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Symmetry and Lattice Dynamics of Oxides with Perovskite-like Structures

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Based on a topological definition the possible space groups for a perovskite-like structure are derived for small unit cells. The irreducible representations are calculated from them for interpretation of the phonon spectra. To compare the character of the bonds in some oxides, Raman spectra have been taken and interpreted on the basis of a simple lattice-dynamical model. It was found that covalent interaction occurs in Na_xWO_3 and XIO_3 ($X=NH_4,K,Rb,Cs$) whereas titanates and niobates are mainly ionic. A model for classification of perovskite-like compounds is discussed.

1. Introduction

Structures with topological similarities to $CaTiO_3$ are called perovskite-like. The highest possible symmetry with the smallest elementary cell is characterized by the space group O_h^1. Nearly all structures observed show lower symmetry caused by deformations of the crystal lattice (Megaw, 1957; Glazer, 1972). These deformation structures are often correlated with important physical effects typical of most of these crystals, such as ferroelectricity, ferroelasticity, piezoelectricity, and optical activity.

In some cases, the deformation vectors can be thought of as amplitudes of frozen phonons in the soft-mode model as derived by Cochran (1960), Cowley (1964) and others. The most critical phonons are the Slater mode (Slater, 1950) T_{1u} in the centre of the Brillouin zone ($BaTiO_3$), the corresponding M-phonon at the zone surface (WO_3), and the R_{25} mode ($SrTiO_3$). The resulting deformation structures are typical for structures with strongly electrostatic bonds. In fact, as in WO_3, these effects are often superposed by covalent interactions leading to complex structures of the perovskite type.

In this paper the related space groups and their irreducible representations are given for $Z=1$, 2, and fourfold elementary cells. The results are compared with measurements made by Raman spectroscopy. A separation of the bonding types is then possible by examination of the effective ionic charges.

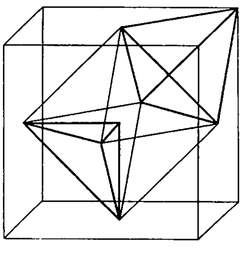


Fig. 1. Simplexes AO_3' and BO_3 (left side) in a simple unit cell ($Z=1$).

II. The possible space groups

A consideration of the topological similarities of these ABO_3 structures must be based on the types of coordination polyhedra and their mutual relationships and not on lattice constants. In the concept of algebraic topology, this can be defined with the help of simplexes, considering the periodic repetition of the elementary cell in the lattice. If the equivalent sides of the cell are identified, the structure is built up of $8Z$ three-dimensional simplexes $(BO)_3$ with:

$$\text{ex. } \{BO_3^i, i=1\cdots 8\}:\ \bigcap_i BO_3^i = B_0$$
$$\forall BO_3^i:\ BO_3^j \in \{BO_3^i\},\ j=1,2,3 \quad \text{with } \bigcap_i BO_3^i,\ BO_3^j = BO_1$$
$$\forall BO_3^i:\ BO_3^j \in \{BO_3^i\},\ j=1,2,3 \quad \text{with } BO_3^i \cap BO_3^j = BO_2.$$

Each simplex BO_3^i connects six complexes with zero-dimensional section 0_0.

Analogously:

$$\text{ex. } \{AO_3^i, i=1\cdots 8\}:\ \bigcap_i AO_3^i = A_0$$
$$\forall AO_3^i:\ AO_3^j \in \{AO_3^i\} \text{ with } \bigcap_i AO_3^i,\ AO_3^j = AO_2^k$$
$$\forall AO_3^i:\ AO_3^m \in \{AO_3^j\} \text{ with } \bigcap_i AO_3^i,\ AO_3^m = AO_1^l,$$
$$l=1,2,\ m=1\cdots 4.$$

The subscripts denote the dimension of the simplexes; Z is the number of complexes in the unit cell.

