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An X-Ray Diffraction Study of Barium Titanate

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AN X-RAY DIFFRACTION STUDY OF BARIUM TITANATE

by

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Irvington-on-Hudson, New York

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Abstract: An X-ray diffraction investigation was carried out in an attempt to determine in detail the atomic positions and temperature motions in the crystal structure of the tetragonal ferroelectric form of barium titanate. The basic experimental data used in the analysis consisted of the integrated intensities of 99 Bragg reflections of the type (hk0). The intensities were carefully measured by means of a scanning technique using a Geiger counter assembly especially designed for this study, a small (0.1 mm) untwinned single crystal, and MoK α radiation. The intensities were corrected for absorption and secondary extinction effects determined by special techniques worked out for this particular crystal.

The search for a structure which will adequately account for these data was carried out by the methods of trial and error and least-squares analysis. A model was finally defined in terms of 3 structure and 9 anisotropic temperature parameters. It was found that in the general intensity function for all reflections there is an interaction between the structure parameter of an atom (displacement along the tetragonal axis) and the temperature motion of the atom in this direction. Therefore, in order to determine the value of one from the observed intensity data, it is necessary to assume a fixed value for the other. Consequently, within a rather wide range, it is not possible to determine uniquely the structure of tetragonal barium titanate.

Certain temperature parameters do not interact with other parameters, and these are uniquely determined. From these, reasonable

*A considerable portion of the work described here has been reported in Technical Reports Nos. 39 and 54, Philips Laboratories, Inc.

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values have been assigned to the other temperature motions, and the structure consistent with these assumptions determined. The reliability factor R for this structure is 0.0367. These results are compared with those published by other workers.

1. Introduction

Barium titanate (BaTiO_3) is one of a large family of compounds having the perovskite (CaTiO_3) structure, or a close approximation to it. The ideal cubic structure, realized by BaTiO_3 above 120°C , is very simple and is illustrated in Fig. 1b. Most compounds of the perovskite type actually have slight distortions of this ideal, highly symmetrical structure, and barium titanate, in particular, becomes polar below 120°C . At this point BaTiO_3 shows most unusual dielectric properties (dielectric constants as high as 20,000 have been measured), and becomes piezo- and ferroelectric. Because of its simple structure, and convenient chemical and unusual physical properties, barium titanate has been subjected in the last eight years to intensive theoretical and experimental investigation in many laboratories throughout the world as an outstanding problem in solid state physics.¹⁾

It has been commonly stated that the polar properties arise from a slight displacement of the titanium atom from its symmetrical position in the center of any oxygen octahedron toward one of the oxygen atoms (in the direction of a cube axis). Actually, all atoms may be displaced, and a theoretical understanding of the properties of BaTiO_3 must depend on an exact knowledge of these displacements. At first glance it appears that the methods of X-ray diffraction should readily yield this information, but many unexpected difficulties and special features of the diffraction problem have delayed the appear-

1) A. R. von Hippel, "Ferroelectricity, Domain Structure and Phase Transitions in Barium Titanate," Technical Report No. 23, Laboratory for Insulation Research, March, 1950.

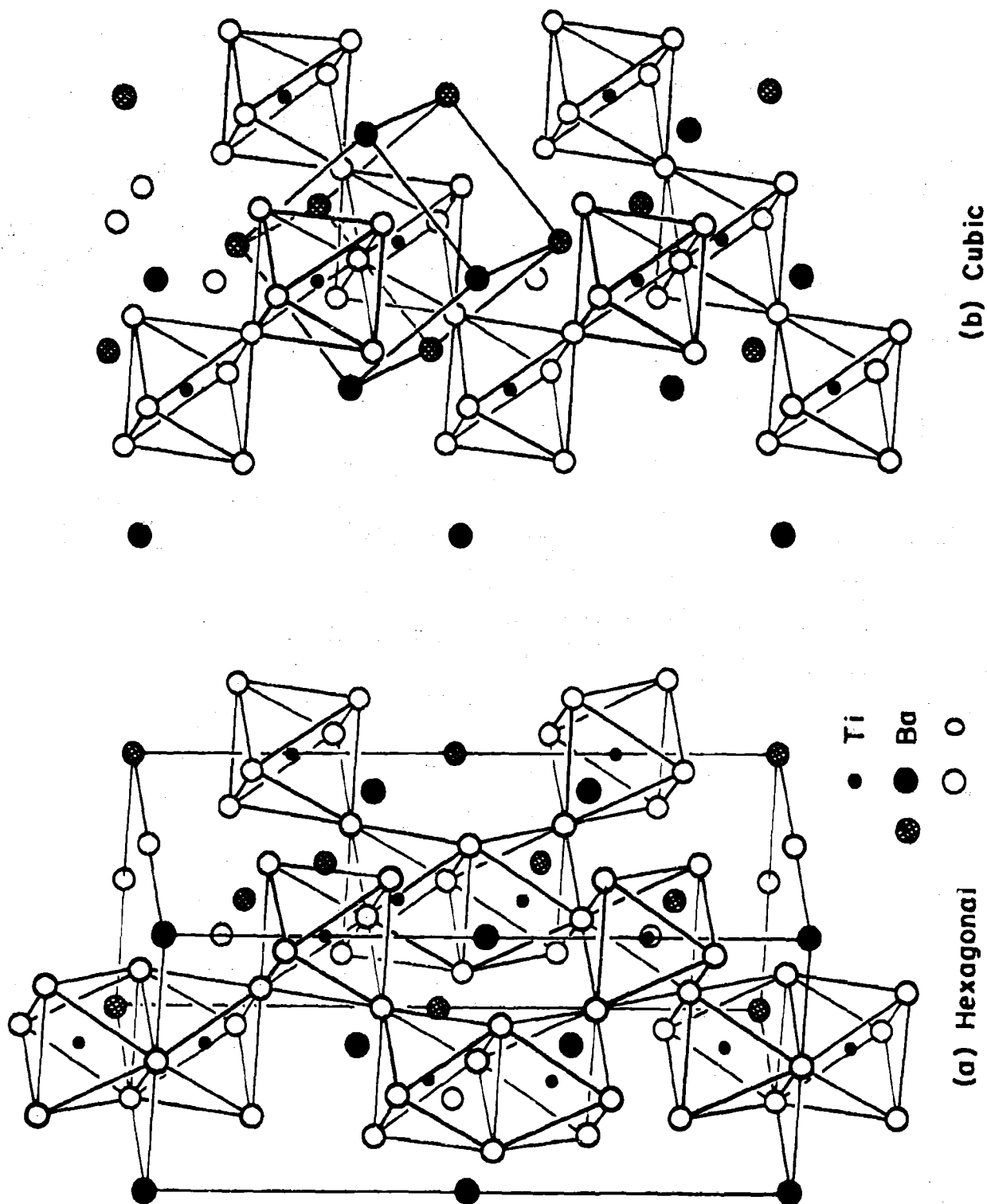


Fig. 1. Crystal structures of barium titanate.

ance of, and qualified, the desired results.

2. Phases and Structure of Barium Titanate

Two polymorphs of barium titanate are well known, one hexagonal and one cubic or pseudocubic. According to Burbank and Evans²⁾ these structures are both based on close-packed barium and oxygen ions, which are practically the same size but having different stacking sequences (Figs. 1a and 1b). The titanium ions are found in octahedral oxygen interstices between close-packed layers. In the cubic form, the close-packing is cubic, and the TiO_6 octahedra are linked by corners in straight rows throughout the structure, unlike the hexagonal form where the titanium distribution is more complex. The cubic form therefore presents the possibility of a uniform interaction between Ti-O dipoles through the structure, producing various polar deformations of the cubic structure at various temperatures.

In the perovskite type of barium titanate, four phases are known, well established by optical and X-ray measurements,^{3, 4)} and are defined⁵⁾ as follows:

I. Cubic; space group $O_h^1 = \text{Fm}\bar{3}\text{m}$; $a_0 = 3.9860\text{\AA}$

Cell contents: BaTiO_3

Ba in (a), 0, 0, 0

Ti in (b), $1/2, 1/2, 1/2$.

3 O in (c), $1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2$

No parameters; stable above 120°C .

2) R.D. Burbank and H. T. Evans, Jr., Acta Cryst. 1, 330(1948).

3) P.W. Forsberg, Jr., Phys. Rev. 76, 1187(1949).

4) R.G. Rhodes, Acta Cryst. 2, 417(1949).

5) Terminology according to the "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Berlin, Gebruder Borntraeger, 1935.

II. Tetragonal; space group $C_{4v}^1 = P4mm$; $a_o = 3.9860$, $c_o = 4.0259\text{\AA}$

Cell contents: $BaTiO_3$

Ba in (a), 0, 0, 0 (Origin)

Ti in (b), $1/2$, $1/2$, $(1/2 + z_{Ti})$

OI in (b), $1/2$, $1/2$, z_{OI}

2 OII in (c), 0, $1/2$, $(1/2 + z_{OII})$; $1/2$, 0, $(1/2 + z_{OII})$

Three parameters; stable between 120° and -5°C .

III. Orthorhombic; space group $C_{2v}^{14} = Amm$; at 4°C , $a_o = 4.0185$,
 $b_o = 3.9860$, $c_o = 4.0162\text{\AA}$

Cell contents: $2BaTiO_3$

2 Ba in (a), 0, 0, 0 (Origin); 0, $1/2$, $1/2$

2 Ti in (b), $1/2$, 0, $(1/2 + z_{Ti})$; $1/2$, $1/2$, z_{Ti}

2 OI in (a), 0, 0, $(1/2 + z_{OI})$; 0, $1/2$, z_{OI}

4 OII in (e), $1/2$, $(1/4 + y_{OII})$, $(1/4 + z_{OII})$; $1/2$, $(3/4 + z_{OII})$;
 $1/2$, $(3/4 - y_{OII})$, $(1/4 + z_{OII})$; $1/2$, $(1/4 - y_{OII})$,
 $(3/4 + z_{OII})$

Four parameters; stable between -5° and -90°C .

