, ○ model of Frazer *et al.*

Table 2. *Crystal structure models proposed for tetragonal BaTiO₃*

	Theoretical*		X-rays	Neutrons	Frazer <i>et al.</i>	Evans (1)	Evans (2)
Δz_{Ti}			0.0135 ± 0.0004	0.0135	0.013	0.015	0.012
$\Delta z_{O(1)}$			-0.024 ± 0.001	-0.0250 ± 0.0004	-0.023	-0.024	-0.026
$\Delta z_{O(2)}$			-0.0150 ± 0.0009	-0.0150 ± 0.0003	-0.013	-0.020	0.0
B_{33} (Å ²)	Ba	0.29	0.21	0.32 ± 0.007	0.34 ± 0.04	0.37	0.28
	Ti	0.29	0.21	0.32 ± 0.02	0.33 ± 0.04	0.42	0.30
	O(1)	0.29	0.21	0.32	0.32 ± 0.03	0.40	0.50
	O(2)	0.29	0.21	0.32	0.33 ± 0.03	0.42	0.90
B_{11} (Å ²)	Ba			0.51 ± 0.06	0.53 ± 0.06	0.31	0.27
	Ti			0.30 ± 0.2	0.27 ± 0.06	0.67	0.46
	O(1)			0.57	0.57 ± 0.06	0.45	0.90
	O(2)			0.67	0.67 ± 0.01	0.62	0.60
B_{22} (Å ²)	O(2)			0.56	0.56 ± 0.01	0.45	0.90
R				0.024	0.027		
wR				0.028	0.026		
S^\dagger				0.35	2.96		

* Left-hand column corresponds to the case of constant E , the right-hand column corresponds to constant P .

† $S = \frac{1}{N-M} \sum w|F_{obs} - F_{calc}|^2$ where $w = 1$ for X-rays and $1/\sigma_{obs}^2$ for neutrons; N is the number of observations and M is the number of variable parameters.

At the end of the refinement the neutron scattering lengths of Ba and Ti were varied. Best results ($R = 0.027$, $wR = 0.022$, $S = 2.51$) were obtained with

$$b(\text{Ba}) = 0.522 \pm 0.001^* \times 10^{-12} \text{ cm},$$

$$b(\text{Ti}) = -0.359 \pm 0.001 \times 10^{-12} \text{ cm}.$$

Table 3(a) lists the calculated and observed structure factors for the neutron diffraction.

* This is in agreement with the value obtained by Cooper, Rouse & Willis (1968).

Table 3. *Calculated and observed structure factors*

(a) Neutron diffraction, for crystals CJ and $C4$

* Denotes reflexions omitted in the structure analysis.

hkl	CJ		$C4$		hkl	$F(\text{obs})$	$F(\text{calc})$	$F(\text{obs})$	$F(\text{calc})$
	$F(\text{obs})$	$F(\text{calc})$	$F(\text{obs})$	$F(\text{calc})$					
010	0.291	0.295	0.276*	0.296	210	0.286	0.289	0.275*	0.290
020	1.300*	1.786	1.150*	1.794	220	1.353*	1.718	1.256	1.726
030	0.289	0.296	0.283	0.297	230	0.279	0.290	0.280	0.291
040	1.339*	1.590	1.111*	1.597	240	1.356*	1.529	1.229*	1.536
050	0.295	0.295	0.261	0.297	250	0.277	0.289	0.296	0.290
060	1.203*	1.308			310	0.382	0.380	0.374	0.382
001	0.305	0.295	0.293	0.295	320	0.279	0.290	0.279	0.291
002	1.532*	1.831	1.890	1.839	330	0.347	0.359	0.348	0.361
003	0.312	0.296	0.299	0.297	340	0.278	0.272		
004	1.694*	1.753	1.781	1.761	410	0.263	0.271		
005	0.319	0.309	0.324	0.311	420	1.371*	1.529		
006	1.601	1.608	1.630	1.626	430	0.278	0.272		
101	0.420	0.401	0.428	0.403	440	1.106*	1.360		
102	0.390	0.386	0.399	0.387	111	1.909*	2.497	2.505	2.508
103	0.378	0.357	0.387*	0.359	112	0.404	0.396	0.389	0.398
104	0.554	0.542	0.543	0.544	113	1.836*	2.340	2.280	2.350
105	0.301	0.291	0.286	0.292	114	0.372	0.377	0.365	0.378
201	0.295	0.295	0.292	0.296	115	1.952*	2.053	2.065	2.063
202	1.580*	1.762	1.886	1.770	221	0.292	0.295	0.295	0.295
203	0.287	0.294	0.298	0.296	222	1.585*	1.696	1.795	1.703
204	1.602*	1.688	1.729	1.696	223	0.293	0.293	0.295	0.294
205	0.304	0.305	0.300	0.306	224	1.510*	1.626	1.520	1.633
					225	0.306	0.301	0.278	0.302

