The Structure of Sodium Niobate at Room Temperature, and the Problem of Reliability in Pseudosymmetric Structures

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The structure of $NaNbO_3$ has been refined from three-dimensional X-ray data. It is a distorted perovskite, with space group *Pbma* and 8 formula units in an orthorhombic unit cell about $5.5 \times 15 \times 5.5$ Å. Electron-density projections constructed with only the Nb atoms displaced from their ideal positions gave approximate magnitudes for all the larger displacement parameters. With the help of an additional projection, assuming one oxygen parameter to fix the sense of the y axis, the signs of all these displacement parameters could be found by several different arguments allowing cross-checking. The trial model thus set up proved to be a very good approximation and refined easily both by Fourier difference syntheses and by least-squares.

The NbO_6 octahedra, which are the asymmetric units, are in fact very regular, though tilted appreciably ($\sim 10°$) about both the [010] and the [100] directions. The Nb atoms are off-centre, with their displacement vector inclined at about $20°$ to [100], nearly in the (010) plane. There are thus two short, two long, and two intermediate Nb–O bonds; each O has only one short bond to Nb. Deviations from regularity of the octahedron shape, though of second-order magnitude, are systematic and can be correlated with the Nb displacement. Along any column of octahedra parallel to [010], a pair of Nb displacements related by the (010) mirror plane is followed by an antiparallel pair, but in adjacent columns the displacements are not exactly parallel. The two independent Na atoms have very different environments; Na(1) has 3 very near neighbours in a triangle, and 6 distinctly more distant, while Na(2) has 4 nearest in a tetrahedron and 4 slightly more distant. Thermal vibration amplitudes are in general greatest at right angles to strong bonds. The structure is compared with the ferroelectric phase (Phase Q), and some suggestions are made as to how the Na environment may determine the relative stabilities of the two phases.

Introduction

Sodium niobate, $NaNbO_3$, belongs to the perovskite structure family. The cell dimensions and symmetry were found by Wood (1951). Early work by Vousden (1951) established the Nb atom positions to a good approximation, but his space-group determination and other features of his structure were incorrect, as shown by Megaw & Wells (1958). A short account of a revised structure was given by Wells & Megaw (1961), but neither the data nor the refinement were very complete. The present determination is based on new data. It is concerned only with the normal room-temperature structure of pure $NaNbO_3$; the other structure studied by Wells & Megaw (1961), whose history is given in detail by Wood, Miller & Remeika (1962), will be the subject of a separate paper.

Experimental

The studies were carried out on single-domain crystals of pure $NaNbO_3$ selected from material kindly provided by Dr L. E. Cross. They were pieces, about 0·1 mm in their longest dimension, cut from good few-domain crystals which showed sharp extinction in

polarized light. Three crystals were used, one with [101] and [001] directions in turn as rotation axes, the others with [100] and [010] respectively. Although sharpness of extinction under the polarizing microscope and absence of any visible domain structure indicated that the crystals were single-domain, the final confirmation came from X-ray photographs. Twinning in the crystals was most easily detected by observing back reflexions taken with Cu $K\alpha$ radiation. In the case of the three crystals discussed above there was no sign of splitting of the back reflexions nor any other indication of twinning.

Equi-inclination Weissenberg photographs were taken of zones hkh, $h0l$, $hk0$ and $0kl$, and layer lines hkl with $h = 1$ to 5, using Zr-filtered Mo $K\alpha$ radiation with the multi-layer film technique. Exposures of about 100 hr were needed. Intensities were measured visually from a standard scale. Absorption corrections were found to be small compared with random errors, and were neglected. A comparison of all pairs of F_o's measured on different photographs gave a mean discrepancy value of 10% (or 7% if one photograph, whose scaling factor was subsequently questioned, was omitted).

In the early stages of the work, two-dimensional data, using the intensities collected for four zones hkh, $h0l$, $0kl$, and $hk0$, were used to establish a suitable model. The tactics of this procedure are discussed below. Re-

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Table 1(a). *Observed and calculated intensities of reflexions used in refinement*

H	K	L	FU	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	20	0	103.84	-90.85	1	16	1	149.43	-141.20	1	12	10	31.41	-26.98	2	9	6	34.19	-29.16
0	24	0	128.15	111.97	1	20	1	124.86	125.80	1	16	10	32.17	31.44	2	11	6	25.07	-19.52
0	28	0	65.09	-55.09	1	24	1	107.13	-101.66	1	0	11	63.06	60.94	2	12	6	105.36	-108.43
0	32	0	78.01	66.59	1	28	1	86.62	79.13	1	4	11	73.96	-75.75	2	13	6	29.13	20.57
0	36	0	41.03	-33.42	1	32	1	72.69	-67.29	1	8	11	54.96	57.04	2	15	6	33.94	23.69
0	4	1	18.24	15.79	1	40	1	38.75	-41.83	1	12	11	64.33	-66.03	2	16	6	99.03	105.50
0	6	1	69.40	-59.42	1	0	2	27.35	26.84	1	16	11	49.13	47.22	2	17	6	28.87	-23.31
0	10	1	39.26	32.59	1	1	2	30.14	-30.66	1	20	11	47.11	-51.31	2	20	6	76.49	-82.12
0	14	1	45.84	-40.54	1	2	2	39.00	28.00	1	24	11	32.93	35.43	2	28	6	58.76	-55.98
0	18	1	26.09	18.73	1	3	2	22.79	-21.61	1	28	11	34.44	-36.84	2	36	6	38.50	-36.07
0	4	2	75.47	86.35	1	4	2	12.92	-14.35	1	0	12	31.15	-34.30	2	0	7	34.95	-29.79
0	12	2	104.09	112.18	1	5	2	23.30	17.88	1	4	12	23.55	26.53	2	4	7	43.06	38.94
0	20	2	107.13	104.51	1	6	2	31.41	16.29	1	8	12	30.90	-32.55	2	8	7	33.94	-28.52
0	24	2	134.23	-126.17	1	8	2	25.58	21.45	1	12	12	23.30	24.41	2	12	7	39.00	33.54
0	28	2	76.49	78.31	1	9	2	14.69	-13.15	1	0	13	47.87	-44.10	2	16	7	29.13	-24.84
0	32	2	83.33	-82.68	1	10	2	30.39	19.31	1	4	13	47.11	49.46	2	20	7	27.35	25.88
0	36	2	51.92	49.09	1	12	2	15.96	-11.18	1	8	13	39.26	-41.78	2	0	8	113.47	-109.45
0	2	3	48.12	40.42	1	14	2	17.48	6.26	1	12	13	45.59	44.05	2	1	8	31.41	24.08
0	4	3	35.96	-37.55	1	16	2	19.50	14.16	1	16	13	33.94	-35.83	2	3	8	24.06	17.85
0	8	3	17.98	17.18	1	1	3	13.93	-13.13	1	20	13	34.44	35.58	2	4	8	105.36	100.91
0	10	3	50.15	46.80	1	3	3	37.23	-34.06	1	0	14	27.35	28.32	2	5	8	27.61	-19.56
0	12	3	28.62	-26.40	1	5	3	19.76	13.46	1	4	14	22.54	-23.23	2	7	8	32.93	-21.26
0	18	3	38.75	31.41	1	7	3	30.90	27.78	1	8	14	28.62	27.04	2	8	8	100.30	-99.76
0	12	4	119.54	-132.93	1	11	3	38.50	-34.17	1	12	14	18.49	-21.54	2	9	8	30.14	23.60
0	16	4	134.23	148.13	1	15	3	28.11	23.43	1	16	14	17.98	23.66	2	11	8	26.59	14.87
0	20	4	87.63	-92.81	1	16	3	116.50	123.56	2	5	0	30.39	-29.03	2	13	8	32.93	-18.03
0	24	4	88.39	92.65	1	19	3	33.18	-23.03	2	7	0	59.01	-63.26	2	15	8	23.81	-17.30
0	28	4	68.13	-59.68	1	20	3	107.39	-118.96	2	9	0	34.70	32.13	2	17	8	24.06	19.45
0	32	4	60.03	56.20	1	24	3	83.83	88.44	2	11	0	42.55	41.40	2	20	8	61.54	66.86
0	36	4	39.26	-37.37	1	28	3	74.21	-75.33	2	13	0	23.30	-18.77	2	24	8	52.93	-53.72
0	40	4	32.42	34.99	1	32	3	61.80	58.30	2	15	0	41.54	-43.34	2	28	8	46.86	47.37
0	2	5	20.77	-15.44	1	36	3	47.11	-45.89	2	17	0	24.82	21.80	2	32	8	37.23	-35.51
0	4	5	40.78	41.97	1	40	3	40.27	36.91	2	19	0	31.66	28.39	2	0	9	34.44	32.49
0	6	5	28.62	-23.45	1	0	4	39.51	-40.09	2	20	0	93.20	97.80	2	4	9	44.83	-38.20
0	8	5	24.57	-24.00	1	1	4	32.67	-20.32	2	23	0	32.17	-26.73	2	8	9	33.43	30.84
0	12	5	31.15	33.85	1	2	4	28.11	-19.42	2	28	0	75.73	73.59	2	12	9	40.27	-33.41
0	14	5	26.34	-20.68	1	3	4	29.13	-24.54	2	32	0	83.83	-82.07	2	16	9	27.35	26.39
0	16	5	20.51	-21.26	1	4	4	24.57	23.11	2	36	0	44.07	46.03	2	0	10	75.47	68.05
0	0	6	141.07	-154.56	1	5	4	29.89	21.47	2	1	1	24.57	21.46	2	1	10	30.90	-16.60
0	4	6	111.19	121.13	1	6	4	30.90	-21.42	2	2	1	33.18	29.19	2	4	10	69.40	-65.15
0	8	6	139.05	-140.92	1	7	4	22.54	11.02	2	3	1	25.07	20.07	2	8	10	68.13	66.03
0	12	6	116.50	109.04	1	8	4	35.46	-34.73	2	4	1	19.50	-11.95	2	12	10	61.80	-62.65
0	16	6	124.36	-111.24	1	9	4	17.48	-8.24	2	5	1	23.30	-15.46	2	16	10	59.77	59.16
0	20	6	97.76	88.03	1	10	4	17.48	-11.21	2	6	1	29.38	-20.14	2	20	10	56.73	-55.13
0	24	6	85.35	-79.39	1	12	4	18.49	20.49	2	7	1	19.00	-11.09	2	24	10	48.37	47.34
0	28	6	67.12	63.62	1	14	4	23.55	-14.60	2	10	1	46.60	42.63	2	28	10	49.13	-42.67
0	32	6	56.73	-52.26	1	16	4	26.59	-25.53	2	11	1	16.97	3.68	2	0	11	31.66	-29.89
0	36	6	41.03	42.22	1	3	5	17.48	11.99	2	14	1	25.58	-22.33	2	4	11	38.50	33.53
0	0	7	33.68	32.65	1	5	5	34.95	-27.74	2	18	1	30.14	26.71	2	8	11	27.61	-28.38
0	4	7	38.24	-44.37	1	9	5	32.42	27.21	2	22	1	15.45	-11.33	2	12	11	30.65	29.75
0	8	7	29.89	30.99	1	12	5	138.79	151.04	2	1	2	44.07	-55.71	2	16	11	25.07	-24.50
0	16	7	23.30	26.41	1	13	5	38.24	-28.83	2	3	2	23.55	-31.11	2	0	12	75.47	-66.97
0	0	8	113.72	110.54	1	16	5	94.47	-101.43	2	5	2	37.99	43.29	2	4	12	63.82	60.96
0	4	8	103.08	-100.73	1	17	5	32.42	23.31	2	7	2	34.70	38.91	2	8	12	60.78	-59.97
0	8	8	107.13	103.61	1	20	5	102.57	111.19	2	9	2	45.59	-51.82	2	12	12	48.63	49.46
0	12	8	94.93	-92.15	1	21	5	24.82	-19.72	2	13	2	35.71	36.32	2	16	12	45.59	-44.07
0	16	8	90.67	85.59	1	24	5	79.02	-75.48	2	17	2	41.28	-35.49	2	20	12	33.18	34.31
0	20	8	78.51	-75.47	1	28	5	72.44	74.76	2	20	2	84.09	-87.18	2	24	12	30.14	-28.90
0	24	8	64.33	62.70	1	40	5	28.62	-31.43	2	24	2	105.61	99.68	2	0	13	27.35	24.68
0	28	8	59.77	-54.82	1	0	6	38.50	44.36	2	28	2	56.48	-53.63	2	4	13	29.89	-27.60
0	32	8	43.31	41.25	1	1	6	21.27	-25.42	2	32	2	56.48	59.82	2	12	13	27.10	-25.49
0	36	8	35.20	-36.17	1	2	6	18.49	11.29	2	1	3	19.00	15.90	2	0	14	33.18	30.06
0	0	9	42.30	-32.82	1	4	6	27.10	-28.62	2	2	3	29.13	-16.95	2	4	14	26.09	-25.10
0	4	9	28.62	40.11	1	7	6	17.48	19.75	2	4	3	33.18	31.06	2	8	14	30.14	31.09
0	8	9	38.75	-31.17	1	8	6	37.74	39.94	2	6	3	47.87	-38.52	2	12	14	26.34	-27.39
0	0	10	109.67	-93.56	1	10	6	25.07	14.18	2	7	3	13.68	-11.62	2	0	15	16.72	-22.71
0	4	10	97.76	87.74	1	12	6	26.59	-25.55	2	8	3	17.73	-16.36	3	5	1	57.49	74.09
0	8	10	87.13	-83.98	1	16	6	33.68	30.97	2	12	3	24.82	22.89	3	7	1	37.23	44.51
0	12	10	77.50	72.59	1	0	7	104.35	106.31	2	14	3	38.50	-31.63	3	9	1	30.90	-35.48
0	16	10	68.13	-62.30	1	3	7	28.11	-18.63	2	20	3	21.53	15.58	3	11	1	53.95	-65.77
0	20	10	56.23	52.13	1	4	7	138.03	-150.31	2	22	3	28.11	-19.39	3	13	1	44.07	51.72
0	24	10	44.07	-41.34	1	7	7	30.14	21.77	2	3	4	31.66	30.72	3	15	1	39.26	36.91
0	28	10	33.94	35.77	1	8	7	91.94	98.32	2	5	4	28.87	-25.01	3	19	1	50.40	-45.31
0	32	10	25.83	-27.52	1	11	7	34.44	-24.68	2	7	4	44.58	-42.95	3	20	1	91.94	-103.94
0	0	11	25.33	30.52	1	12	7	110.68	-124.60	2	9	4	36.47	31.31	3	21	1	41.79	36.03
0	4	11	25.33	-35.24	1	15	7	25.07	22.39	2	11	4	29.38	28.77	3	23	1	25.58	27.51
0	8	11	25.33	29.39	1	16	7	73.70	78.78	2	13	4	21.27	-19.31	3	24	1	75.98	87.51
0	12	11	30.39	-31.83	1	20	7	86.37	-90.65	2	15	4	36.47	-33.40	3	27	1	32.42	-29.53
0	0	12	60.53	47.24	1	24	7	53.95	56.05	2	17	4	23.81	22.45	3	32	1	55.47	57.80
0	8	12	53.69	47.94	1	28	7	61.54	-61.00	2	19	4	23.81	22.13	3	36	1	41.79	-39.05
0	12	12	44.07	-44.76	1	32	7	40.78	37.20	2	23	4	25.07	-22.60	3	40	1	35.20	36.74
0	16	12	48.12	47.31	1	36	7	37.74	-39.80	2	24	4	93.71	-96.91	3	0	2	24.57	-20.28
0	24	12	43.06	41.33	1	0	8	44.07	-43.49	2	32	4	63.32	-64.08	3	1	2	19.50	-2.87
0	0	13	25.58	-28.12	1	1	8	25.83	-10.82	2	36	4	40.78	44.10	3	2	2	19.76	-15.15
0	4	13	26.34	31.45	1	3	8	24.57	-12.38	2	40	4	34.19	-38.82	3	3	2	20.51	-13.91
0	8	13	21.53	-26.46	1	4	8	35.96	30.54	2	0	5	24.06	26.68	3	4	2	17.48	13.24
0	12	13	24.82	27.68	1	7	8	23.55	7.28	2	2	5	25.58	18.67	3	5	2	18.49	12.90
0	0	14	55.47	-53.98	1	8	8	44.07	-40.57	2	3	5	14.69	-4.04	3	6	2	26.34	-22.50
0	4	14	41.54	46.97	1	12	8	32.67	27.97	2	5	5	14.69	3.78	3	7	2	12.92	-1.93
0	8	14	46.86	-48.11	1	16	8	37.23	-33.43	2	6	5	14.69	6.87	3	8	2	18.24	-17.33
0	12	14	32.93	37.31	1	0	9	83.07	-74.66	2	8	5	22.79	25.11	3	14	2	21.27	-16.19
0	0	15	19.25	20.32	1	4	9	102.32	103.80	2	10	5	31.66	23.35	3	1	3	40.27	45.49
0	4	15	22.79	-23.44	1	8	9	44.32	-71.26	2	12	5	36.98	-31.78	3	7	3	28.37	-32.24
1	1	1	16.46	19.78	1	12	9	86.37	91.83	2	16	5	25.58	21.35	3	9	3	45.34	47.87
1	3	1	29.13	32.33	1	16	9	65.09	-61.38	2	18	5	33.43	20.07	3	11	3	41.79	44.06
1	5	1	37.48	-39.76	1	20	9	70.92	72.67	2	20	5	28.62	-23.06	3	13	3	49.39	-56.79
1	7	1	10.89	-8.98	1	24	9	46.35	-47.13	2	1	6	34.70	-31.95	3	15	3	27.10	-24.30
1	9	1	23.81	21.61	1	28	9	51.41	52.21	2	3	6	25.83	-22.36	3	16	3	110.93	-110.07
1	11	1	19.76	18.64	1	0	10	37.74	40.57	2	5	6	31.66	22.95	3	17	3	42.04	38.40
1	13	1	33.14	-26.97	1	4	10	31.15	-30.05	2	7	6	41.03	29.48	3	19	3	33.68	31.15