IV. Rhombohedral; space group $C_{3v}^5 = R3m$; $a_o = 4.035\text{\AA}$;
 $\alpha = 90^\circ 19'$

Hexagonal cell contents: $3BaTiO_3$

3 Ba in (a), 0, 0, 0 (Origin); $1/3$, $2/3$, $1/3$; $2/3$, $1/3$, $2/3$

3 Ti in (a), 0, 0, $(1/2 + z_{Ti})$; $1/3$, $2/3$, $(5/6 + z_{Ti})$;

$2/3$, $1/3$, $(1/6 + z_{Ti})$

9 O in (b), $(5/6 + x_o)$, $(1/6 - x_o)$, z_o ; $(1/6 + x_o)$, $(5/6 - x_o)$,

$(1/3 + z_o)$; $(1/2 + x_o)$, $(1/3 - x_o)$, $(2/3 + z_o)$; $(5/6 + x_o)$,

$(2/3 + x_o)$, z_o ; $(1/6 + x_o)$, $(1/3 + x_o)$, $(1/3 + z_o)$;

$(1/2 + x_o)$, x_o , $(2/3 + z_o)$; $(1/3 - x_o)$, $(1/6 - x_o)$, z_o ;

$$(2/3 - x_0), (5/6 - x_0), (1/3 + z_0); -x_0, (1/3 - x_0), (2/3 + z_0)$$

Three parameters; stable below -90°C .

All these structures are based on the familiar perovskite type, with the pseudocube edge always close to $4\text{\AA}$. The exact variations of cell dimensions of all the phases have been accurately measured by Megaw⁶⁾ and Rhodes.⁷⁾ The attempt to determine exactly the three parameters of the tetragonal phase II (at room temperature) is described in the following sections.

3. The Tetragonal Structure Factors

While the parameters z_{TI} , z_{OI} and z_{OII} as described above for the tetragonal phase are small, they are appreciable (of the order of $0.1\text{\AA}$), and one would believe at first that the ordinarily sensitive crystal-structure methods would measure them in a straight-forward manner. The intensities of the diffracted beams, which constitute our ultimate experimental data, are a function of the square of the structure factors F which express the manner in which X rays scattered by the individual atoms are combined into the beams scattered by the crystal as a whole.

$$\begin{aligned} F_{(hkl)} &= \sum_j f_j e^{-2\pi i(hx_j + ky_j + lz_j)} \\ &= \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j) \quad (1) \\ &= \sum_j f_j a_j + i \sum_j f_j b_j \end{aligned}$$

in which h , k and l are the order numbers of the diffracting plane in the three-dimensional grating of the crystal; x_j , y_j and z_j are the co-ordinates of the j^{th} atom in fractions of the unit-cell edges; and f_j is the scattering power of the j^{th}

6) H.D.Megaw, Proc.Phys.Soc. 58, 133(1946).

7) R.G.Rhodes, Acta Cryst. 4, 105(1951).

atom for the particular reflection (hkl) (a function of the Bragg angle 2θ).

The summation is taken over all the j atoms in the unit cell. The cubic unit cell above 120°C contains five atoms with the co-ordinates:

$\frac{j}{\text{Ba}}$	$\frac{x_j}{0}$	$\frac{y_j}{0}$	$\frac{z_j}{0}$
Ti	1/2	1/2	1/2
O	1/2	1/2	0
O	0	1/2	1/2
O	1/2	0	1/2

If these co-ordinates are substituted in Eq.(1), the b_j terms vanish and F is determined as shown in Table 1, according as h and l are odd or even, respectively.

Table 1

Structure Factors for ($h0l$) Reflections For Cubic Barium Titanate

	h odd	h even
l odd	$f_{\text{Ba}} + f_{\text{Ti}} - f_{\text{O}}$	$f_{\text{Ba}} - f_{\text{Ti}} - f_{\text{O}}$
l even	$f_{\text{Ba}} - f_{\text{Ti}} - f_{\text{O}}$	$f_{\text{Ba}} + f_{\text{Ti}} + 3f_{\text{O}}$

We now consider only reflections with $k = 0$, since these are the only ones measurable in this study (cf. Section 4).

In the tetragonal crystal, the unit cell contains five atoms with the following co-ordinates:

$\frac{j}{\text{Ba}}$	$\frac{x_j}{0}$	$\frac{y_j}{0}$	$\frac{z_j}{0}$
Ti	1/2	1/2	$1/2 + z_{\text{Ti}}$
OI	1/2	1/2	z_{OI}
OII	0	1/2	$1/2 + z_{\text{OII}}$
OII	1/2	0	$1/2 + z_{\text{OII}}$

The new z_j co-ordinates modify the structure factors in Table 1 according to Eq.(1), by multiplying the f_j terms by $\cos 2\pi\ell z_j$ and adding an imaginary component in $f_j \sin 2\pi\ell z_j$. But since the co-ordinate parameters z_{Ti} , z_{OI} and z_{OH} are all near zero, it is apparent that the absolute values of the structure factors, $|F|$, will change very little for relatively large changes in the parameters. Thus, the structure factors of Table 1 are a very good approximation to those of the tetragonal structure. In fact, the approximation is so good that the parameters z_j cannot be determined by ordinary means.

4. Range of X-Ray Measurements

In order to get the most out of the function of Eq.(1), the value of ℓ in the Bragg reflections measured must be extended as far as possible. In addition, it is desirable to have as many Bragg reflections measured as possible so that random errors will be minimized. To this end, MoK α radiation was used, giving a range of $(\sin \theta)/\lambda$ from 0 to 1.41. The crystal is sufficiently hard so that reflections are not markedly damped by temperature vibration, and are still appreciably strong even at the limits of this range. The number of $(hk\ell)$ reflections in this range is about 6,000, but because of the difficulties of correcting for absorption, we must be content with measuring only the $(h0\ell)$ reflections, of which there are 405. With the Geiger counter instrumentation we have been able to measure 356 of these, and these data, after averaging, yield 99 symmetrically nonequivalent Bragg reflections.

5. Experimental Source of the Data

The essential data (99 F terms) were taken from a single untwinned crystal of barium titanate at room temperature. This crystal, whose dimensions are $0.071 \times 0.160 \times 0.193$ mm, was taken from a preparation made by B.M. Matthias.⁸⁾ The crystals were grown in a flux of barium chloride, with

8) B. Matthias, Phys. Rev. 73, 808(1948).

a small excess of barium oxide over titanium dioxide, in the presence of one mole ratio of boron oxide to barium titanate to minimize twinning. The crystal was mounted on a glass fiber and placed on the standard Weissenberg camera for X-ray study. A Geiger counter was used to measure 356 integrated reflections as described briefly in Section 6. These measurements were corrected for Lorentz and polarization effects in the standard manner. Corrections were also made for absorption and secondary extinction of the X rays in the crystal according to the method described in Section 7. These corrections may be summarized in the following expression:

$$\left. \begin{aligned} I &= AVQI_0 \\ Q &= K L p |F|^2 \end{aligned} \right\} \quad (2)$$

where I is the integrated intensity; I_0 is the intensity of the incident beam; K is a constant; L is the Lorentz factor, which is a measure of the time in which a set of planes has an opportunity to diffract as the crystal rotates; p is the polarization factor, introduced because an unpolarized beam is partially polarized in the diffraction process to a degree dependent on the Bragg angle; V is the volume of the crystal; A is the absorption factor, dependent on the linear absorption coefficient μ (a function of I in this case, where secondary extinction is important, and different for each reflection), the shape of the crystal and the geometry of diffraction; and F is the structure amplitude from which it is hoped to determine the details of the structure itself through Eq.(1).

The 99 symmetrically independent structure amplitudes obtained by averaging the 356 measured reflections, together with Lp and A corrections and the Bragg parameter $s^2 = (\sin \theta)^2 / \lambda^2$, are listed in Table 2. The final set of calculated values of F as derived in the following sections is also given.

