Raman- and infrared-active phonons in hexagonal YMnO₃: Experiment and lattice-dynamical calculations

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Raman-scattering and far-infrared-transmission spectra of hexagonal YMnO₃ (space group $P6_3cm$) are reported and discussed. In the Raman spectra measured in several exact scattering configurations, lines of A_1 (at 148, 190, 257, ~300, 433, 459, and 681 cm⁻¹), E_1 (at 376, 408, and 632 cm⁻¹), and E_2 (at 135, and ~215 cm⁻¹), symmetries have been observed. Maxima in the infrared absorption have been found at 211, 238, 265, 281, 308, 398, 428, 457, 491, 596, and 612 cm⁻¹. An assignment of the phonon lines to definite atomic vibrations has been made on the basis of their symmetries in close comparison with results of latticedynamical calculations for YMnO₃ in its ferroelectric ($P6_3cm$, Z=6) and high-temperature paraelectric ($P6_3/mmc$, Z=2) phases. [S0163-1829(97)06329-7]

I. INTRODUCTION

The rare-earth and yttrium manganites, $RMnO_3$, for R with smaller ionic radius (R = Ho, Er, Tm, Yb, Lu, Y)crystallize in hexagonal structure [space group $P6_3cm$ $(C_{6v}^3), Z=6$], whereas the compounds with R of larger ionic radius (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, or Dy) are orthorhombic [space group $Pnma(D_{2h}^{16})$, Z=4].¹⁻³ A hexagonal-to-orthorhombic phase structural transition can also take place upon annealing under high pressure.⁴ The hexagonal RMnO₃ compounds belong to the class of ferroelectromagnet materials characterized by the coexistence of magnetic, and ferroelectric orderings.⁵ This is not the case in the orthorhombic RMnO₃ compounds where the magnetic ordering also occurs but not the ferroelectric one. The properties of manganites attracted significant interest since colossal magnetoresistance was observed in $R_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba).⁶ Recently, clear indications for coupling between the ferroelectric and magnetic orders have been found in YMnO₃.⁷

The variations of Raman and/or IR phonon spectra with magnetic, and ferroelectric orderings can help understand the interplay of structural, magnetic and ferroelectric properties. However, with the exception of an earlier work on infrared absorption,⁹ no results concerning Raman or IR phonons in $RMnO_3$ compounds are available. In this work we present results of our Raman and infrared absorption studies on hexagonal YMnO₃ [T_M =80 K, T_E >900 K (Refs. 5 and 8)]. The experimentally observed lines from the Raman and farinfrared-transmission spectra in the ferroelectric phase are assigned to definite atomic vibrations on the basis of their

symmetry and/or by comparison with the results of latticedynamical calculations for both the ferroelectric $(P6_3cm)$ and the high-temperature paraelectric $(P6_3/mmc)$ structures.

II. SAMPLES AND EXPERIMENTAL

The samples investigated were prepared by the solid-state reaction technique at ambient pressure. Cation oxides of Y_2O_3 (99.99%) and MnO₂ (99.99%) were thoroughly mixed in a 1:2 molar ratio to achieve the cation stoichiometry of YMnO₃. The mixture was then compacted and calcinated in air at 1100 °C for 13 h. The reacted product was ground, compacted, and reheated at 1100-1300 °C for 12 h to ensure homogeneity. The powder x-ray-diffraction data show that these polycrystalline samples are single phase of hexagonal YMnO₃ within a resolution of \sim 3%. The lattice parameters are a = 6.13 Å and c = 11.4 Å, in agreement with previous reports.^{2,11} Some single crystals of hexagonal YMnO₃ were also obtained by heating the above stoichiometric oxide mixture of YMnO₃ in Bi₂O₃ flux at 1200 °C for \sim 48 h, followed by a slow cooling to room temperature over a period of 24-40 h. Plateletlike single crystals with the c axis perpendicular to the surfaces, according to the x-ray diffraction results, were found to grow on top of the melt. The size of these crystals was $\sim 4 \times 4 \times 0.05$ mm³.

The Raman spectra were obtained at room temperature with a Mole S3000 triple spectrometer, equipped with a Sidiode array and a microscope. The 514.5 and 496.5 nm Ar⁺ laser lines were used for excitation, the laser power in the focus spot (2–3 μ m in diameter) being kept below 1 mW to avoid overheating of the sample. An objective of ×100

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FIG. 1. Unit cells of YMnO₃ in its *ferroelectric* $P6_3cm$ (left) and *paraelectric* $P6_3/mmc$ (right) phases. The correspondence between the oxygen atoms in the two structures is indicated. Empty circles stay for atoms outside the unit cell.

magnification was used both to focus the laser beam on the sample surface and to collect the scattered light.