Table 1 (a) (cont.)

H	K	L	FO	FC
3	20	3	108.65	105.79
3	24	3	85.86	-84.35
3	28	3	73.20	70.89
3	32	3	30.65	-56.52
3	36	3	44.32	42.88
3	40	3	37.99	-34.31
3	0	4	26.85	31.02
3	1	4	19.00	-30.66
3	2	4	28.87	21.60
3	4	4	17.48	-21.07
3	8	4	24.57	27.33
3	10	4	33.68	26.35
3	1	5	33.68	-56.69
3	3	5	48.88	-52.13
3	5	5	40.78	39.64
3	7	5	40.27	44.58
3	9	5	23.55	-25.84
3	11	5	56.73	-52.07
3	13	5	37.48	27.76
3	16	5	79.02	87.53
3	17	5	28.62	-20.03
3	19	5	42.55	-40.62
3	20	5	85.61	-89.52
3	21	5	22.79	21.19
3	24	5	58.00	58.72
3	28	5	61.54	-56.63
3	32	5	35.96	38.01
3	36	5	37.23	-36.32
3	3	6	22.03	-9.76
3	4	6	25.33	26.99
3	5	6	22.79	9.83
3	6	6	22.03	-17.03
3	7	6	17.73	-3.12
3	8	6	34.70	-33.94
3	9	6	17.73	1.31
3	12	6	33.68	24.73
3	14	6	25.33	-17.62
3	16	6	25.33	-27.73
3	0	7	76.99	-74.73
3	1	7	38.24	34.13
3	3	7	42.04	32.14
3	5	7	43.31	-40.58
3	7	7	22.79	-23.33
3	8	7	73.73	-74.60
3	9	7	43.31	39.55
3	11	7	22.79	21.65
3	12	7	95.48	102.52
3	13	7	42.55	-39.47
3	16	7	68.64	-69.60
3	17	7	35.71	34.90
3	20	7	79.78	84.26
3	24	7	50.91	-56.31
3	28	7	63.32	61.24
3	32	7	35.46	-38.76
3	36	7	38.24	39.39
3	0	8	32.67	37.81
3	4	8	26.85	-29.05
3	8	8	40.02	34.90
3	0	9	84.85	76.86
3	1	9	31.41	-25.21
3	3	9	33.43	-29.49
3	5	9	27.35	22.15
3	7	9	33.94	30.23
3	8	9	70.16	69.55
3	9	9	22.79	-18.01
3	11	9	36.47	-31.50
3	12	9	89.29	-83.77
3	15	9	30.90	28.58
3	16	9	54.20	52.57
3	20	9	62.05	-60.01
3	24	9	43.56	35.32
3	28	9	42.30	-40.27
3	32	9	19.76	23.45
3	0	10	32.67	-34.27
3	8	10	35.20	-32.61
3	0	11	51.92	-46.84
3	4	11	66.10	60.97
3	8	11	48.37	-45.35
3	12	11	56.48	55.85
3	16	11	43.31	-40.70
3	20	11	49.39	46.63
3	24	11	31.66	-33.12
3	28	11	28.87	35.35
3	0	12	27.35	31.02
3	8	12	30.65	29.25
3	0	13	40.52	38.80
3	4	13	39.51	-44.03
3	8	13	35.71	36.91
3	12	13	37.48	-39.45
3	16	13	32.93	31.76
3	20	13	26.59	-31.82
4	11	0	35.20	-38.86
4	13	0	57.75	66.71
4	15	0	39.76	45.47
4	19	0	35.96	-31.61
4	20	0	70.16	-72.33
4	21	0	57.75	47.93
4	23	0	41.28	34.41
4	24	0	85.10	86.60
4	25	0	43.31	-39.03
4	28	0	45.08	-43.73
4	32	0	60.28	52.42
4	36	0	28.87	-25.47
4	40	0	33.43	32.59
4	1	1	31.66	27.16
4	3	1	15.70	24.30
4	5	1	14.44	-21.02
4	6	1	26.85	-20.50
4	7	1	23.05	-17.79
4	9	1	18.49	13.24
4	10	1	17.73	11.08
4	9	2	44.32	54.20
4	11	2	48.37	61.17
4	13	2	34.19	-36.47
4	15	2	62.05	-65.93
4	17	2	43.06	39.17
4	19	2	36.98	46.83
4	20	2	54.96	76.74
4	21	2	29.13	-30.54
4	23	2	51.67	-44.21
4	24	2	72.69	-91.43
4	25	2	28.87	30.26
4	27	2	27.35	30.09
4	28	2	49.39	56.85
4	29	2	19.50	-25.61
4	31	2	19.25	-25.96
4	32	2	52.17	-61.64
4	33	2	18.24	23.42
4	36	2	32.42	36.56
4	40	2	27.86	-38.02
4	0	3	17.48	15.84
4	1	3	16.46	7.73
4	2	3	25.07	18.45
4	3	3	25.33	6.61
4	4	3	25.33	-19.73
4	5	3	28.37	-5.76
4	6	3	8.86	3.88
4	7	3	15.96	-2.03
4	8	3	18.74	15.48
4	9	3	9.88	1.93
4	10	3	31.91	24.26
4	11	3	18.24	-1.93
4	12	3	21.78	-17.10
4	13	3	11.14	1.63
4	18	3	27.10	20.35
4	5	4	54.96	53.58
4	7	4	60.28	57.87
4	8	4	160.44	148.40
4	9	4	61.80	-65.20
4	11	4	37.74	-36.78
4	12	4	114.98	-100.59
4	13	4	48.12	49.65
4	16	4	121.32	107.63
4	17	4	52.93	-52.16
4	20	4	77.50	-72.18
4	21	4	53.68	37.79
4	23	4	31.91	32.96
4	25	4	32.67	-35.39
4	27	4	19.50	-23.12
4	29	4	19.25	24.37
4	36	4	34.44	-28.77
4	0	5	17.99	-23.94
4	2	5	15.20	-9.62
4	3	5	10.89	16.81
4	4	5	29.89	28.02
4	5	5	15.70	-14.59
4	6	5	23.05	-14.81
4	8	5	24.57	-22.40
4	12	5	26.09	23.47
4	14	5	24.82	-15.11
4	16	5	17.22	-18.74
4	0	6	114.23	-107.97
4	1	6	59.52	54.66
4	3	6	48.37	40.98
4	4	6	92.19	92.71
4	5	6	50.65	-39.52
4	7	6	55.72	-52.64
4	8	6	81.81	-100.06
4	9	6	46.35	48.48
4	12	6	73.96	63.63
4	13	6	38.75	-33.87
4	15	6	48.37	-43.51
4	16	6	68.13	-81.05
4	17	6	41.54	38.34
4	19	6	35.46	29.65
4	20	6	55.72	67.53
4	21	6	29.63	-26.29
4	23	6	32.93	-31.86
4	24	6	53.95	-58.88
4	25	6	29.89	28.22
4	27	6	19.00	21.02
4	28	6	42.80	49.03
4	29	6	18.24	-19.07
4	31	6	17.22	-21.33
4	32	6	32.93	-39.23
4	36	6	28.11	32.76
4	4	7	37.48	-31.63
4	8	7	24.06	26.72
4	12	7	31.15	-27.34
4	16	7	18.74	22.57
4	20	7	19.50	-21.11
4	0	8	85.10	82.63
4	1	8	45.84	-40.98
4	3	8	35.46	-33.02
4	4	8	66.61	-79.81
4	7	8	49.64	41.19
4	8	8	67.62	76.85
4	9	8	41.79	-36.01
4	11	8	31.66	-31.14
4	12	8	68.89	-71.30
4	13	8	32.17	25.85
4	15	8	44.07	35.21
4	16	8	54.96	62.45
4	17	8	32.93	-29.81
4	19	8	30.14	-24.83
4	20	8	53.69	-57.00
4	21	8	19.25	21.34
4	23	8	26.85	25.83
4	24	8	42.80	45.25
4	28	8	38.24	-41.30
4	0	9	26.59	-27.30
4	1	9	17.22	2.51
4	3	9	17.22	10.34
4	4	9	32.67	29.62
4	5	9	19.00	-9.06
4	7	9	19.00	-5.10
4	8	9	27.10	-26.25
4	12	9	27.61	25.74
4	0	10	73.96	-66.32
4	1	10	33.18	30.78
4	3	10	27.61	23.71
4	4	10	59.52	64.58
4	5	10	33.68	-28.69
4	7	10	27.61	-24.70
4	8	10	61.54	-60.67
4	9	10	33.68	33.10
4	11	10	27.61	17.99
4	13	10	33.43	-28.34
4	16	10	45.34	-47.15
4	17	10	26.34	28.95
4	19	10	17.98	14.65
4	20	10	40.52	41.77
4	21	10	24.57	-22.26
4	24	10	31.66	-32.63
4	28	10	25.07	29.24
4	0	11	19.25	26.04
4	4	11	19.25	-27.81
4	8	11	19.00	24.97
4	12	11	18.49	-24.59
4	16	11	17.73	21.36
4	0	12	43.56	38.38
4	1	12	25.58	-20.31
4	3	12	25.58	-21.95
4	4	12	31.41	-35.24
4	5	12	17.98	16.85
4	7	12	17.98	23.68
4	8	12	33.65	37.72
4	11	12	24.06	-22.56
4	12	12	33.43	-34.54
4	15	12	22.29	21.59
4	16	12	34.19	35.09
4	19	12	19.25	-18.14
4	20	12	26.09	-31.66
4	23	12	14.69	15.40
4	4	13	15.96	23.82
4	8	13	15.20	-21.78
4	12	13	13.93	21.95
4	16	13	11.90	-19.54
4	0	14	33.68	-39.82
4	4	14	28.62	34.21
4	8	14	29.13	-36.16
4	12	14	19.00	28.22
5	6	1	10.13	-8.82
5	9	1	41.28	57.25
5	10	1	12.92	13.65
5	11	1	58.51	76.19
5	12	1	80.93	102.14
5	13	1	66.10	-74.29
5	15	1	47.36	-46.93
5	16	1	73.96	-95.37
5	17	1	46.35	46.93
5	19	1	48.12	55.52
5	20	1	64.08	75.48
5	21	1	49.39	-54.51
5	23	1	39.26	-34.74
5	24	1	68.64	-71.19
5	25	1	40.52	34.22
5	27	1	39.26	37.99
5	28	1	53.95	49.89
5	29	1	39.51	-37.43
5	31	1	33.18	-24.24
5	33	1	31.66	22.72
5	35	1	24.06	24.94
5	36	1	32.67	29.92
5	37	1	21.27	-24.55
5	40	1	27.61	-29.84
5	0	2	8.61	10.93
5	2	2	17.48	14.59
5	10	2	24.31	18.25
5	18	2	17.98	13.99
5	2	3	8.13	-3.87
5	7	3	44.83	57.83
5	8	3	94.22	112.56
5	9	3	44.07	-51.21
5	11	3	64.33	-72.29