A picture of a possible choice of simplexes is given in Fig. 1. Here AO_3' denotes the hole between the simplexes. With the help of these it is possible to define a 'degree of interaction'. This degree is called n if a way can be constructed from two positions, containing n three-dimensional simplexes as a minimum. The number of equivalent ways is typical for the type of structure. In the case of perovskite-like structures there are three minimal ways A to B (A–O–B) and only one minimal way B_1 to B_2 (B_1–O–B_2) and A_1 to A_2 (A_1–O–A_2) respectively. This definition is analogous to that of

Megaw (1957), who considers $LiNbO_3$ as a compound with a perovskite-like structure in contrast to Keith & Roy (1954).

If the topologically defined structure is set into metrical space, it is possible to evaluate the resulting symmetries and hence the space groups. For small cells ($Z \leq 4$) which correspond to the classes 1 and 2 defined by Megaw (1957); this is done in Table 1. The space groups are derived according to the choice of the elementary cell and the zellengleichen Obergruppen-relation (Boyle & Lawrenson, 1972). The irreducible representations of some of the space groups are derived by a factor group analysis and compiled in Table 2.

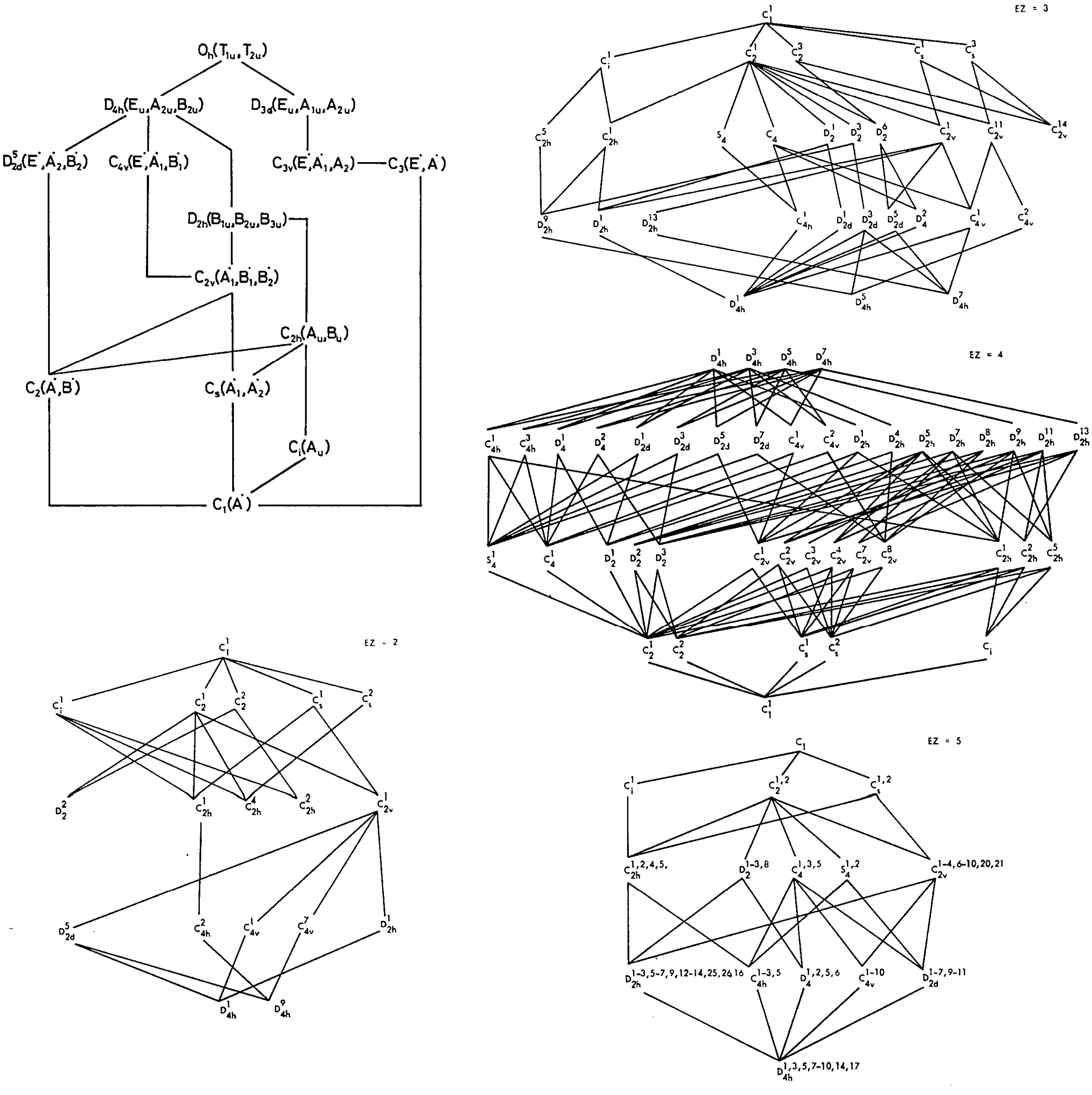
III. Lattice-dynamical models

As a consequence of the symmetry, the transformation behaviour of the lattice-dynamical interaction matrices changes from isotropy. The secular equation in the rigid-ion model (Born & Huang, 1954) is given by:

$$M\omega^2 U = (R + Z'CZ)U\ .$$

For computing the real phonon frequencies ω, the more complex shell model (Cochran, 1960) has to be

Table 1. *The zellengleiche Obergruppenrelation for the space groups with* $Z=1$, $Z=2$ $(EZ=2,3)$, *and* $Z=4$ $(EZ=4,5)$