Table 2
X-Ray Diffraction Data For Tetragonal Barium Tetanate

h0l	s ²	I(rel.)	I/Lp	μ	A	F obs.	F calc.	ΔF	ψ	A calc.	B calc.
000	0	—	—	—	—	—	104.0	—	0	104.0	0
100	0.0156	1630	0.180	253	0.169	18.8	24.2	-5.4	0	24.2	0
200	0.0625	3140	0.373	407	0.066	60.1	65.5	-5.4	0	65.5	0
300	0.141	587	0.593	208	0.237	17.3	20.9	-3.6	0	20.9	0
400	0.250	1492	0.855	237	0.197	36.3	40.3	-4.0	0	40.3	0
500	0.392	244	1.168	200	0.247	15.4	15.6	-0.2	0	15.6	0
600	0.564	496	1.525	208	0.228	23.3	27.8	-4.5	0	27.8	0
700	0.771	81	1.856	198	0.233	11.5	10.7	0.8	0	10.7	0
800	1.002	198	2.000	203	0.213	19.5	18.7	0.8	0	18.7	0
900	1.268	40	1.773	198	0.204	8.4	8.1	0.3	0	8.1	0
1000	1.568	130	1.207	203	0.182	13.2	12.8	0.4	0	12.8	0
001	0.0154	880	0.178	253	0.043	27.3	24.2	3.1	-5.9	24.1	-2.5
101	0.0310	3410	0.256	405	0.058	55.1	55.0	0.1	2.1	55.0	2.0
201	0.0778	1042	0.422	215	0.212	20.5	21.9	-1.4	-4.2	21.8	-1.6
301	0.157	1820	0.632	248	0.177	38.2	38.6	-0.4	1.6	38.6	1.1
401	0.266	403	0.891	203	0.234	17.6	17.5	0.1	-2.6	17.5	-0.8
501	0.407	642	1.203	215	0.216	27.0	27.8	-0.8	1.4	27.8	0.7
601	0.581	118	1.557	199	0.232	12.7	12.7	0	-2.3	12.7	-0.5
701	0.806	203	1.877	204	0.217	18.9	19.0	-0.1	1.2	19.0	0.4
801	1.014	49	1.997	198	0.208	9.7	8.9	0.8	-2.0	8.9	-0.3
901	1.281	98	1.750	202	0.199	13.2	13.4	-0.2	1.3	13.4	0.3
1001	1.583	32	1.172	198	0.180	6.5	6.8	-0.3	-1.7	6.8	-0.2
002	0.0615	2510	0.369	407	0.035	73.4	65.4	8.0	0.5	65.4	0.6
102	0.0767	742	0.418	215	0.144	20.9	22.7	-1.8	-1.7	22.7	-0.7
202	0.124	2610	0.550	294	0.104	53.0	52.8	0.2	0.6	52.8	0.6
302	0.203	493	0.743	205	0.202	19.2	19.2	0	-1.8	19.2	-0.6
402	0.312	1280	0.994	223	0.202	35.8	36.9	-1.1	0.9	36.9	0.6
502	0.450	168	1.308	200	0.219	14.2	14.7	-0.5	-2.4	14.7	-0.6
602	0.626	421	1.640	207	0.212	25.7	26.1	-0.4	1.1	26.1	0.5
702	0.826	57	1.925	198	0.218	10.1	10.6	-0.5	-2.2	10.6	-0.4
802	1.065	176	1.982	202	0.204	18.7	17.7	1.0	1.0	17.7	0.3
902	1.332	36	1.672	198	0.197	7.9	7.6	0.3	-2.3	7.6	-0.3
1002	1.628	141	1.071	205	0.176	13.2	12.3	0.9	0.9	12.3	0.2
003	0.138	400	0.586	208	0.126	19.5	21.0	-1.5	-9.6	20.7	-3.5
103	0.153	1200	0.626	248	0.085	42.5	39.3	3.2	4.8	39.2	3.3
203	0.200	393	0.740	205	0.148	20.0	19.1	0.9	-8.7	18.9	-2.9
303	0.280	919	0.920	219	0.164	32.4	31.7	0.7	4.3	31.6	2.4
403	0.387	196	1.163	200	0.194	15.5	15.3	0.2	-7.5	15.2	-2.0
503	0.527	388	1.459	209	0.183	25.1	24.7	0.4	4.2	24.6	1.8
603	0.701	77	1.767	198	0.217	11.3	11.4	-0.1	-7.5	11.3	-1.5
703	0.903	156	1.979	203	0.196	17.9	17.5	0.4	3.9	17.5	1.2
803	1.136	41	1.929	198	0.188	9.2	8.3	0.9	-6.9	8.2	-1.0
903	1.407	89	1.534	202	0.181	12.4	12.3	0.2	3.7	12.3	0.8
1003	1.698	32	0.900	198	0.179	5.7	6.4	-0.7	-5.4	6.4	-0.6

Table 2 - Continued

h0l	s ²	I(rel.)	I/Lp	μ	A	F obs.	F calc.	ΔF	ψ	A calc.	B calc.
004	0.246	1232	0.844	237	0.137	40.9	39.9	1.0	1.9	39.9	1.3
104	0.260	283	0.879	203	0.143	19.5	18.0	1.5	-3.8	18.0	-1.2
204	0.308	891	0.985	223	0.112	39.9	36.7	3.2	1.9	36.7	1.2
304	0.386	172	1.160	200	0.172	15.4	15.6	-0.2	-4.0	15.6	-1.1
404	0.500	529	1.390	210	0.168	29.8	29.5	0.3	2.1	29.5	1.1
504	0.634	78	1.661	199	0.184	12.0	12.4	-0.4	-4.6	12.4	-1.0
604	0.810	245	1.905	204	0.191	22.2	21.8	0.4	2.4	21.8	0.9
704	1.008	41	1.920	198	0.174	9.4	9.4	0	-4.9	9.4	-0.8
804	1.250	137	1.803	202	0.179	16.7	15.4	1.3	2.3	15.4	0.6
904	1.513	35	1.314	198	0.184	7.2	7.2	0	-4.0	7.2	-0.5
005	0.384	231	1.152	200	0.193	16.7	15.5	1.2	-13.8	15.1	-3.7
105	0.398	562	1.187	215	0.173	20.0	28.4	-0.4	7.1	28.2	3.5
205	0.448	136	1.287	200	0.193	13.5	14.6	-1.1	-13.5	14.2	-3.4
305	0.521	288	1.448	209	0.141	24.5	25.1	-0.6	6.9	24.9	3.0
405	0.629	73	1.657	199	0.210	10.9	12.4	-1.5	-12.6	12.1	-2.7
505	0.774	172	1.868	204	0.157	20.1	19.5	0.6	7.1	19.4	2.4
605	0.951	38	1.996	198	0.172	9.4	9.4	0	-11.7	9.2	-1.9
705	1.158	103	1.920	202	0.174	15.2	14.6	0.6	6.3	14.5	1.6
805	1.385	27	1.572	198	0.179	7.0	7.4	-0.4	-10.1	7.3	-1.3
905	1.646	104	1.017	206	0.197	10.4	11.0	-0.6	10.0	10.9	1.1
006	0.546	493	1.500	208	0.214	26.5	27.6	-1.1	3.3	27.6	1.6
106	0.564	121	1.535	199	0.221	13.1	13.4	-0.3	-7.3	13.3	-1.7
206	0.610	397	1.622	207	0.200	25.5	25.8	-0.3	3.6	25.8	1.6
306	0.692	83	1.754	198	0.200	12.2	11.9	0.3	-6.8	11.8	-1.4
406	0.797	229	1.900	204	0.181	22.1	21.7	0.4	3.4	21.7	1.3
506	0.945	46	1.994	198	0.181	10.1	9.9	0.2	-7.0	9.8	-1.2
606	1.121	142	1.950	202	0.180	17.6	16.7	0.9	3.4	16.7	1.0
706	1.311	39	1.691	198	0.198	8.2	8.1	0.1	-6.4	8.0	-0.9
806	1.548	140	1.230	203	0.214	12.8	12.6	0.2	3.6	12.6	0.8
007	0.755	99	1.838	198	0.261	11.9	11.2	0.7	-18.2	10.7	-3.5
107	0.771	256	1.858	204	0.242	20.0	20.0	0	10.1	19.7	3.5
207	0.815	71	1.911	198	0.251	10.5	10.4	0.1	-18.5	9.9	-3.3
307	0.897	184	1.973	203	0.230	17.9	18.0	-0.1	9.6	17.7	3.0
407	1.004	48	1.999	198	0.229	9.2	9.3	-0.1	-16.9	8.9	-2.7
507	1.141	129	1.927	202	0.220	15.2	15.0	0.2	9.2	14.8	2.4
607	1.306	33	1.698	198	0.230	7.1	8.0	-0.9	-14.5	7.7	-2.0
707	1.513	137	1.308	203	0.232	12.5	11.8	0.7	8.8	11.7	1.8
807	1.750	56	0.788	198	0.264	5.8	6.5	-0.7	-12.4	6.3	-1.4
008	0.982	224	2.000	203	0.275	18.2	18.2	0	5.1	18.2	1.6
108	0.998	69	2.000	198	0.283	9.9	9.7	0.2	-9.5	9.7	-1.6
208	1.042	201	1.990	202	0.268	17.4	17.4	0	5.3	17.4	1.6
308	1.124	56	1.944	198	0.269	9.4	9.0	0.4	-8.9	9.0	-1.4
408	1.232	169	1.825	202	0.264	15.4	15.2	0.2	4.9	15.2	1.3
508	1.374	50	1.596	198	0.261	7.9	8.0	-0.1	-7.9	8.0	-1.1
608	1.543	142	1.248	203	0.263	11.7	12.5	-0.8	4.6	12.5	1.0
708	1.750	62	0.796	198	0.284	5.9	6.8	-0.9	-7.6	6.7	-0.9

Table 2 - Continued

h0l	s ²	I(rel.)	I/Lp	μ	A	F obs.	F calc.	ΔF	ψ	A calc.	B calc.
009	1.250	61	1.810	198	0.304	8.6	8.1	0.5	-21.0	7.6	-2.9
109	1.254	160	1.787	202	0.305	13.8	14.1	-0.3	11.5	13.8	2.8
209	1.304	44	1.715	198	0.298	7.2	8.0	-0.8	-19.7	7.5	-2.7
309	1.381	150	1.576	202	0.290	12.8	12.8	0	11.3	12.6	2.5
409	1.491	56	1.357	198	0.290	7.3	7.3	0	-19.2	6.9	-2.4
509	1.633	148	1.055	206	0.287	10.6	11.2	-0.6	10.8	11.0	2.1
0010	1.538	172	1.274	203	0.315	11.9	12.4	-0.5	7.0	12.3	1.5
1010	1.545	72	1.239	198	0.321	7.5	7.5	0	-11.5	7.3	-1.5
2010	1.593	171	1.137	205	0.316	11.2	12.1	-0.9	6.7	12.0	1.4
3010	1.672	73	0.964	198	0.325	6.7	7.2	-0.5	-11.2	7.1	-1.4

6. Geiger Counter Intensity Measurements

Special apparatus and techniques were devised to measure diffraction intensities given by the crystal mentioned in Section 5, with the greatest possible accuracy. Much time was expended in an attempt to use film photometric methods to evaluate intensities but these were finally abandoned because it was felt that random errors in the measurements were intolerably high. The Geiger counter was finally resorted to as the most sensitive and accurate instrument for measuring diffraction intensities.