5	12	3	87.13	-104.98
5	15	3	51.67	50.68
5	16	3	78.26	82.89
5	17	3	21.27	-41.93
5	19	3	57.24	-55.72
5	20	3	63.57	-68.77
5	21	3	47.11	45.77
5	23	3	39.76	38.60
5	24	3	57.75	55.05
5	25	3	38.24	-31.42
5	28	3	48.12	-41.80
5	29	3	32.93	32.40
5	32	3	36.22	35.46
5	33	3	24.31	-22.11
5	35	3	19.25	-23.64
5	36	3	25.33	-25.99
5	37	3	13.68	22.27
5	0	4	20.26	-23.90
5	1	4	16.46	9.60
5	2	4	9.62	-10.60
5	3	4	17.22	-3.37
5	4	4	21.27	19.76
5	5	4	16.46	4.77
5	6	4	28.37	-23.52
5	8	4	23.05	-20.88
5	9	4	15.45	7.72
5	12	4	20.51	16.85
5	13	4	21.53	2.05
5	14	4	35.71	-24.32
5	0	5	70.41	-67.58
5	1	5	56.73	55.98
5	3	5	32.67	63.04
5	4	5	90.16	92.02
5	5	5	70.16	-66.12
5	9	5	53.69	55.59
5	11	5	52.93	50.78
5	12	5	89.66	86.95
5	13	5	56.48	-57.97
5	15	5	37.48	-36.93
5	16	5	66.36	-67.66
5	17	5	44.58	46.96
5	19	5	42.04	37.08
5	20	5	79.53	74.30
5	21	5	43.31	-44.21
5	23	5	25.58	-27.27
5	24	5	54.71	-56.54
5	25	5	29.13	34.68
5	28	5	57.49	54.52
5	29	5	29.13	-30.35
5	31	5	21.27	-20.30
5	32	5	37.99	-39.25
5	33	5	19.25	23.26
5	35	5	13.93	19.24
5	36	5	31.66	34.32
5	2	6	17.22	13.52
5	8	6	27.61	23.16
5	10	6	33.18	22.64
5	12	6	16.97	-19.55
5	16	6	22.79	19.55
5	18	6	30.90	-19.67
5	0	7	86.87	83.10
5	1	7	31.41	-45.19
5	3	7	51.41	-50.06
5	4	7	97.51	-105.21
5	5	7	40.39	45.09
5	7	7	49.64	46.93
5	8	7	66.36	72.93
5	9	7	37.48	-39.51
5	11	7	51.15	-49.49
5	12	7	72.44	-83.63
5	13	7	39.26	36.93
5	15	7	40.02	42.52
5	16	7	49.89	50.53
5	17	7	38.50	-32.48
5	19	7	41.23	-40.05
5	21	7	33.43	28.72
5	24	7	37.99	29.99
5	25	7	26.34	-25.55
5	27	7	25.07	-29.14
5	28	7	36.72	-34.00
5	29	7	20.26	21.69
5	32	7	19.76	19.36
5	33	7	18.24	-19.59
5	0	8	30.90	-27.84
5	1	8	28.37	8.31
5	3	8	22.03	4.21
5	4	8	31.15	24.91
5	5	8	22.03	-2.35
5	7	8	18.24	-11.19
5	8	8	34.44	-26.31
5	9	8	22.79	7.04
5	16	8	19.25	-22.31
5	0	9	42.30	-37.53
5	1	9	39.76	37.12
5	3	9	36.47	35.71

Table 1 (a) (cont.)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	4	9	55.72	58.47	5	0	14	13.93	20.42	7	1	3	70.16	64.87	8	13	8	33.94	34.91
5	5	9	40.78	-39.39	5	4	14	11.14	-18.22	7	0	5	84.09	71.47	9	0	1	35.20	-36.99
5	7	9	31.91	-30.74	5	8	14	9.88	19.49	7	1	5	63.82	-59.39	9	1	1	63.57	61.19
5	8	9	41.03	-38.62	6	0	0	140.57	-118.23	7	0	7	35.46	-23.67	9	0	3	48.63	43.32
5	9	9	41.03	38.58	6	1	0	85.10	81.61	7	1	7	56.23	51.70	9	1	3	63.82	-61.24
5	11	9	30.90	28.27	6	3	0	61.54	76.32	7	4	7	34.44	40.30	9	1	5	63.06	54.79
5	13	9	39.00	-36.98	6	4	0	62.81	66.56	7	5	7	51.92	-52.43	9	0	7	37.17	27.13
5	15	9	29.63	-23.11	6	5	0	53.95	-62.63	7	7	7	50.15	-47.46	9	1	7	42.80	-49.02
5	16	9	39.76	-38.85	6	7	0	71.17	-89.58	7	8	7	34.70	-26.34	9	1	9	35.46	37.97
5	17	9	38.50	34.16	6	8	0	84.09	-107.71	7	9	7	55.97	49.44	9	3	9	32.17	37.52
5	19	9	22.79	21.04	6	9	0	61.80	62.46	7	11	7	49.39	44.84	9	5	9	31.91	-37.20
5	20	9	48.63	51.07	6	11	0	69.40	75.92	7	13	7	49.39	-46.48	9	7	9	31.41	-35.68
5	21	9	28.37	-29.90	6	12	0	75.47	60.52	7	16	7	34.95	-30.15	9	9	9	30.90	36.42
5	23	9	20.01	-17.36	6	13	0	57.49	-50.02	7	17	7	41.28	42.84	10	0	0	34.44	-29.63
5	24	9	35.71	-34.11	6	15	0	78.77	-76.93	7	20	7	33.68	41.13	10	3	0	65.60	62.61
5	25	9	22.79	26.39	6	16	0	95.99	-85.91	7	0	9	40.27	41.83	10	5	0	61.80	-59.02
5	27	9	14.69	16.15	6	17	0	50.91	47.68	7	1	9	41.79	-39.62	10	7	0	64.58	-60.01
5	28	9	36.47	39.86	6	19	0	65.09	60.57	8	0	0	64.84	63.34	10	9	0	56.99	51.63
5	29	9	12.92	-21.53	6	20	0	61.80	48.86	8	1	0	78.51	-82.38	10	11	0	65.34	60.33
5	0	10	27.35	26.53	6	21	0	49.13	-41.96	8	3	0	75.47	-72.66	10	13	0	54.45	-53.01
5	4	10	19.25	-23.50	6	23	0	59.27	-54.07	8	4	0	41.03	-38.38	10	15	0	57.24	-54.48
5	8	10	19.25	24.89	6	24	0	76.49	-63.41	8	5	0	82.57	85.63	10	17	0	35.96	44.28
5	0	11	43.06	44.17	6	25	0	51.41	37.87	8	7	0	70.66	66.89	10	19	0	53.19	50.24
5	1	11	32.67	-26.37	6	28	0	50.91	35.27	8	8	0	58.51	60.23	10	21	0	42.30	-46.10
5	3	11	31.91	-29.04	6	32	0	52.17	-43.98	8	9	0	80.03	-83.53	10	1	2	68.89	-65.92
5	5	11	30.39	26.33	6	0	2	131.19	126.82	8	11	0	59.77	-54.54	10	1	6	50.65	-54.60
5	7	11	29.38	27.38	6	1	2	88.14	-87.16	8	12	0	47.61	-35.50	10	1	8	43.31	45.43
5	9	11	26.09	-23.16	6	0	4	100.30	-89.57	8	13	0	79.01	78.80	11	1	1	46.86	-50.71
5	11	11	31.15	-28.37	6	1	4	80.79	73.84	8	15	0	54.96	48.55	11	1	3	48.12	46.82
5	12	11	44.58	-46.18	6	0	6	88.39	77.41	8	16	0	61.04	51.17	11	1	5	44.83	-49.04
5	13	11	24.82	22.24	6	1	6	68.38	-64.33	8	17	0	70.92	-69.20	11	1	9	27.86	-33.83
5	15	11	24.06	24.82	6	3	6	45.08	-48.20	8	19	0	40.27	-39.46	12	0	0	32.42	-11.65
5	16	11	29.63	30.19	6	4	6	87.13	-72.33	8	20	0	40.52	-28.08	12	1	0	47.36	-48.67
5	17	11	16.21	-19.52	6	5	6	47.61	50.22	8	21	0	67.88	61.65	12	3	0	55.97	-51.07
5	19	11	21.78	-23.87	6	7	6	55.47	58.86	8	23	0	38.75	35.40	12	5	0	55.72	57.22
5	20	11	29.89	-33.32	6	8	6	77.50	70.72	8	24	0	35.96	37.74	12	7	0	49.64	40.22
5	23	11	12.66	19.33	6	9	6	56.99	-61.39	8	25	0	50.40	-48.26	12	9	0	51.92	-50.09
5	0	12	21.27	-22.77	6	11	6	44.07	-41.46	8	0	2	63.32	-60.69	12	13	0	52.68	55.41
5	4	12	17.22	20.07	6	12	6	72.94	-62.19	8	1	2	72.69	71.91	12	1	2	39.00	42.34
5	8	12	16.72	-21.95	6	13	6	41.28	45.96	8	0	4	58.00	49.96	12	4	2	43.06	-3.78
5	0	13	29.89	-27.41	6	15	6	42.04	47.94	8	1	4	74.97	-73.79	12	1	6	35.46	40.22
5	1	13	21.02	18.55	6	16	6	58.76	54.87	8	0	6	38.50	-33.88	12	1	8	31.15	-35.92
5	3	13	23.55	19.26	6	17	6	42.30	-51.48	8	1	6	69.65	62.16	13	1	3	32.93	-38.83
5	4	13	30.90	32.27	6	20	6	49.39	-46.81	8	0	8	36.98	30.28	13	1	7	23.81	-34.59
5	5	13	20.77	-21.42	6	24	6	48.37	37.48	8	1	8	52.65	-49.88	14	0	2	34.95	-23.77
5	7	13	17.48	-15.58	6	0	8	55.97	-52.50	8	3	8	36.72	-38.42	14	1	2	27.10	-31.73
5	8	13	28.62	-26.09	6	0	10	46.60	40.43	8	5	8	36.47	38.12	14	1	4	23.81	29.07
5	12	13	25.83	29.03	6	1	10	42.04	-35.92	8	7	8	39.51	47.73	14	0	6	17.22	-18.12
5	13	13	17.48	-21.18	6	0	12	33.68	-32.68	8	8	8	34.70	26.92	14	1	6	18.24	-30.76
5	15	13	11.14	-12.47	6	1	12	28.62	27.18	8	9	8	39.26	-47.38	15	0	1	19.50	-18.03
5	16	13	21.78	-22.70	7	0	1	90.42	86.41	8	11	8	33.94	-35.06	15	1	1	20.77	-24.48
5	17	13	9.62	18.66	7	0	3	58.76	-56.82	8	12	8	33.94	-29.31	15	0	3	16.72	17.24