The sample used for Raman studies was a plateletlike single crystal with top and bottom surfaces parallel to the ab planes. The thickness of the platelet was about 50 μ m c axis, and, with the microscope, Raman spectra could also be obtained from the side crystal surfaces, which were parallel to the c axis. Therefore, Raman spectra could be measured in $z(xx)\overline{z}$, $z(xy)\overline{z}$, $y(zz)\overline{y}$, and $y(xz)\overline{y}$ scattering configurations, where the z axis coincides with the c axis, and the mutually orthogonal x and y axes are located in the ab plane. Comparative Raman studies of hexagonal YMnO₃ were also done using polycrystalline samples. In that case the Raman signal was either integrated over several grains in the laser spot, or was obtained from a grain surface of unknown orientation. Transmission spectra of YMnO₃ powder in CsI matrix (weight ratio 1:300) were measured at room temperature in the phonon range from 180 to 700

 $E_1 \rightarrow \alpha_{xz}^x, \alpha_{yz}^y \\ E_2 \rightarrow \alpha_{xx} - \alpha_{yy}, \alpha_{xy}$

 cm^{-1} by means of a Fourier-transform IR Bomem DA8 spectrometer.

III. CRYSTAL STRUCTURE AND Γ-POINT PHONONS IN HEXAGONAL YMNO3

The unit cell of the *ferroelectric* $P6_3cm$ structure is shown in Fig. 1 (left). This structure contains layers of corner-sharing MnO₅ bipyramids with a triangular base of nonequivalent O(3) and O(4) atoms, whereas the O(1) and O(2) are at the apexes. The Mn-O(1) and Mn-O(2) bonds are slightly tilted with respect to the c axis. The Y(2) and Y(1)atoms are between the bipyramidal layers. The elementary cell contains six formula units. Table I summarizes the results of a group-theoretical analysis¹² for the Γ -point phonon modes of hexagonal $(P6_3cm)$ YMnO₃. It follows from Table I that out of in total 60 Γ -point modes $(10A_1 + 5A_2 + 10B_1 + 5B_2 + 15E_1 + 15E_2), 38 (9A_1 + 14E_1)$ $+15E_2$) are Raman active. The modes of A_1 and E_1 symmetries are also infrared active, whereas the modes of A_2 , B_1 , and B_2 symmetries are inactive (silent) modes. Given that some crystallographic directions in the sample are known and Raman spectra can be measured in some exact scattering configurations, the symmetry of a line and hence the symmetry of the corresponding Raman mode can be determined. For the scattering configurations available in our experiments, modes of the following symmetries are allowed:

$$y(zz) \overline{y} \rightarrow A_{1}(\text{TO}),$$
$$y(xz) \overline{y} \rightarrow E_{1}(\text{TO}),$$
$$z(xy) \overline{z} \rightarrow E_{2},$$
$$z(xx) \overline{z} \rightarrow A_{1}(\text{LO}), E_{2}$$

TABLE I. Wyckoff notations, atomic site symmetries, and the irreducible representations for the atoms in hexagonal *ferroelectric* YMnO₃ [space group $P6_3cm$, Z=6].

Atom	Wyckoff notation	Site symmetry	Irreducible representations
Y(1)	2(<i>a</i>)	C^v_{3v}	$A_1 + B_1 + E_1 + E_2$
Y(2)	4(<i>b</i>)	C_3	$A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2$
Mn	6(<i>c</i>)	C_s^v	$2A_1 + A_2 + 2B_1 + B_2 + 3E_1 + 3E_2$
O(1)	6(<i>c</i>)	C_s^v	$2A_1 + A_2 + 2B_1 + B_2 + 3E_1 + 3E_2$
O(2)	6(<i>c</i>)	C_s^v	$2A_1 + A_2 + 2B_1 + B_2 + 3E_1 + 3E_2$
O(3)	2(a)	C_{3v}^v	$A_1 + B_1 + E_1 + E_2$
O(4)	4(<i>b</i>)	C_3	$A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2$
		Modes classification	
$\Gamma_{\text{Raman}} = 9A_1 + 14A_2$	$E_1 + 15E_2$		$\Gamma_{\rm ir} = 9A_1 + 14E_1$
$A_1 \rightarrow \alpha_{xx}^z + \alpha_{yy}^z, \alpha_z^z$	7		$\Gamma_{\text{silent}} = 5A_2 + 10B_1 + 5B_2$
$E_1 \rightarrow \alpha_{x_7}^x, \alpha_{y_7}^y$	~		$\Gamma_{\text{acoustic}} = A_1 + E_1$

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TABLE II. Wyckoff notations, atomic site symmetries, and the irreducible representations for the atoms in hexagonal *paraelectric* YMnO₃ [space group $P6_3/mmc$, Z=2].