Table 3 (cont.)

hkl	$F(\text{obs})$	$F(\text{calc})$	$F(\text{obs})$	$F(\text{calc})$
301	0.394	0.391		
302	0.384	0.377		
303	0.356	0.347		
304	0.522	0.519		
401	0.286	0.294	0.281	0.294
402	1.550	1.570	1.667	1.577
403	0.292	0.290	0.290	0.291
404	1.371	1.508	1.428	1.515
110	0.398	0.402	0.395	0.404
120	0.288	0.289	0.276*	0.290
130	0.382	0.380	0.374	0.382
140	0.285	0.271	0.265	0.273
150	0.326	0.340	0.311	0.342
210	0.286	0.289	0.275*	0.290
220	1.353*	1.718	1.256	1.726
230	0.279	0.290	0.280	0.291
240	1.356*	1.529	1.229*	1.536
250	0.277	0.289	0.296	0.290
310	0.382	0.380	0.374	0.382
320	0.279	0.290	0.279	0.291
330	0.347	0.359	0.348	0.361
340	0.278	0.272		
410	0.263	0.271		
420	1.371*	1.529		
430	0.278	0.272		
440	1.106*	1.360		
111	1.909*	2.497	2.505	2.508
112	0.404	0.396	0.389	0.398
113	1.836*	2.340	2.280	2.350
114	0.372	0.377	0.365	0.378
115	1.952*	2.053	2.065	2.063
221	0.292	0.295	0.295	0.295
222	1.585*	1.696	1.795	1.703
223	0.293	0.293	0.295	0.294
224	1.510*	1.626	1.520	1.633
225	0.306	0.301	0.278	0.302

Table 3 (cont.)

<i>hkl</i>	<i>CJ</i>		<i>C4</i>	
	<i>F</i> (obs)	<i>F</i> (calc)	<i>F</i> (obs)	<i>F</i> (calc)
331	1.900*	2.194	2.223	2.205
332	0.352	0.354	0.359	0.356
333	1.758*	2.056	2.001	2.064
121	0.401	0.389	0.404	0.391
122	0.386	0.376	0.390	0.378
123	0.361	0.346	0.341	0.347
124	0.528	0.528	0.512*	0.531
125	0.286	0.279	0.285	0.281
131	2.000*	2.341	2.450	2.352
132	0.390	0.374	0.376	0.376
133	1.851*	2.193	2.200	2.202
134	0.350	0.356		
141	0.347	0.356	0.334*	0.357
142	0.369	0.351	0.364	0.353
143	0.304	0.313	0.302	0.314
144	0.487	0.490		
151	1.828	2.060	2.150	2.068
152	0.352	0.336	0.323	0.338
231	0.385	0.379	0.378	0.381
232	0.369	0.368	0.369	0.370
233	0.000*	0.336	0.000*	0.337
234	0.499	0.506	0.510	0.509
241	0.303	0.293	0.275*	0.294
242	1.558	1.511	1.558	1.518
243	0.302	0.288		
251	0.329	0.360	0.322	0.361
252	0.348	0.351	0.350	0.353
341	0.315	0.348	0.316	0.349
342	0.352	0.343	0.350	0.344

