

Zone Center Phonons of Orthorhombic Perovskite YAlO_3

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A short range force constant model has been applied to investigate the phonons in YAlO_3 perovskite in the orthorhombic phase. The calculations with six stretching and one bending force constants provide a satisfactory agreement for the available Raman frequencies. Based on the present calculations, the infrared frequencies have been assigned for the first time. © 1999 Academic Press

INTRODUCTION

The properties of distorted perovskite YAlO_3 have recently become quite important as manganese doped yttrium orthoaluminate is seen as a potential material for holographic recording and data storage (1), Nd doped YAlO_3 is used for medical laser applications (Moncargb *et al.* (2)), titanium doped YAlO_3 had found application as a laser material (3), and $\text{YAlO}_3(\text{YAP})$ camera has been found suitable for radio-pharmaceutical research (4). Further, YAlO_3 exhibits a lot of similarity with another distorted perovskite YMnO_3 where substitution of Y by Ca, Sr, or Ba results in structural changes and the occurrence of colossal magnetoresistance near the temperatures of spin ordering of Mn ions (5). Since the properties like magnetic ordering and structural phase changes will effect the phonon frequencies, in this paper, an attempt is being made to investigate the phonon frequencies at the zone center, i.e., the Raman and the infrared frequencies in the case of YAlO_3 in its orthorhombic phase.

A Raman study of YAlO_3 in its orthorhombic phase was made experimentally by Udagawa *et al.* (6). They observed and assigned 19 Raman modes out of 24 in case of YAlO_3 . However, to our knowledge, no theoretical calculations of the zone center frequencies of YAlO_3 have been made. Hence, we have applied a short range force constant model involving various stretching and bending force constants to evaluate the Raman and the infrared frequencies in the case of orthorhombic YAlO_3 . The calculated Raman modes exhibit a satisfactory agreement with the experimental observations of Diehl *et al.* (7). Also, for the first time, an

assignment of infrared frequencies to specific modes has been made. It is expected that such a calculation will provide an insight into the understanding of the structural phase transition in these perovskites.

THEORY

The structure of YAlO_3 is orthorhombic with space group $Pnma$, $Z = 4$ ($a = 5.330 \text{ \AA}$, $b = 7.375 \text{ \AA}$, $c = 5.180 \text{ \AA}$) (7). The orthorhombic unit cell of the crystal structure of YAlO_3 with subunits corresponding to the ideal cubic perovskite unit cell are shown in Fig. 1. The Al atoms are present at the centers of distorted octahedra formed by O atoms.

Group theoretical treatment of the zone center phonons yield

$$\Gamma = 7A_g \oplus 5B_{1g} \oplus 7B_{2g} \oplus 5B_{3g} \oplus 8A_u \oplus 10B_{1u} \oplus 8B_{2u} \oplus 10B_{3u}$$

with four Raman active modes of the species A_g , B_{1g} , B_{2g} , B_{3g} ; three infrared active modes of the species B_{1u} , B_{2u} , B_{3u} , and A_u as the inactive mode.

The lattice dynamics calculations were carried out according to the Wilson-GF matrix method (8) on the basis of cartesian symmetry coordinates. The dynamical matrix is given by

$$D = M^{1/2}FM^{1/2},$$

where M is a diagonal matrix specifying the masses of the atoms involved. The force constant matrix F is represented by the short range stretching interactions with valence and repulsive force constants K_i and f_i and the bending force constants H_i .

