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An X-Ray Diffraction Study of Tetragonal Barium Titanate

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In order accurately to determine the parameters of the crystal structure of ferroelectric tetragonal barium titanate, X-ray diffraction intensity data were gathered from a small, untwinned, single crystal by means of a Geiger counter apparatus specially built for the purpose. 99 independent $h0l$ data were collected, and corrected for absorption and secondary extinction by an exact integration method. Of these, 83 were used for the structure refinement, the remainder (with $(\sin\theta)^2/\lambda^2 \leq 0\cdot250$) being subject to primary extinction effects. The structure was refined first by trial and error methods, then by least-squares analysis; first on the basis of a 4-parameter model, and finally with a 12-parameter model. When an attempt was made to solve the full least-squares matrix of the 12-parameter model (plus scale factor), anomalous results were obtained, and it became apparent that the structure is essentially indeterminate. This situation is caused by gross interactions between the z and B_{33} parameters, among others, for each of the atoms. Anomalously large standard deviations for these parameters have been calculated from the least-squares matrix.

It is suggested that such anomalous errors may be encountered in crystals having a polar space group, but which deviate only by small atomic displacements from a higher symmetry group. Ferroelectric crystals are generally of this type and may be generally indeterminate with any reasonable, true accuracy.

Introduction

Perhaps no other substance has been more extensively studied in all aspects of its physical properties than barium titanate. Interest in the compound was first aroused in 1945 when its unusual ferroelectric properties were discovered by von Hippel, Breckenridge, Chesley and Tisza (1946). This was the third crystal, after the classical cases of Rochelle salt and potassium dihydrogen phosphate, found to have such properties. A theoretical study of barium titanate appeared to be especially promising because its crystal structure is extremely simple. For the first time there seemed to be a reasonable possibility of directly relating the gross vectorial electrical and other physical properties directly to the atomic arrangement and crystal fields on an atomic scale, in a case where few structural parameters are involved and the mathematics might be numerically manageable. Unfortunately, this hope has since been only partly realized. Of pivotal importance in such treatments is an exact knowledge of the crystal structure parameters, of which there are only three in tetragonal barium titanate. This paper describes an attempt to measure these parameters, an attempt which failed because of an inherent instability in the basic structure factor functions which was discovered late in the investigation.

The study was begun by the author in 1948 at the Laboratory for Insulation Research at Massachusetts Institute of Technology. Here, from a melt prepared by B. T. Matthias, an untwinned specimen was selected which was used for all the measurements of this study. Attempts to measure the diffraction intensities from this crystal by film methods were carried on for a year and finally abandoned when it became apparent that the most careful photographic techniques could never give the accuracy required for the structure determination of barium titanate. At that laboratory the method for the correction of the diffraction intensities for absorption was developed (Evans, 1952*a*). When the author transferred to Philips Laboratories in Irvington-on-Hudson, New York in November, 1949, the study was continued with the development of Geiger counter techniques for diffraction intensity measurement (Evans, 1952*b*). In late 1951 a reliable set of diffraction intensity data was finally obtained in this way, and the numerical calculation begun. After an early, overoptimistic result (Evans, 1951), these calculations revealed the unstable character of the diffraction functions in the case of tetragonal barium titanate. Since computing facilities adequate for a complete analysis of the least-squares error functions involved were not available, the work was stopped at the end of 1952. A detailed summary of the work was published in two internal reports (Evans, 1952*c*, 1953), which have been widely circulated.

With the advent of large scale computing machinery in recent years, it has become possible to complete the analysis of the barium titanate problem. This work has been done by S. Geller of the Bell Telephone Laboratories using the data set forth herein, and is described in a separate paper (Geller, 1961). The author gratefully acknowledges his interest and co-

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Experimental data

The phase transitions of barium titanate have been traced in detail by Forsbergh (1949) by optical methods, and by Rhodes (1949) by X-ray diffraction methods. The simple cubic nonferroelectric structure becomes tetragonal at 120 °C., orthorhombic at -5 °C., and rhombohedral at -90 °C. All the forms below 120 °C. are polar and ferroelectric, and the displacive transformations are very sensitive to external forces. All diffraction measurements in this study were made at room temperature, with the crystal in the tetragonal form.

The space group of tetragonal barium titanate is $P4mm(C_{4v}^1)$. The unit cell has

$$a = 3{\cdot}9945 \quad \text{and} \quad c = 4{\cdot}0335 \text{ Å},$$

and contains one formula unit of $BaTiO_3$ (Rhodes, 1949). The atoms are located as follows:

Ba in (a): 0, 0, 0 (selected origin);
Ti in (b): $\frac{1}{2}, \frac{1}{2}, [\frac{1}{2}+z(\text{Ti})]$;
O_1 in (b): $\frac{1}{2}, \frac{1}{2}, z(O_1)$;
2 O_2 in (c): $0, \frac{1}{2}, [\frac{1}{2}+z(O_2)]$; $\frac{1}{2}, 0, [\frac{1}{2}+z(O_2)]$.

