

Soft modes and the structure, spontaneous polarization and Curie constants of perovskite ferroelectrics: tetragonal potassium niobate

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Abstract. The structure of potassium niobate KNbO_3 in the ferroelectric tetragonal phase has been determined at 270°C by neutron diffraction. The atomic displacements along $[001]$ from the cubic perovskite positions are $\Delta(\text{K}) = -0.030 \pm 0.035 \text{ \AA}$, $\Delta(\text{Nb}) = 0.064 \text{ \AA}$, $\Delta(\text{O}_I) = -0.095 \pm 0.012 \text{ \AA}$ and $\Delta(\text{O}_{II}) = \Delta(\text{O}_{III}) = -0.102 \pm 0.012 \text{ \AA}$. The phase transition is seen as the condensation of a soft lattice vibrational mode in which comparatively rigid oxygen octahedra vibrate against the K and Nb atoms. The spontaneous polarization, Curie constant and entropy change for this and the other perovskite ferroelectrics BaTiO_3 , PbTiO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ have been calculated according to Cochran's soft mode theory. The agreement with experiment is satisfactory.

1. Introduction

KNbO_3 , like BaTiO_3 undergoes a series of ferroelectric structural phase changes as the temperature is lowered. Above 435°C , the structure is cubic perovskite with K at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, Nb at (000) and the O atoms on the cube faces at $(00\frac{1}{2})$, $(0\frac{1}{2}0)$ and $(\frac{1}{2}00)$. At 435°C , according to Cochran's theory of ferroelectricity (Cochran 1960), a soft optic mode of atomic vibration condenses as a spontaneous tetragonal distortion of the structure along one of the cube axes: the direction and sense of this cell polarization can be switched by an applied electric field. There are further transitions, at 225°C to an orthorhombic phase and at -10°C to a rhombohedral phase.

We have determined the atomic displacements in the cubic-tetragonal transition and used them to calculate the spontaneous polarization and Curie constant for comparison with the other ferroelectric perovskites BaTiO_3 , PbTiO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$. These latter quantities are also available from measurements on the bulk materials. The formulae given by Cochran (1960), together with the effective ionic charges obtained from lattice dynamical calculations (Cowley 1964), give satisfactory agreement with experiment.

Our results lend additional support to the soft mode picture, and we conclude that in KNbO_3 this soft mode consists of a vibration of a comparatively rigid oxygen octahedron against the rest of the structure.

2. Neutron diffraction experiment on KNbO_3

The crystal, which was grown at the Bell Telephone Laboratories, New Jersey, was cut to produce a thin [001] axis plate of approximate dimensions $2 \times 2 \times 0.5$ mm. The smallest possible specimen weighing 9.2 mg was chosen so as to reduce extinction corrections in the data analysis. Aluminium electrodes were evaporated onto the polished [001] faces, and the crystal was mounted on a thin ceramic rod. Thin aluminium foil contacts pressed onto these electrodes because of electrostatic attraction when a field was applied across them. The crystal had been seen to consist of a number of differently oriented domains when examined between crossed polarizers, and it was necessary to cool it from about 100°C above the transition temperature while applying a field of 5000 V cm^{-1} to ensure complete domain alignment. In KNbO_3 the ratio $c/a = 1.017$ is such that the 006 and 600 reflexions can be resolved on our neutron diffractometer; it was possible then, to check that at least 90% of the domains were aligned parallel with the field.

Table 1. Structure factors, on an arbitrary scale, for KNbO_3 with tetragonal axis along [001]. Observed F_o with statistical standard deviation $\pm\sigma_o$, and calculated F_c corrected by up to 3% for extinction.