Table 3 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> (obs)	<i>F</i> (calc)
1	1	7	14.07	13.96
1	1	8	15.25	15.84
1	1	9	9.85	10.20
1	1	10	10.76	11.14
1	1	11	7.01	7.34
1	2	7	18.90	18.84
1	2	8	9.32	9.16
1	2	9	13.94	13.65
1	2	10	6.89	7.27
1	3	7	12.79	12.44
1	3	8	14.64	14.39
1	3	9	9.21	9.23
1	3	10	9.95	10.21
1	4	7	16.11	16.12
1	4	8	8.12	7.78
1	4	9	11.85	11.95
1	4	10	6.25	6.32
2	2	7	9.95	9.27
2	2	8	16.40	16.49
2	2	9	7.36	7.16
2	2	10	10.75	11.12
2	3	7	17.17	16.97
2	3	8	8.60	8.21
2	3	9	12.43	12.49
2	3	10	6.61	6.63
2	4	7	8.28	7.78
2	4	8	14.47	14.24
2	4	9	6.64	6.23
2	4	10	9.48	9.73
3	3	7	11.08	11.02
3	3	8	13.27	13.10
3	3	9	8.49	8.37
3	3	10	8.70	9.38

Table 3 (cont.)

(b) Calculated and observed structure factors (X-rays)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> (obs)	<i>F</i> (calc)
0	0	5	15.42	14.77
0	0	6	27.17	27.11
0	0	7	10.93	10.33
0	0	8	18.58	18.26
0	0	9	8.00	7.91
0	0	10	12.14	12.17
1	0	8	9.99	9.68
1	0	9	13.85	14.31
1	0	10	7.23	7.63
1	0	11	8.87	9.75
2	0	7	9.82	9.86
2	0	8	17.10	17.35
2	0	9	7.67	7.51
3	0	7	18.10	17.87
3	0	8	8.21	8.67
3	0	9	11.99	13.05
3	0	10	6.65	6.94
4	0	7	8.68	8.21
4	0	8	15.34	14.95
4	0	9	6.69	6.53
4	0	10	10.28	10.17

Because of the differing quality of the two faces of the crystal used for the X-ray measurements, no attempt was made to determine the polarity of the crystal experimentally. Instead, calculations with Cromer's (1965) dispersion corrections were carried out in the last stages of the refinement of the X-ray data, assuming that all the *l* indices were positive or negative, as well as a calculation in which it was assumed that fifty per cent of the crystal face consisted of 00*l* domains and the other fifty per cent of 00*l* domains. The latter assumption and the assumption that all *l* indices are positive yielded essentially the same results, the standard errors being somewhat lower when all *l* indices were assumed to be positive. The assumption that all *l* indices are negative resulted in larger standard errors and a slightly higher value of the reliability indices. Tables 2 and 3(b) list the results obtained when it was assumed that all *l* indices are positive.

Although our model was obtained by assuming the individual β_{33} temperature parameters of all the atoms to be approximately equal, it can be shown that the analysis is to some extent independent of this initial

Table 4. The effect of different values of z_{Ti} on the B_{33} temperature parameters for the X-ray (X) and neutron (N) diffraction data

