refinement) an increase in the range of initial parameters from which the refinement will converge.

In the refinement of biologically important structures (such as many of the antibiotics) the introduction of constraints should prove particularly valuable. In disordered structures where refinement of individual atoms is impossible, the application of reasonable constraints to the system could allow satisfactory refinement without the limitations imposed by a completely constrained (rigid-group) refinement (Bailey & Dahl, 1965).

Fortran 4 and Fortran 63 versions of *ORFLSE* are available through Dr L. F. Dahl, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53706.

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Determination of the Normal Vibrational Displacements in Several Perovskites by Inelastic Neutron Scattering*

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Relative displacements of the atoms corresponding to the lowest frequency long wavelength transverse optic phonon of several materials with the perovskite structure were determined directly by a least-squares refinement of the integrated intensity of inelastic neutron scattering. The modes of $KTaO_3$ and $SrTiO_3$ were identified as being of the Slater type, in which oxygen atoms vibrate against Ta and Ti atoms. In the case of $RbMnF_3$, however, an entirely different vibrational motion was obtained, in which Rb ions vibrate out of phase with the rigid MnF_3 group.

Introduction

The lattice dynamical theory of ferroelectric phase transitions in perovskite structures predicts that there exists a close relationship between the vibrational displacement associated with soft optic phonons at the Brillouin zone center (wave-vector $\mathbf{q}=0$), and the static structure of the ferroelectric phase (Cochran, 1960). It is of great interest to see what kind of atomic vibrational displacements exist for soft optic modes in such substances and, where possible, to compare with static spontaneous displacements.

In connection with this idea, approximate mode assignments of the three infrared active modes for $BaTiO_3$, $SrTiO_3$ and other related substances have been made by several authors, with results which are in wide disagreement. Last (1957) originally suggested a vibration of the cation out of phase with a rigid TiO_3 group vibration as the possible mode of the lowest frequency $q=0$ transverse optic (TO) phonon for $BaTiO_3$. This suggestion was later supported by Perry & Khanna (1964) and Perry, McCarthy & Rupprecht (1965), who showed as evidence that the mode frequencies for several titanium perovskites depended systematically upon the cation mass. Spitzer, Miller, Kleinman & Howarth (1962), however, deduced a stretching type motion in which Ti atom vibrates against the O_6 octahedron, from the fact that the infrared resonance strengths for the soft mode are the same order of magnitude for the three substances, $BaTiO_3$, $SrTiO_3$ and TiO_2. (Hereafter, we shall call this type of vibration a 'Slater mode', since it was originally pointed out by Slater (1950) that the structure resulting from such a distortion is energetically favorable because of strong local field effects.) This argument recently has been extended by Axe

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(1967) in a more quantitative way. He concluded that displacements reasonably close to the Slater type occur in the lowest TO mode for oxide type perovskites but suggested that a Last-type mode was of lowest frequency in fluoride perovskites.

Cowley (1964) has calculated the displacements of atoms in $q=0$ modes of $SrTiO_3$ on the basis of a lattice dynamical shell model in which force constants were made to fit experimental phonon dispersion curves. These results, which are by far the most reliable to date, show nearly a Slater-type mode for the lowest TO branch of this substance, but it is not easy to extend his results to other interesting perovskite substances.

It is possible to obtain more experimentally direct information about the vibrational motions by a (neutron, X-ray, electron) diffraction method (Cole, 1953), because the scattering of an incident beam resulting from excitation of a single phonon is proportional to the square of an inelastic structure factor which involves the polarization vectors of the phonon. By observing the relative intensity of the X-ray diffuse scattering from tetragonal $BaTiO_3$, an attempt was made by Harada & Honjo (1967) to deduce the approximate atomic motion in the soft TO mode for small q values, and the results favored a Slater-type mode for the soft TO branch.