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
020	1.986 ± 11	1.982	315	0.833 ± 11	0.845
002	1.931 ± 11	1.943	135	0.828 ± 7	0.845
220	1.954 ± 11	1.914	315	0.826 ± 19	0.845
202	1.902 ± 11	1.874	100	0.711 ± 7	0.713
022	1.876 ± 14	1.877	010	0.725 ± 7	0.712
222	1.754 ± 9	1.794	001	0.704 ± 7	0.706
400	1.717 ± 14	1.744	210	0.712 ± 7	0.699
040	1.724 ± 15	1.743	120	0.689 ± 7	0.699
004	1.595 ± 9	1.585	201	0.721 ± 7	0.696
240	1.631 ± 11	1.654	021	0.693 ± 8	0.696
042	1.569 ± 15	1.617	102	0.675 ± 7	0.673
204	1.505 ± 11	1.501	012	0.676 ± 8	0.673
024	1.511 ± 11	1.501	300	0.674 ± 10	0.672
242	1.521 ± 9	1.530	030	0.642 ± 10	0.672
224	1.445 ± 11	1.419	003	0.607 ± 10	0.616
044	1.242 ± 19	1.269	221	0.682 ± 10	0.680
244	1.219 ± 9	1.197	212	0.650 ± 10	0.655
060	1.317 ± 18	1.328	122	0.665 ± 9	0.654
006	0.939 ± 31	1.047	160	0.514 ± 13	0.528
260	1.227 ± 12	1.255	162	0.468 ± 14	0.493
062	1.209 ± 12	1.223	110	0.396 ± 7	0.376
206	0.972 ± 17	0.984	101	0.396 ± 7	0.403
026	0.913 ± 28	0.986	011	0.416 ± 7	0.403
111	1.053 ± 9	1.079	211	0.413 ± 12	0.377
311	0.963 ± 9	0.954	112	0.426 ± 11	0.452
131	0.956 ± 8	0.954	310	0.344 ± 20	0.313
311	0.948 ± 7	0.954	130	0.316 ± 19	0.313
131	0.948 ± 7	0.954	031	0.353 ± 18	0.346
113	1.041 ± 7	1.038	103	0.483 ± 13	0.497
133	0.903 ± 7	0.917	013	0.490 ± 13	0.497
151	0.790 ± 9	0.733	015	0.564 ± 12	0.568
115	0.945 ± 8	0.950	253	0.377 ± 19	0.323
351	0.667 ± 8	0.642	235	0.497 ± 15	0.480
153	0.709 ± 9	0.714			

The furnace (Hewat 1973), mounted on a standard UNICAM goniometer head, consisted of an evacuated silica glass aluminized globe, with a nichrome element heating the crystal from below by radiation. The temperature and background scattering of this furnace are independent of furnace orientation, and in any case neutron absorption and scatter from the furnace and electrodes is very small ($<1\%$ of the Bragg reflexion intensities).

The data were collected on the Ferranti automated 4-circle diffractometer (Channel 1), connected on line to a PDP-8 computer at the PLUTO high-flux reactor. The monitor count was adjusted so that each reflexion was collected with a statistical error of about 1% , taking between eight minutes and one hour per reflexion. The values of F_{obs} in table 1 represent averages over at least two equivalent reflexions (usually hkl and $\overline{h\overline{k}l}$). There is evidence of slight extinction of the strong (even,even,even) reflexions, reducing their intensities by up to 6% . Extinction of the weaker (odd,odd,odd), (odd,even,even) and (odd,odd,even) reflexions appears to be negligible.

Background corrections were made by offsetting the crystal by 3° and repeating the scan over the same angular range. No corrections were made for absorption or for thermal diffuse scattering. The former is negligible for such a small crystal, and the latter will mean that the Debye-Waller factors will be slightly underestimated in the refinement, the coordinate parameters being unaffected.