The equipment used consisted of an adaptation of the standard Norelco Wide-Range X-Ray spectrometer and circuits to a standard Supper Weissenberg camera. The overall assembly is shown in Fig. 2. The Geiger counter is attached to a bracket pivoted on an axis coincident with the spindle axis of the Weissenberg camera as shown in Fig. 3. The angular position of the Geiger counter is indicated with a vernier on a large graduated circle. The tilting adjustment shown in the illustration is intended for equi-inclination settings on upper levels, not used in this investigation. A back-gearred cam and lever arrangement fastened to the spindle-dial end of the Weissenberg camera per-



Fig. 3. Detail view of Geiger counter attachment to Weissenberg camera.

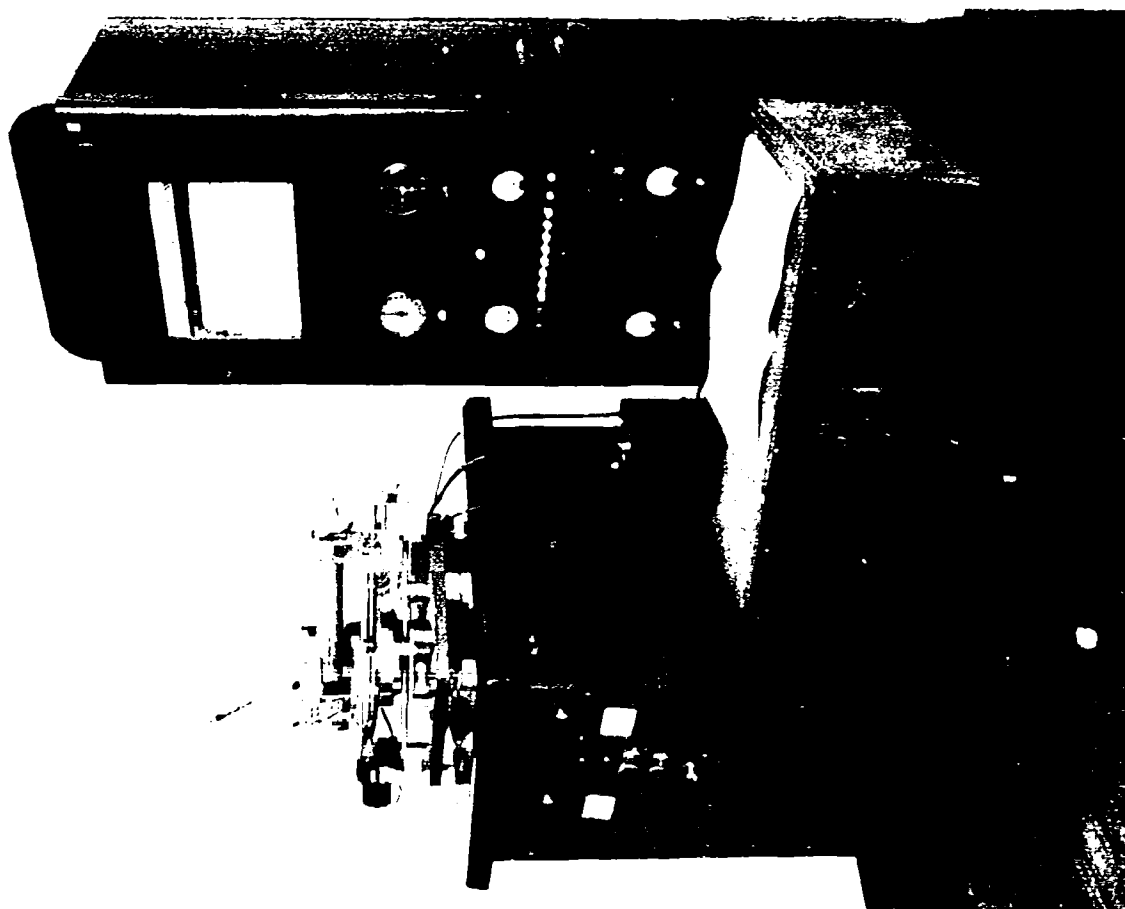


Fig. 2. Geiger counter-Weissenberg camera assembly for intensity measurements on barium titanate single crystals.

mitted an accurately uniform oscillation of the crystal through a 0° to 3° range (continuously selectable), and the operation of a switch to start and stop the counting circuits. The intensity was integrated by scanning the MoK α peak in the spectrum produced by the diffracting planes under study. If a 1° oscillation of the crystal was used, a Geiger counter slit opening corresponding to ca. 3° with the counter at a fixed angular position was ample to insure that all of the spectrum produced passed into the tube.

Typical scans as recorded on the strip chart are shown in Fig. 4. Counting was started and stopped at a precise moment of the scanning cycle, and the counts were accumulated on the count register during one oscillation cycle, with one scan forward and one backward (1 to 2 degrees oscillation, 256 seconds of time). The total of counts was then proportional to the area under the strip chart record, made simultaneously. The effect of background was measured by determining the background height from the chart, and subtracting this value (multiplied by a suitable factor) from the count total. The result was proportional to the integrated intensity for the reflection corresponding to molybdenum K α monochromatic radiation. This background correction allowed the use of unfiltered radiation with the consequent gain in intensity. An attempt to use crystal-monochromatized radiation was found to be useless because only 16 out of 99 reflections could be detected at such low intensity levels.

Considerable care was taken to insure the accuracy and reproducibility of these measurements. It was found that close regulation of the primary X-ray beam was necessary; 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. A standard reflection was remeasured periodically throughout the work. Intensity measurements were reproducible to about 1 percent where the statis-

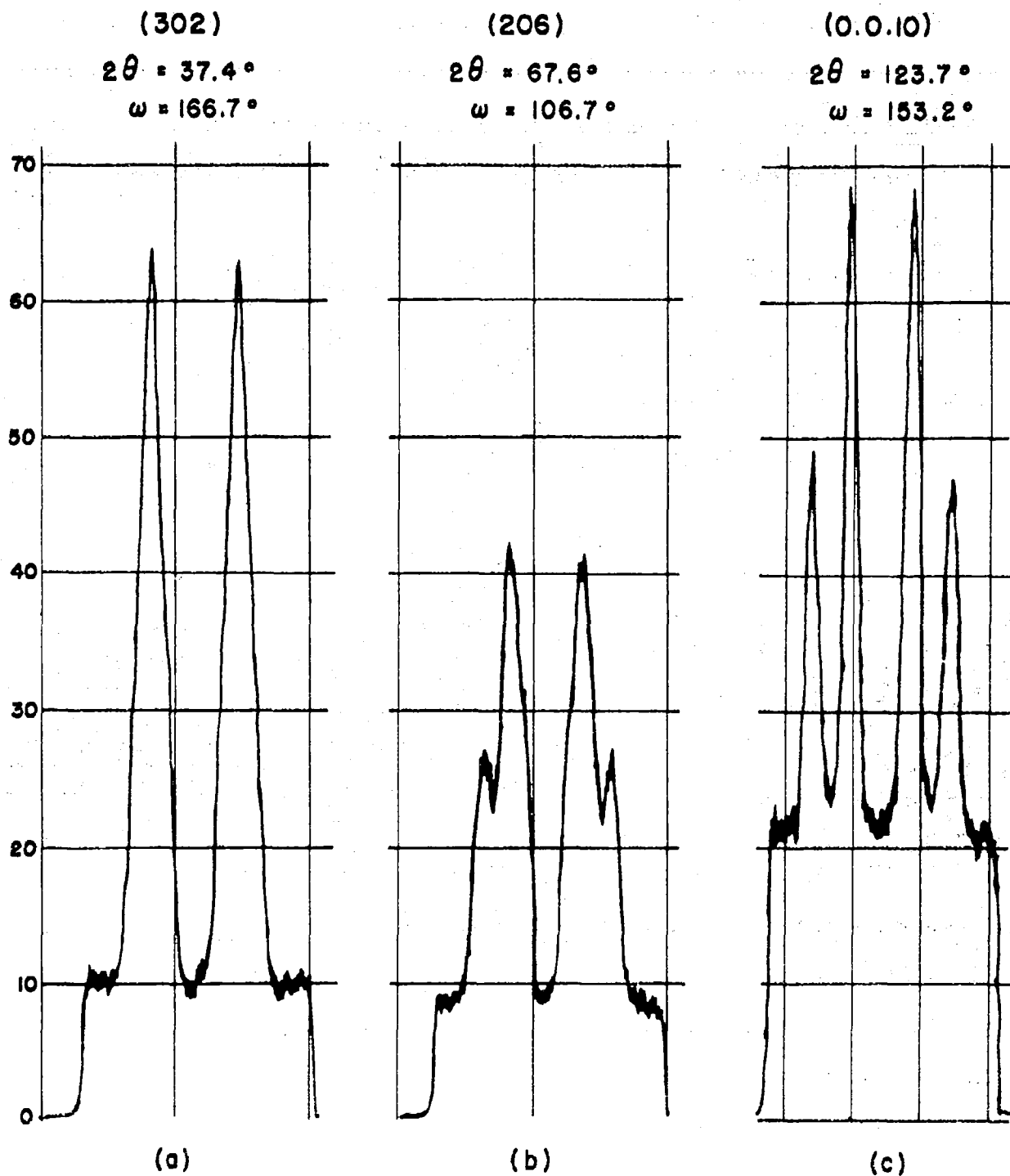


Fig. 4. Typical scans of tetragonal barium titanate reflections: (a) (302) reflection ($2\theta = 37.4^\circ$); (b) (206) reflection ($2\theta = 106.7^\circ$); (c) $(0.0.10)$ reflection ($2\theta = 153.2^\circ$).

tical error would be about 0.3 percent. Variations among equivalent reflections, resulting probably from slight variations in absorption and extinction conditions, were frequently higher, sometimes as much as 5 percent, and occasionally, for very strong reflections, up to 10 percent.