	A		B		C		D		E		F	
	$\Delta z_{\text{Ti}}=0.016$		$\Delta z_{\text{Ti}}=0.015$		$\Delta z_{\text{Ti}}=0.014$		$\Delta z_{\text{Ti}}=0.0135$		$\Delta z_{\text{Ti}}=0.013$		$\Delta z_{\text{Ti}}=0.012$	
	X	N	X	N	X	N	X	N	X	N	X	N
B_{33} (\AA^2)												
Ba	0.33	0.52	0.33	0.48	0.33	0.42	0.32	0.34	0.32	0.34	0.32	0.32
Ti	0.19	0.34	0.24	0.34	0.29	0.34	0.31	0.33	0.33	0.33	0.38	0.35
O(1)	0.44	0.27	0.40	0.29	0.34	0.30	0.33	0.32	0.31	0.32	0.28	0.33
O(2)	0.57	0.34	0.57	0.34	0.57	0.33	0.54	0.33	0.54	0.33	0.54	0.32
R	0.024	0.028	0.024	0.027	0.024	0.027	0.023	0.027	0.023	0.027	0.023	0.028
wR	0.027	0.027	0.027	0.026	0.027	0.026	0.027	0.026	0.027	0.026	0.027	0.026
S	0.34	2.97	0.34	2.96	0.34	2.96	0.34	2.96	0.34	2.96	0.34	2.97

assumption. As an example, Table 4 shows the effect of different values of z_{Ti} on the β_{33} parameters. Model D with equal values of the individual temperature parameters is the only model which yields consistent results for both X-rays and neutrons, in agreement with our previous conclusion.

Discussion

Table 4 summarizes the present model, previous models and the results of the theoretical calculations. Table 5 lists the atomic shifts and bond distances in Angstrom units.

Table 5. Atomic shifts and bond distances

Bond lengths		Atomic shifts	
Ti-O(1)	2.1720 \AA	Δz (Ti)	0.0544 \AA
Ti-O(2)	2.0300	Δz [O(1)]	0.1008
Ba-O(1)	2.8425	Δz [O(2)]	0.0617
Ba-O(2)	2.7948		

In view of the fact that we have only used X-ray intensities obtained at high 2θ angles no knowledge of the exact ionic state of the atoms was required.

From Table 2, we see that the theoretical calculation gives two different values for the temperature parameters corresponding to the two different values of the elastic constants, constant electric field E and constant polarization P . For the condition $P=\text{const.}$ to be fulfilled, the crystal must be completely insulated, as is the case for substances like KDP where the ferroelectric phase occurs at such low temperatures that both the crystal and the surrounding medium can be considered to be perfect insulators (Shirane & Jona, 1962). In BaTiO_3 , however, this is no longer the case. It is not yet certain which elastic constants correspond more closely to the acoustic phonon dispersion curve at wave number $q=0$. The present results, $B_{33}=0.32 \pm 0.03$ for X-rays and $0.33 \pm 0.04 \text{\AA}^2$ for neutrons, are very close to the theoretically expected value ($B_{33}=0.29 \text{\AA}^2$) using $E=\text{const.}=0$.

Previously it was expected from the experimental results of Evans (1961) and Danner *et al.* (1960) that

the contribution of the optic vibrations to the temperature parameters of the heavy atoms would be very small. The present analysis, however, shows that $\beta_{11}(\text{Ba}) > \beta_{11}(\text{Ti})$.

Calculation of $\sum_k m_k B(k)$, where m_k is the mass of the k th atom, for the B_{11} temperature parameters gives $\bar{B}_{11}=0.50 \text{\AA}^2$ which is slightly lower than the value expected from the theoretical calculations (0.70\AA^2) (Harada & Pedersen, 1968).

The model that we propose was obtained by least-squares refinement of both X-ray and neutron data. [No attempt has been made to correct the data for TDS, the effect of which is apparently similar in the two techniques (Coppens, 1968).] Because of the high correlation between some parameters, it would appear that the structure of BaTiO_3 cannot be reliably solved by either neutron or X-ray diffraction alone. Inspection of the correlation matrices (see Appendix) shows that there are in the case of X-rays seven, and in the case of neutrons ten, elements greater than 0.8. Except for one instance (where correlation is avoided through our initial assumption that the β_{33} are independent of atomic mass) these are different elements in the case of X-rays and neutrons – where the neutron data exhibit strong correlation, the correlation in the X-ray data is small and *vice versa*.