3. Structure refinement for KNbO_3

The tetragonal phase has symmetry $P4mm$ with $c = 4.063$ and $a = 3.997 \text{ \AA}$ (Shirane *et al* 1954). The structure is obtained from cubic perovskite by displacing the atoms κ by $\Delta(\kappa)$ along the z axis, giving the coordinates,

$$\text{K at } \frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}c + \Delta(\text{K})$$

$$\text{Nb at } 0, 0, 0 + \Delta(\text{Nb})$$

$$\text{O}_I \text{ at } 0, 0, \frac{1}{2}c + \Delta(\text{O}_I)$$

$$\text{O}_{II} \text{ at } 0, \frac{1}{2}a, \Delta(\text{O}_{II})$$

$$\text{O}_{III} \text{ at } \frac{1}{2}a, 0, \Delta(\text{O}_{III}).$$

One of the parameters $\Delta(\kappa)$ (we chose $\Delta(\text{Nb})$) must be fixed, since the refinement yields only relative atomic displacements. This parameter is determined by a relation involving the atomic mass m_κ ,

$$m_K \Delta(\text{K}) + m_{\text{Nb}} \Delta(\text{Nb}) + m_{\text{O}} (\Delta(\text{O}_I) + 2\Delta(\text{O}_{II})) = 0$$

which states that the centre of mass of the KNbO_3 cell is unmoved by the ferroelectric transition.

The refinement, using the Pawley constrained-parameter program, proceeded as described for $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ (Hewat *et al* 1972). We took care to select reasonable starting values for the parameters and to try all possible combinations of signs for the atomic displacements $\Delta(\kappa)$, which were expected to be $1\text{--}5\%$ of the cell dimension c . In this way we were able to ascertain that our solution for the structure was truly unique.

The agreement between calculated (F_c) and observed (F_o) structure factors (table 1) was improved slightly for the stronger reflexions when a small extinction correction was applied to the data. According to Zachariasen (1967), the corrected $F^2 = yF_c^2$ where $y \simeq (1 + x^2)^{1/2} - x$ and $x \simeq \epsilon F_o^2 \text{ cosec } 2\theta$; ϵ is the extinction parameter, which depends

of course on the scale factor used for F_o . Strictly, these formulae are true only for a spherical crystal, but in practice, because the correction is small even for the strongest reflexions, little improvement can be expected if a more exact expression for x is used.

The largest parameter correlation coefficients were 0.81 and 0.89 between the pairs ($\Delta(K)$, $U_{33}(K)$) and ($\Delta(K)$, $U_{33}(Nb)$) respectively (table 2). These large coefficients mean

Table 2. Structural parameters for tetragonal KNbO_3 . The $\Delta(\kappa)$ are the atomic displacements along [001] from the parameters for cubic perovskite, relative to the centre of mass of the KNbO_3 cell. The $U_{jj}(\kappa) = \langle u_j(\kappa)^2 \rangle \text{Å}^2$ are the mean square amplitudes of vibration along the j axes. The absolute magnitude of the extinction parameter is determined by the F scale, and the reliability indices are $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = \Sigma w |F_o| - |F_c| / \Sigma w |F_o|$ where $w = 1/\sigma_o$ (table 3)

$\Delta(K)$	=	-0.030	± 0.035	Å
$\Delta(Nb)$	=	0.064	(origin)	Å
$\Delta(O_I)$	=	-0.095	± 0.012	Å
$\Delta(O_{II}) = \Delta(O_{III})$	=	-0.102	± 0.012	Å
$U_{11}(K) = U_{22}(K)$	=	0.021	± 0.005	Å ²
$U_{33}(K)$	=	0.015	± 0.006	Å ²
$U_{11}(Nb) = U_{22}(Nb)$	=	0.010	± 0.002	Å ²
$U_{33}(Nb)$	=	0.003	± 0.002	Å ²
$U_{11}(O_I) = U_{22}(O_I)$	=	0.012	± 0.003	Å ²
$U_{33}(O_I)$	=	0.016	± 0.006	Å ²
$U_{11}(O_{II}) = U_{22}(O_{II})$	=	0.011	± 0.003	Å ²
$U_{22}(O_{II}) = U_{11}(O_{III})$	=	0.010	± 0.001	Å ²
$U_{33}(O_{II}) = U_{33}(O_{III})$	=	0.016	± 0.006	Å ²
ϵ	=	0.00023	± 0.00003	
R	=	0.019		
R_w	=	0.019		

that these parameters cannot be independently obtained with high accuracy from this data alone. They are responsible for the relatively large error limits assigned to $\Delta(K)$ when all parameters were refined simultaneously. This does not however have a serious effect on our calculations (§ 5 and § 6) because of the relatively small mass and charge of the potassium atom.