The integrated intensities measured as described were averaged for the 99 nonequivalent reflections, and are listed in Table 2 under the heading I (rel). These numbers, corrected for background, are the count totals divided by the scale factor of 128. Further details of the measurement of integrated intensities with a Geiger counter are described elsewhere.⁹⁾

7. Correction of Intensities for Absorption and Extinction

Among the most important factors which influence the final value of the diffracted beam intensity are absorption and extinction effects (A in Eq. 2). This factor is a function of the linear absorption coefficient μ , the shape of the crystal, the position of the crystal in the beam and the Bragg angle. For this crystal it was derived from an exact evaluation of the expression

$$A = \frac{\int e^{-\mu t} dv}{\int dv} \quad (3)$$

over the whole volume of the crystal, where t is the path length of the X rays into and out of the crystal for the volume element dv . In order to make the calculation feasible, only diffraction beams normal to the prism axis, corresponding to the ($h0\ell$) reflections, were considered. Reducing the problem in this way to the two dimensions of the right-prism section, it was possible to subdivide this section into areas for which the integral of Eq. (3) is continuous, with boundaries determined primarily by the edges of the crystal. Two typical subdivisions are shown in Fig. 5. The limits of the exponential integral in Eq. (3) are different for each area j , so that Eq. (3) becomes

9) H. T. Evans, Jr., Technical Report No. 39, Philips Laboratories, Inc., 1951; Rev. Sci. Instr., in press.

$$A = \frac{\sum_j \int_j e^{-\mu t} ds}{\int ds} = \frac{\sum_j Z_j}{\mu^2 s}, \quad (4)$$

where Z_j is the exponential integral of each subdivision multiplied by μ^2 and s is the area of the section for the two-dimensional case. In practice, for each reflection the integrations Z_j were set up and carried out (4 to 9 per reflection), evaluated and summed. These tedious calculations were carried out for 99 reflections using the calculated value of $\mu = 198 \text{ cm}^{-1}$.

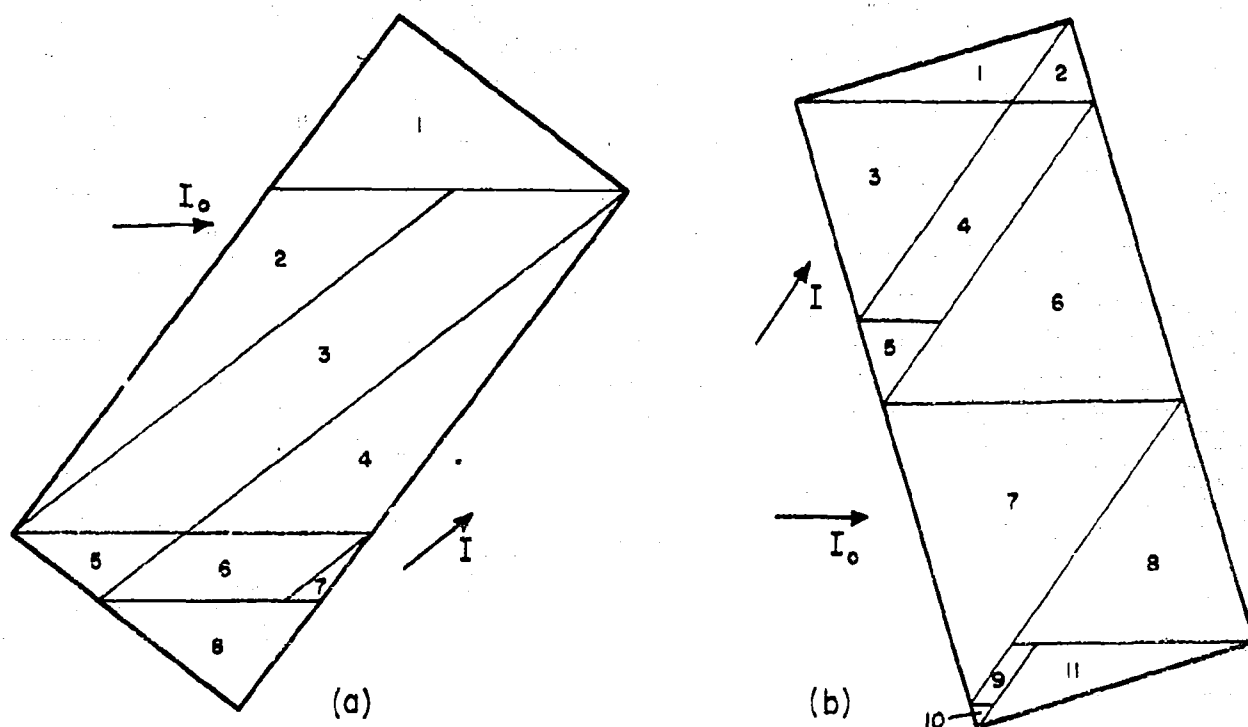


Fig. 5. Typical subdivisions of crystal section for determination of X-ray absorption effects: (a) for (203) reflection; (b) for (501) reflection.

Application of these values of A to the measured intensities showed by comparison with calculated structure factors that secondary extinction is an important factor. According to this effect the drain of the energy of the primary X-ray beam into the diffracted beam resulted in increasing the apparent absorption coefficient μ by an amount proportional to the intensity of

the diffracted beam. The effective μ becomes under these conditions

$$\mu = \mu_0 + gQ \quad (5)$$

where Q is a function of the structure factor and includes the Lorentz and polarization effects (Eq. 2) and g is a pure number, determined experimentally for a given crystal. An attempt was made to determine the value of g by making integrated intensity measurements of the strongest reflections with the wide-range spectrometer, using a flat powdered specimen. It was found that preferred orientation effects made it impossible to account for the intensities obtained, even though extinction effects are presumably absent. The value of the factor was therefore determined by trial, using calculated values of Q . Different values of g were used to determine μ for 12 strong reflections until the best fit between calculated and observed intensities was obtained. This process is demonstrated in Table 3. The reliability factor R

Table 3

Determination of Secondary Extinction In Barium Titanate

$g \times 10^{-3} =$		1.45		2.90		4.35		5.06		5.80		6.50	
$h0l$		μ	A	μ	A	μ	A	μ	A	μ	A	μ	A
100	214	0.230	230	0.208	246	0.179	254	0.169	262	0.159	270	0.151	
200	258	0.175	318	0.117	378	0.079	409	0.066	438	0.056	467	0.048	
300	202	0.248	206	0.242	210	0.236	211	0.235	214	0.230	217	0.229	
001	214	0.062	230	0.052	246	0.045	254	0.043	262	0.041	270	0.039	
002	258	0.071	318	0.050	378	0.039	409	0.035	438	0.033	467	0.031	
003	202	0.131	206	0.128	210	0.125	211	0.124	214	0.122	215	0.122	
101	257	0.137	317	0.094	376	0.080	406	0.058	436	0.050	466	0.044	
102	205	0.149	210	0.147	216	0.145	218	0.144	222	0.142	229	0.141	
103	211	0.109	224	0.097	237	0.088	243	0.085	250	0.081	257	0.078	
201	204	0.228	210	0.220	216	0.212	219	0.208	222	0.205	225	0.201	
202	226	0.159	254	0.132	282	0.111	296	0.104	310	0.097	324	0.092	
301	211	0.222	224	0.205	237	0.187	243	0.177	250	0.168	256	0.161	
R =		0.129		0.097		0.083		0.079		0.082		0.089	

(see Section 8) is used as the criterion of fit, and, on this basis, the value $g = 5.06 \times 10^3$ was chosen. All absorption factors A were then recalculated and these values were used to establish the final observed structure factors. Table 3 lists the values of A so obtained, and also, under μ , the effective absorption coefficient as determined by the secondary extinction effect, which was used in the calculation of A .

In spite of the rather drastic thermal history of the crystal,⁸⁾ the use of molybdenum radiation, and the excellent overall agreement between observed and calculated structure factors, certain of the strongest reflections are anomalously out of line with this general agreement. For example, the (200) and (002) reflections, which have calculated structure factors both equal to 65.5, are observed to have values of 60.1 and 73.4, respectively. Such an effect must result from the influence of an appreciable amount of primary extinction. This effect will be observed in regions of the crystal (within the "mosaic blocks" of the normally imperfect crystal) which are so perfect that the doubly-reflected Bragg reflection, 180° out of phase with the incident beam, will tend to cancel out this beam. Since there is no way to account quantitatively 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 $(\sin \theta)^2 / \lambda^2 < 0.250$ have been excluded, thus leaving 83 reflections to constitute the basic data.

The matter of extinction, secondary and primary, will not be further treated in this discussion. These phenomena have been thoroughly investigated by Känzig¹⁰⁾ with results which have a highly significant bearing on textural phenomena which occur in barium titanate single crystals as they are

10) W. Känzig, *Helv. Phys. Acta* 24, 175(1951).

heated and cooled through the Curie point at 120°C.

The absorption calculations described above (and in more detail elsewhere¹¹⁾ can be carried out with some effort in cases where the plane of diffraction is normal to the prism axis of the crystal, but become prohibitively involved for inclined reflections. Therefore, of the nearly 6,000 reflections of the type $(hk\ell)$ available, only those with $k = 0$ can be corrected for absorption. It should be noted also that the crystal must be treated as it stands, since any attempt to change its shape would fill the crystal with glide twin lamellae.

8. Calculation of Structure Factors

The structure amplitude F for reflection $(hk\ell)$ is a function of the atomic co-ordinates x_j , y_j and z_j and the scattering factor f_j of each atom, according to Eq.(1). The scattering factors used in this investigation are those of Hartree,⁵⁾ and Pauling and Sherman⁵⁾ for the stationary atom modified by a temperature factor, thus

$$f_j = f_{(T)j} e^{-B_j s^2}, \quad (6)$$

where $f_{(T)}$ is the tabulated scattering factor for the atom j at rest, B_j is a constant proportional to the square of the mean amplitude of vibration $\bar{u}$ of the atom, and $s = (\sin \theta)/\lambda$. According to the Debye-Waller theory this relation is approximately $B = 8\pi^2 \bar{u}^2$. The complete form of Eq.(1) will contain 12 free parameters: 3 structure and 9 anisotropic temperature parameters.