used. To understand the crystal chemistry of perovskite-like compounds the most interesting parameter is the relation between the short range forces R and the Coulomb forces $\mathbf{Z}'\mathbf{C}\mathbf{Z}$; $\mathbf{Z}$ is the vector of the effective ionic charges and $\mathbf{C}$ the matrix containing the Coulomb coefficients (Cowley, 1964). Neglecting the additional shell polarizabilities in the shell model, a simple model has been used to compare the bonding behaviour of the compounds investigated experimentally. Hence only the relative values of R and $\mathbf{Z}$ can be taken into account and it is incorrect to use these values for other types of structure.

As the Coulomb coefficients C have a smooth dependence on the deformation of the structure, they are assumed to be constant. It is then possible to give a simple approximation for the phonon frequencies:

$$T_{1u}(\mathrm{A{-}BO_3}):\ A_1+2B_1=\tfrac{1}{2}[1/(3m_\mathrm{O}+m_\mathrm{B})+1/m_\mathrm{A}{}^{-1}\omega_4^2$$

$$T_{1u}(\mathrm{B{-}O,\ O{-}O}):\ \omega_3^2=B_2(1/m_\mathrm{BO}+\tfrac{1}{2}m_\mathrm{O}) + 2A_3/m_\mathrm{O},\ B_3\approx 0$$

$$T_{2u}(\mathrm{O{-}O}):\ \omega_1^2=B_2(1/m_\mathrm{B}+1/m_\mathrm{O})+2A_3/m_\mathrm{O},\ B_3\approx 0$$

$$B_2\approx(\omega_1^2-\omega_3^2)\ [1/(m_\mathrm{B}+m_B^2/m_\mathrm{O})+\tfrac{1}{2}m_\mathrm{O}]$$

$$T_{1u}(\mathrm{B{-}O}):\ A_2=(1/m_\mathrm{O}+1/m_\mathrm{B})^{-1}\omega_2^2 + (3/m_\mathrm{O}+1/m_\mathrm{B})^{-1}\omega_3^2$$

Table 2. *Space groups, Wykoff position* (W), *number of symmetry coupled positions* (N), *maximum local symmetry* (*symm.*), *degree of interaction* (*d.i.*), *and the irreducible representations for simple and twofold unit cells*