There are three position parameters, $z(\text{Ti})$, $z(O_1)$ and $z(O_2)$. Ba, Ti and O_1 all lie on fourfold rotation axes, while the O_2 atoms lie on twofold axes. If the thermal motion of each atom is represented in terms of a triaxial ellipsoid, these may be defined in terms of two parameters each for Ba, Ti and O_1, and three parameters for O_2. The structure may thus be completely described in terms of 12 parameters.

Nearly all of the diffraction intensities of the type $h0l$ within reach of Mo $K\alpha$ radiation were measured to provide the basic experimental data for the measurement of these parameters. The crystal is sufficiently hard that Bragg reflections are not markedly damped by temperature vibration and are still fairly strong even at the highest angles where $(\sin\theta)/\lambda$ approaches 1·41. The total number of hkl reflections to be expected in this range is about 6,000, but, mainly because of the difficulties of correcting for absorption, we had to be content with measuring only the $h0l$ reflections, of which there are 405. With the Geiger counter instrumentation it was possible to measure 356 of these, and the resulting data, after averaging, yield 99 symmetrically non-equivalent Bragg amplitudes.

All measurements were made with a euhedral, optically untwinned single crystal, having the dimensions 0·071 (c axis) × 0·160 × 0·193 mm. This crystal was taken from a preparation made by B. T. Matthias, and was grown in a flux of $BaCl_2$ with a small excess of BaO over TiO_2, in the presence of one mole ratio of B_2O_3 to $BaTiO_3$ to minimize twinning (Matthias, 1948). The crystal was mounted on a glass fiber and placed on a standard Weissenberg camera for X-ray study. As mentioned earlier, film was not used for the intensity measurements, but rather, special counter apparatus and techniques were devised in order to obtain measurements of the greatest possible accuracy. To this end, a Geiger counter was mounted on a bracket set in place of the film holder on the Weissenberg camera in such a way that the bracket pivot is coincident with the crystal-spindle axis of the camera. Standard Norelco Wide-Range X-ray Diffractometer circuits were used to record the counter impulses. Measurements were made by rocking the crystal through a sufficiently large angle to register the α_1 and α_2 peaks for each reflection, while accumulating the total number of counts on a register. The counting rate was recorded simultaneously on a strip chart recorder in order to establish the purity of the reflection, and determine the background level. The total background calculated from the strip chart record was then subtracted from the registered count total to obtain the number of counts corresponding to the area under the diffraction peaks. No filter was used, so that maximum intensity could be gained.

Considerable care was taken to insure the accuracy and reproducibility of these measurements. An X-ray tube space current regulator was used to maintain this current constant without drift to 0·1 percent. This regulation together with 0·1 percent primary voltage regulation was found to be adequate without monitoring the X-ray beam. A standard reflection was remeasured periodically throughout the work. Intensity measurements were reproducible to about 1 percent where the predicted statistical error would be about 0·3 percent. Variations among equivalent reflections, resulting probably from variations in absorption and extinction conditions, were frequently higher, sometimes as high as 5 percent, and occasionally, for very strong reflections (excluded from subsequent calculations) up to 10 percent. A detailed description of the apparatus and technique used to make these measurements has been published elsewhere (Evans, 1952b).

The integrated intensities measured in this way for 356 reflections were averaged for the 99 nonequivalent reflections. The latter are listed in Table 1 under the heading I(rel), where the numbers are the count totals (background subtracted) divided by the scale factor of 128.