The evaluation of the parameters has been carried out by means of a combination of trial-and-error operations and least-squares analysis. The quality of the given structure is tested by comparing the observed and calculated structure amplitudes. The usual criterion used in statistics is the sum of the squares of the residuals, or quadratic mean error ϵ defined as

11) H. T. Evans, Jr., Technical Report No.45, Laboratory for Insulation Research, 1951; J. Appl. Phys. 23, 663(1952).

$$\epsilon^2 = \frac{\sum (|F|_{\text{obs}} - |F|_{\text{calc}})^2}{n - p}, \quad (7)$$

where n is the number of observations (reflections) and p the number of degrees of freedom (free parameters). The scale of $|F|_{\text{obs}}$ is established by multiplying by the factor K :

$$K = \sum |F|_{\text{obs}} \times |F|_{\text{calc}} \div \sum |F|_{\text{obs}}^2$$

It is the quantity $(|F|_{\text{obs}} - |F|_{\text{calc}})^2$ which is minimized analytically in least-squares analysis.

Crystallographers have been in the habit of using another criterion, the reliability factor R , defined as follows:

$$R = \sum ||F|_{\text{obs}} - |F|_{\text{calc}}| \div \sum |F|_{\text{obs}} \quad (8)$$

where the scale for $|F|_{\text{obs}}$ is established by

$$K = \sum |F|_{\text{calc}} \div \sum |F|_{\text{obs}}$$

The factor R is dimensionless and therefore useful to some extent in comparing the relative degree of refinement of structures of different crystals and substances. As a general rule, a value of R as low as 0.20 is considered satisfactory proof that a given structure is nearly correct. In recent years structure determinations giving reliability factors of 0.12 and 0.15 have become more common and are considered extremely good. Only by means of ionization chambers and Geiger counters has it been possible in a few cases to obtain values of R as low as 0.06 (see, for example, Cochran,¹²⁾ and Brill, Grimm, Hermann, and Peters.¹³⁾

12) W. Cochran, *Acta Cryst.* 4, 81(1951).

13) R. Brill, H. G. Grimm, C. Hermann and C. Peters, *Ann. Physik* 34, 393(1939).

9. Factors Influencing the Values of the Structure Amplitude

The values of the observed structure amplitude are affected by: (1) The relative location of the atoms; (2) the scattering factor of each atom; (3) errors in the experimental determination of the F values. We try to reduce the latter factor as much as possible in order to be able to learn more about the first two.

The scattering factor f_j is, to a first approximation, a function only of the Bragg parameter s (i.e., spherically symmetrical), and is similar in form to the function Ze^{-ks^2} (Z = atomic number). The Gaussian function is modified, of course, by the modern statistical mechanical treatment and has been calculated by Pauling and Sherman, Hartree and others for all atoms in free space at rest. In the environment of the crystal, the scattering factor will be altered; first, by the polarization of the atom due to the electric field in which it exists and bond formation with other atoms; and second, by the heat motion of the atom; both these effects will be aspherical. The temperature effect makes the electron cloud of the atom generally more diffuse, and consequently lowers the scattering factor at high Bragg angles approximately according to Eq.(6). The polarization of the atom, on the other hand, will affect almost exclusively the outer shell of electrons, and therefore will alter the scattering factor primarily at low Bragg angles, while these electrons make almost no contribution to the high-angle scattering. We may note in passing, that one may expect to obtain a higher degree of agreement between observed and calculated structure factors in structures containing heavy atoms, where a higher proportion of the X-ray scattering arises from dense, closed-shell atom cores, than in the case of organic structures, say, where a higher proportion of electrons are influenced by polarization, since polarization is the hardest factor to define in terms of

the structure factor.

In the case of barium titanate, because of the considerable influence of primary extinction, it was necessary to discard from consideration all reflections for which $(\sin \theta)^2 / \lambda^2 < 0.250$. This means that with 83 data from which to determine 12 parameters, we may expect to learn in some detail the structure (atomic displacements) and temperature motions of barium titanate, but will not be able to learn anything directly about the electronic polarizations of the atoms or the distribution of electrons between the atoms.

10. First Approximate Model

The first step in the analysis of the 83 data was to make the usual assumption that all atoms vibrate spherically with the same amplitude, giving a structure defined by 1 temperature parameter B , and 3 structure parameters z_{Ti} , z_{OI} , z_{OH} . By trial, each was varied in turn by small intervals, a set of structure factors calculated at each step and compared with the observed set by the criterion of the reliability factor R (Eq. 8). With $z_{Ti} = z_{OI} = z_{OH} = 0$ (cubic structure) and $B = 0.30 \times 10^{-16} \text{ cm}^2$, the reliability factor was determined as 0.0892, already a very low value as ordinary crystal structure standards go. After 28 trials, the lowest value for R for this model was found for the following parameters: $z_{Ti} = 0.015 \text{ cycles} = 0.061 \text{ \AA}$, $z_{OI} = -0.024 \text{ cycles} = -0.081 \text{ \AA}$, $z_{OH} = -0.020 \text{ cycles} = -0.097 \text{ \AA}$, $B = 0.30 \text{ \AA}^2$, $R = 0.0473$. This value for R was considered to be so unusually low that the results were published in a note¹⁴⁾ before further refinement of the model was carried out. It may be noted that the value of B is quite low, corresponding to a hard, covalently bound crystal with a high melting point, in contrast to molecular crystals (such as organic crystals), where B commonly may be as high as $2.5 \text{ \AA}^2$.

14) H. T. Evans, Jr., Acta Cryst. 4, 377(1951).

11. Anisotropic Temperature Motions in Barium Titanate

The next step in the refinement of the model was the assumption of different temperature vibration amplitudes (still spherically symmetrical) of each type of atom, thus increasing the number of temperature parameters to four: B_{Ba} , B_{Ti} , B_{OI} , B_{OII} . Starting with the previous model in which all these parameters are taken as $0.30 \text{ \AA}^2$, appropriate corrections ΔB_{Ba} , ΔB_{Ti} , ΔB_{OI} , and ΔB_{OII} were calculated by the method of least squares (Section 12), to give a 7-parameter structure for which $R = 0.0455$, a slight improvement over the first structure. The final model adopted assumes anisotropic temperature motion in all atoms, and is defined by 3 structure and 9 temperature parameters. Assuming that B_j varies elliptically with direction, the temperature parameters are designated as α_{Ba} , β_{Ba} , α_{Ti} , β_{Ti} , α_{OI} , β_{OI} , for the three atoms on the fourfold symmetry axes, where α corresponds to the $[a]$ -direction vibration and β to the $[c]$ -direction vibrations; and α_{OII} , β_{OII} , γ_{OII} for the oxygen atom on the two-fold rotation axis, where α_{OII} corresponds to the $[a]$ -direction vibration normal to the titanium-oxygen bond, γ_{OII} to the $[a]$ -direction vibration parallel to the bond, and β_{OII} to the $[c]$ -direction vibration. These parameters, which are shown in Fig. 6, appear in the temperature factor in place of B_j in Eq. (6), as, for example,

$$f_{Ba} = f_{(T)Ba} e^{-(\alpha_{Ba} \cos^2 \phi + \beta_{Ba} \sin^2 \phi) s^2}$$

where ϕ is the angle between an $(h0\ell)$ diffracting plane and the a crystallographic axis. In setting up the structure factors it is now necessary to consider the two OII atoms separately, since their temperature motions contribute in a different way to the amplitude. The complete expression for the structure factor is now written