It is possible to obtain a slightly different model with a somewhat lower R value ($R=0.022$) from the X-ray data, but since this model differs in the $\beta_{33}(\text{O})$ parameters only, the difference is not significant. This model can furthermore be rejected by testing it with the neutron data ($R=0.035$).

The present structure analysis is based on the assumption that tetragonal barium titanate can be described in terms of the previously listed 12 parameters. An alternative model has very recently been proposed by Comes, Lambert & Guinier (1968) in which the tetragonal phase of barium titanate is regarded as a partially disordered phase of the rhombohedral structure. They suggest that the difficulties encountered in solving the tetragonal structure may arise from a wrong assignment of structure parameters. This does not take into account Geller's considerations (Geller, 1961) which indicate that the structure is difficult to solve because of the high correlation between some of the

APPENDIX
Correlation matrix from BaTiO₃ least-squares calculation for X-ray and neutron diffraction data
Correlation matrix – X-ray diffraction data

S	$\beta_{11}(\text{Ba})$	$\beta_{33}(\text{Ba})$	z_{Ti}	$\beta_{11}(\text{Ti})$	$\beta_{33}(\text{Ti})$	$z\text{O}(1)$	$\beta_{11}[\text{O}(1)]$	$\beta_{33}[\text{O}(1)]$	$z\text{O}(2)$	$\beta_{11}[\text{O}(2)]$	$\beta_{22}[\text{O}(2)]$	$\beta_{33}[\text{O}(2)]$	S
1.00	0.29	0.61	0.14	0.04	-0.07	0.12	-0.17	0.37	0.11	-0.01	0.02	0.14	$\beta_{11}(\text{Ba})$
	1.00	0.01	0.18	-0.33	-0.12	0.06	-0.63	0.48	0.17	-0.07	0.14	0.16	$\beta_{33}(\text{Ba})$
		1.00	0.79	0.32	-0.76	0.54	0.07	0.52	0.66	-0.08	-0.16	0.66	z_{Ti}
			1.00	0.27	-0.98	0.64	-0.02	0.64	0.87	0.13	-0.18	0.84	$\beta_{11}(\text{Ti})$
				1.00	-0.38	0.22	0.46	-0.01	0.23	0.01	-0.39	0.29	$\beta_{33}(\text{Ti})$
					1.00	-0.62	-0.04	-0.57	-0.86	0.13	0.22	-0.84	$z\text{O}(1)$
						1.00	0.08	0.57	0.60	-0.09	-0.15	0.58	$\beta_{11}[\text{O}(1)]$
							1.00	-0.54	-0.03	0.08	-0.20	-0.01	$\beta_{33}[\text{O}(1)]$
								1.00	0.57	-0.12	-0.02	0.54	$z\text{O}(2)$
									1.00	-0.14	-0.18	0.94	$\beta_{11}[\text{O}(2)]$
										1.00	-0.34	-0.25	$\beta_{22}[\text{O}(2)]$
											1.00	-0.30	$\beta_{33}[\text{O}(2)]$
												1.00	