Accurate correction for absorption was early recog-

Table 1. *X-ray diffraction data for tetragonal barium titanate*

$|F|$(calc.), α and $\Delta|F|$ are based on Model 5, Table 2

* denotes reflections omitted in the structure analysis

$h0l$	I (rel.)	μ (cm.$^{-1}$)	A	$\|F\|$ (obs.)	$\|F\|$ (calc.)	α (deg.)	$\Delta\|F\|$	$\sigma\|F\|$ (stat.)	$\sigma\|F\|$ (sym.)
000	—	—	—	—	104·0	0	—	—	—
100*	1630	253	0·169	18·8	24·2	0	−5·4	0·09	0·83
200*	3140	407	0·066	60·1	65·5	0	−5·4	0·16	1·74
300*	587	208	0·237	17·3	20·9	0	−3·6	0·06	0·07
400*	1492	237	0·197	36·3	40·3	0	−4·0	0·13	1·33
500	244	200	0·247	15·4	15·6	0	−0·2	0·10	0·06
600	496	208	0·228	23·3	27·8	0	−4·5	0·06	0·08
700	81	198	0·233	11·5	10·7	0	0·8	0·09	0·14
800	198	203	0·213	19·5	18·7	0	0·8	0·07	0·12
900	40	198	0·204	8·4	8·1	0	0·3	0·14	0·15
10,0,0	130	203	0·182	13·2	12·8	0	0·4	0·05	0·04
001*	880	253	0·043	27·3	24·2	−5·9	3·1	0·18	7·35
101*	3410	405	0·058	55·1	55·0	2·1	0·1	0·12	4·80
201*	1042	215	0·212	20·5	21·9	−4·2	−1·4	0·07	1·26
301*	1820	248	0·177	38·2	38·6	1·6	−0·4	0·08	0·32
401	403	203	0·234	17·6	17·5	−2·6	0·1	0·04	0·08
501	642	215	0·216	27·0	27·8	1·4	−0·8	0·04	0·17
601	118	199	0·232	12·7	12·7	−2·3	0	0·05	0·06
701	203	204	0·217	18·9	19·0	1·2	−0·1	0·03	0·05
801	49	198	0·208	9·7	8·9	−2·0	0·8	0·10	0·12
901	98	202	0·199	13·2	13·4	1·3	−0·2	0·07	0·12
10,0,1	32	198	0·180	6·5	6·8	−1·7	−0·3	0·09	0·05
002*	2510	407	0·035	73·4	65·4	0·5	8·0	0·24	6·93
102*	742	215	0·144	20·9	22·7	−1·7	−1·8	0·09	1·19
202*	2610	294	0·104	53·0	52·8	0·6	0·2	0·11	3·00
302*	493	205	0·202	19·2	19·2	−1·8	0	0·04	0·13
402	1280	223	0·202	35·8	36·9	0·9	−1·1	0·09	0·56
502	168	200	0·219	14·2	14·7	−2·4	−0·5	0·04	0·05
602	421	207	0·212	25·7	26·1	1·1	−0·4	0·06	0·12
702	57	198	0·218	10·1	10·6	−2·2	−0·5	0·08	0·04
802	176	202	0·204	18·7	17·7	1·0	1·0	0·06	0·07
902	36	198	0·197	7·9	7·6	−2·3	0·3	0·11	0·17
10,0,2	141	205	0·176	13·2	12·3	0·9	0·9	0·06	0·05
003*	400	208	0·126	19·5	21·0	−9·6	−1·5	0·10	0·32
103*	1200	248	0·085	42·5	39·3	4·8	3·2	0·10	2·34
203*	393	205	0·148	20·0	19·1	−8·7	0·9	0·05	0·08
303	919	219	0·164	32·4	31·7	4·3	0·7	0·05	0·18
403	196	200	0·194	15·5	15·3	−7·5	0·2	0·04	0·02
503	388	209	0·183	25·1	24·7	4·2	0·4	0·04	0·07
603	77	198	0·217	11·3	11·4	−7·5	−0·1	0·06	0·07
703	156	203	0·196	17·9	17·5	3·9	0·4	0·06	0·06
803	41	198	0·188	9·2	8·3	−6·9	0·9	0·10	0·09
903	89	202	0·181	12·4	12·3	3·7	0·2	0·07	0·10
10,0,3	32	198	0·179	5·7	6·4	−5·4	−0·7	0·08	0·07
004*	1232	237	0·137	40·9	39·9	1·9	1·0	0·19	2·28
104	283	203	0·143	19·5	18·0	−3·8	1·5	0·06	0·12
204	891	223	0·112	39·9	36·7	1·9	3·2	0·06	0·15
304	172	200	0·172	15·4	15·6	−4·0	−0·2	0·04	0·03
404	529	210	0·168	29·8	29·5	2·1	0·3	0·07	0·35
504	78	199	0·184	12·0	12·4	−4·6	−0·4	0·07	0·12
604	245	204	0·191	22·2	21·8	2·4	0·4	0·05	0·12
704	41	198	0·174	9·4	9·4	−4·9	0	0·09	0·03
804	137	202	0·179	16·7	15·4	2·3	1·3	0·06	0·05
904	35	198	0·184	7·2	7·2	−4·0	0	0·07	0·05
005	231	200	0·193	16·7	15·5	−13·8	1·2	0·09	0·26
105	562	215	0·173	28·0	28·4	7·1	−0·4	0·48	0·37
205	136	200	0·193	13·5	14·6	−13·5	−1·1	0·37	0·04
305	288	209	0·141	24·5	25·1	6·9	−0·6	0·41	0·07
405	73	199	0·210	10·9	12·4	−12·6	−1·5	0·07	0·05
505	172	204	0·157	20·1	19·5	7·1	0·6	0·07	0·02
605	38	198	0·172	9·4	9·4	−11·7	0	0·10	0·09