4. Rigidity of the oxygen octahedra in perovskites

According to Cochran's (1960) soft-mode theory, the tetragonal phase of KNbO_3 is produced by the condensation at 435 °C of a soft transverse $q = 0$ optic mode polarized along [001]. Figure 1a shows the resulting displacements relative to the centre of mass origin. The equivalent soft modes polarized along [010] and [100] are stabilized by this transition, until at 225 °C one of them condenses giving a net polarization along [011] or [101] in the orthorhombic phase (figure 1b). Finally the remaining soft mode condenses at -10 °C to give a net polarization along [111] in the rhombohedral phase.

Megaw (1957) has pointed to the essential rigidity of the oxygen octahedra in the perovskite structure, and has discussed the distorted perovskites in terms of displacements and tilts of these rigid octahedra. According to lattice dynamics theory (Cowley 1964), zone boundary vibrational modes such as Γ_{25} at $q = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and M_3 at $q = (\frac{1}{2}\frac{1}{2}0)$,

Table 3. Atomic displacements in Å from the cubic perovskite positions for various ABO₃ ferroelectrics.

	KNbO ₃		BaTiO ₃		K(Ta, Nb)O ₃		PbTiO ₃
	Tetragonal (1)	Orthorhombic (2)	Tetragonal (3)	Orthorhombic (4)	Tetragonal (5)	Tetragonal (5)	Tetragonal (6)
$\Delta z(A)$	-0.030 ± 35	-0.030 ± 5	0.004	0.002	0.048 ± 12	0.100 ± 2	0.100 ± 2
$\Delta z(B)$	0.064	0.067	0.058 ± 2	0.059	0.001	-0.066 ± 7	-0.066 ± 7
$\Delta z(O_I)$	-0.095 ± 12	-0.133 ± 10	-0.093 ± 4	-0.072	-0.040 ± 4	-0.365 ± 7	-0.365 ± 7
$\Delta z(O_{II})$	-0.102 ± 12	-0.133 ± 10	-0.057 ± 4	-0.072	-0.044 ± 4	-0.365 ± 7	-0.365 ± 7
$\Delta z(O_{III})$	-0.102 ± 12	-0.053 ± 10	-0.057 ± 4	-0.055	-0.044 ± 4	-0.365 ± 7	-0.365 ± 7
$\Delta y'(O_I)$		0.023 ± 11		0.017			

(1) This paper

(2) Katz and Megaw (1967)

(3) Harada *et al* (1970)(4) Shirane *et al* (1957)(5) Hewat *et al* (1972)(6) Shirane *et al* (1956)

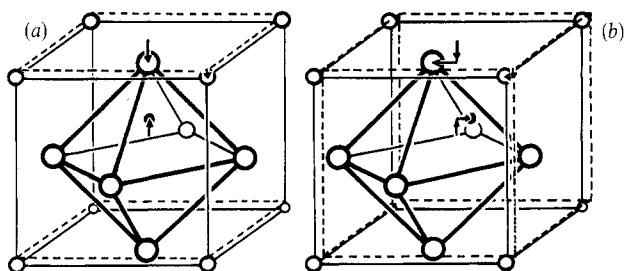


Figure 1. (a) Displacements in the cubic-tetragonal ferroelectric transition of KNbO_3 relative to the centre of mass origin. (b) The structure of the orthorhombic phase. \circ potassium, \bullet niobium, \circ oxygen.