In an ABO_3 orthorhombic perovskite structure, the rigid network is formed from the linkage of BO_6 octahedra where B -O bonds are relatively strong and short (at distances 1.9015, 1.9105, and 1.9208 \AA). The B cations exhibit an electronegativity (1.5 for Al) such that B -O bonds are rather covalent whereas A cations with low electronegativity (1.2 for Y) generally establish A -O bonds exhibiting an ionic

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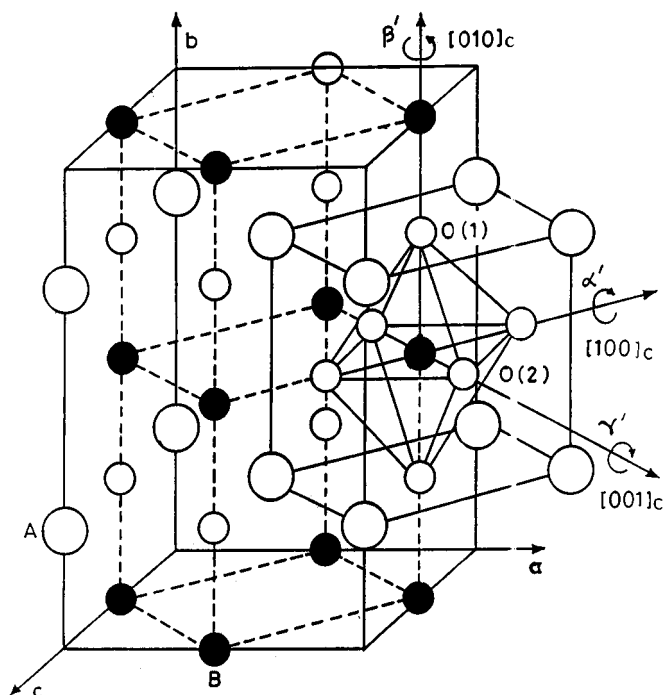


FIG. 1. Crystal structure of ABO_3 . An orthorhombic unit cell with subunits corresponding to the ideal cubic perovskite unit cell are drawn. The pseudocubic subcell directions (subscript c) define the directions of rotations of the octahedra.

character. Further, in a perovskite structure, all $B-O$ bonds ($Al-O1$, $Al-O2$) play an equivalent role in the structure and thus they all are assigned the same force constant value, as their bond lengths are also nearly the same. However, in AO_{12} polyhedra, the $A-O$ bond lengths exhibit significant differences due to larger distortion in the perovskite structure. The $Y-O1$ bond at length (2.237 \AA) has ionic character, and hence the interatomic force constant $Y-O1$ at this bond length has been considered to be slightly weaker. The $Y-O2$ bonds in YO_{12} polyhedra have been considered to play an equivalent role as their bond lengths do not significantly differ. Further, two stretching force constants between $O1-O2$ (bond lengths 2.6805 , 2.7249 \AA) and $O2-O2$ (bond lengths 2.7091 , 3.0385 \AA) have been considered explicitly. Thus, in all, six stretching force constants at various interatomic force distances as given in Table 1 have been used in the present calculations. In order to account for the distortion in perovskite structure, especially the YO_{12} polyhedra, one bending force constant for $O1-Y-O2$ (angle 108.495) has been considered.

The input parameters are the unit cell dimensions, the fractional coordinates as given in Diehl *et al.* (7), the masses of the atoms, the symmetry coordinates, and the phonon frequencies. The interatomic force constants given in Table 1 were obtained by having a best fit to the measured Raman frequencies.

RESULT AND DISCUSSION

The Raman frequencies evaluated using the force constants as given in Table 1 are presented in Table 2 along with the observed values due to Udagawa *et al.* (6). The atomic displacements for atoms are also given in the table. It should be pointed out that a very good fitting of the Raman frequencies to obtain the physically reasonable interatomic force constants according to the structural dynamics of more distorted perovskite structure $YAIO_3$ has been quite difficult. The only significant discrepancy is for the lowest Raman frequencies, which could not be corrected by incorporating other interatomic force constants also. It may be pointed out that for these lowest frequencies, Iliev *et al.* (9) had obtained even worse agreement with the shell model lattice dynamics calculations in the case of $YMnO_3$ and $LaMnO_3$.

In Table 3, we exhibit the presently calculated infrared frequencies for the first time to our knowledge along with the atomic displacements for various atoms. Precise infrared experiments are needed to verify these theoretical values in case of $YAIO_3$.