Atom	Wyckoff notation	Site symmetry	Irreducible representations
Y	2(<i>a</i>)	$D_{3d}(3C_2+3\sigma_d)$	$A_{2u} + B_{2u} + E_{1u} + E_{2u}$
Mn	2(c)	$D'_{3h}(3C'_2+3\sigma_d)$	$A_{2u} + B_{1g} + E_{1u} + E_{2g}$
O _{plane}	2(b)	$D'_{3h}(3C'_2+3\sigma_d)$	$A_{2u} + B_{1g} + E_{1u} + E_{2g}$
O _{apex}	4(f)	$C^d_{3v}(\sigma_d)$	$A_{1g} + A_{2u} + B_{1g} + B_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}$
		Modes classif	fication
$\Gamma_{\text{Raman}} = A_{1g}$	$+E_{1g}+3E_{2g}$		$\Gamma_{ir} = 3A_{2u} + 3E_{1u}$
$A_{1g} \rightarrow \alpha_{xx} + \alpha$	α_{vv}, α_{zz}		$\Gamma_{\text{silent}} = 3B_{1g} + 2B_{2u} + 2E_{2u}$
$E_{1g} \rightarrow \alpha_{xz}, \alpha_y$	22		$\Gamma_{\text{acoustic}} = A_{2u} + E_{1u}$
$E_{2g} \rightarrow \alpha_{rr} - \alpha$	α_{vv}, α_{vv}		

A LO-TO splitting is expected for the A_1 and E_1 modes, as these modes may induce a nonzero dipole moment both parallel and perpendicular to the phonon propagation direction.

Figure 1 (right) shows the crystal structure of YMnO₃ in its high-temperature *paraelectric* phase space group $P6_3/mmc$ (Ref. 11). Although high-temperature Raman measurements were not performed in our study, the comparative phonon mode analysis and lattice-dynamical calculations for the ferroelectric and paraelectric phases make the assignment of experimentally observed Raman lines of ferroelectric YMnO₃ less ambiguous. Note that the $P6_3cm$ structure can easily be obtained from the more simple $P6_3/mmc$ by a small rotation of the MnO₅ bipyramids around axes which are parallel to one of the base-triangle sides and pass through the Mn site.

The elementary cell of the $P6_3/mmc$ structure contains only two formula units, has two inequivalent oxygen sites (O_{pl} and O_{ap}), and only one site for Y and Mn (see Fig. 1 and Table II). The Y sites are now centers of inversion and therefore Y atoms cannot participate in Raman-active Γ -point phonons. Note that while for the $P6_3cm$ structure there is a large number of Γ -point phonon modes, the A_1 and E_1 modes being both Raman- and infrared-active, in the $P6_3/mmc$ structure the number of phonons is strongly reduced and, if allowed in the Raman scattering, the modes are forbidden in the infrared absorption, and vice versa.

The symmetry of a given phonon line can easily be determined from its appearance or disappearance in the spectra of known scattering configurations. The assignment of a Raman line of known symmetry to definite atomic vibrations, however, requires additional argumentation, such as atomic mass and bond considerations or/and calculations of the lattice dynamics.

IV. CALCULATIONS OF THE LATTICE DYNAMICS

Calculations of the lattice dynamics of oxides within a shell model yield valuable information about the phonon eigenmodes and can be used to support the assignment of the experimentally observed features in the Raman and infrared spectra.¹⁰ This model is appropriate for ionic compounds, such as the oxides, because it describes the ionic interactions

by sums of long-range Coulomb potentials and short-range potentials, the latter usually chosen in the Born-Mayer-Buckingham form

$$V = a \exp(-br) - \frac{c}{r^6},\tag{1}$$

where *r* is the interionic separation. The parameters *a*, *b*, and *c* can be derived from simpler, well-studied compounds and transferred to more complex ones.¹⁰ The deformations of the electronic density of the ions affect the frequency of the higher energy modes and have to be accounted for. In the shell model this is done in the dipole approximation representing each ion as a point core with charge Z coupled with a force constant *k* to a massless shell with charge *Q* around it. The free ionic polarizability α , given by $\alpha = Q^2/k$, is additionally "dressed" by the ionic interactions.

The shell model parameters used in the calculations for YMnO₃, derived as described in Ref. 10, are presented in Table III. To obtain the interatomic distances in the $P6_3cm$ structure, we assumed that the relative atomic positions in YMnO₃ and LuMnO₃ are the same, and the data for the former compound were obtained from the available data for the latter one,² accounting for only the weak difference of the lattice parameters a=b and c. The relative atomic positions for the centrosymmetric $P6_3/mmc$ structure were obtained neglecting the deformations that result in the appearance of nonequivalent Y, O_{ap}, and O_{pl} atoms. To obtain the absolute interatomic distances in this case we used lattice parameters $a'=b'=(1/\sqrt{3})a$ and c'=c.