corresponding to pure rotations (or tilts) of the oxygen octahedra, can also become unstable; octahedra distortion and displacements of other atoms are excluded from these soft modes simply because of symmetry requirements. However, the oxygen octahedra are not restricted by symmetry to be rigid in the zone centre $q = 0$ soft mode which is responsible for the ferroelectric transition. Table 3 shows though, that in the tetragonal phases of KNbO_3 , $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ and PbTiO_3 the oxygen octahedra are in fact undistorted; the oxygen atoms move in the same direction with much the same amplitude. In tetragonal BaTiO_3 , and in the orthorhombic phases, there are small distortions of the oxygen octahedra, but these distortions are still much smaller than those which must occur in the two highest frequency transverse modes.

Table 4. Dynamic force matrix elements $M_{zz}(\kappa, \kappa')$ in units of 10^{24} atomic weight units/ s^2 for SrTiO_3 perovskite at $q = 0$. This matrix determines the relative atomic displacements $u_z(\kappa)$ in the mode of frequency ω through the equation $\omega^2 m_\kappa u_z(\kappa) = \sum_{\kappa'} M_{zz}(\kappa, \kappa') u_z(\kappa')$. The large forces binding O_I to $\text{O}_{II} \equiv \text{O}_{III}$ mean that the oxygen octahedra will be relatively undistorted in the soft ferroelectric mode.

κ	$\kappa' = \text{Sr}$	Ti	O_I	O_{II}	O_{III}
Sr	1053	-676	-420	23	23
Ti	-676	568	-260	184	184
O_I	-421	-260	3253	-1286	-1286
O_{II}	23	184	-1286	1054	25
O_{III}	23	184	-1286	25	1054

This rigidity of the oxygen octahedra in the low frequency mode indicates strong forces between the oxygen atoms, as suggested by Megaw. The strength of these forces can be illustrated by constructing the $q = 0$ lattice dynamical matrix for SrTiO_3 (table 4) from the eigenvectors and frequencies given by Cowley (1964). An element of the submatrix $M_{zz}(\kappa, \kappa')$ (table 4) represents the force on atom κ in direction z when atom κ' is displaced by one unit along the z axis, in a transverse mode propagating along the x or y axes. Obviously there is a relatively large force binding O_I and $\text{O}_{II} \equiv \text{O}_{III}$ together. (O_{III} is tied to O_{II} by the symmetry requirements of the soft mode, so that the small shearing force between O_{III} and O_{II} is irrelevant for this mode).

Cowley's eigenvectors, used in the construction of this matrix, do in fact contain a small distortion of the oxygen octahedron in the soft $q = 0$ mode of SrTiO_3 , in disagreement with the experimental results of Harada *et al* (1970) which indicate an even more rigid oxygen octahedron. However this discrepancy can probably be removed by improvements to the model, without altering the essential fact that the oxygen atoms are held together by strong forces: the relative strength of these forces for the different perovskite oxides is probably indicated by the relative rigidity of the oxygen octahedra in the soft $q = 0$ modes.

Yelon *et al* (1971) have suggested that distortion of the oxygen octahedron in BaTiO_3 and KNbO_3 is associated with the fact that these materials undergo first order ferroelectric transitions, whereas in PbTiO_3 and in $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ ($x > 0.66$) this octahedron is undistorted and the transition is second order. However there is insufficient evidence to show that the oxygen octahedron is distorted in the soft ferroelectric mode in KNbO_3 (G Shirane, private communication 1972), and indeed our results show that there is only a very small distortion in the cubic-tetragonal transition of this material. Rigidity of the oxygen octahedron is not confined then to perovskite materials which undergo, or have a tendency toward, second order transitions.

A more accurate picture of the interatomic forces can be obtained experimentally. For a given material, the dynamic force matrix can be obtained directly if the eigenvectors as well as the frequencies of all the $q = 0$ modes are determined from inelastic neutron scattering and infrared/Raman scattering experiments.