finement was done with three-dimensional data. Altogether about 1150 reflexions were used [Table 1(a)]. In addition there were about 90 near-in reflexions which were too strong for accurate measurement, or unreliable because of extinction, or were missing because of camera geometry. These are recorded in Table 1(b). They were not used in refinement, and their F_o's were replaced by F_c's in constructing electron-density maps. There are systematic weaknesses, because of the pseudosymmetric character of the structure. A rough analysis of reflexions according to their reciprocal-space radius and the character of their indices gave the following ratios of numbers observed to numbers possible in each category:

	h+l even		h+l odd	
	k=4n	k≠4n	k=4n	k≠4n
sin θ less than 0.33	1.0	0.5	0.7	0.6
sin θ between 0.33 and 0.67	1.0	0.4	0.6	0.2
sin θ greater than 0.67	0.8	0.15	0.3	0

Unobservably weak reflexions were neglected during refinement, but in the final stages their F_c values were all inspected, and none were found to be significantly greater than the F_c's of the weakest observable reflex-ions. Details of the refinement procedures are given below. Computing facilities were provided by the Cambridge University Mathematical Laboratory, and at a later stage the IBM 7090 computer at Imperial College, London, was used in addition.

Symmetry, space group, and lattice parameters

The structure is orthorhombic, with space group Pbma (No. 57, in yzx setting) (Megaw & Wells, 1958) and lattice parameters $a = 5.566$ Å, $b = 15.520$ Å, $c = 5.506$ Å (Lefkowitz, Łukaszewicz & Megaw, 1966). The relation of the unit cell to that of ideal perovskite (a cube with side a_0 of about 4 Å) is given by the matrix

$$\begin{array}{ccc} 1 & 0 & \bar{1} \\ 0 & 4 & 0 \\ 1 & 0 & 1 \end{array}.$$

Two symmetry directions [001] and [100] are thus face diagonals of the original cube, and the third, [010], is parallel to a cube edge but is now quadripartite. The cell contains eight formula units and there are seven atoms in an asymmetric unit. It is convenient to write the atomic parameters in terms of displacements u, v, w, from the special positions of the ideal

Table 1(b). Observed and calculated structure factors, not used in synthesis

(Scaling of F_{obs} to match Table 1(a) only done approximately.)

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	0	—	584	3	16	1	78	124
0	4	0	120	−254	3	0	3	83	−134
0	8	0	150	377	3	3	3	40	62
0	12	0	89	−144	3	4	3	83	174
0	16	0	122	196	3	5	3	44	−72
0	0	2	125	−279	3	8	3	66	−127
0	0	2	132	−243	3	12	3	78	143
0	16	2	114	−179	3	0	5	78	131
0	0	4	126	273	3	4	5	90	−172
0	4	4	118	−173	3	8	5	67	118
0	8	4	139	223	3	12	5	91	−134
1	0	1	—	−253	3	4	7	77	112
1	4	1	98	277	4	0	0	—	259
1	8	1	89	−199	4	1	0	—	−89
1	12	1	99	194	4	3	0	23	−57
1	0	3	81	194	4	4	0	52	−139
1	4	3	110	−251	4	5	0	38	75
1	8	3	93	163	4	7	0	43	62
1	12	3	103	−180	4	8	0	86	210
1	0	5	72	−123	4	9	0	57	−88
1	4	5	102	185	4	12	0	67	105
1	8	5	—	−118	4	16	0	86	138
2	0	0	—	−277	4	0	2	72	−174
2	1	0	—	57	4	1	2	42	77
2	3	0	36	49	4	3	2	40	62
2	4	0	45	72	4	4	2	58	87
2	8	0	99	−240	4	5	2	32	−49
2	12	0	69	102	4	7	2	55	−80
2	16	0	92	−176	4	8	2	93	−158
2	0	2	113	367	4	12	2	62	89
2	4	2	110	−193	4	16	2	85	−126
2	8	2	106	276	4	0	4	94	169
2	12	2	139	−131	4	1	4	—	−69
2	16	2	85	166	4	3	4	31	−46
2	0	4	104	−187	4	4	4	71	−122
2	4	4	70	112	5	0	1	37	−123
2	8	4	94	−170	5	1	1	23	61
2	12	4	71	109	5	2	1	—	3
2	16	4	81	−134	5	3	1	36	93
2	0	6	82	155	5	4	1	49	122
2	4	6	74	−127	5	5	1	42	−94
2	8	6	72	139	5	8	1	54	−114
3	0	1	63	201	5	0	3	66	127
3	1	1	19	−44	5	1	3	31	−57
3	3	1	39	−84	5	3	3	41	−81
3	4	1	72	−216	5	4	3	67	−137
3	8	1	80	167	5	5	3	43	77
3	12	1	85	−157					

structure. They are then as in Table 2(a). All the u, v, w's are small, but their signs as well as their magnitudes have to be found.

Table 2(a). Atomic coordinates in terms of displacement parameters

	x	y	z
Nb	$\frac{1}{4} + u_{Nb}$	$\frac{1}{8} + v_{Nb}$	$\frac{1}{4} + w_{Nb}$
Na(1)	$\frac{1}{4}$	0	$\frac{1}{4} + w_{Na(1)}$
Na(2)	$\frac{3}{4} + u_{Na(2)}$	$\frac{1}{4}$	$\frac{1}{4} + w_{Na(2)}$
O(1)	$\frac{1}{4}$	0	$\frac{1}{4} + w_{O(1)}$
O(2)	$\frac{1}{4} + u_{O(2)}$	$\frac{1}{4}$	$\frac{1}{4} + w_{O(2)}$
O(3)	$u_{O(3)}$	$\frac{1}{8} + v_{O(3)}$	$\frac{1}{2} + w_{O(3)}$
O(4)	$\frac{1}{2} + u_{O(4)}$	$\frac{1}{8} + v_{O(4)}$	$w_{O(4)}$

Table 2(b). Displacement parameters from initial electron-density projections

	u	v	w
Nb	+0.022	+0.000	+0.007
Na(1)	0	0	−0.00
Na(2)	+0.03	0	−0.00
O(1)	0	0	+0.06
O(2)	+0.00	0	−0.06
O(3)	+0.03	+0.015	+0.03
O(4)	−0.03	−0.015	−0.03

It is convenient to notice that the b-glide plane lies at $x = \frac{1}{4}$, the m plane at $y = \frac{1}{4}$, and the a-glide plane at $z = 0$.

Method of establishing the trial structure

The principles involved in dealing with pseudosymmetric structures have been discussed by Katz & Megaw (1967). Here it need only be emphasized that in a trial structure suitable for automatic refinement not only must the magnitudes of all displacement parameters be approximately known but the signs of all the important ones must also be known. The detailed procedure by which this was achieved is described here.

Preliminary studies, and comparison with other materials, suggested values for the isotropic temperature factors as follows: $B(Nb) = 0\cdot3$ Å², $B(Na) = 1\cdot3$ Å², $B(O) = 0\cdot7$ Å². These were kept unchanged during the initial stages of refinement, except for one or two test syntheses to check that reasonable changes in them made no significant difference to the other parameters. The f-curves used in these early stages were those of Forsyth & Wells (1959).

The displacement parameters of Nb can be estimated independently of the others, since Nb is much the heaviest atom. A preliminary study of a photograph of a twinned crystal showed that the values of Megaw & Wells (1958) and of Vousden (1951) were better than those of Wells & Megaw (1961). Arbitrary allocation of signs merely fixes the origin and sense of the axes. The trial values adopted were:

$$u(Nb) = 0\cdot020, \quad v(Nb) = 0, \quad w(Nb) = 0\cdot007 .$$

The first set of electron-density maps was made with these displacement parameters for Nb, and all others zero, for the set of projections $h0l$, hkh, $0kl$ and $hk0$ (see Figs. 1–4). They and the corresponding difference maps agreed in showing:

(i) that the Nb displacements were essentially correct,
(ii) that O(3) and O(4) both had displacements of approximate magnitude $|u| = 0\cdot03$, $|v| = 0\cdot015$, $|w| = 0\cdot03$,
(iii) that the signs of all three displacements of O(3) were the same as each other and opposite to the signs of all three O(4) displacements.