In the case of X-rays, however, atomic motion cannot be reliably determined because of the inherent difficulty in resolving the scattering due to a phonon in a particular branch from that due to other phonon branches, two phonon processes and Compton scattering. Moreover, the intensity from the most interesting $\mathbf{q}\simeq 0$ phonons is concealed by elastic Bragg scattering. As first pointed out by Brockhouse (1961), neutron diffraction has the advantage in atomic motion determination that a particular phonon can, in most cases, easily be resolved by energy analysis. This method has not been applied to systems of any complexity partially because of the time required to collect a sufficient number of accurately measured phonon 'reflections' to define the vibrations. Recently, however, several experiments have been performed at Brookhaven, exploring the practicality of direct phonon mode determination in moderately complex lattices utilizing least-square fitting techniques (Skalyo, Frazer & Shirane, 1970; Axe & Shirane, 1970). In the present experiments, the atomic motions in the lowest frequency TO mode of three perovskites, two oxides, $KTaO_3$, and $SrTiO_3$ and one fluoride, $RbMnF_3$ have been analyzed. In this paper we show the results of the analysis and discuss them in comparison with previous mode assignments for these substances.

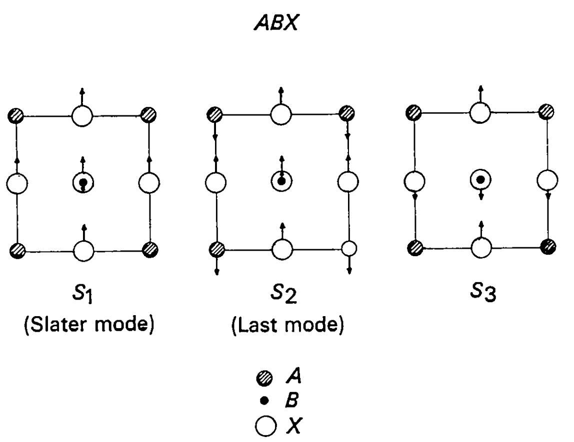

Fig. 1. Three symmetry coordinates for atomic motions of the perovskite ABX_3.

The inelastic structure factor

The intensity of inelastic scattering for a one phonon process integrated over the energy is directly proportional to the square of the inelastic structure factor, which may be written as

$$F_{\text{inel}}(\mathbf{Q},j)=\sum_{\kappa}[\mathbf{Q}\cdot\xi_\kappa(\mathbf{q},j)]b_\kappa\exp\{-W_\kappa\}\exp\{i\mathbf{G}\cdot\mathbf{R}_\kappa\}\quad(1)$$

providing $\mathbf{Q}=$constant.

Here b_κ is the neutron scattering length and $\exp\{-W_\kappa\}$ is the familiar Debye–Waller factor for the κth atom with the coordinate $\mathbf{R}_\kappa$. The momentum transfer $\mathbf{Q}$ is given by

$$\mathbf{Q}=\mathbf{q}+\mathbf{G}\,,\quad(2)$$

where $\mathbf{q}$ and $\mathbf{G}$ are wave numbers of the phonon and the reciprocal lattice vector, respectively. $\xi_\kappa(\mathbf{q},j)$ is the normalized displacement vector for κth atom of mass m_κ and is related to the atomic displacement $\mathbf{u}_{\kappa l}$ and the polarization vector $\mathbf{e}_\kappa(\mathbf{q},j)$ for the phonon of $\mathbf{q}$ in the jth branch,

$$\mathbf{u}_{\kappa l}^{(t)}=(Nm_\kappa)^{-1/2}\sum_{p,j}\mathbf{e}_\kappa(\mathbf{q},j)Q(\mathbf{q},j;t)\exp\{i\mathbf{q}\cdot(\mathbf{R}_l+\mathbf{R}_\kappa)\}\,.\quad(3)$$

where

$$\xi_\kappa(\mathbf{q},j)=(m_\kappa)^{-1/2}\cdot\mathbf{e}_\kappa(\mathbf{q},j)\,.\quad(4)$$

$Q(\mathbf{q},j;t)$ is the normal coordinate of the phonon, $\mathbf{R}_l$ indicates the position of lth cell. For the Brillouin zone center phonon, $\mathbf{q}=0$, accordingly $\mathbf{Q}=\mathbf{G}$, and furthermore $\xi_\kappa(0,j)$ may be chosen to be real.