Space group	EZ	W	N	Symm.	d.i.	Irreducible representations
C_1^1	1	*a*	1	1	–	$12A$
C_i^1	1	*aefgh*	1	$\bar{1}$	–	$12A_u$
C_{1h}^1	1	*ab*	1	*m*	–	$8A'$, $4A''$
C_2^1	1	*abcd*	1	2	–	$4A$, $8B$
C_{2h}^1	1	*ahefg*	1	$2/m$	–	$4A_u$, $8B_u$
C_{2v}^1	1	*abcd*	1	*mm*	–	$4A_1$, $4B_1$, $4B_2$
D_{2d}^5	1	*abdg*	2	$\bar{4}2m$	1	$4B_2$, $4E$
C_{4v}^1	1	*abc*	2	$4mm$	1	$3A_1$, B_1, $4E$
D_{2h}^1	1	*ahfdg*	1	*mmm*	–	$4B_{1u}$, $4B_{2u}$, $4B_{3u}$
D_{4h}^1	1	*adce*	2	$4/mmm$	1	$3A_{2u}$, $4E_u$, $1B_{2u}$
O_h^1	1	*abc*	3	$m3m$	1	$3T_{1u}+T_{2u}$
D_{4h}^1	2	*abhcdi*	4	$4/mmm$	2	$2A_{1g}$, B_{1g}, B_{2u}, $6E_u$, $3E_g$, $5A_{2u}$
D_{4h}^9	2	*abif*	4	$\bar{4}2m$	2	B_{2g}, A_{1g}, B_{1g}, $3E_g$, A_{1u}, $2A_{2u}$, $2B_{2u}$, B_{1u}, $6E_u$
D_{2d}^5	2	*absdfg*	2	$\bar{4}2m$	3	$3A_1$, $6B_2$, $9E$
D_{4v}^1	2	*abc*	2	$4mmm$	1	$7A_1$, $2B_1$, $9E$
C_{4v}^7	2	*abc*	2	*mm*	3	$4A_1$, $5B_1$, $9E$
D_{2h}^1	2	*actfhsr*	2	*mmm*	2	$3A_g$, $3B_{2g}$, $6B_{1u}$, $3B_{3g}$, $6B_{2u}$, $6B_{3u}$
C_{4h}^2	2	*afbi*	4	$\bar{4},2/m$	2	$3A_u$, $3B_u$, $6E_u$, A_g, $2B_g$, $3E_g$
D_2^2	2	*adbc*	2	2	2	$5A$, $6B_1$, $4B_2$, $9B_3$
C_{2h}^2	2	*aed*	2	m, $\bar{1}$	2	$11A_u$, $7B_u$, $3A_g$, $6B_g$
C_{2h}^4	2	*abef*	2	$2,\bar{1}$	2	$4A_u$, $3A_g$, $6B_u$, $6B_g$
C_{2v}^1	2	*ablghkj*	2	$2/m$	2	$9(A_1B_1B_2)$
D_{4h}^7	3	*ace*	4	$\bar{4}2m$ $4mm$	2	A_{1g}, B_{1g}, B_{2g}, $2E_g$, A_{1u} $2A_{2u}$, B_{1u}, $2B_{2u}$, $5E_u$
D_{4h}^5	3	*acdh*	4	$4/m,mmm$	2	A_{1u}, $4A_{2u}$, $4B_{2u}$, $9E_u$
D_{4h}^1	3	*acefk*	4	$4/mmm$	2	A_{1g}, B_{1g}, $3E_g$, $4A_{2u}$, $3B_{2u}$, $7E_u$
D_{2d}^5	3	*abgi*	4	$\bar{4}2m$	2	$3A_1$, A_2, B_1, $4B_2$, $9E$
D_{2d}^3	3	*ace*	4	$\bar{4},mm$	2	$3A_1$, $3A_2$, $4B_1$, $3B_2$, $7E$
D_{2d}^1	3	*adfen*	4	$\bar{4}2m$	2	A_1, $5A_2$, $3B_1$, $4B_2$, $7E$
C_{4v}^2	3	*abc*	4	$4,mm$	2	$5A_1$, $2A_2$, $5B_1$, B_2, $7E$
C_{4v}^1	3	*abcd*	4	$4mm$	2	$6A_1$, A_2, $5B_1$, B_2, $7E$
D_4^2	3	*acf*	4	4,222	2	$3A_1$, $5A_2$, B_1, $4B_2$, $7E$
C_{4h}^1	3	*acefk*	4	$4/m$	2	$4A_u$, $3B_u$, $3E_u$, $2A_g$, $2B_g$, E_g
S_4^1	3	*acgh*	4	4	2	$5A$, $6B$, $8E$
C_4^1	3	*abcd*	4	4	2	$6A$, $5B$, $8E$
D_{2h}^{13}	3	*abd*	4	$mm,\bar{1}$	2	$3(A_g, B_{2g}, B_{3g}, A_u)$, $5(B_{1u}, B_{2u}, B_{3u})$
D_{2h}^9	3	*acdh*	4	$2/m$	2	$2A_g$, $2B_{1g}$, B_{2g}, B_{3g}, $4A_u$, $3B_{1u}$, $7B_{2u}$, $7B_{3u}$
D_{2h}^1	3	*afdgbez*	4	*mmm*	2	$2A_g$, $2B_{1g}$, B_{2g}, B_{3g}, A_u, $6B_{1u}$, $7B_{2u}$, $7B_{3u}$
C_{2v}^{14}	3	*abe*	4	*mm*	2	$13A_1$, $13B_2$, $9B_1$, $4A_2$
C_{2v}^{11}	3	*abc*	4	$mm,2$	2	$9A_1$, $4A_2$, $13B_1$, $13B_2$
C_{2v}^8	3	*abc*	4	2	2	$5A_1$, $6A_2$, $8B_1$, $8B_2$
C_{2v}^1	3	*adcbi*	4	*mm*	2	$8A_1$, $3A_2$, $8B_1$, $8B_2$
D_2^6	3	*abck*	4	222	2	$2A$, $7B_1$, $9B_2$, $9B_3$
D_2^3	3	*abc*	4	2	2	$6A$, $5B_1$, $8B_2$, $8B_3$
D_2^1	3	*abcefgu*	4	222	2	$3A$, $8B_1$, $8B_2$, $8B_3$
C_{2h}^5	3	*adce*	4	$\bar{1}$	2	$3A_g$, $3B_g$, $11A_u$, $10B_u$
C_{2h}^1	3	*abdgefo*	4	$2/m$	2	$3A_g$, $3B_g$, $8A_u$, $8B_u$
C_s^3	3	*ab*	4	*m*	2	$11A'$, $16A''$
C_s^1	3	*abc*	2	*m*	2	$18A'$, $9A''$
C_2^3	3	*abc*	4	2	2	$11B$, $16A$
C_2^1	3	*abcde*	2	2	2	$18A$, $9B$