However, because of two 'accidental' effects, the zero value of $v(Nb)$ and the near equality in magnitude of the O(3) and O(4) displacements, the projections could

not distinguish the sense of the y axis. The $0kl$ projection, while confirming the estimated magnitudes of the displacements, showed the need for giving a sign to one of the v's to destroy the false remanent symmetry of this model; taking $v_{O(3)}$ as positive fixed the sign of all the O(3) and O(4) displacements.
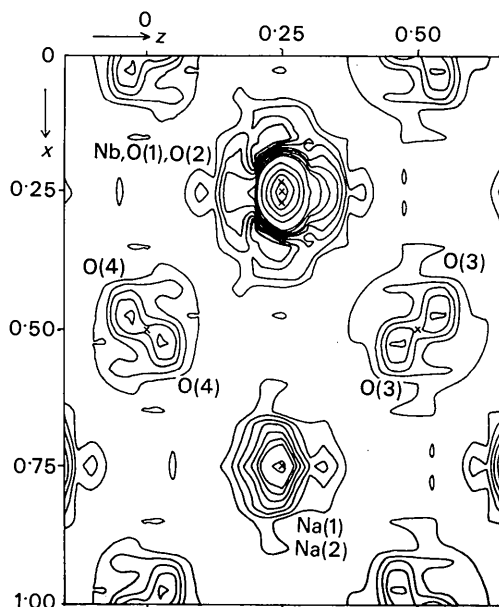
Fig. 1. [010] electron-density projection. Trial model has all atoms in ideal positions, except Nb with displacement parameters $u = 0.020$, $v = 0$, $w = 0.007$. Contours at intervals of 10 e.Å^{-3} from 10 to 70 e.Å^{-3}, and intervals of 100 e.Å^{-3} from 100 e.Å^{-3} upwards.
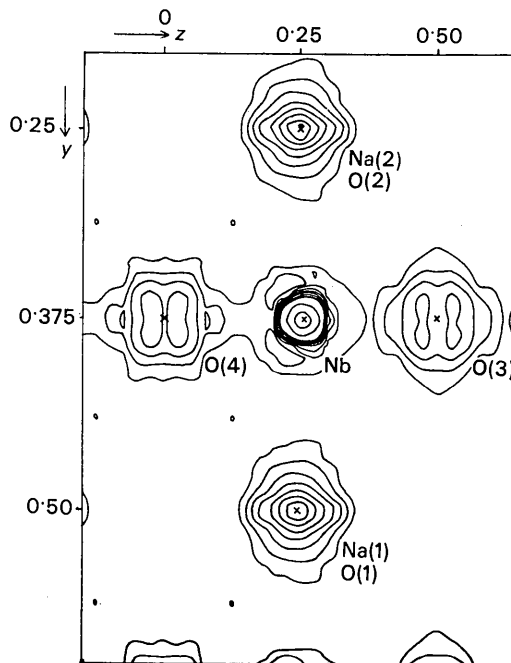
Fig. 3. [100] electron-density projection. Trial model as in Fig. 1. Contours at intervals of 5 e.Å^{-3} from 5 to 40 e.Å^{-3}, and at intervals of 50 e.Å^{-3} thereafter.
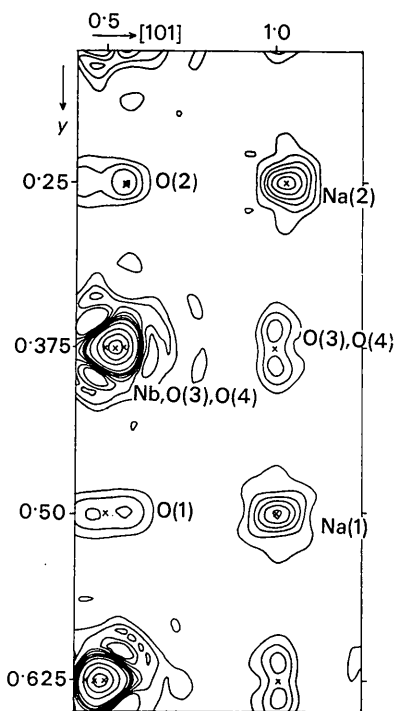
Fig. 2. [10$\bar{1}$] electron-density projection. Trial model and contours as in Fig. 1.
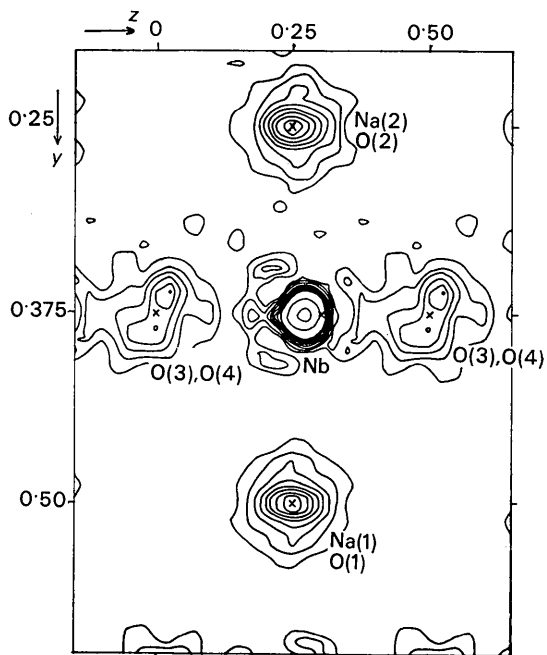
Fig. 4. [001] electron-density projection . Trial model as in Fig. 1; contours as in Fig. 3.

The displacements of Na(1) and Na(2), O(1) and O(2), gave more difficulty because of overlaps. Here,
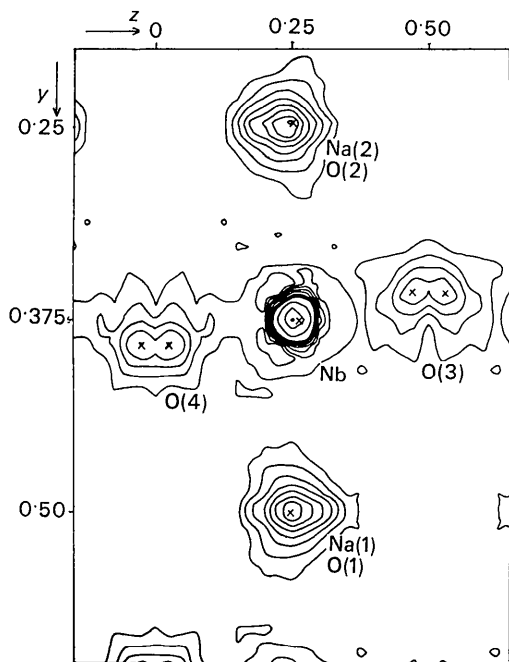
Fig. 5. [100] electron-density projection. Trial model has all atoms in ideal positions except Nb as in Fig. 1 and O(3), O(4) with displacement parameters $v_{O(3)} = v_{O(4)} = 0.015$, $w_{O(3)} = -w_{O(4)} = 0.03$. Contours as in Fig. 3.

however, the *hkh* projection – *i.e.* the projection* down [10$\bar{1}$] on the plane containing [101] and [010] – proved particularly useful. In this, the repeat distance along [101] is approximately $a/\sqrt{2}$, and if the corresponding coordinate is denoted by x', $x' = x + z$. Operation of the *a*-glide plane gives symmetry-related peaks at $(x+z,y)$ and $(\frac{1}{2}+x-z,y)$. Because the atoms we are considering all lie near positions with x and z equal to $\frac{1}{4}$ or $\frac{3}{4}$, pairs project nearly on top of one another, forming doublets with peaks at $(u \pm w,y)$ for Na and $(\frac{1}{2}+u \pm w,y)$ for O. Each crystallographically-independent atom thus forms a doublet in a different part of the projection. The separation of the doublet gives the magnitude of w, but not its sign; the displacement of its mid point from that with $x' = 0$ or $\frac{1}{2}$ gives the magnitude and sign of u.

Inspection of Fig. 2 gives the following results. From the symmetrically elongated peaks for O(1) and O(2), it follows that $|w_{O(1)}|$ and $|w_{O(2)}|$ must be large and roughly equal, and $|u_{O(2)}|$ small. From the nearly round peaks for Na(1) and Na(2) and the unsymmetrical displacement of the latter, $|w_{Na(1)}|$ and $|w_{Na(2)}|$ must be small, and $u_{Na(2)}$ moderately large and positive. Estimated magnitudes were 0·06 for $|w_{O(1)}|$ and $|w_{O(2)}|$, 0·03 for $u_{Na(2)}$.

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* Strictly this is a non-orthogonal projection, but the deviation from 90° is too small to matter.

There are also O(3)/O(4) peaks at $(\frac{1}{2}+u+w,\frac{1}{8}+v)$ and $(u-w,\frac{1}{8}+v)$, the former overlapping with the Nb doublet at $(\frac{1}{2}+u \pm w,\frac{1}{8}+v)$. These give independent confirmation of the conclusions drawn concerning O(3) and O(4) from other projections. In particular we may notice, from the O(3)/O(4) complex, that $u-w \simeq 0$ for both atoms, while the Nb/O(3)/O(4) complex serves to confirm the signs of the O(3) and O(4) displacements.

Confirmation that $w_{O(1)}$ and $w_{O(2)}$ were both fairly large came from the *h0l* projection (Fig. 1), which, moreover, showed them to be of opposite sign. The overlap with Nb made it difficult to estimate their magnitude, and only after refinement of u_{Nb} to 0·022 was it possible to do so. The value of 0·06 for both was then confirmed, as was the value of 0·03 for $|u_{Na(2)}|$.

New syntheses introducing the O(3) and O(4) displacements gave difference maps which were greatly improved round the sites of these particular atoms but little altered elsewhere, except that the 0*kl* projection could now distinguish not only between O(3) and O(4) but also between Na(1)/O(1) and Na(2)/O(2). There was still, however, a tendency for effects at each of the two latter sites to imitate those at the other. This was partly due to the fact that all the displacements had not yet been introduced into the trial structure, and partly that the evidence which should distinguish between them is all carried in difference reflexions, a high proportion of which are too weak to be observed. This ghost effect means that caution is needed in interpretation. However, it was clear that the centres of the peaks had moved in opposite directions from $z = \frac{1}{4}$ (see Fig. 5). Though it was impossible in this projection to distinguish between displacements of Na and displacements of O (and continued so on refinement), introduction of the evidence from *hkh* that the $|w_{Na}|$ were small and the $|w_O|$ large allowed the conclusion to be drawn that $w_{O(1)}$ and $w_{O(2)}$ were of opposite sign (in agreement with the *h0l* evidence), with $w_{O(1)}$ positive and $w_{O(2)}$ negative.

Approximate parameters were then as in Table 2(*b*).

Difference maps calculated for this trial model showed no conspicuous features, and the model was regarded as satisfactory. *R* values ranged from 9% for *h0l* to 13% for *hk0*.

It should be emphasized that, in this first stage of setting up a trial model, no importance was attached to making estimates of the parameters to better accuracy than about ± 0.02 for u and w, ± 0.005 for v, except for Nb, where the accuracy needs to be better by a factor of about 10. The refusal to allow any of the parameters to vary continuously from their initial values was deliberate, because of the danger of refining to a false minimum if some of them were released before others, equally important, had been introduced into the model or if the latter had been introduced with a wrong sign. An example occurred when automatic refinement of *h0l* was tried with a model where only Nb, O(3), and O(4), had been given displacement parameters; the program was unable to in-

troduce large enough shifts for O(1) and O(2), and so allowed w_{Nb} to refine wrongly. Some errors due to this cause affected the accuracy of the parameters previously published (Wells & Megaw, 1961). On the other hand, with our new data, a model very similar to the above trial structure had previously been derived by more conventional methods in which some parameters had been allowed to refine while new ones were being introduced. The method described above has, however, the advantage of allowing direct justification from the experimental evidence of each step involved in setting up the model.

Refinement

Stages of refinement were as follows.

(i) Difference syntheses were used, with a standard crystallographic program on the TITAN computer. The initial parameters were those of the trial model described above [Table 2(b)] with isotropic temperature factors $B_{Nb} = 0.3$, $B_{Na} = 1.3$, $B_O = 0.7$ Å^2, kept constant during the refinement. The f-curves were those of Forsyth & Wells (1959). The R value dropped very little, from 13.02 to 12.98%, in 7 cycles.