5. Spontaneous polarization calculations

When a rigid ion κ of charge z_κ electrons is displaced by $\Delta(\kappa)$ from its cubic perovskite position, the resulting dipole moment is $z_\kappa\Delta(\kappa)$. In fact the ions are not rigid, and become polarized in the field resulting from their displacements: the charge z_κ must then be replaced by an apparent charge z'_κ (Cochran 1960). The total polarization can be written

$$P = \frac{e}{v_c} \sum_{\kappa} z'_\kappa \Delta(\kappa). \quad (5.1)$$

The apparent charges z'_κ allow for the contribution of the ionic polarizability, which is measured by the high frequency dielectric constant ϵ_∞ . For a diagonally cubic crystal such as cubic perovskite (Cochran 1960),

$$z'_\kappa = \frac{1}{3}(\epsilon_\infty + 2) z_\kappa \quad (5.2)$$

where z'_κ is the effective ionic charge obtained from rigid-ion model calculations of the lattice dynamics. These z'_κ can also be obtained directly from the splitting of the frequencies of the longitudinally and transversely polarized infrared/Raman modes.

Strictly, equation (5.2) does not apply for a non-cubic crystal such as tetragonal KNbO_3 , but Axe (1967) has shown that it is still a very good approximation for the apparent charges on the cations. He obtained the z'_κ for BaTiO_3 and other tetragonal perovskites directly from the infrared dipole strengths, and showed that there is a large anisotropy in the apparent charges on the two types of oxygen ions O_I and $\text{O}_{II} \equiv \text{O}_{III}$. Fortunately this anisotropy need not concern us if all oxygens are displaced in the same direction with the same amplitude, as in KNbO_3 : equation (5.1) can then be evaluated using the mean apparent oxygen charge $(z''_{\text{O}_I} + 2z''_{\text{O}_{II}})/3$, which can be obtained from the cation charges because of the requirements for total charge neutrality for ABO_3 .

$$z'_A + z'_B + z'_{O_1} + 2z'_{O_n} = 0.$$

Since there do not appear to be sufficient infrared/Raman data available for KNbO_3 , we have used Cowley's (1964) SrTiO_3 results to estimate z'_k for use in our calculation. According to Axe's (1967) calculations, BaTiO_3 (and presumably PbTiO_3) can be expected to have essentially the same apparent cation charges as SrTiO_3 , while in KTaO_3 (and presumably KNbO_3 and K(Ta, Nb)O_3) only half of the charge appears on K, the remainder being transferred to the other cation. The refractive index $n = \epsilon_\infty^{1/2} \simeq 2.4$ for these materials so that equation (5.2) yields the apparent charges of table 5. The differences

Table 5. Apparent charges z'_k for perovskite ferroelectrics ABO_3 estimated from equation (5.2) with $\epsilon_\infty = 5.76$, and the effective charges z'_k given for SrTiO_3 by Cowley (1964) modified as explained in the text for the different cation valencies in the case of KNbO_3 and K(Nb, Ta)O_3 .

	z'_A	z'_B	$\overline{z'_O}$	z''_A	z''_B	$\overline{z''_O}$
KNbO_3 K(Ta, Nb)O_3	0.7 ± 0.1	2.9 ± 0.5	-1.2 ± 0.2	1.8 ± 0.3	7.5 ± 1.2	-3.1 ± 0.3
BaTiO_3 PbTiO_3	1.4 ± 0.2	2.2 ± 0.4	-1.2 ± 0.2	3.6 ± 0.5	5.7 ± 0.9	-3.1 ± 0.3

between our results for SrTiO_3 and those of Axe (1967) are not large, and are mainly due to the choice by Axe of $z'_{\text{Ti}}/z'_{\text{Sr}} = 2$, whereas Cowley's (1964) calculations and electron energy band analysis support our choice of $z'_{\text{Ti}}/z'_{\text{Sr}} \simeq 1.6$.