Correlation matrix – neutron diffraction data

S₁*	S_2^*	$\beta_{11}(\text{Ba})$	$\beta_{33}(\text{Ba})$	z_{Ti}	$\beta_{11}(\text{Ti})$	$\beta_{33}(\text{Ti})$	$z\text{O}(1)$	$\beta_{11}[\text{O}(1)]$	$\beta_{33}[\text{O}(1)]$	$z\text{O}(2)$	$\beta_{11}[\text{O}(2)]$	$\beta_{22}[\text{O}(2)]$	$\beta_{33}[\text{O}(2)]$	S ₁
1.00	0.46	-0.10	-0.16	-0.21	0.62	0.00	0.10	-0.05	0.35	0.10	-0.05	-0.07	0.03	S_2
	1.00	0.06	-0.31	-0.38	0.31	-0.13	0.13	0.08	0.54	0.23	0.09	0.09	0.24	$\beta_{11}(\text{Ba})$
		1.00	-0.19	-0.15	-0.21	-0.15	-0.19	0.98	0.03	0.04	0.99	0.99	0.03	$\beta_{33}(\text{Ba})$
			1.00	0.96	-0.17	0.62	-0.57	-0.21	-0.65	-0.74	-0.19	-0.19	0.27	z_{Ti}
				1.00	-0.15	0.43	-0.38	-0.17	-0.79	-0.56	-0.16	-0.16	0.35	$\beta_{11}(\text{Ti})$
					1.00	-0.24	0.26	-0.05	0.13	0.26	-0.15	-0.16	0.14	$\beta_{33}(\text{Ti})$
						1.00	-0.88	-0.21	-0.06	-0.94	-0.16	-0.15	-0.15	$z\text{O}(1)$
							1.00	-0.14	0.07	0.94	-0.17	-0.18	0.14	$\beta_{11}[\text{O}(1)]$
								1.00	0.02	0.09	0.98	0.00	0.00	$\beta_{33}[\text{O}(1)]$
									1.00	0.19	0.04	-0.28	-0.28	$z\text{O}(2)$
										1.00	0.05	0.05	0.15	$\beta_{11}[\text{O}(2)]$
											1.00	0.99	0.03	$\beta_{22}[\text{O}(2)]$
												1.00	-0.03	$\beta_{33}[\text{O}(2)]$
													1.00	

* S₁, S₂ scale factors for crystals C_J and C₄ respectively.

parameters. While we cannot reject the proposal of Comes, Lambert & Guinier, the present analysis does show that it is in fact possible to determine the structure with reasonable accuracy when the correlation problem is avoided by the use of both X-ray and neutron diffraction data.

After this work was completed, the authors became aware of an unpublished refinement of a previous neutron diffraction analysis by Frazer (1962) with the following results:

$$\begin{array}{ll} \Delta z_{\text{Ti}} = 0.014 \pm 0.002 & B_{33}(\text{Ba}) = 0.42 \pm 0.08 \text{ \AA}^2 \\ \Delta z_{\text{O}(1)} = 0.0249 \pm 0.0006 & B_{33}(\text{Ti}) = 0.45 \pm 0.05 \\ \Delta z_{\text{O}(2)} = 0.0156 \pm 0.0007 & B_{33}[\text{O}(1)] = 0.35 \pm 0.04 \\ & B_{33}[\text{O}(2)] = 0.47 \pm 0.02 \\ & B_{11}(\text{Ba}) = 0.30 \pm 0.02 \\ & B_{11}(\text{Ti}) = 0.56 \pm 0.06 \\ & B_{11}[\text{O}(1)] = 0.46 \pm 0.02 \\ & B_{11}[\text{O}(2)] = 0.55 \pm 0.04 \\ & B_{22}[\text{O}(2)] = 0.45 \pm 0.02 \end{array}$$

The position parameters of this refinement are in excellent agreement with our results, but the temperature parameters are not. Use of the above values with our X-ray and neutron data results in higher values of the reliability indices than those obtained with our position and temperature parameters.

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X-ray Diffraction from Hexagonal Close-Packed Crystals with Deformation Stacking Faults. II. Effect of Change in Layer Spacing at Faults

BY SHRIKANT LELE

Department of Metallurgy, Banaras Hindu University, Varanasi, India

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The Christian-Gevers theory of X-ray diffraction from hexagonal close-packed crystals with deformation stacking faults is extended to include the effect of change in layer spacing at the faults. The results show that integral breadths as well as integrated intensities remain unaffected to a first approximation. The principal effect is to introduce peak shifts, the magnitude and direction of which depend on the reflexion.

Introduction

Diffraction effects due to the presence of deformation stacking faults in h.c.p. crystals are predicted under

the following assumptions (Christian, 1954; Gevers, 1954; Lele, Anantharaman & Johnson, 1967):

- (1) the crystal is infinite in size and is free from distortions;