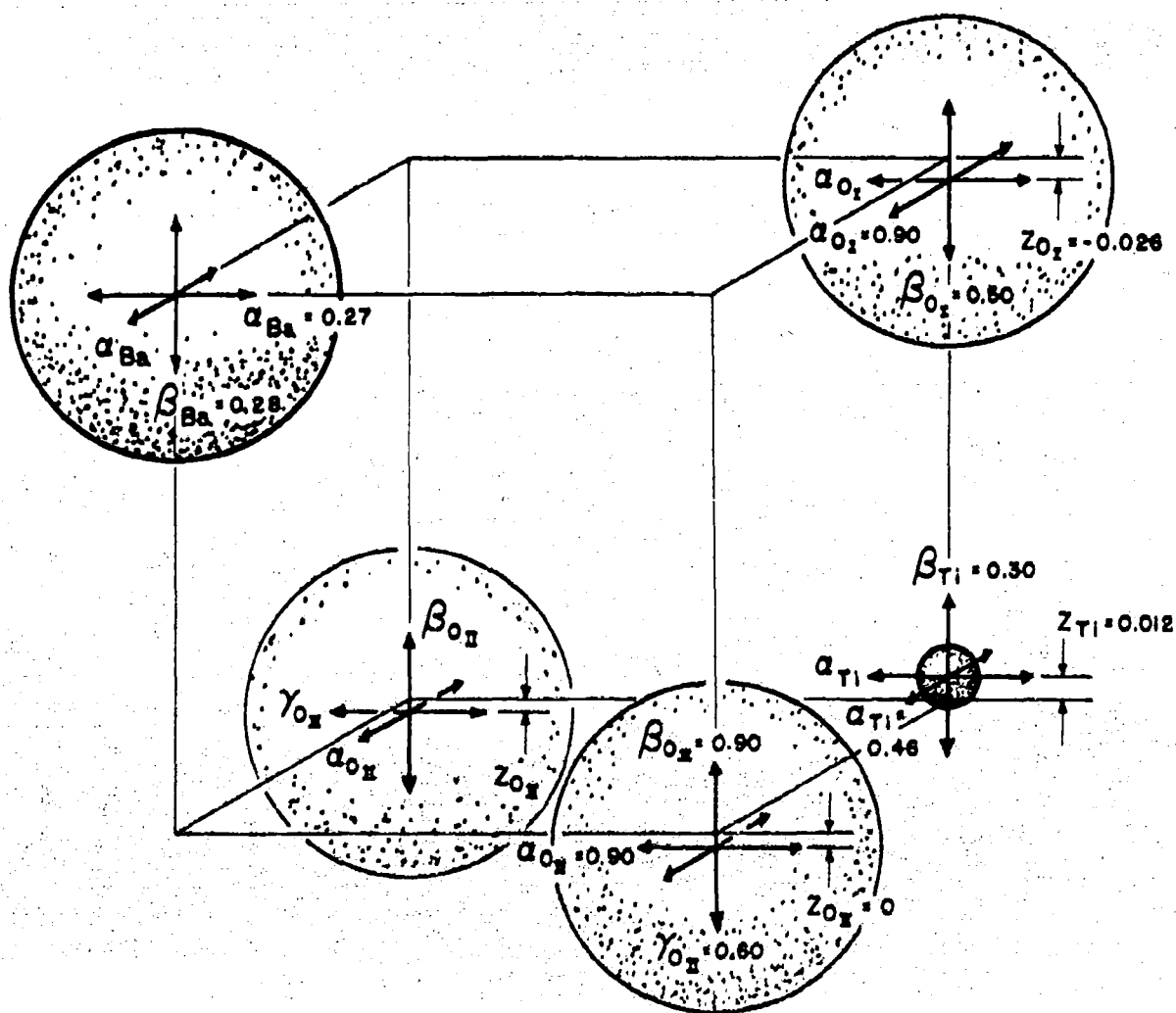


Fig. 6. Parameters in ultimate structure of tetragonal barium titanate.

$$\begin{aligned}
 A = & e^{-(\alpha_{Ba} \cos^2 \phi + \beta_{Ba} \sin^2 \phi)s^2} f_{(T)Ba} \\
 & + e^{-(\alpha_{Ti} \cos^2 \phi + \beta_{Ti} \sin^2 \phi)s^2} f_{(T)Ti} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \cos 2\pi l z_{Ti} \right] \\
 & + e^{-(\alpha_{OI} \cos^2 \phi + \beta_{OI} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & - \\ + & - \end{pmatrix} \cos 2\pi l z_{OI} \right] \\
 & + e^{-(\alpha_{OH} \cos^2 \phi + \beta_{OH} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \cos 2\pi l z_{OH} \right] \\
 & + e^{-(\gamma_{OH} \cos^2 \phi + \beta_{OH} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & + \\ - & - \end{pmatrix} \cos 2\pi l z_{OH} \right] \quad (9) \\
 B = & e^{-(\alpha_{Ti} \cos^2 \phi + \beta_{Ti} \sin^2 \phi)s^2} f_{(T)Ti} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} \right] \\
 & + e^{-(\alpha_{OI} \cos^2 \phi + \beta_{OI} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & - \\ + & - \end{pmatrix} \sin 2\pi l z_{OI} \right] \\
 & + e^{-(\alpha_{OH} \cos^2 \phi + \beta_{OH} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{OH} \right] \\
 & + e^{-(\gamma_{OH} \cos^2 \phi + \beta_{OH} \sin^2 \phi)s^2} f_{(T)O} \left[\begin{pmatrix} + & + \\ - & - \end{pmatrix} \sin 2\pi l z_{OH} \right]
 \end{aligned}$$

The sign matrices in Eq.(9) show the appropriate sign for the following cosine or sine term depending upon whether h and l are odd or even, according to the scheme:

		h	
		even	odd
l	even	+	-
	odd	-	+

12. Least-Squares Analysis

We have defined a function for the structure amplitude, F , in terms of 12 parameters:

$$F = f(z_{Ti}, z_{OI}, z_{OH}, \alpha_{Ba}, \beta_{Ba}, \alpha_{Ti}, \beta_{Ti}, \alpha_{OI}, \beta_{OI}, \alpha_{OH}, \beta_{OH}, \gamma_{OH}).$$

Approximate values of each of these parameters are known from which, by

Eq.(9), can be calculated a set of $|F|_{\text{calc}}$ values to be compared with the observed set of data $|F|_{\text{obs}}$. It can be shown analytically that these parameters may be altered by correction terms Δz_{Ti} , Δz_{OI} , Δz_{OH} , Δa_{Ba} , etc., such that the standard deviation will be a minimum when the correction terms are derived from a series of simultaneous equations of the form:

$$\frac{\partial |F|}{\partial z_{\text{Ti}}} \Delta z_{\text{Ti}} + \frac{\partial |F|}{\partial z_{\text{OI}}} \Delta z_{\text{OI}} + \frac{\partial |F|}{\partial z_{\text{OH}}} \Delta z_{\text{OH}} + \dots = |F|_{\text{obs}} - |F|_{\text{calc}} = \Delta |F|.$$

We may set up as many of these so-called "normal" equations as there are parameter corrections to determine. All of the data can be used by forming coefficients for the correction terms by summing cross-products. Thus, if

$$\frac{\partial |F|}{\partial z_{\text{Ti}}} = A, \quad \frac{\partial |F|}{\partial z_{\text{OI}}} = B, \quad \frac{\partial |F|}{\partial z_{\text{OH}}} = C, \text{ etc.,}$$

then the normal equations may be formed as follows:

$$\begin{aligned} (\sum A^2) \Delta z_{\text{Ti}} + (\sum AB) \Delta z_{\text{OI}} + (\sum AC) \Delta z_{\text{OH}} + \dots &= (\sum Ax \Delta |F|) \\ (\sum BA) \Delta z_{\text{Ti}} + (\sum B^2) \Delta z_{\text{OI}} + (\sum BC) \Delta z_{\text{OH}} + \dots &= (\sum Bx \Delta |F|) \quad (10) \\ (\sum CA) \Delta z_{\text{Ti}} + (\sum CB) \Delta z_{\text{OI}} + (\sum C^2) \Delta z_{\text{OH}} + \dots &= (\sum Cx \Delta |F|) \end{aligned}$$

The solution of these symmetrical equations should lead directly to the set of parameters which will give the best fit with the observed data since our approximate model is presumably already very near to the best one.¹⁵⁾

The differentials used in the least-squares treatment of barium titanate were derived as follows:

15) For further treatment of least-squares methods see A.C. Worthing and J. Geffner, "Treatment of Experimental Data," New York, John Wiley and Sons, Inc., 1943; E.T. Whittaker and G. Robinson, "Calculus of Observations," London, Blackie and Son, Ltd., 1944.

$$\left. \begin{aligned}
 F &= A + iB \\
 |F|^2 &= A^2 + B^2 \\
 2|F| \frac{\partial |F|}{\partial x} &= 2A \frac{\partial A}{\partial x} + 2B \frac{\partial B}{\partial x} \\
 \frac{\partial |F|}{\partial x} &= \frac{A}{|F|} \frac{\partial A}{\partial x} + \frac{B}{|F|} \frac{\partial B}{\partial x} = \cos \psi \frac{\partial A}{\partial x} + \sin \psi \frac{\partial B}{\partial x}
 \end{aligned} \right\} \quad (11)$$

where ψ is the phase angle of the noncentrosymmetric structure factor.

In the next stage of the analysis of barium titanate, the 13 differentials were calculated for the 83 ($h0\ell$) reflections, their cross-products summed to form the normal equations according to Eq.(10), and these equations solved by the method of Crout.¹⁶⁾ Until the last stages of the work, all these operations were accomplished with a hand computing machine, and were checked by a complete, independent recalculation. The results of the first complete calculations proved to be inconclusive for reasons to be described in the next section.

13. Interactions between Parameters

When an attempt was made to solve the 13 normal equations, results were obtained which were obviously without any significance, i.e., the corrected parameters gave a standard deviation much higher than the previous set. A study of the differential coefficients shows that, for the values of the parameters used, certain pairs of the derivatives are nearly equal in value for all $|F|$ terms, except for a common factor. This means that all the values change in the same way with changes in either one or the other of the pair of parameters. There are 4 such pairs of derivatives among the 13: $\partial|F|/\partial z_{Ti}$ and $\partial|F|/\partial \beta_{Ti}$; $\partial|F|/\partial z_{OI}$ and $\partial|F|/\partial \beta_{OI}$; $\partial|F|/\partial z_{OII}$ and $\partial|F|/\partial \beta_{OII}$; $\partial|F|/\partial a_{Ti}$ and $\partial|F|/\partial a_{OII}$. Thus, the atomic displacement

16) P. Crout, Trans. Am. Inst. Elect. Eng. 60, (1941).

parameter z and the $[c]$ -direction temperature parameter for the atom β , have an effect in the function Eq. (9) which does not permit their separation. In addition, the $[a]$ -direction vibration parameter for titanium cannot be distinguished from that of oxygen II which is superposed on it in the $(h0l)$ projection.