These apparent ionic charges, together with the experimental ionic displacements (table 3) have been used to estimate the expected spontaneous polarization for the various ferroelectric perovskites (table 6). If we compare these estimated values, with the results of dielectric measurements of P , the agreement is satisfactory. This comparison is a useful check on the correctness of the magnitudes and directions of the displacements, and also on the magnitudes of the apparent ionic charges.

6. Curie constant and entropy change calculation

The importance for the theory of ferroelectricity of the Lyddane-Sachs-Teller relation

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod_j \left(\frac{\omega_{Lj}}{\omega_{Tj}} \right)^2 \quad (6.1)$$

between the ratios of the frequencies ω_{Tj} and ω_{Lj} of the transversely and longitudinally polarized $q = 0$ optic lattice vibrational modes, and the static and high frequency dielectric constants ϵ_0 and ϵ_∞ , was realized by Cochran (1959). He pointed out that the observed Curie law increase of ϵ_0 near the transition temperature T_0 ,

$$\epsilon_0 = \frac{C}{T - T_c} \quad (6.2)$$

means that one of the frequencies ω_{Tj}^2 of (6.1) must go linearly to zero at $T_c \leq T_0$

$$\omega_T^2 = A(T - T_c) \quad (6.3)$$

Table 6. Calculated spontaneous polarizations P and Curie constants C compared with measurements for the ABO_3 ferroelectrics, together with changes P_0 in P and S in entropy at the transition. Superscripts refer to (d) dielectric, (s) specified heat, (n) neutron scattering and (i) infrared experimental data. The values of the frequency constant A of equation (6.3) have been estimated for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ —see text.

ABO ₃ (Temperature)	Polarization P		ΔS cal mol ⁻¹ K ⁻¹	A 10 ⁻²⁴ rad s ⁻²	Curie constant C	
	P_0 μC cm ⁻²	Measured μC cm ⁻²			10 ⁵ K Measured	Calculated
KNbO ₃ (tetrag.) 270°C	26 ^d (2)	30 ± 2 ^d (2)	0.32† (2)	0.3 ± 0.1	1.6 ^s	1.6 ± 0.5 (5)
		32 ± 3 ^d (2)	0.28 (3) 0.19 (4)		2.4 ^d	
BaTiO ₃ (tetrag.) 20°C	18 ^d (6)	26 ^d (6)	0.125† (7) 0.12 (1)	0.48 ^{n†} (8) 0.43 ^d (9, 10) 0.56 ^d (9, 11) 0.66 ⁱ (9, 12)	1.54 ^d (13) 1.7 ± 0.2 ^s	1.5 ± 0.3
		30 (6)				
PbTiO ₃ (tetrag.) (20°C)	40 ^d (16)	75 ^{d†} (16) 57 ^d (17)	1.51 (18) 0.46 (19) 1.0 ± 0.5†	0.30 (20)	1.1 ^{d†} (21) 1.1 ^d (22) 4.1 ^d (17) 4.4 ^d (19) 1.1 ± 0.4 ^s	1.1 ± 0.4
		≥ 10 (15)	0.03 ^c	0.3 ± 0.1	1.2 (5)	1.4 ± 0.4
KTa _x Nb _{1-x} O ₃ (tetrag.) $x = 0.55$ (20°C)	8.6 ^d (14) ($x = 0.65$)					

† indicates preferred values.

- (1) Jona and Shirane (1962),
 (2) Triebwasser (1956),
 (3) Shirane *et al* (1954),
 (4) Triebwasser and Halpern (1955),
 (5) Triebwasser (1959),
 (6) Merz (1953),

- (7) Shirane and Takeda (1952),
 (8) Harada *et al* (1971),
 (9) Barker (1966),
 (10) Stern and Lurio (1961),
 (11) Benedict and Durand (1958),
 (12) Ballantyne (1964),

- (13) Shirane and Sawaguchi (1951),
 (14) Samara (1971),
 (15) Shirane *et al* (1970),
 (16) Shirane and Hoshino (1951),
 (17) Bhide *et al* (1962),