(ii) A full-matrix least-squares program was used with EDSAC II. The initial parameters were those obtained from two-dimensional work. (An attempt to use a model with all displacement parameters zero except for Nb proved unsuccessful, as some of the smaller shifts continued to oscillate – not unexpectedly.) Isotropic temperature factors were allowed to refine. The f-curves were those of Forsyth & Wells (1959), corrected for anomalous scattering ($\Delta f = -2.1$). The R value dropped from 12.69 to 12.47% in 6 cycles.

(iii) The Busing–Martin–Levy least-squares program was used with the IBM 7090 computer. Initial parameters were those at the end of stage (ii); temperature factors were refined anisotropically. The f-curve used for Nb was that of Cromer & Waber (1965) for Nb^{3+}, without correction for anomalous scattering. The R value dropped from 26.9 to 11.0% in 9 cycles, and stayed constant thereafter.

(iv) The same program was used as in stage (i), but with the initial parameters reached at the end of stage (iii), including the anisotropic temperature factors, which were however held constant. The f-curve for Nb was as in stage (iii). During a few cycles R dropped from 11.58 to 11.42%.

(v) The same program was used, with the initial parameters as at the end of stage (iv), but correcting for anomalous scattering by Nb (Cromer, 1965). A few cycles of refinement gave no changes of position outside the estimated error, except for Nb, where the maximum difference, 0.0003 in z, was still very small.

The parameters given in Table 3 are those obtained at the end of stage (iii).

Accuracy

The final R value of 11.0% is very reasonable in comparison with the experimental error, allowing for the fact that weak difference reflexions contribute proportionately more.

Standard deviations of parameters calculated by the least-squares program are included in Table 3. The accuracy of the x parameters is lower than that of the others because few reflexions with $h > 5$ were used.

Table 3. *Atomic position parameters and thermal parameters*

The temperature factor is taken as exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)]$.

Coordinates	Nb	Na(1)	Na(2)	O(1)	O(2)	O(3)	O(4)
x	0.2722	0.750	0.782	0.250	0.233	0.032	0.467
error	0.0002	—	0.003	—	0.003	0.002	0.002
y	0.1262	0	0.250	0	0.250	0.140	0.110
error	0.0002	—	—	—	—	0.001	0.001
z	0.2566	0.243	0.239	0.304	0.191	0.536	0.966
error	0.0001	0.002	0.002	0.003	0.003	0.001	0.001
β_{11}	0.0021	0.0246	0.0086	0.0011	0.0009	0.0008	0.0093
error	0.0002	0.0085	0.0031	0.0040	0.0024	0.0015	0.0029
β_{22}	0.0004	0.0018	0.0007	0.0003	0.0004	0.0008	0.0007
error	0.0000	0.0008	0.0004	0.0005	0.0005	0.0003	0.0004
β_{33}	0.0023	0.0064	0.0072	0.0089	0.0064	0.0033	0.0018
error	0.0001	0.0041	0.0036	0.0027	0.0023	0.0012	0.0010
β_{12}	−0.0006	−0.0009	0	−0.0006	0	0.0007	0.0015
error	0.0001	0.0011	—	0.0007	—	0.0006	0.0008
β_{13}	−0.0004	0	−0.0051	0	0.0024	0.0013	0.0022
error	0.0002	—	0.0024	—	0.0025	0.0013	0.0016
β_{23}	−0.0003	0	0	0	0	0.0002	0.0004
error	0.0001	—	—	—	—	0.0005	0.0004

Systematic errors might be introduced by an incorrect f-curve. There was some uncertainty about the best curve to use for Nb, considering that it is 5-valent but certainly not fully ionic. The choice of the Cromer–Waber curve for Nb^{3+} was somewhat arbitrary; it differs little from their curve for Nb, and only slightly more from the Thomas–Umeda curve in *International Tables for X-ray Crystallography* (1962) (on which the Wells–Forsyth curve was based), but is quite appreciably different, at values of $(\sin\theta)/\lambda$ above $1\cdot0$ Å^{-1}, from their curve for Nb^{5+}.* The differences, which were comparable in some regions with the anomalous scattering correction, could cause systematic errors in thermal parameters, though negligible for position parameters. Even for the thermal parameters, any such errors are not likely to affect their order-of-magnitude values, nor the conclusions drawn from them.

Two small effects may be mentioned. (i) It was noticed that refinement by least squares with anisotropic temperature factors always gave a smaller value for u_{Nb} and a greater value for v_{Nb} than did refinement by difference synthesis with isotropic temperature factors. (ii) There were about 30 very weak reflexions (just above the limit of observation) for which F_c was systematically less than F_o. This could perhaps be due to errors in the f-curve either for Nb or for Na or O,

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* *Note added in proof:*– Larson (private communication, 1968) states that the values for Nb^{5+} are subject to revision.

or it might be an indication that the assumption of ellipsoids for the thermal parameters (harmonically vibrating atoms) is not quite good enough. The effect was too close to the limit of error to justify investigation in more detail.

Description of the structure

The structure is of the perovskite type, consisting of NbO_6 octahedra connected by shared corners, with Na atoms in the spaces between them. Projections on (010), (001), and (100), are shown in Fig.6. Bond lengths and bond angles calculated from the parameters of Table 3 are given in Table 4.

All octahedra are identical, and though they contain no symmetry elements they are remarkably regular [Fig. 7(a)]. (Indeed their increasing approach to regularity with successive cycles of refinement was a rather striking feature of the process). The four edges lying nearly in the (010) plane, which join two O(3) atoms and two O(4) atoms to each other, and are almost coplanar by symmetry, are all of length $2\cdot81\pm0\cdot01$ Å; the mean of all twelve edges is $2\cdot80$ Å, with a mean deviation of $\pm0\cdot02$ Å and extreme values of $2\cdot76$ Å and $2\cdot83$ Å. Inside each octahedron the Nb atom is displaced from the geometrical centre by $0\cdot13$ Å in a direction lying almost exactly in the plane of the O(3), O(4) square, between the direction of the x axis and one diagonal of the square, and making an angle of 21° with the latter. This displacement of Nb results

Table 4. *Bond lengths (Å) and bond angles (degrees)*

(Figures in round brackets after lengths give errors; figures in square brackets give the numbers of symmetry-equivalent Na–O bonds).

Nb–O(1)	1·980 (3)		O(1)–O(3a)	2·799 (18)	
–O(2)	1·967 (3)		–O(3b)	2·825 (18)	
–O(3a)	2·049 (14)		–O(4a)	2·798 (18)	
–O(3b)	1·857 (14)		–O(4b)	2·755 (18)	
–O(4a)	1·950 (14)		Mean	2·795 (12)	
–O(4b)	2·110 (14)				
			O(2)–O(3a)	2·785 (18)	
			–O(3b)	2·817 (18)	
			–O(4a)	2·822 (18)	
Na(1)–O(1) [2]	2·804 (3)		–O(4b)	2·770 (18)	
–O(1) [1]	2·496 (22)		Mean	2·798 (10)	
–O(1) [1]		3·009 (22)			
–O(3a)[2]		3·128 (15)	O(3a)–O(3b)	2·812 (3)	
–O(3b)[2]	2·772 (15)		–O(4b)	2·825 (18)	
–O(4a)[2]	2·778 (15)		O(4a)–O(3b)	2·807 (18)	
–O(4b)[2]	2·383 (15)		–O(4b)	2·810 (3)	
Mean of 9	2·663		Mean	2·813 (4)	
Mean of 12		2·769			
Na(2)–O(2) [1]		3·068 (30)	Nb—O(1)—Nb	164·9	
–O(2) [1]	2·524 (30)		Nb—O(2)—Nb	155·3	
–O(2) [1]		3·150 (30)			
–O(2) [1]	2·386 (30)		O(1)—Nb—O(2)	169·6	
–O(3a)[2]	2·740 (18)				
–O(3b)[2]	2·524 (18)		O(3a)–Nb—O(4b)	85·6	
–O(4a)[2]		3·171 (18)	O(4a)–Nb—O(3b)	95·0	
–O(4b)[2]	2·658 (18)				
Mean of 8	2·595		O(3b)–O(3a)–O(4b)	89·4	
Mean of 12		2·776			
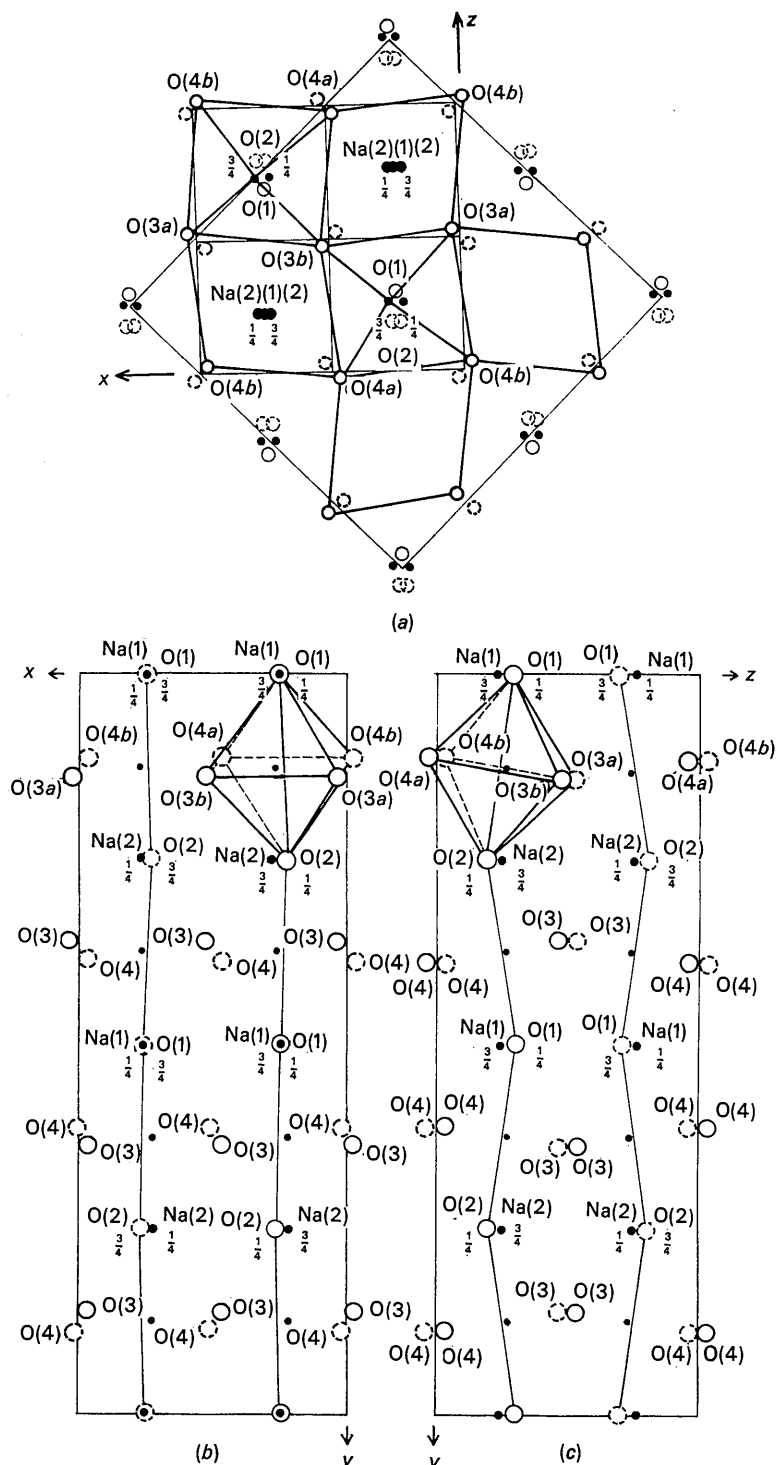
Fig. 6. Projection of structure on three principal planes. Small black circles Nb, larger black circles Na, open circles (full or dashed lines) O. (a) Heavy full circles are O(3) and O(4), superposed pairs, at heights near $\frac{1}{4}$, $\frac{3}{4}$; heavy dashed circles similar pairs near $\frac{5}{8}$, $\frac{7}{8}$. Light full circles are O(1) at heights 0 and $\frac{1}{2}$, light dashed circles O(2) at either $\frac{1}{4}$ or $\frac{3}{4}$. Atoms marked as Na(1) are superposed pairs at heights 0 and $\frac{1}{2}$. Full lines joining Nb–O and O–O lie near $\frac{1}{4}$ and $\frac{3}{4}$; Nb atoms not so joined lie near $\frac{5}{8}$ and $\frac{7}{8}$. Base of primitive cell outlined (together with lines at $x=\frac{1}{2}$ and $z=\frac{1}{2}$) and orthorhombic x, z, axial directions marked (y axis upward). Larger square at 45° is base of B-centred pseudocubic cell. (b) and (c). Oxygens at heights 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ are shown respectively by heavy dashed circles, thin full circles, heavy full circles, thin dashed circles. One octahedron is outlined in each diagram, and lines joining apical oxygen atoms are shown for all octahedra. Areas outlined represent projection of one unit cell.

in the formation of two short and two long bonds approximately in the (010) plane, of length 1·86, 1·95, 2·05, 2·11 Å respectively; the two Nb bonds to the other vertices of the octahedra, O(1) and O(2), are 1·98 Å and 1·97 Å [Fig. 7(b)]. It is interesting to notice how very little effect the Nb displacement has on the regularity of the octahedron. This point will be discussed further below.