$$\mathbf{Z}_\mathrm{A}^2 \approx [1/(3m_\mathrm{O}+m_\mathrm{B})+1/m_\mathrm{A}]^{-1}[\omega_4^2(\mathrm{LO})-\omega_4^2(\mathrm{TO})]/4\pi$$

$$\mathbf{Z}_\mathrm{B}\mathbf{Z}_\mathrm{O} \approx \{[1/m_\mathrm{O}+1/m_\mathrm{B}]^{-1}[\omega_2^2(\mathrm{LO})-\omega_2^2(\mathrm{TO})] + [3/m_\mathrm{O}+1/m_\mathrm{B}]^{-1} \times [\omega_3^2(\mathrm{LO})-\omega_3^2(\mathrm{TO})]\}1/34{\cdot}3$$

$$\mathbf{Z}_\mathrm{A}+\mathbf{Z}_\mathrm{B}+3\mathbf{Z}_\mathrm{O}=0\,.$$

These formulae hold good if the effective ionic charges are small and the BO_6 groups can be taken as separated complexes. The principal form of the resulting terms is given in Fig. 2. However, if the intramolecular forces A_2 and B_2 are too strong, this approximation corresponds to the molecular force approximation. In the latter case the BO_x complex is taken as a rigid molecule. Hitherto we have observed two types of complexes: a nearly pyramidal complex (*e.g.* IO_3) and an approximately tetragonal complex (*e.g.* WO_4 in WO_3). The connexion between both approximations is:

Pyramidal:

$$\omega_{2,1}^2+\omega_{3,1}^2=\left(1+3\frac{m_\mathrm{O}}{m_\mathrm{B}}\cos^2\beta\right)A_2/m_\mathrm{O}+3A_3'/m_\mathrm{B},\quad A_3'=A_3(B_2)$$

$$\omega_{2,1}^2\omega_{3,1}^2=\left(3+9\frac{m_\mathrm{O}}{m_\mathrm{B}}\right)\cos^2\beta A_2A_3'/m_\mathrm{O}^2$$

$$\omega_{2,2}^2+\omega_{3,2}^2=(1+3m_\mathrm{O}/2m_\mathrm{B}\sin^2\beta)A_2/m_\mathrm{O}+3A_3'/2m_\mathrm{B}$$

$$\omega_{2,2}^2\omega_{3,2}^2=\left(\tfrac{3}{2}-\tfrac{3}{4}\sin^2\beta+\tfrac{9}{4}\frac{m_\mathrm{O}}{m_\mathrm{B}}\sin^2\beta\right)A_2A_3'/m_\mathrm{O}^2$$

Tetrahedral:

$$\omega_{2,1}^2=A_2/m_\mathrm{O},\ \omega_{3,1}^2=3B_2'/m_\mathrm{O},\ B_2'=B_2(A_3)$$

$$\omega_{2,2}^2+\omega_{3,2}^2=\frac{A_2}{m_\mathrm{O}}(1+4m_\mathrm{O}/3m_\mathrm{B})+2\frac{B_2}{m_\mathrm{O}}(1+8m_\mathrm{O}/3m_\mathrm{B})$$

$$\omega_{2,2}^2\omega_{3,2}^2=2A_2B_2'/m_\mathrm{O}^2(1+4m_\mathrm{B}/m_\mathrm{O})\,.$$

The ionic charges vanish in this pure covalent model.

IV. Experimental

Crystals of Na_xWO_3 ($x \le 0{\cdot}28$), NH_4IO_3, KIO_3, $CsIO_3$, $RbIO_3$, and (Ba, Sr) NbO_3 have been examined by Raman spectroscopy. The experimental arrangement has been described (Salje, 1974). All crystals had a minimum size of 0·01 mm^3, and it was possible to use single crystals for spectroscopy. No correction for the spatial dependence of the scattering frequency has been made. In Na_xWO_3, the separation of low-frequency longitudinal and transverse phonons was made with the forward scattering arrangement (Salje, 1975). For cooling the crystals a commercial cryostat was used. The temperature during the cycle of measurement of approximately 30 min was kept constant to ± 2°.

V. Results

The Raman spectra of the iodates and (Ba, Sr) NbO_3 are shown in Fig. 3. The latter shows strong irregular line-broadening effects like $BaTiO_3$. The phonon frequencies of the iodates are compared in Fig. 4. The high-frequency band near 750 cm^{-1}, typical for octa-

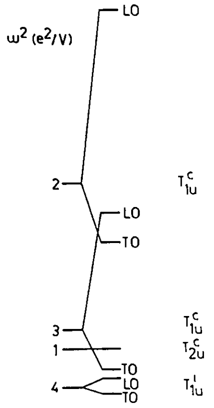


Fig. 2. A schematic diagram showing the phonon frequencies in a pure covalent (left) and an ionic crystal (right) in the approximation used.