Table 1 (*cont.*)

$h0l$	I (rel.)	μ (cm.$^{-1}$)	A	$\|F\|$ (obs.)	$\|F\|$ (calc.)	α (deg.)	$\Delta\|F\|$	$\sigma\|F\|$ (stat.)	$\sigma\|F\|$ (sym.)
705	103	202	0·174	15·2	14·6	6·3	0·6	0·06	0·02
805	27	198	0·179	7·0	7·4	−10·1	−0·4	0·12	0·16
905	104	206	0·197	10·4	11·0	10·0	−0·6	0·05	0·06
006	493	208	0·214	26·5	27·6	3·3	−1·1	0·06	0·23
106	121	199	0·221	13·1	13·4	−7·3	−0·3	0·05	0·04
206	397	207	0·200	25·5	25·8	3·6	−0·3	0·06	0·12
306	83	198	0·200	12·2	11·9	−6·8	0·3	0·07	0·02
406	229	204	0·181	22·1	21·7	3·4	0·4	0·05	0·12
506	46	198	0·181	10·1	9·9	−7·0	0·2	0·09	0·08
606	142	202	0·180	17·6	16·7	3·4	0·9	0·07	0·05
706	39	198	0·198	8·2	8·1	−6·4	0·1	0·09	0·08
806	140	203	0·214	12·8	12·6	3·6	0·2	0·05	0·03
007	99	198	0·261	11·9	11·2	−18·2	0·7	0·10	0·06
107	256	204	0·242	20·0	20·0	10·1	0	0·04	0·07
207	71	198	0·251	10·5	10·4	−18·5	0·1	0·07	0·07
307	184	203	0·230	17·9	18·0	9·6	−0·1	0·05	0·05
407	48	198	0·229	9·2	9·3	−16·9	−0·1	0·09	0·07
507	129	202	0·220	15·2	15·0	9·2	0·2	0·06	0·09
607	33	198	0·230	7·1	8·0	−14·5	−0·9	0·10	0·19
707	137	203	0·232	12·5	11·8	8·8	0·7	0·05	0·03
807	56	198	0·264	5·8	6·5	−12·4	−0·7	0·06	0·04
008	224	203	0·275	18·2	18·2	5·1	0	0·06	0·03
108	69	198	0·283	9·9	9·7	−9·5	0·2	0·07	0·11
208	201	202	0·268	17·4	17·4	5·3	0	0·10	0·03
308	56	198	0·269	9·4	9·0	−8·9	0·4	0·08	0·08
408	169	202	0·264	15·4	15·2	4·9	0·2	0·05	0·08
508	50	198	0·261	7·9	8·0	−7·9	−0·1	0·07	0·02
608	142	203	0·263	11·7	12·5	4·6	−0·8	0·05	0·14
708	62	198	0·284	5·9	6·8	−7·6	−0·9	0·05	0·15
009	61	198	0·304	8·6	8·1	−21·0	0·5	0·11	0·07
109	160	202	0·305	13·8	14·1	11·5	−0·3	0·05	0·04
209	44	198	0·298	7·2	8·0	−19·7	−0·8	0·08	0·08
309	150	202	0·290	12·8	12·8	11·3	0	0·05	0·03
409	56	198	0·290	7·3	7·3	−19·2	0	0·06	0·03
509	148	206	0·287	10·6	11·2	10·8	−0·6	0·04	0·04
0,0,10	172	203	0·315	11·9	12·4	7·0	−0·5	0·06	0·04
1,0,10	72	198	0·321	7·5	7·5	−11·5	0	0·05	0·08
2,0,10	171	205	0·316	11·2	12·1	6·7	−0·9	0·04	0·02
3,0,10	73	198	0·325	6·7	7·2	−11·2	−0·5	0·05	0·04

nized to be essential to the successful interpretation of these data. The absorption correction was determined for each reflection by exact integration, by a method which has already been described in detail (Evans, 1952*a*). When values of A (ratio of intensity of a reflection with absorption to the intensity without absorption) calculated using the computed linear absorption coefficient $\mu = 198$ cm.$^{-1}$ were applied to the measured intensities, it became apparent upon comparison with calculated intensities that secondary extinction is an important factor. Setting $\mu = \mu_0 + gQ$ (where Q is the calculated diffraction intensity without absorption), the best value of g to account for this effect was determined by trial calculations on the 12 strongest reflections. The lowest value for the reliability factor was found to correspond to the value of $g = 5{\cdot}06 \times 10^3$ (see Evans, 1952*a*). All absorption factors A were then recalculated, and these values were used to establish the final observed structure amplitudes, which are listed in Table 1 under $|F|$ (obs.). The values of A used are also listed, as well as the effective absorption coefficient μ (as determined by the secondary extinction effect) which was used to calculate A.