It is known that there are three triply degenerate infrared active lattice vibrations (F_{1u}) and a single inactive one (F_{2u}) in the perovskite ABX_3 structure if we neglect acoustic vibrations. (For the polar modes, the degeneracy is partially removed giving rise to distinct longitudinal and transverse frequencies.) Although there is only a single possible mode of F_{2u} symmetry, no unique set of symmetry coordinates for F_{1u} exists. But it is possible to describe the eigenvectors in terms of a complete set of coordinates constructed to form a basis for irreducible representation of the point group but otherwise arbitrary. One possible set of such symmetry coordinates is shown in Fig. 1, in which Slater ($\mathbf{s}_1$) and Last ($\mathbf{s}_2$) type modes are included as irreducible symmetry coordinates. We shall adopt this set of coordinates in this paper, since it is convenient to discuss the atomic motion in the lowest TO branch of the perovskite in terms of the Slater or Last modes, which have been used already by several authors.

The displacements $\xi_\kappa(j)$ for the infrared active jth branch, therefore, are given as a linear combination of these coordinates $\mathbf{s}_{\lambda\kappa}$

$$\xi_\kappa(j)=\sum_{\gamma=1}^{3} S_\lambda(j)\,.\,\mathbf{s}_{\kappa\lambda} \qquad (5)$$

where $S_\lambda(j)$ indicates the contribution of the λth symmetry coordinate, $\mathbf{s}_{\kappa\lambda}$, to the eigenvector, $\xi(j)$. They are parameters to be determined in this analysis. Summation over λ is a summation over all three symmetry coordinates $\mathbf{s}_{\kappa\lambda}$ which are listed together with atomic positions of the perovskite ABX_3 in Table 1. Because only the relative ratio of these three parameters has a significant meaning (the normalization is arbitrary) the actual number of parameters to be determined is reduced to two in the present case.

Table 1. *Symmetry coordinates for the perovskite ABX_3*

For the displacement along [001] axis, $k=3m_X/m_B$, $k'=(m_B+3m_X)/m_A$.

Atom	Position	$s_{\kappa 1}$	$s_{\kappa 2}$	$s_{\kappa 3}$
A	(0,0,0)	0	$-k'$	0
B	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$-k$	1	0
X_1	$(\frac{1}{2},0,\frac{1}{2})$	1	1	$-\frac{1}{2}$
X_2	$(0,\frac{1}{2},\frac{1}{2})$	1	1	$-\frac{1}{2}$
X_3	$(\frac{1}{2},\frac{1}{2},0)$	1	1	1

Experimental

Dimensions of the three single-crystal specimens used were

	Dimension (cm^3)	Mosaic spread
$KTaO_3$	2·2	less than 3′
$SrTiO_3$	7·6	less than 8′
$RbMnF_3$	4	less than 4′

Integrated intensities for the lowest transverse optic phonon of $q=0$ ($\pm$0·07 Å^{-1}) were measured on a triple-axis crystal spectrometer at the Brookhaven High Flux Beam Reactor, using 'constant Q' scanning. The lowest $q=0$ phonon energies of these three substances are 10·8, 11·5 and 13·8 meV for $KTaO_3$, $SrTiO_3$ and $RbMnF_3$, respectively. Incident energies used were 45 meV for $KTaO_3$ and 55 meV for $SrTiO_3$ and $RbMnF_3$, which enabled us to observe 12, 18 and 13 reflections of a type (hhl), respectively. These data were collected at room temperature, 22 ± 2 °C.

Four equivalent reflections were usually measured for one or two reflections in order to estimate the possible spurious scattering and to check the uniformity of the incident neutron beam. Agreement between intensities of the equivalent reflections was found to be about 10% which was less than the error due to counting statistics. Error due to counting statistics was then employed in the weighting scheme for the least-square analysis.

Analysis

The mode analysis was carried out using a least-squares fitting routine '*POWLS*' (Hamilton, 1964) which was modified so as to be suitable for present mode analysis.