The main results of the lattice dynamical calculations are:

1. The same kind of atoms (like $Y-O2$, $O1-O2$, $Al-O2$) behave similarly at nearly the same distances as these were combined together satisfactorily to reduce the interatomic force constants.
2. The stretching interatomic force constant between $O1-O2$ and $O2-O2$ atoms should be considered explicitly.
3. The bending force constants should be taken into account in the case of YO_{12} polyhedra, but not for AlO_6 octahedra.

TABLE 1
Interatomic Distances, Coordination Number, and Interatomic Force Constant Values

Interatomic interaction between	Interatomic distances (\AA)	Angle	Coordination number	Force constant	Force constant value (N/cm)
$Al-O1$	1.9015		8	K1	0.967
$Al-O2$	1.9105		8		0.967
$Al-O2$	1.9208		8		0.967
$Y-O1$	2.237		4	K2	0.590
$Y-O1$	2.3061		4	K3	0.839
$Y-O2$	2.2843		8	K4	0.457
$Y-O2$	2.4807		8		0.457
$Y-O2$	2.5691		8		0.457
$Y-O2$	3.2604		8		0.457
$O1-O2$	2.6805		8	f1	0.451
$O1-O2$	2.7249		8		0.451
$O2-O2$	2.7091		4	f2	0.386
$O2-O2$	3.0385		8		0.386
$O1-Y-O2$		108.4958		H1	0.385

TABLE 2
Calculated Zone Center Frequencies (in cm⁻¹) in the Orthorhombic Phase of YAIO₃ Compared to Experimental Values Obtained by Udagawa *et al.* (6) and Atomic Displacements for Various Atoms

Species	Present calculated values	Experimental values	Atoms							
			Y	Y	O1	O1	O2	O2	O2	
<i>A_g</i>	554.0	553.0	0.07	0.05	-0.36	0.56	-0.07	0.45	-0.58	
	539.8		-0.16	0.21	0.30	0.44	0.54	0.37	0.46	
	423.9		412.0	-0.05	-0.26	-0.38	0.28	-0.55	0.11	0.63
	343.7		345.0	0.03	-0.14	0.28	-0.48	-0.23	0.78	-0.01
	288.5		278.0	-0.06	-0.34	0.72	0.41	-0.36	-0.17	-0.18
	185.2		197.0	-0.83	0.46	0.01	-0.06	-0.30	-0.01	-0.09
<i>B_{1g}</i>	110.3	540.0	0.52	0.74	0.18	0.07	-0.37	-0.03	0.11	
	629.8		-0.02		0.89		0.35	0.28	-0.03	
	572.4		-0.06		-0.27		-0.04	0.94	0.18	
	410.4		0.39		-0.33		0.84	-0.00	-0.17	
	377.1		0.12		0.03		0.15	-0.16	0.97	
	147.7		0.91		0.14		-0.38	0.09	-0.04	
<i>B_{2g}</i>	635.9	616.0	0.06	-0.10	-0.13	0.90	0.10	0.35	-0.14	
	536.6	552.0	0.09	0.15	0.46	0.12	0.46	0.05	0.73	
	424.6		0.20	-0.17	0.40	-0.21	0.58	0.22	-0.59	
	378.8		-0.12	-0.03	-0.14	-0.32	-0.15	0.90	0.19	
	287.1	283.0	0.08	-0.20	0.73	0.11	-0.63	0.06	-0.05	
	209.2	219.0	-0.48	0.80	0.22	0.08	-0.01	0.08	-0.26	
<i>B_{3g}</i>	138.3	157.0	0.84	0.51	-0.10	-0.03	-0.17	0.08	-0.04	
	582.3		0.05		0.23		0.23	0.94	0.12	
	527.1	555.0	-0.11		0.72		0.58	-0.28	-0.23	
	388.2	403.0	-0.13		0.22		-0.00	-0.17	0.95	
	334.8		0.06		-0.60		0.78	-0.07	0.14	
	203.8	150.0	0.98		0.14		0.05	-0.09	0.08	