Although the overall agreement between observed and calculated structure factors was excellent even in early stages of refinement, certain of the strongest reflections were anomalously out of line with this general agreement. For example, 200 and 002, which have calculated structure factors both equal to 65·5, are observed to have values of 60·1 and 73·4 respectively. In spite of the drastic thermal history of the crystal and the use of molybdenum radiation, this effect probably results in part, at least, from the influence of an appreciable amount of primary extinction. Since there is no way to account for this effect under the present conditions, it has been necessary to exclude the seriously affected reflections from consideration in the structure analysis. To keep this selection otherwise impartial, all reflections (16) with a value of $(\sin\theta)^2/\lambda^2$ less than 0·250 have been excluded, thus leaving 83 reflections to constitute the basic data.

The matter of extinction, primary and secondary, cannot be further treated in this paper. These phenomena have been thoroughly investigated by Känzig (1951) with results which have a highly significant bearing on the textural phenomena which occur in barium titanate single crystals as they are heated and cooled through the transition point at 120 °C.

The quality of these data has been evaluated by the estimation of the standard deviation $\sigma_{|F|}$ of each structure amplitude directly from the measurements, by methods described by Evans (1961). Two estimates were made, one based on the statistics of pulse counters (Evans, 1961, equation (12)), and one based on variations among measurements of the four (or two) symmetrical reflections (Evans, 1961, equation (9)). They are listed in Table 1 under $\sigma_{|F|}$ (stat.) and $\sigma_{|F|}$ (sym.) respectively. Not including the 16 low angle reflections, the root-mean-square averages of these standard deviations are 0·07 and 0·12 respectively. These values are considerably lower than those obtained from the $\Delta|F|$ values of the best structure factor calculations (Table 2). It is possible, of course, that errors are present in the measurements which are not revealed by the estimates of standard deviation given above. The high values of $\sigma_{|F|}$ (sym.) obtained for the low angle reflections confirm the need for excluding these data from the calculations.

First refinement of the structure

The refinement of the structure parameters of barium titanate was carried out first by trial-and-error calculations and then by least squares analysis. The model first used was based on the three structure parameters and one over-all temperature factor, followed by more complicated models in which more temperature parameters were introduced. The Thomas–Fermi scattering factor for barium and the Hartree factors for oxygen and titanium, as given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935), were used for all the earlier calculations. Since all data at low scattering angles had to be excluded from the calculations as explained above, no attempt has been made to determine the effect of bond polarization of the atoms on the scattering factor.

With

$$z(\mathrm{Ti})=z(\mathrm{O}_1)=z(\mathrm{O}_2)=0 \quad \text{and} \quad B=0{\cdot}30\times10^{-16}\ \text{cm.}^{-2}\ ,$$

the reliability factor already had a value of $R=0{\cdot}089$. After 28 trials, the lowest value of R was obtained for the 4-parameter model shown as Model 2 in Table 2. This value of R (0·047) was considered to be sufficiently low to justify the publication of the results in a note (Evans, 1951). Unfortunately, these results were repudiated subsequently by the least squares analysis.

As a next step, individual isotropic temperature parameters were assumed for each atom, in a 7-parameter model. Least squares calculations for the temperature factors gave a slight improvement of the reliability factor. The temperature parameters obtained in this way are shown as Model 3 in Table 2.

Finally, anisotropic temperature factors were introduced, B_{11} and B_{33} for Ba, Ti and O_1 and B_{11}, B_{22} and B_{33} for O_2. For all atoms except O_2, B_{11} is the temperature factor corresponding to the a axis direction and B_{33} that corresponding to the c axis. For O_2, B_{11} corresponds to the a axis direction toward the