In the computations the following neutron scattering lengths were used (in units of 10^{-12} cm)

$b(\mathrm{K})=0{\cdot}35$ $\quad b(\mathrm{Sr})=0{\cdot}57$ $\quad b(\mathrm{Rb})=0{\cdot}705$†

$b(\mathrm{Ta})=0{\cdot}70$ $\quad b(\mathrm{Ti})=-0{\cdot}36$* $\quad b(\mathrm{Mn})=-0{\cdot}36$

$b(\mathrm{O})=0{\cdot}58$ $\quad b(\mathrm{F})=0{\cdot}55$.

In the structure factor expression, equation (1), there are two anisotropic temperature parameters for X atoms which are located at non-cubic symmetry positions of the structure and one for each of the other atoms, *i.e.* A and B in ABX_3. Hence, there are seven parameters in all, to be determined; two mode parameters among S_1, S_2, and S_3, four temperature parameters and a scale factor.

Since it is not easy in practice to obtain a sufficient number of phonon 'reflections' with great accuracy, we employed a single isotropic crystal temperature parameter instead of the individual ones. Thus, four parameters were refined for $SrTiO_3$ and $KTaO_3$ by the

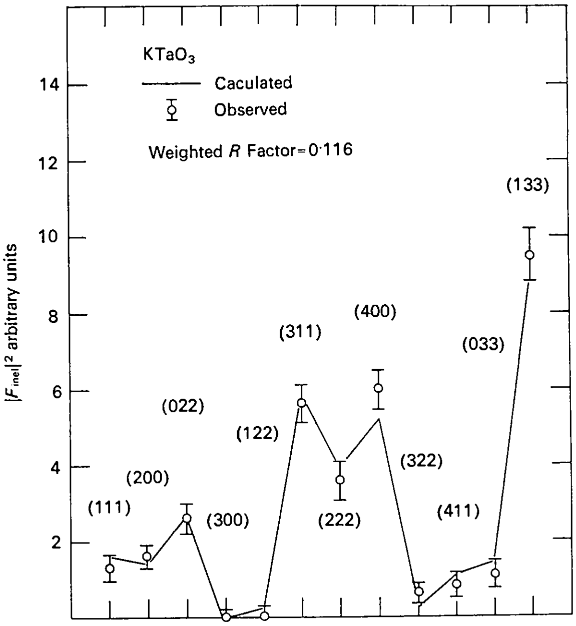

Fig. 2. Comparison between the observed integrated intensities and the square of the inelastic structure factors for the lowest frequency $q=0$ optic phonon of KTAO$_3$.

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* An average of the two values curently accepted $b(\mathrm{Ti})=-0{\cdot}34\pm0{\cdot}02$ (Shull, Wilkinson & Muller, 1960); $b(\mathrm{Ti})=-0{\cdot}37\pm0{\cdot}01$ (Brookhaven National Laboratory, 1968).

† Wang & Cox (1970).

least-squares minimization at $\sum W(F^2_{\text{obs}}-F^2_{\text{cal}})$. For $RbMnF_3$, however, temperature parameters were fixed to the value obtained from elastic data. Final reliability R values defined by

$$R=\frac{\sum|F^2_{\text{obs}}-F^2_{\text{cal}}|}{\sum|F^2_{\text{cal}}}$$

were 9·6%, 15%, and 19% for $KTaO_3$, $SrTiO_3$ and $RbMnF_3$, respectively.

In Fig. 2 we compare the observed relative intensity for $KTaO_3$ with the square of the inelastic structure factors. The resulting final mode parameters and their standard deviations are listed in Table 2. The observed intensities and calculated square of the structure factors are given in Table 3.

Table 2. *Mode parameters and reliability factors for the three perovskites*

The temperature parameter B (Å^2) is defined in the Debye–Waller factor $\exp\{-B(\sin\theta/\lambda)^2\}$, R and R_w are the unweighted and weighted reliability values, respectively.