TABLE 3
Calculated Zone Center Frequencies (in cm⁻¹) in the Orthorhombic Phase of YAIO₃ Along with the Atomic Displacements for Various Atoms

Species	Present calculated values	Atoms										
		Al	Al	Al	Y	Y	O1	O1	O2	O2	O2	
<i>B_{1u}</i>	681.4	-0.08	-0.37	-0.03	0.02	-0.03	-0.19	0.81	-0.02	0.40	-0.07	
	503.1	-0.15	0.07	-0.08	-0.10	0.25	-0.29	0.06	-0.52	-0.11	0.72	
	471.7	-0.22	-0.09	0.08	0.10	-0.18	0.50	0.10	0.51	0.03	0.61	
	434.6	0.22	-0.38	0.04	0.01	-0.15	-0.05	-0.50	-0.13	0.69	0.16	
	381.4	-0.13	-0.09	0.78	0.01	0.21	0.40	0.05	-0.38	0.01	-0.12	
	328.0	0.92	-0.04	0.15	-0.01	0.10	0.05	0.20	0.08	-0.18	0.21	
	290.6	-0.02	0.43	0.55	-0.01	-0.40	-0.53	0.03	0.21	0.12	0.11	
	209.6	0.10	0.40	-0.16	0.76	-0.19	0.21	0.11	-0.32	0.18	0.01	
	127.0	-0.10	-0.42	0.17	0.64	0.29	-0.38	-0.16	0.23	-0.26	0.02	
	0.0	0.0	0.41	0.0	0.0	0.74	0.0	0.0	0.31	0.44	0.0	
<i>B_{2u}</i>	684.6	-0.13	-0.32	0.17	0.07		0.73		0.37	-0.42	0.02	
	635.7	0.06	-0.23	-0.40	0.02		0.37		0.16	0.76	-0.20	
	437.2	-0.38	0.25	-0.22	-0.23		0.38		-0.49	0.06	0.55	
	420.0	-0.03	-0.36	-0.14	-0.31		-0.34		0.50	0.05	0.62	
	324.0	0.89	-0.01	0.14	-0.22		0.22		-0.20	-0.01	0.24	
	230.0	0.23	0.32	-0.70	0.44		0.01		0.20	-0.31	0.13	
	153.5	-0.01	0.74	0.26	-0.23		0.14		0.52	0.20	0.01	
	0.0	0.0	0.0	0.41	0.74		0.0		0.0	0.31	0.44	
	<i>B_{3u}</i>	623.9	-0.45	0.08	-0.14	-0.03	0.08	-0.24	0.63	-0.05	0.54	-0.13
		501.9	-0.07	-0.18	-0.04	0.01	-0.01	-0.19	0.04	-0.35	0.02	0.89
466.7		-0.26	-0.08	0.09	-0.21	-0.03	0.58	0.17	0.62	0.02	0.35	
402.3		-0.20	0.49	0.29	0.25	-0.13	0.28	-0.44	-0.19	0.50	0.06	
367.1		-0.21	-0.21	0.75	-0.11	0.12	0.17	0.25	-0.40	-0.25	-0.14	
320.3		0.26	0.79	0.11	-0.27	0.19	-0.11	0.29	0.02	-0.26	0.19	
260.5		0.16	-0.08	0.56	0.17	-0.13	-0.56	-0.03	0.51	0.18	0.08	
222.2		0.25	-0.16	0.04	-0.07	0.88	0.07	-0.15	0.04	0.33	0.04	
123.7		0.58	-0.15	0.07	-0.47	-0.38	0.17	0.14	-0.18	0.44	0.01	
0.0		0.41	0.0	0.0	0.74	0.0	0.31	0.44	0.0	0.0	0.0	

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