Table 2. *Crystal structures proposed for tetragonal* $\mathrm{BaTiO_3}$

Atom	Ti	O_1	O_2	Ba		Ti		O_1			O_2			
Model	z	z	z	B_{11}	B_{33}	B_{11}	B_{33}	B_{11}	B_{22}	B_{11}	B_{22}	B_{33}	R	$[\overline{(\Delta\|F\|)^2}]^{\frac{1}{2}}$
1	0	0	0	0·30		0·30		0·30			0·30		0·0892	1·838
2	0·015	−0·024	−0·020	0·30		0·30		0·30			0·30		0·0473	1·158
3	0·015	−0·024	−0·020	0·29		0·39		0·88			0·49		0·0455	1·053
4	0·015	−0·024	−0·020	0·27	0·28	0·53	0·21	0·90	0·08	0·60	0·49	0·07	0·0375	0·861
5	0·012	−0·026	0	0·27	0·28	0·46	0·30	0·90	0·50	0·60	0·90	0·90	0·0372	0·924
6	0·014	−0·032	0	0·48		0·13		0·13			0·48		0·123	
7	0·014	−0·023	−0·014	0·273		0·152		0·334			0·267		0·0296	
σ_4(est.)	0·0012	0·0062	0·0035	0·013	0·013	0·047	0·062	0·34	0·55	0·23	0·23	0·22		
σ_5	0·018	0·017	0·097	0·05	0·07	0·51	0·63	0·65	0·87	0·24	1·48	1·02		

Remarks:

Model 1. Cubic, undistorted structure; single, overall temperature factor.
Model 2. 4-parameter tetragonal structure; single, overall temperature parameter.
Model 3. 7-parameter structure; isotropic temperature factors.
Model 4. 12-parameter structure: z parameters fixed as in Model 3, anisotropic temperature parameters varied by least squares analysis.
Model 5. Alternative 12-parameter structure: temperature parameters fixed as shown, z parameters varied by least squares analysis.
Model 6. Final structure of Känzig (1951); isotropic temperature parameters.
Model 7. Structure of Frazer, Danner & Pepinsky (1955), from neutron diffraction; isotropic temperature parameters.

σ_4(est.) are standard deviations estimated for Model 4 from $\Sigma(\Delta|F|)^2$, assuming no parameter interaction.
σ_5 are standard deviations of parameters calculated for Model 5 by inversion of the full least squares matrix.

Ti atom, B_{22} to the *a* axis direction normal to B_{11}, and B_{33} to the *c* axis direction. At this stage the complete normal equations were set up, one for each of 13 parameters, including a scale factor. All weights were assumed to be unity. When these equations were solved, obviously anomalous results were obtained for the parameter corrections. The parameter shifts were many times larger than any previously calculated shifts, and lead to a wholly unreasonable structure. Some of the temperature factors became impossibly large while others were shifted to negative values.

This was the first point at which any suspicion had been aroused that there might be a basic instability in the structure factor function. It was soon verified that variations in certain of the parameters could not be distinguished from one another in their effect on the structure factors. For these parameters, the derivatives of the structure factors are approximately in proportion, so that the determinant of the normal equations tends to vanish. In other words, equally good explanations of the experimental data may be obtained with widely different sets of parameters. This impasse is inherent in the structure factor function itself and must lead us to the conclusion that the crystal structure of barium titanate is indeterminate with data of the type developed for this study.

Limits of the crystal structure analysis

The anomalous results obtained in the least squares treatment can be reasonably accounted for by a direct interaction between the following pairs of parameters:

$$\begin{aligned} z(\mathrm{Ti}) &\ \text{and}\ B_{33}(\mathrm{Ti}) \\ z(\mathrm{O}_1) &\ \text{and}\ B_{33}(\mathrm{O}_1) \\ z(\mathrm{O}_2) &\ \text{and}\ B_{33}(\mathrm{O}_2) \\ B_{22}(\mathrm{O}_2) &\ \text{and}\ B_{11}(\mathrm{Ti})\,. \end{aligned}$$

Thus, only B_{11} and B_{33} of Ba, B_{11} of O_1 and B_{33} of O_2 might be expected to be independently capable of refinement. Least squares calculations were therefore continued for 8 parameters, holding the left-hand one of each of the pairs of interacting parameters listed above fixed at the values used for the last trial and error calculation, Model 3 in Table 2. This computation led in a straightforward way to Model 4 of Table 2, with a reliability factor $R = 0{\cdot}038$. However, the great uncertainty of these results was demonstrated by structure factor calculations for another model which was obtained by fixing all the temperature factors as shown in Table 2 for Model 5 and varying the *z* parameters. The result of this refinement gave $R = 0{\cdot}037$.

At this point the work was stopped with no hope of reaching any definite conclusion about the structure of barium titanate. It was only suggested (Evans, 1952*c*, 1953) that the last model (Model 5) was perhaps the most reasonable one with regard to the temperature factors. Structure factors for this model are given in Table 1.