	$KTaO_3$	$SrTiO_3$	$RbMnF_3$
B (Å^2)	$0{\cdot}19\pm0{\cdot}07$	$0{\cdot}51\pm0{\cdot}06$	$0{\cdot}86$
S_1	$1{\cdot}0$	$1{\cdot}0$	$-0{\cdot}28\pm0{\cdot}06$
S_2	$-0{\cdot}02\pm0{\cdot}02_5$	$0{\cdot}3\ \pm0{\cdot}1$	$1{\cdot}0$
S_3	$0{\cdot}06\pm0{\cdot}08$	$0{\cdot}01\pm0{\cdot}08$	$-0{\cdot}09_5\pm0{\cdot}06_5$
R	$0{\cdot}096$	$0{\cdot}15$	$0{\cdot}19$
R_w	$0{\cdot}116$	$0{\cdot}18$	$0{\cdot}19$

Although the temperature parameters were refined by the least-squares analysis of the inelastic scattering data, they can also be determined independently by measuring elastic Bragg scattering. An analysis of powder diffraction data of $KTaO_3$ was carried out at room temperature, similarly assuming a single isotropic crystal temperature parameter. The analysis yielded essentially the same temperature parameter $\bar{B}=0{\cdot}2\pm0{\cdot}1$ Å^2, the standard error being rather higher in this case. Similar analyses for $SrTiO_3$ and $RbMnF_3$ were not attempted, but the temperature parameter of $SrTiO_3$ ($B=0{\cdot}51\pm0{\cdot}06$ Å^2) showed very good agreement with the value $B=0{\cdot}45\pm0{\cdot}02$ Å^2 obtained from single crystal X-ray measurements by Harada & Barnea (1970). It was also observed that substantial trial changes of the temperature parameter do not greatly affect the mode parameters although the reliability R value changes. These facts confirm that the least-square refinement of the mode analysis has been carried out in a reasonable way.

Discussion

From Table 2 we see that the atomic motion of the soft optic modes is predominantly a Slater mode for $KTaO_3$ and $SrTiO_3$, namely Ta and Ti atoms move against O_6 octahedron. But, considerably different atomic motions are obtained for the lowest frequency TO mode for $RbMnF_3$, in which case cations vibrate out of phase to the rigid MnF_3 group. Such different atomic motions for oxide and fluoride perovskites can be understood, as already discussed by Axe (1967), as to be due to greater enhancement of the local field for the long-range coupling between B and X_3 ions in the oxide, because of the fact that the oxide ion is roughly twice as polarizable as in the fluoride ion. Therefore, in the fluoride by comparison, the long-range force is not sufficient to cancel out to the short-range repulsive forces.

In principle, it is possible to directly determine such sublattice coupling constants once all the eigenfrequencies and eigenvectors are known by inversion of the lattice dynamical equation. In the present instance, only the three polar mode eigenvectors need to be determined since symmetry considerations uniquely fix the $q=0$ TA mode vector as well as that of the remaining

Table 3. *Observed integrated intensities and calculated square of the inelastic structure factors for the three perovskites, where α is the scale factor*

$KTaO_3$

(h	k	l)	I_{obs}	$\alpha\|F_{\text{inel}}(\text{cal})\|$
1	1	1	128	166
2	0	0	158	139
0	2	2	264	270
3	0	0	5	8
1	2	2	0	15
3	1	1	566	580
2	2	2	361	395
4	0	0	597	513
3	2	2	64	22
4	1	1	88	109
0	3	3	111	141
1	3	3	958	951

$\alpha=15{\cdot}2\pm0{\cdot}6$

$SrTiO_3$

(h	k	l)	I_{obs}	$\alpha\|F_{\text{inel}}(\text{cal})\|^2$
1	1	1	344	483
2	0	0	1158	961
2	1	1	148	116
0	2	2	1628	1758
3	0	0	534	441
1	2	2	624	454
3	1	1	1242	1482
2	2	2	2534	2410
4	0	0	3119	2936
3	2	2	946	706
4	1	1	346	262
0	3	3	455	275
1	3	3	1630	2137
2	3	3	444	304
4	2	2	3525	3679
5	0	0	827	855
3	3	3	2063	2537
5	1	1	2205	2537