The most conspicuous distortion of the structure from that of ideal perovskite is the tilting of the octahedra relative to one another. This can be seen in Fig. 6(a), (b) and (c). The detailed geometry of the tilt is shown in stereographic projection in Fig. 8; it comprises a rotation of $\omega = 8°$ about the y axis and a tilt of $\varphi = 9\frac{1}{2}°$ about the x axis (the octahedron being taken as defined by the O(3), O(4) square and its normal for calculating these figures). This crumpling of the framework provides quite a different environment for the Na cation from the 12-coordinated position it would have in the ideal perovskite structure. The two Na atoms behave differently. Taking the octahedron centre as reference point, Na(1) remains almost undisplaced, while Na(2) has a large displacement of 0·18 Å in the same direction as the two parallel Nb displacements in the planes above and below it. In the ideal structure of the same volume, each Na would have had 12 neighbours at a distance of about 2·8 Å; in the actual structure, the corresponding distances range from 2·38 Å to 3·19 Å. The environments of the two Na atoms are shown in Figs. 9(a) and (b). Na(1), which lies on the diad axis parallel to [001], has 9 near neighbours at 2·81 Å or less, and 3 more distant at more than 3 Å; Na(2), on the mirror plane, has 8 near neighbours at 2·74 Å or less, and 4 more distant at more than 3 Å. For Na(1), the three nearest neighbours, at distances less than 2·50 Å (marked with a cross in the Figure) form a triangle co-planar with Na(1), and there are no other neighbours nearer than 2·77 Å. Taking all twelve neighbours, the set of directions is very like that in ideal perovskite; thus the only conspicuous feature

of the distortion is the movement in towards Na(1) of the three nearest. Two of these are O(4) atoms, related to each other by the rotation diad parallel to [001]; the third is O(1), lying on the diad. For Na(2), the four nearest neighbours, at distances less than 2·55 Å, form a tetrahedron, but the next nearest are not much farther away. The eight neighbours at distances less than 2·75 Å form a trigonal prism with its axis along [010], with extra atoms inserted in the middle of two rectangular faces. The directions to O(1) and O(2) remain as in ideal perovskite, but the other directions are considerably skewed. As compared with Na(1), the

Table 5. *Thermal vibration amplitudes: magnitudes u_{tt}, and angles of inclination to the crystallographic axes*

(Figures in brackets after u_{tt} indicate error.)

	u_{tt} (Å)	α_{tx}	α_{ty} (degrees)	α_{tz}
Nb	0·046 (2)	42	57	67
	0·073 (2)	121	33	101
	0·061 (2)	116	93	26
Na(1)	0·20 (3)	7	97	90
	0·15 (3)	83	7	90
	0·10 (3)	90	90	0
Na(2)	0·13 (3)	38	90	128
	0·10 (3)	90	0	90
	0·09 (3)	52	90	38
O(1)	0·03 (3)	29	61	90
	0·06 (6)	119	29	90
	0·12 (3)	90	90	0
O(2)	0·03 (3)	12	90	102
	0·07 (6)	90	0	90
	0·10 (3)	78	90	12
O(3)	0·03 (3)	21	96	110
	0·09 (2)	78	19	75
	0·07 (1)	73	108	25
O(4)	0·13 (2)	25	66	82
	0·08 (2)	114	24	89
	0·05 (2)	97	94	8

(a)

(b)
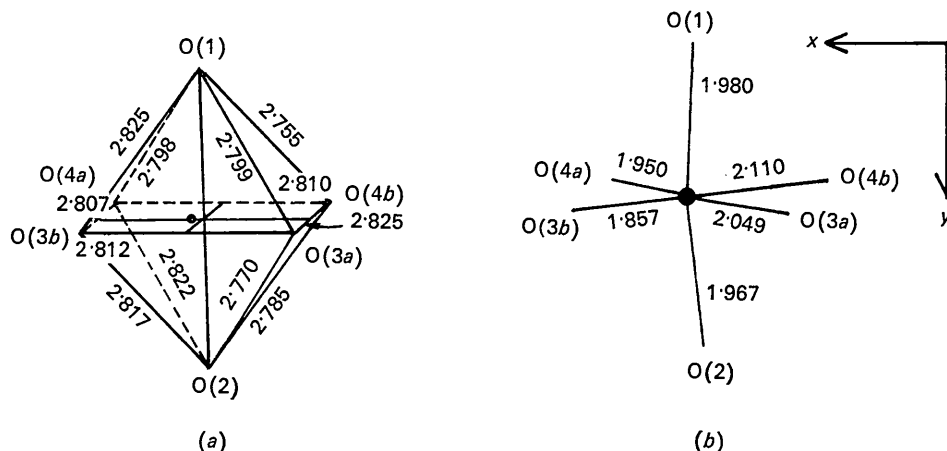
Fig. 7. Projection of octahedron outlined in 6 (b), showing (a) edge lengths (b) Nb–O bond lengths.

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near neighbours are more uniformly but less symmetrically distributed in space.

The thermal vibration amplitudes derived from the anisotropic thermal parameters of Table 3 are given in Table 5. The principal axes of the ellipsoids lie nearly enough in and normal to the (010) plane for a diagram in this plane to be of interest. Sections are shown in Fig. 10, drawn approximately to scale but magnified by a factor of 5.

For Nb, the smallest amplitude lies between the two shortest Nb–O bonds, in the general direction of the shorter, Nb–O(3); it is tilted up out of the plane of the diagram by 33°, while Nb–O(3) is tilted up by 7°. The exact angles are not significant, because the anisotropy is small and the possible errors in direction therefore rather large; the general agreement in direction between strong bonds and small amplitudes is, however, very satisfactory.

The O(3) and O(4) ellipsoids are flattened discs, with their axes in the [010] direction nearly equal to each other, and also (less exactly) to the two long axes in the (010) plane, which are nearly at right angles to the Nb–O bonds. This is what we should have predicted on the assumption that the only important modes of vibration were those in which the octahedra remained rigid but tilted relative to one another, producing bending of the Nb–O–Nb angles. Though a useful approximation, it is not exactly true. The ellipsoid for O(4) is larger in the (010) plane than that for O(3), and makes a larger angle with its Nb–O bond (26° as compared with 18°). These differences can be associated with the fact that Nb–O(4) is longer (and therefore weaker) than Nb–O(3), and perhaps also with the role of the short Na–O(4) bond, considered below.

For O(1) and O(2), though the experimental error is larger, it seems clear that the largest amplitudes are

along [001], and that they are of the same order of magnitude as those of O(3) and O(4), while the smallest amplitudes, which lie along [100], are [like those of O(3)] too small for reliable measurements. The large amplitudes are those which would result from tilting the octahedra about [100] but not about [001].

The amplitudes of Na are larger than those for the other atoms, and those for Na(1) are significantly larger than for Na(2), as might have been predicted from the fact that the average Na(1)–O length (count-
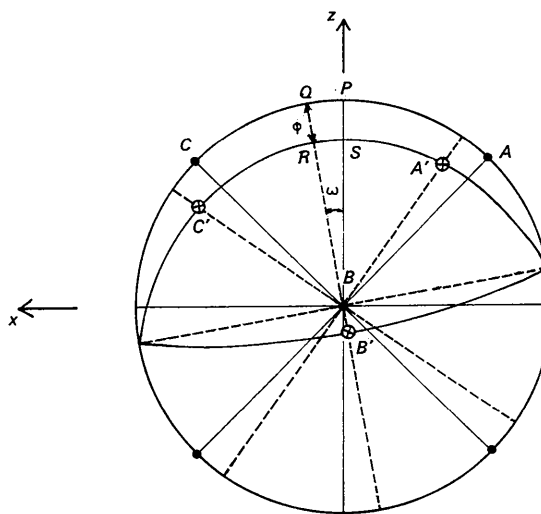
Fig. 8. Stereogram showing tilt of octahedron. *ABC*, tetrad axes of octahedra in ideal perovskite, $A'B'C'$, pseudo-tetrad axes of an octahedron in NaNbO$_3$. Angles of tilt: ω about y axis, φ about a direction very close to the x axis, zero about the z axis. (To this approximation, differences between opposite sides of the quadrilateral *PQRS* are negligible).
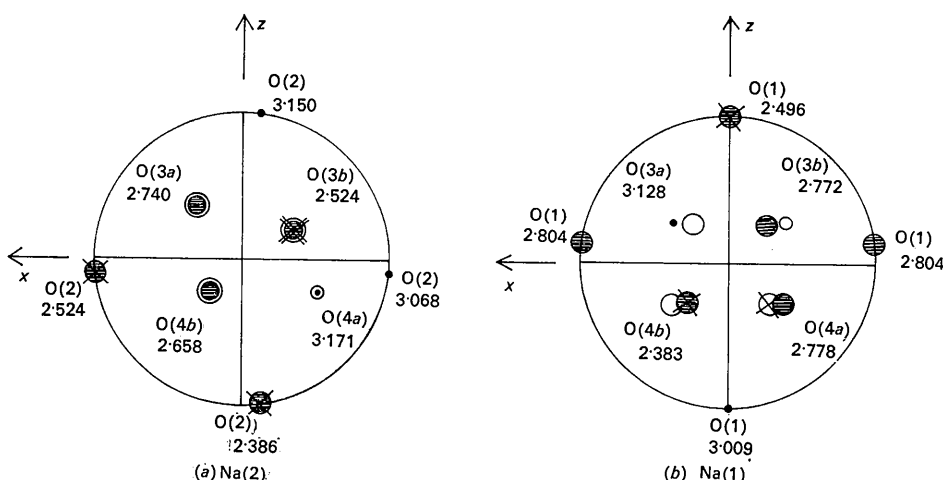
Fig. 9. Stereograms of oxygen environment of (*a*) Na(2), (*b*) Na(1), with Na–O distances in Å. Black and hatched circles are above plane of projection or in it, open circles below it. Large and small circles (whether black, hatched or open) represent neighbours at less or more than 2·85 Å respectively; neighbours at less than 2·55 Å are marked by crosses. In (*a*) atoms above and below the plane of projection are related by the mirror plane; the double cross marks a pair of atoms at the same distance. In (*b*), distances marked refer to atoms above plane of projection, related to those below by diad axis along *z*.

ing neighbours within 2·9 Å) is greater than the average Na(2)–O length. The anisotropy of Na(2) is probably not outside experimental error, but Na(1) is elongated along [100]. It was noted above that the three nearest neighbours to Na(1) are symmetrical about the [001] diad axis through it; one of them, shown in the diagram, is O(4a), and the others are vertically below O(4b) and the translation repeat of O(1) at $z = -\frac{3}{4}$. Thus the smallest vibration amplitude of Na(1) is in the direction symmetrically related to the shortest Na–O bonds. The existence of the fairly strong Na(1)–O(4a) bond can also explain why the short axis of the O(4a) ellipse is tilted away from the direction of Nb–O(4). If the ellipse, keeping its same size and shape, had lain symmetrically about Nb–O(4), the amplitude along Na–O(4) would have been considerably greater, in contradiction to what is expected in the direction of a bond.