The most direct and conclusive evidence for the uncertainty of the parameters is obtained by direct calculation of their standard deviations from the diagonal terms of the inverse of the full least squares matrix. Recently, such a calculation was made on the IBM 704 computer using a program which develops these standard deviations (Busing & Levy, 1959). In this calculation the parameters of Model 5 were used as a starting point for one cycle of refinement. Scattering factors were now taken from Thomas & Umeda (1957) for barium and from Berghuis *et al.* (1955) for titanium and oxygen, but no correction was made for anomalous dispersion. The data were all given equal weight. The parameter adjustments obtained were erratic as in the earlier calculations, but the standard deviations, given as σ_5 in Table 2, are of particular significance.

We may estimate standard deviations of the parameters to be expected on the basis of the root-mean-square of the $\Delta|F|$ values (last column of Table 2) by the relation:

$$\sigma_x^2 = \overline{(\Delta|F|)^2} / \Sigma(\partial|F|/\partial x)^2\,.$$

This is the estimate usually made in the least squares analysis method when the non-diagonal terms of the matrix of the normal equations are neglected. It is generally valid when there are no interactions among parameters. In Table 2, estimates made in this way are given as σ_4(est.) for the 12 parameters (based on the parameters of Model 4). The standard deviation of the parameters resulting from the Busing–Levy calculations mentioned above, by comparison with the σ_4(est.) values, fully confirm the uncertainty of the foregoing structure analysis. Geller (1961), in a separate paper, has calculated the full inverse matrix for this structure using the data of Table 1 of this paper. His calculations further substantiate these findings by an analysis in detail of the cross correlation coefficients derived from the non-diagonal terms. In addition to the interactions postulated above (except for that between $z(O_2)$ and $B_{33}(O_2)$ which is shown to be relatively weak), several other seriously high parameter correlations were found. According to Geller's calculations, only $B_{11}(O_1)$ and $B_{11}(O_2)$ are free of serious interaction with other parameters.

Other studies of the barium titanate structure

With a structure as significant as that of barium titanate, it is natural that its refinement would be attempted independently by several workers. The first work reported which was based on technique of sufficient precision to have any hope of success was that of Känzig (1951). He measured X-ray diffraction intensities from a large single crystal plate, using Mo $K\alpha$ radiation. The structure he proposed is given as Model 6 in Table 2. Unfortunately, his work suffers from several handicaps. One serious limitation was imposed by the small number of data that were measured: 8 $h00$-type reflections which would depend on B_{11} for Ba, Ti, O_1 and O_2 and B_{22} for O_2; and 10 $00l$-type reflections which would depend on z for Ti, O_1 and O_2, and B_{33} for Ba, Ti, O_1 and O_2. Also, all calculations were made under the assumption that $z(O_2)=0$, and that only two spherical temperature factors applied, one for Ti and O_1, and one for Ba and O_2. It would appear that Känzig's structure determination is quite incomplete. On the other hand, as mentioned earlier, his measurements were made over a range of temperatures extending from 20° to 350 °C. and indicate some very significant diffraction phenomena in the vicinity of the Curie point. Here all extinction effects suddenly disappear, and from this he was able to deduce very useful information about the domain structure in the crystal, and the transformation process at the Curie point.

Another detailed structure study of barium titanate has been made recently by Frazer, Danner and Pepinsky (1955), using the technique of neutron diffraction. Using a large crystal aligned in a single domain by an applied electric field, they collected data for 50 nonequivalent $h0l$ reflections. The refinement was carried out assuming the 7-parameter model (isotropic temperature parameters), with the results shown for Model 7, Table 2. Least square methods were used, but no standard errors were cited. These preliminary results have since been modified by Danner, Frazer & Pepinsky (1960) by a full least squares analysis based on the 12-parameter model, just as the preliminary results of Evans (1951) were subsequently revised. In particular, serious interaction was found between z(Ti) and B_{33}(Ba), as predicted for X-rays by Geller (1961). On the other hand, an analysis of the errors in the neutron diffraction case indicates that the situation is generally much better than in the X-ray diffraction case (Frazer & Danner, private communication). Apparently the different circumstances of scattering power and form factors of the atoms to a large degree prevent the coupling of parameters in the structure factor function, except in the case mentioned. But even with neution diffraction, Frazer & Danner have had to conclude, in agreement with the author (Evans, 1952*c*, 1953), that the complete structure of barium titanate cannot be accurately determined independantly of some limiting assumption concerning the thermal vibrations. Fortunately, for the neutron diffraction case such assumptions primarily involve the barium atom and can be made with some confidence, so that a useful model may finally be determined. While such assumptions were attempted for the X-ray diffraction case (Model 5, Table 2), no real confidence can be placed on them and no useful result obtained.