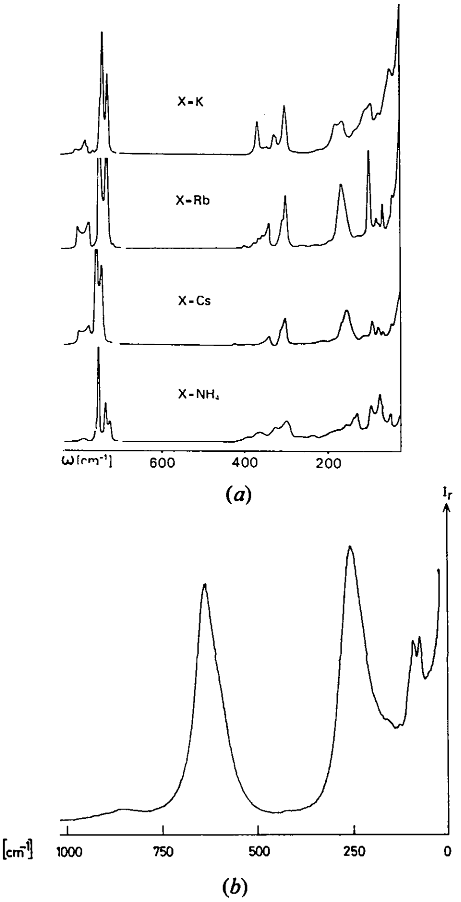


Fig. 3. Raman spectra of (*a*) XIO_3 ($X=K,Rb,Cs,NH_4$) and (*b*) $(Ba,Sr)NbO_3$. The intensities of all high-frequency Raman lines are $\times 10^{-1}$ in the iodates.

hedrally coordinated I, is nearly the same for all these crystals. It was discussed earlier (Salje, 1975; Viswanathan & Salje, 1975) that the fine structure of this band can be understood for NH_4IO_3 by the scattering of nearly pyramidal IO_3 groups. The typical aspect of the iodates is therefore the deformation of the I positions from the octahedra centre in one of the [111] directions, accompanied by a destruction of the octahedra. Hence the iodates are examples of a perovskite-like structure with deformations caused by short-range covalent effects.

An analogous deformation was found in the Na–W bronzes. These compounds are semiconductors at room temperature and insulators in the low-temperature phase (Salje & Viswanathan, 1975). The structure of pure WO_3 at room temperature was solved by Tanisaki (1960) and at low temperatures by Salje (1976). The main feature of the structures is the quasi-tetrahedral coordination of W. In accordance with this rather unusual environment the Raman spectrum shows four lines directly correlated to W–O interactions of nearest neighbours at 719, 808, 275 and 330 cm^{-1}. These lines can be interpreted as due to the tetrahedral bonds of WO_4. On the other hand, it is also possible to describe the spectrum as a group of well-split T_{1u} lines with lost parity. In both models the effective ionic charge of W is small. A longitudinal–transverse splitting can be detected in the low-frequency range. These phonons are approximately Γ-phonons detectable in the Raman experiment. Really they must be seen as M-phonons (in the smaller subcell) which become Raman active as a result of the superstructure, caused by the zig-zag arrangement of the W positions and the torsions of the deformed octahedra. Hence this splitting is correlated with the acoustic branches. The effective ionic charges (with $C_T = -4\pi/3$ and $C_L = +8\pi/3$) in Table 3 are now attributed to the WO_4 complexes.

With increasing Na content in Na_xWO_3 only a small change can be detected in the high-frequency part of

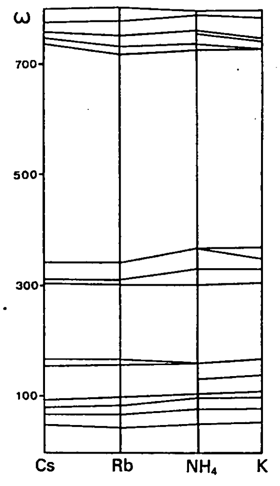


Fig. 4. Measured Raman frequencies in some iodates.