- (18) Roberts (1949),
 (19) DiDomenico and Wemple (1968),
 (20) Chen *et al* (1966),
 (21) Gavrilianchenko *et al* (1970),
 (22) Remeika and Glass (1970),

Cochran's (1960) lattice dynamical theory provides a relation between the Curie constant C of (6.2) and the displacements u_{κ} of the atoms in the 'soft mode' (6.3), which can be tested for KNbO_3 with our data.

$$C = \frac{4\pi v_c P^2}{A \sum_{\kappa} m_{\kappa} u_{\kappa}^2} \quad (6.4)$$

Here v_c is the unit-cell volume containing the atoms of masses m_{κ} , and $u_{\kappa} \equiv \Delta(\kappa)$ since the soft-mode displacements u_{κ} 'freeze' into the ferroelectric displacements $\Delta(\kappa)$ which we have obtained. For BaTiO_3 equation (6.4) yields a value for C in good agreement with experiment (Cochran 1969), but for PbTiO_3 two quite different experimental values have been obtained for C and the test is inconclusive (Shirane *et al* 1970). It is useful therefore to test (6.4) for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ (Hewat *et al* 1972), the only other perovskite oxides for which the displacements in the tetragonal phase are now available.

In table 6 the values of C predicted by the lattice dynamical theory (equation 6.4) are compared with the results of measurements of the temperature dependence of the dielectric constants (equation 6.2). The lower experimental value of C for PbTiO_3 is preferred, because the many experiments on BaTiO_3 (Jona and Shirane 1962) indicate that the higher values are usually obtained for poor or impure specimens. (The PbTiO_3 specimens yielding the higher values had been doped with uranium to help with crystal growth.) As well, the entropy change measurements for PbTiO_3 support the lower value for C .

The change ΔS in the entropy of a ferroelectric material when it passes through the phase transition is related to the Curie constant and the change P_0 in the polarization (Jona and Shirane 1962)

$$\Delta S = \frac{2\pi P_0^2}{C} \quad (6.5)$$

ΔS is available for BaTiO_3 , PbTiO_3 and KNbO_3 from specific heat measurements and the corresponding values calculated for C from (6.5) are labelled s in table 6. These serve as a useful check on the dielectric measurements.

The only parameter in equation (6.4) which presents some difficulty is the soft-mode frequency constant A of equation (6.3). In KNbO_3 , as in BaTiO_3 , the soft mode is overdamped, and the infrared reflectivity data must be fitted by a damped oscillator if ω_T is to be extracted (Barker 1966). Alternatively ω_T and thence A can be obtained from (6.1) if the dielectric constants and the frequencies of all of the other $\mathbf{q} = 0$ modes are known (Barker 1966). Unfortunately, for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ there are insufficient infrared/Raman data for either of these methods to be applied. The constant A has also been obtained for BaTiO_3 and PbTiO_3 from neutron scattering measurements, labelled N in table 6, but again insufficient data are available for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$. If we assume the validity of the lattice dynamical model we can of course calculate A from ΔS using equations (6.4) and (6.5), but for our purposes it is probably best to assume that A is much the same for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ as it is for BaTiO_3 and PbTiO_3 . Although this uncertainty of the precise value of A increases the error limits which must be assigned to the calculated values of C , the agreement with the experimental values is quite encouraging. It is sufficiently good, for example, to exclude the tunnelling mode model as an alternative to Cochran's model, since such a model would give much smaller values of C for the present data (Cochran 1968).

7. Conclusion

The tetragonal structures obtained for KNbO_3 and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ support the idea that in the ferroelectric soft mode, comparatively rigid oxygen octahedra vibrate against the remaining atoms. The rigidity of these octahedra in KNbO_3 is especially interesting since this material, unlike others in which very rigid octahedra have been observed, undergoes a first order transition. These structures yield correct values for the spontaneous polarization and also result in correct predictions of the ferroelectric Curie constants by Cochran's soft-mode theory of ferroelectricity.

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