The interaction can be demonstrated analytically in the following way. In the least-squares analysis, we may expect to have difficulty in determining correction terms for two parameters ϕ if the function varies in the same way for each. In the present case this circumstance will obtain, for example, if the ratio $\partial|F|/\partial z_{Ti} \div \partial|F|/\partial \beta_{Ti}$ is constant or nearly so. It can be shown that for the set of parameters which characterize the barium titanate structure, the derivative

$$\frac{\partial}{\partial l} \left[\frac{\partial|F|}{\partial z_{Ti}} \bigg/ \frac{\partial|F|}{\partial \beta_{Ti}} \right] = \frac{\partial P}{\partial l}$$

tends to vanish. The first derivatives have the following form:

$$\frac{\partial|F|}{\partial z_{Ti}} = -2\pi l e^{-(a_{Ti} \cos^2 \phi + \beta_{Ti} \sin^2 \phi)s^2} f_{(T)Ti} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} \cos \psi \right. \\ \left. + \begin{pmatrix} - & + \\ + & - \end{pmatrix} \cos 2\pi l z_{Ti} \sin \psi \right]$$

$$\frac{\partial|F|}{\partial \beta_{Ti}} = -s^2 \sin^2 \phi e^{-(a_{Ti} \cos^2 \phi + \beta_{Ti} \sin^2 \phi)s^2} f_{(T)Ti} \left[\begin{pmatrix} + & - \\ - & + \end{pmatrix} \cos 2\pi l z_{Ti} \cos \psi \right. \\ \left. + \begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} \sin \psi \right].$$

If we note that $\sin^2 \phi = \frac{\lambda^2 l^2 c^{*2}}{4 \sin^2 \theta}$, and l is the index, then

$$P = \frac{8\pi}{c^2} \cdot \frac{1}{l} \left[\frac{\begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} \cos \psi + \begin{pmatrix} - & + \\ + & - \end{pmatrix} \cos 2\pi l z_{Ti} \sin \psi}{\begin{pmatrix} + & - \\ - & + \end{pmatrix} \cos 2\pi l z_{Ti} \cos \psi + \begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} \sin \psi} \right]$$

$$= \frac{8\pi}{l c^2} \cdot \frac{x}{y}$$

where x is the numerator and y the denominator of the bracketed fraction, then

$$\frac{\partial P}{\partial l} = \frac{8\pi}{c^2} \left[\frac{1}{l} \left(\frac{1}{y} \frac{\partial x}{\partial l} - \frac{x}{y^2} \frac{\partial y}{\partial l} \right) - \frac{1}{l^2} \frac{x}{y} \right]$$

When z_j is small, then approximately

$$\cos 2\pi l z_{Ti} = 1$$

$$\cos \psi = 1$$

$$\partial/\partial l (\cos \psi) = 0$$

$$x = \begin{pmatrix} + & - \\ - & + \end{pmatrix} \sin 2\pi l z_{Ti} + \begin{pmatrix} - & + \\ + & - \end{pmatrix} \sin \psi$$

$$y = \begin{pmatrix} + & - \\ - & + \end{pmatrix} 1$$

$$\sin 2\pi l z_{Ti} = 2\pi l z_{Ti}$$

$$\frac{\partial P}{\partial l} \approx \frac{8\pi}{c^2} \left[\frac{1}{l} \left(2\pi z_{Ti} \cos 2\pi l z_{Ti} - \frac{\partial}{\partial l} \sin \psi \right) - \frac{1}{l^2} \left(\sin 2\pi l z_{Ti} - \sin \psi \right) \right]$$

$$\approx \frac{8\pi}{c^2} \left[\frac{1}{l^2} \sin \psi - \frac{1}{l} \frac{\partial}{\partial l} \sin \psi \right]$$

Since, when the values z_j are all small, $\sin \psi$ is small and changes slowly with l , the derivative $\partial P/\partial l$ is seen to have a negligible value, at least for titanium and oxygen. When $\partial P/\partial l$ approaches zero, the determinant of the coefficients of the normal equations tends to vanish, and consequently the error in the separate determination of the variables involved in P tends to become infinite.

Strictly speaking, if we do not arbitrarily fix the origin of co-ordinates, we should introduce a 13th parameter z_{Ba} , in which case we will find that $\partial|F|/\partial z_{Ba}$ and $\partial|F|/\partial \beta_{Ba}$ tend to interfere with one another. Thus it appears that only 3 parameters can be established unambiguously: α_{Ba} , α_{OI} and γ_{OII} .

14. Final Refinement of the Barium Titanate Structure

The least-squares analysis of the complete model (12 parameters) next was carried out with 8 parameters assuming that one of each of the interfering pairs was fixed. Thus, the z parameters obtained from the original trial-and-error study were assumed to be correct (and also α_{OII}), and corrections were determined for the remaining temperature parameters. The resulting set of parameters gave a considerably improved agreement between observed and calculated structure amplitudes, with $R = 0.0372$. The values obtained for the temperature vibrations did not seem at all reasonable (see Table 4, F 30), however, and it seemed likely that the assumption the z parameters were correct must be abandoned. The calculation of the independent parameters gave results which are reasonable, considering only the binding forces between the atoms. Assuming that temperature vibration will be less in the direction of a bond with an adjacent atom than in other directions, we expect the 12-co-ordinated barium atom to be quite spherical in its vibration, while oxygen, being fairly tightly bound to titanium in one direction, should be rather anisotropic in its vibration. The calculation yields the following results:

$$\alpha_{Ba} = 0.27$$

$$\beta_{Ba} = 0.28$$

$$\alpha_{OI} = 0.90 \text{ (perpendicular to bond)}$$

$$\gamma_{OII} = 0.60 \text{ (parallel to bond)}.$$

Table 4
Trial Structures Of Tetragonal Barium Titanate

F	z_{Ti}	z_{OI}	z_{OH}	α_{Ba}^*	β_{Ba}	α_{Ti}	β_{Ti}	α_{OI}^*	β_{OI}	α_{OH}	β_{OH}	γ_{OH}^*	R	ϵ
0	0	0	0	0.30									.0892	1.838
20	.015	-.024	-.020	0.30									.0473	1.158
29	.015	-.024	-.020	0.29		0.39		0.88		0.49			.0455	1.053
30	.015	-.024	-.020	.27	.28	.53	.21	.90	.08	.49	.07	.60	.0375	0.861
42	.012	-.026	0	.27	.28	.46	.30	.90	.50	.90	.90	.60	.0372	0.924
Känzig	.014	-.032	0	0.48		0.13		0.13		0.48			.123	

We make the following adjustments:

1. Let $\alpha_{OH} = \beta_{OH} = 0.90$ since these all correspond to directions normal to O-Ti bonds.
2. Let $\beta_{OI} = 0.50$, a little smaller than γ_{OH} , because the OI-Ti bond is presumably somewhat stronger than OH-Ti.
3. Since α_{OH} is raised to 0.90, we decrease α_{Ti} to 0.46 in accordance with the relative values of their differentials calculated from Eq.(9).
4. Let $\beta_{Ti} = 0.30$, allowing for the stronger bond in this direction.

Then, by trial and error, the z parameters were redetermined to give a minimum value for R which was substantially equal to that obtained for the previous model. This required rather large adjustments of the structure, and the result is shown under F 42, Table 4. The calculated structure amplitudes for this model are the ones listed in Table 3.

Thus, we have arrived at a final result which is definitely ambiguous. It can be stated simply that unless data can be obtained extending considerably beyond the present limit of $(\sin \theta)/\lambda$ (by the use of shorter wavelengths), the structural displacements in barium titanate cannot be uniquely determined.

The measurement of (hkl) or $(hk0)$ reflections would serve to determine the parameters a_{Ti} and a_{OH} separately, but the z and β parameters will interact for all reflections.

Table 4 shows the course of the structure determinations by listing certain trial structures (serial number under F). The starred parameters are those uniquely determined. Structure 42 represents, we suggest, the most reasonable one consistent with the X-ray measurements.

15. The Work of Känzig

While there have been many investigators working on the barium titanate structure problem, only one has presented a report containing the kind of measurements and analysis capable of solving it. The work of Känzig¹⁰⁾ consists of the measurement of X-ray diffraction intensities from a large single crystal plate of barium titanate. The results of his work on the structure are shown in Table 4. There are several important aspects of Känzig's report which must be considered in evaluating these results:

1. Only 18 reflections were measured: 8 $(h00)$ -type reflections which would depend on a_{Ba} , a_{Ti} , a_{OI} , a_{OH} and γ_{OH} , and 10 $(00l)$ -type which would depend on z_{Ti} , z_{OI} , z_{OH} , β_{Ba} , β_{Ti} , β_{OI} and β_{OH} . These measurements, while they extend to the same range of $(\sin \theta)/\lambda$ as those made here, are hardly enough to lend statistical weight to the determination of the parameters.
2. It was assumed, quite arbitrarily, that $z_{OH} = 0$. While the assumption is apparently nearly correct, no study was made to establish this result.
3. It was assumed that

$$a_{Ti} = \beta_{Ti} = a_{OI} = \beta_{OI}$$

$$a_{Ba} = \beta_{Ba} = a_{OH} = \beta_{OH} = \gamma_{OH},$$

again apparently quite arbitrarily. Thus, only two spherical temperature parameters were considered.

4. No numerical data of any kind are given in Känzig's report.

It would appear that Känzig's structure determination is quite incomplete. On the other hand, as mentioned in Section 7, 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.

16. The Future of the Barium Titanate Structure Problem

It is a considerable disappointment to workers in the theory of ferroelectrics, for whom any new observational data is of the utmost importance, to find that X-ray diffraction fails in this case. One way out of the difficulty, as has been mentioned, is to use shorter wavelengths, as Grimsal¹⁷⁾ has tried to do, but even if sufficient intensity can be achieved to get data in the high ranges, the atomic scattering functions are not known in these regions and must be determined or calculated. Otherwise, recourse may be made to neutron diffraction where the scattering factors are radically different in relative magnitudes and do not damp out at high angles; they may, therefore, give a complete picture of the structure.

Finally, it should be pointed out that this is only the second instance in which the temperature factors have interfered with the X-ray determination of structure. The other case was hydrocyanic acid HCN, worked out by

17) E. G. Grimsal, "Structure of BaTiO₃," U.S. Atomic Energy Commission Report No. AECU-884, Dec. 7, 1950.

Dulmage and Lipscomb,¹⁸⁾ which came to the writer's attention long after the situation was discovered for barium titanate. The phenomenon should be watched for in future determinations, especially when an atom is slightly displaced from a symmetrical position in a polar structure.

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18) W. J. Dulmage and W. N. Lipscomb, Acta Cryst. 4, 330(1951).