Table 3. *Calculated force constants and effective ionic charges*

	$SrTiO_3$	$BaTiO_3$	$LiNbO_3$	$(Ba,Sr)NbO_3$	WO_3	KIO_3	NH_4IO_3	$RbIO_3$	$CsIO_3$
e^2/V	14 14 14								
$\omega_1^2m_O$	138 59 111	130 67 109	190 89 157	183 103 156	161–124	158 136 151	155 140 150	150	150
$\omega_2^2m_O$	47 6 20	56 18 31	48 16 26	71 17 35	26– 17	34 23 26	34 24 26	28	25
$\omega_3^2m_O$	6 2 3	8	10 2 5	2	4 1 2	6	14 6 9	3 – 7	2 – 7
$\omega_4^2m_O$	LO TO O	LO TO O	LO TO O	LO TO O	LO TO O	LO TO O	LO TO O	LO TO O	LO TO O
A_1+2B_1	4·86	13·4	1·0	4·8		5·6	4·6	5 – 13	5 – 17
A_2	89·8	90·9	142	144	156 – 120	142	141	142	141
B_2	−10·2	[−10·2]	−21·3	−8·2	−24 – −39	−22·2	−22·8	−20	−24
A_3	13·9	19·2	[20]	[20]	[20]	[20]	[20]	[20]	[20]
$Z(A)$	1·0		0·5				0·8		
$Z(B)$	2·1	2·2	2·86	2·32	0·4	0·87			
$Z(O)$	−1·05	−1·2	−1·13			−0·56			

the spectrum ($\nu \geq 200$ cm^{-1}). The lowest phonon shows a critical behaviour. This phonon is Raman active in the ($x \leq 0{\cdot}28$) metallic phase. This Γ-phonon becomes really a M-phonon, because the superstructure vanishes. As the deformation structure of WO_3 can be described as caused by a soft-mode behaviour of these phonons, they have to be critical at the point of phase transition to the cubic phase. This transformation is brought about not by temperature but by chemical composition. The application of the lattice-dynamical model to the measured phonon frequencies gives the short-range parameters and effective ionic charges listed in Table 3. For comparison the parameters for $LiNbO_3$, $BaTiO_3$, and $SrTiO_3$ taken from Claus & Schrötter (1971), Burstein (1969), and Cowley (1964) are computed with the same model and collected in Table 3.

VI. Discussion

The calculated strength of B–O bonds, the effective ionic charges, and the symmetry behaviour of the short-range coupling shows that perovskite-like structures can be classified into two types depending upon the deformation: those with primarily covalent B–O interactions (*e.g.* iodates) and those with long-range ionic interactions. If the latter predominate, two typical ionic deformation structures can be distinguished:

(1) the $BaTiO_3$ type with critical behaviour of the Slater mode, and

(2) the $SrTiO_3$ type with freezing of one more of the R_{25} modes at the zone boundary, leading to rotations of the BO_6 octahedra against each other.

Both ionic types should not be restricted to the tetragonal phase of $BaTiO_3$ and $SrTiO_3$, but expanded in other points of the Brillouin zone. Hence also the corresponding M-phonons to the T_{1u} mode causing antiferroelectric structures belong to this type. Similarly all rotational modes (as in $LiNbO_3$) along the various crystallographic axes – clockwise or counterclockwise – are included in type (2). The resulting possible combinations of this type are compared with the symmetries by Glazer (1972).

The torsions of deformed octahedra may also occur in mainly covalent structures such as NH_4IO_3. In such cases an interpretation may be based on a soft-mode behaviour of the R_{25} mode. However, they are more likely to be caused by the tendency of the structure to minimize the Gibbs free energy by minimizing the molar volume.

The appearance of ferroelectricity in perovskite-like structures is correlated to the critical behaviour of soft modes, often leading to distortive phase transformations as discussed by Gränicher & Müller (1971). Helg (1970) has shown in KIO_3 that ferroelectricity is also possible in mainly covalent compounds. The soft-mode behaviour of these crystals is extremely complicated (Salje, 1974) and the phase transformation cannot be interpreted by a critical slowing down of a single mode. Likewise the field-induced transformations do not merely translate the sublattices but reorientate complexes like IO_3. Hence ferroelectricity is not restricted to ionic compounds of type (1) but may also be found in more or less covalent crystals if the BO_x complexes already contain a spontaneous polarization.

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