It is important to take note of the fact that the instability of this structure determination only becomes apparent upon the inversion of the full least-squares matrix for the 12-parameter model. When a simpler model is used, or approximate methods utilized for the least squares calculations, the analysis converges in a seemingly satisfactory way to a particular set of parameters. Unless the full 12-parameter matrix is inverted, there is no clue to the fact that a large number of other widely divergent sets will give equally satisfactory agreement between observed and calculated structure amplitudes. This indeterminacy is inherent in the structure factor function itself, and must be suspected regardless of what type of radiation is used in the diffraction experiment.

The problem of polar structures

The first instance in which a gross interaction between structure and temperature parameters in the structure factor function was detected was the case of the crystal structure of HCN, studied by Dulmage & Lipscomb (1951). In the polar space group *I4mm*, they calculated a surprisingly large standard deviation for the single z parameter (not considering the hydrogen atom) of 0·15 Å, reflecting a large interaction with the thermal vibration parameters in the c axis direction. It is especially disturbing in such cases as HCN and $BaTiO_3$ to find that in spite of the availability of unusually accurate data sufficient to overdetermine the parameters by a ratio of 7 to 1, the atomic positions cannot be determined with an error smaller than 0·1 Å. Such a situation may be expected to occur in a structure which has a polar space group, but which fails to satisfy a space group of higher symmetry because of small atomic displacements.

When interactions have been found to occur for X-ray data of general type, there are two possible ways to reduce their influence. One is to extend the data to higher values of $(\sin\theta)/\lambda$. In the case of barium titanate, by the use of Ag $K\alpha$ radiation, for example, it may be possible to uncouple sufficiently the interacting parameters to reduce the error of determination to a considerable extent. The other possibility lies in repeating the diffraction measurements with neutrons, in which case the behavior of the structure factor function may be improved by a complete redistribution of the weights of the various atomic contributions owing to the different form factors. This approach has apparently been found by Frazer & Danner to lead finally to a useful result for barium titanate.

It is most unfortunate that ferroelectric crystals are generally just of the type referred to above, which show large parameter interactions. In these crystals, where the very accurate structure determinations of which X-ray diffraction techniques are generally considered to be capable are most urgently needed, the structures may be generally indeterminate within wide limits. Two such structures are lead titanate (Shirane, Pepinsky & Frazer, 1956) and potassium dihydrogen phosphate (Frazer & Pepinsky, 1953). The determinations of both these polar structures have been carried out by the same partial methods applied to the earlier neutron diffraction determination of the barium titanate structure referred to above, (Danner, Frazer & Pepinsky, 1955), so that abnormally large standard deviations of the parameters are not revealed. In view of the experience gained with barium titanate, there is good reason to suspect that they may be large, and the models proposed must be accepted with caution.

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Parameter Interaction in Least Squares Structure Refinement

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The correlation matrix gives a good indication of the interdependence of parameters in the course of refinement. Very strong interactions, i.e., high correlations, are essentially independent of the quality of the data, but depend on the trial structure model, including all parameters and atomic scattering factors, and to some extent on the number of data. Very strong interactions imply that the parameters involved could be indeterminate. Detailed illustration of the importance of the correlation matrix is given by results from investigations of the structures of a grossularite, of tetragonal $BaTiO_3$ and of $LiMnPO_4$.

Introduction

Temperature and scale factors obtained in structure refinements are perhaps not as reliable as might be indicated by error estimates. The character of the thermal parameter function whether isotropic or anisotropic is such as to invite into it errors of various sorts. These include errors in intensity measurement, in absorption and extinction correction and in atomic scattering factors, particularly when correction has not been made for dispersion or when the spherical symmetry approximation is not valid.

Templeton (1955) has predicted that neglect of the real part of the dispersion correction would strongly affect the scale and thermal parameters. This is equivalent to saying that strong interaction is expected between the atomic scattering factors and the scale and thermal parameters. In the case of the refinement of the yttrium iron garnet structure it was shown (Geller & Gilleo, 1959) that inclusion of the dispersion corrections resulted only in large changes in the scale factor (from 1·00 to 1·17) and in the thermal parameters of Y^{3+} (from 0·16 to 0·40 Å^2) and of O^{2-} (from 2·05 to 1·19 Å^2). The change in the temperature factor of the Fe^{3+} ion was negligible despite the fact that the real part of the dispersion correction for this ion was $-3{\cdot}7e$ as against $-1{\cdot}3e$ for the Y^{3+} ion.

The effects of the interactions described above, however, are usually not included in the error estimates. As another example, one may say that all theoretical atomic scattering factors are only an approximation particularly for atoms which have electronic clouds which in many structures deviate substantially from spherical symmetry. Such errors as may occur from