$\alpha=44{\cdot}5\pm2{\cdot}0$

$RbMnF_3$

(h	k	l)	I_{obs}	$\|\alpha F_{\text{inel}}(\text{cal})\|^2$
2	1	1	780	577
0	2	2	13	3
1	2	2	220	98
3	0	0	144	156
3	1	1	474	420
2	2	2	91	5
4	0	0	46	6
3	2	2	348	196
4	1	1	1324	1391
0	3	3	1216	1157
1	3	3	378	608
5	0	0	374	305
3	3	3	664	725

$\alpha=45{\cdot}8\pm2{\cdot}6$

nonpolar TO mode. Particularly for the oxides, however, direct determinations of the remaining TO mode eigenvectors is complicated by the near degeneracy of TO and LO modes (Barker, 1966). However, in order to get some qualitative insight into the sublattice coupling constants, we may assume the highest frequency mode to be well approximated by $\mathbf{s}_3$ alone and use the mode orthogonality property to fix the form of the remaining polar mode.

As expected, the results obtained in this manner show that the strongest coupling constant is between X_1 and X_3 sublattices for all the three substances. On the other hand, very weak coupling can be seen between B and X_3 for $SrTiO_3$ and $KTaO_3$, but no such peculiarly weak coupling between any ion pairs in $RbMnF_3$. These results serve to verify our conclusion that the cancellation of long and short range coupling which exists between $B-X_3$ sublattices in the oxides is not present in the fluoride.

The atomic motion of the TO modes for $SrTiO_3$ has been calculated by Cowley (1964), using interatomic force constant obtained from fitting to the experimentally determined phonon dispersion curves. These atomic displacements for the lowest $q=0$ TO mode, decomposed on the basis of the same symmetry coordinates used in this work are:

$$S_1=1{\cdot}0\,,\quad S_2=0{\cdot}287\,,\quad S_3=0{\cdot}247$$

where S_1 is scaled to unity.

Comparing this result with the present one, fairly good agreement can be seen for $\mathbf{s}_1$ and $\mathbf{s}_2$ components, but considerable discrepancy exists for $\mathbf{s}_3$. A substantial $\mathbf{s}_3$ contribution indicates a distortion of the oxygen octahedra and such a distortion is observed to condense into the tetragonal form of $BaTiO_3$ (Frazer, Danner & Pepinsky, 1955; Harada, Pedersen & Barnea, 1970). On the other hand, tetragonal $PbTiO_3$ seems not to involve the condensation of any $\mathbf{s}_3$ component (Shirane, Pepinsky & Frazer, 1956).

In order to investigate more closely vibrational displacements of the $\mathbf{s}_3$ type in $SrTiO_3$ the fit of the reflections with mixed (*i.e.* even–odd) indices (which alone are sensitive to $\mathbf{s}_3$ displacements) were separately refined by adjustment of the scale factor first for the set of displacements given in Table 2, then for those determined from the model calculation. The former (small $\mathbf{s}_3$ contribution) gave an R value of 6·8%, the latter an R value of 40%. We conclude, therefore, that our data do not support the existence of substantial octahedra distortion in the lowest frequency optic mode.

Several anharmonic contributions which would have the effect of introducing a temperature dependence into the apparent harmonic structure factor [equation (1)], can be conceived. However, Yamada & Shirane (1969) found that the intensity of the $q=0$ soft mode scattering in $SrTiO_3$ could be made to fit quite accurately with a temperature independent structure factor over a wide range of temperature even though that is not the case for modes away from $q=0$. A similar effect was also observed in $KTaO_3$ (Axe, Harada & Shirane, 1970). We must, therefore, conclude that anharmonic effects upon the intensity are relatively unimportant for the modes studied here, even though there are large anharmonic effects on the phonon frequencies for the two oxides. The lack of anharmonic effects on the intensity at $q=0$ can be understood as follows. First of all, the acoustic–optic mode interaction vanishes at $q=0$ (Axe, *et al.* 1970). Also the interference between one and multiphonon scattering processes, which has recently been discussed by Cowley, Svensson & Buyers (1969), can be shown to vanish at $q=0$ in centrosymmetric lattices.

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