Discussion

Nb–O *bonds*

The bond lengths resemble those in KNbO₃, though their mean length is 1·985 Å as compared with 2·011 Å in KNbO₃. The most striking difference is in the in-
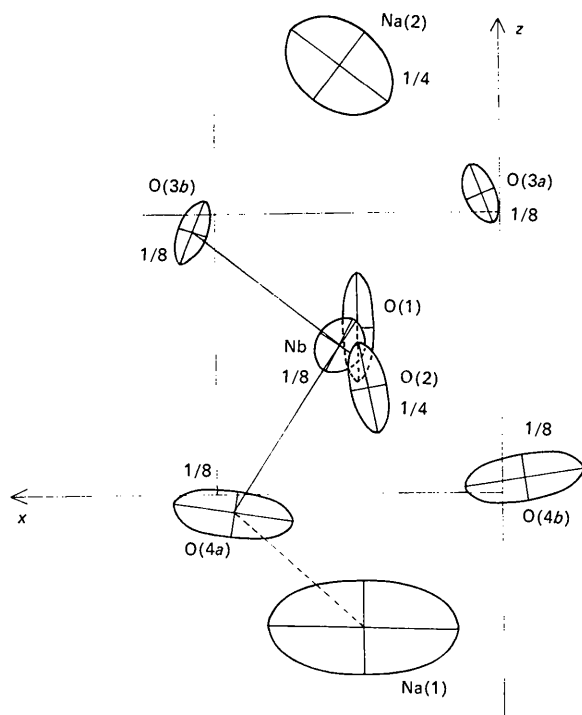
Fig. 10. Sections of thermal ellipsoids in (010) plane. Positions of atomic centres correspond to Fig.6(a), with origin near O(4b), but only a representative part of the structure is shown Heights are marked [except for Na(1) and O(1) at height zero]. The diagram is to scale, except that the axes of the ellipsoids are multiplied by a factor 5. A translation-repeat of Na(1) occurs superposed on Na(2) in the complete projection, and of Na(2) on Na(1), but these are omitted for clarity.

equality between the two shortest bonds in NaNbO₃: 1·860 Å to O(3), 1·958 Å to O(4). This means that the arrangement within the octahedron is intermediate between the one-corner displacement of tetragonal KNbO₃ and the two-corner displacement of orthorhombic KNbO₃. Nevertheless the regularities of the structure are more easily understood if Nb–O(4) is counted as a short bond. With this proviso, the same feature appears as in all other related structures: each O atom is involved in *either* one short and one long Nb–O bond, *or* two bonds of intermediate length. The short and long bonds alternate in the (010) plane in a way which is consistent with their partly covalent character. The weakness of Nb–O(4) as compared with Nb–O(3) has been seen in its effect on the vibration amplitudes of these atoms.

Regularity of octahedra

To a first approximation the most important feature of the octahedra is their good approximation to regularity, commented on above. To a second approximation, we find a difference between the average lengths of octahedron edges in the (010) plane and inclined to that plane, of the same kind and almost the same magnitude as between the equatorial and inclined edges in KNbO₃. Admittedly the difference is smaller than the scatter of the edge lengths involving O(1) and O(2), but experience is accumulating from many different types of structure to show that the average over a set of lengths or angles playing a similar role in a structure is a physically meaningful quantity; whatever forces cause the deviations from a symmetrical arrangement do so in opposite directions on different members of the set, leaving the mean unchanged. Again, though the errors in individual edge lengths are relatively large, they are not independent, and are reduced to second-order small quantities in taking the mean.

The difference in the two types of edge-length means is to be associated with the displacement of Nb in the (010) plane. The evidence from this structure and from other octahedral niobates has been used (Megaw, 1968) to show that there is a linear relation between the edge-length difference and the Nb displacement from the centre, which in this structure is 0·13 Å. The effect is independent of the symmetry of the structure or the nature of the tilts, if any, of the octahedron, as well as of the size of the larger cation.

Na *environment*

The character of the environment of both Na atoms is dependent on the octahedral tilts. Decrease of the angle of tilt enlarges the cavity. Na(2), lying on a mirror plane, can adjust itself in two dimensions to its surroundings; Na(1), on a rotation diad, can only move along a line where its movements are severely restricted by its three closest neighbours. It seems that the Na environment is critical in relation to the stability of this form of NaNbO₃ as compared with other closely related structures.

Relation to the ferroelectric phase

The structure of the ferroelectric phase stabilized by an electric field has not been directly determined, but it is believed (cf. Wood, Miller & Remeika, 1962) to be the same as that of $Na_{0.975}K_{0.025}NbO_3$ ('phase II' – Wells & Megaw, 1961). The structure of the latter has not been fully refined, and details are subject to confirmation, but the main features are known. Its space group is $P2_1ma$; the cell dimensions are like those of $NaNbO_3$, except that b has half the value; the octahedra remain fairly regular; their tilts are about the same axes, but are rather smaller; the Nb displacement has about the same magnitude. As a consequence of the shorter b-repeat and lower symmetry, both octahedra with the same x,z coordinates are rotated in the same sense about [010]; hence the projection of the whole structure looks like that of the part between $y=0$ and $y=\frac{1}{2}$ in $NaNbO_3$, and the environment of $Na(2)$ is little changed, but that of $Na(1)$, which now lies on a mirror plane instead of a rotation diad, has altered considerably. Fig.11(a) and (b) show these environments in $NaNbO_3$. With the reversal of direction of octahedral tilt about [010] goes reversal of sense of the Nb displacement within the same octahedra, so that now all the x-components of the dipoles are parallel instead of antiparallel in successive pairs of layers. However, the resultant Nb displacement does not now lie nearly along a one-corner Nb–O direction – instead, it is very nearly symmetrical, directed towards the mid point of an edge. (This important feature of the structure has been checked by an independent analysis of the original phase II data – Megaw, unpublished work).

It is easy to see why the sense of the tilt about [010] is affected by substitution of K for Na. Consider the effect of one replacement in a Na(1) site, as shown in Fig.11(b). The short distances of 2·38 Å and 2·50 Å become impossible. They can be increased sufficiently, without loss of symmetry, by decreasing the tilts. But if the octahedra behave as rigid units, this means enlarging all the other cavities in the structure; even allowing for some elasticity of the octahedra, which will gradually smooth out the strain, the cavities in the neighbourhood of the foreign atom will certainly be enlarged. At a composition of 2·5% K, about one site in three along each cube edge direction will contain K, and it is reasonable to suppose that all the intervening sites are seriously affected. They will, therefore, be too large for their Na atoms, which can only obtain a suitable environment by moving off the rotation diad. Suppose, in Fig.11(b), Na(1) moves to the right. (The distances marked are those for the undistorted cavity in pure $NaNbO_3$, but the qualitative features of the drawing remain, even when the tilts are reduced.) In maintaining a reasonable distance from A, its original close neighbour, it comes too close to B, which moves outward. This means a rotation about [010] of the octahedra whose equatorial planes lie below Na(1), reducing the angle ω. By reducing it to zero, and then increasing it with a reversed sign, B is brought below C, and D,E,F below G,H,A. (It is not suggested that the process is truly a continuous one; actually the angle of the tilt is likely to click through abruptly from a positive ω to a negative ω.) The octahedra above and below Na(1) are now related by a mirror plane of symmetry instead of a rotation diad. The configuration is in fact very like that of Na(2) [Fig.11(b)]. To obtain
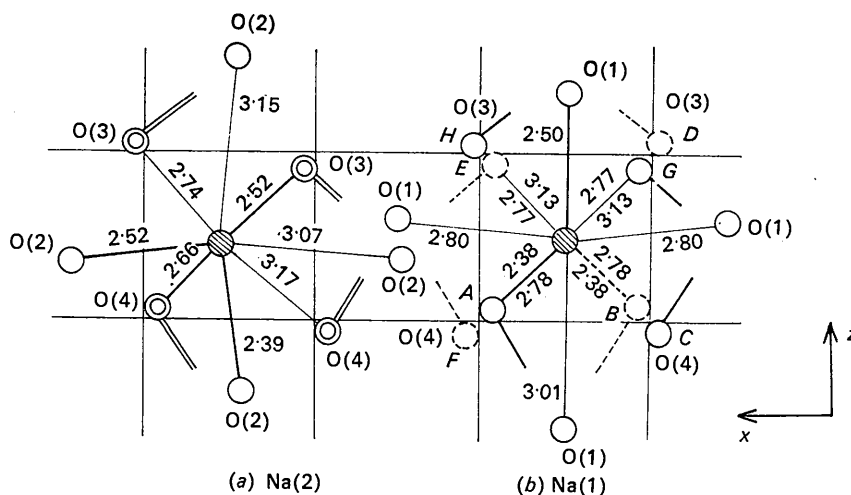

Fig. 11. Projection on (010) of environments of (a) Na(2) near $\frac{3}{4},\frac{1}{4},\frac{1}{4}$, (b) Na(1) near $-\frac{1}{4},0,\frac{1}{4}$. Na atoms shown by hatched circles' short Na–O bonds by heavier lines, direction of Nb–O bonds by unfinished lines from O. In (a) there is a plane of symmetry through Na, and O(3) and O(4) are superposed in pairs near heights $\frac{1}{8},\frac{3}{8}$, and so are the Na–O bonds to them. In (b) there is a diad axis; O atoms at height $+\frac{1}{8}$ are shown as full circles, at height $-\frac{1}{8}$ as dashed circles, and only the shorter of each nearly superposed pair of bonds is drawn in, though the lengths of both are marked. (The upper figure in each case refers to the upper bond, that to atoms at $+\frac{1}{8}$).

the complete structure of Phase II, we have to suppose the reversal of tilt happening cooperatively for the complete double layer of octahedra below Na(1), and for every alternate double layer below that.

It is not possible to explain directly why the direction of the Nb displacement reverses with the sense of the ω tilt. It must, of course, depend on changes in the polarization of the O atoms which are associated with changes in the Na–O bonds. If, however, we assume that Na(1) can find a position in which the Na(1)–O bonds to the layer above it are in satisfactory balance with the Nb–O bonds in that layer, then because there is a plane of symmetry relating the positions of the O atoms in the layer below to those in the layer above, the same set of Nb–O bonds in the layer below will also give a good balance, i.e. the plane of symmetry of the oxygen array will be a true symmetry plane of the structure. Hence all the large components of the Nb displacements are parallel.

In destroying the very short Na(1)–O(4) distance, the transition destroys the reason for distinction between the Nb–O(4) and Nb–O(3) bonds. Weakening Na(1)–O(4) changes the polarization of O(4) until Nb–O(4) becomes equal in strength to Nb–O(3), and therefore equal in length; hence the change in direction of the Nb displacement follows.

Entry of K into Na(2) sites also causes initial decrease of tilts to open up the sites, but here the short bonds are not quite so short, nor so closely fixed in direction by symmetry; Na(2) has more freedom of movement without destruction of symmetry, and there is no special discrimination between O(3) and O(4) atoms, as there was at the Na(1) site.

The effect of an electric field can be explained if it is assumed that polarization by an external field tends to act equally on O(3) and O(4). As these become more nearly equal, the two Nb–O bonds also become equal, and the short Na(1)–O(4) bond becomes impossible. Movement of Na(1) off its rotation diad takes place, just as described above for the result of K substitution, and the transition results. In directions within a single (010) layer of octahedra it is propagated by the direct action of the strong Nb–O bonds on the shared O(3) and O(4) atoms, but from layer to layer it depends on the effect of polarization in the Na–O bonds.

In view of the rather unusual environment of Na(1), it is perhaps a little puzzling why the structure in which it occurs should be the normally stable structure. There may be some stabilizing effect in the planar arrangement of three near neighbours. On the other hand, it may simply be due to the fact that a structure with symmetry giving antiparallel displacements is, other things being equal, more stable than one with polar symmetry, because of its better mechanical balance. This effect may, under normal circumstances, more than compensate for a less stable Na(1) environment, so that only under the influence of extraneous strain, whether caused by a large substituted ion or by an electric field (or possibly by the elastic compressions or tensions due to neighbouring domains in a polycrystal) is the polar structure favoured.

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