V. RESULTS AND DISCUSSION

Figure 2 shows the Raman spectra of hexagonal YMnO₃ ($P6_3cm$) as obtained in $y(zz)\overline{y}$, $y(xz)\overline{y}$,

TABLE III. Shell-model parameters for YMnO₃.

				Ionic			
Ion	Z(e)	$Q(\left e\right)$	α (Å ³)	pair	a (eV)	$b (\text{\AA}^{-1})$	$c \text{ (eV Å}^6)$
Y	2.85	1.7	2.0	Y-0	1695	2.966	0
Mn	2.85	3.0	3.0	Mn-O	2020	3.345	0
0	-1.90	-3.0	2.0	0-0	22764	6.711	20.37



FIG. 2. Raman spectra of YMnO₃ single crystal ($P6_3cm$) in various scattering configurations. The spectrum of polycrystalline YMnO₃ is also shown.

 $y(xx)\overline{y}, z(xy)\overline{z}$, and $z(xx)\overline{z}$ scattering configurations. Following the considerations of Sec. II, the experimentally observed lines at 148, 190, 257, ~300, 433, 459, and 681 cm ⁻¹ are of A_1 symmetry, those at 376, 408, and 632 cm ⁻¹ are of E_1 symmetry, and the lines at 135 and ~215 cm ⁻¹ are of E_2 symmetry.

The spectrum of infrared optical density between 190 and 700 cm⁻¹ of YMnO₃ in the CsI matrix is shown in Fig. 3. The spectral line shape has clearly pronounced absorption maxima and can be fitted in a rather good approximation by 11 Lorentzians centered at 211, 238, 265, 281, 308, 398, 428, 457, 491, 596, and 612 cm⁻¹. The symmetry of the lines in the infrared spectrum, however, is unknown.

A comparison of the spectra of Figs. 2 and 3 shows that, as a rule, the strong lines in the Raman spectra are not seen in the infrared absorption and *vice versa*. Therefore, the structure behaves like a centrosymmetric. Another interesting observation is the existence of a A_1 line (at 681 cm⁻¹) and a E_1 line (at 408 cm⁻¹) which are much stronger than the remaining lines of A_1 and E_1 symmetries, respectively.

To explain these peculiarities which are of key importance for the phonon line assignments we mention here that a phonon mode is a Raman-active one provided its atomic displacements modulate the macroscopic polarizability. The stronger the phonon-mode-induced polarizability, the higher the intensity of the corresponding Raman line. For the *silent* and infrared active (in a centrosymmetrical structure) modes, the atomic-motion-induced polarizabilities are mutually compensated within the elementary cell and these modes are Raman inactive. The noncentrosymmetric structure



FIG. 3. Absorption (optical density) spectrum of YMnO₃ ($P6_3cm$) in the phonon range between 190 and 700 cm⁻¹.

 $(P6_3cm)$ of YMnO₃ differs by only small distortions from the centrosymmetric $(P6_3/mmc)$ structure, and to each Γ -point phonon mode of the former structure one can juxtapose a $P6_3/mmc$ Γ -point or zone-boundary counterpart mode involving similar atomic motions. As the $P6_3/mmc \rightarrow P6_3mc$ transition reduces the atomic site symmetries, the counterparts of some modes, otherwise Raman inactive in the parent $P6_3/mmc$ structure, become Raman active in $P6_3cm$. In particular, the following $P6_3/mmc \rightarrow P6_3mc$ phonon mode correlations are valid:

$$A_{1g} \rightarrow A_1, \quad E_{1g} \rightarrow E_1, \quad E_{2g} \rightarrow E_2,$$

 $A_{2u} \rightarrow A_1, \quad E_{1u} \rightarrow E_1, \quad E_{2u} \rightarrow E_2.$

Given that the distortion is small, it is plausible to expect weak polarizability modulation and hence low Raman intensities for these A_1 , E_1 , and E_2 modes, which correspond, respectively, to the Raman-inactive A_{2u} , E_{1u} , and E_{2u} modes in the parent $P6_3/mmc$ structure. In contrast, the A_1 and E_1 modes, which correspond to the Raman-active A_{1g} and E_{1g} modes in $P6_3/mmc$, should give rise to much stronger lines in the Raman spectra of $P6_3cm$.

In a similar manner, some conclusions concerning the infrared-active modes in the $P6_3cm$ structure can be drawn by considering the correspondence between the $P6_3cm$ and parent $P6_3/mmc$ modes. The integrated absorption (or oscillator strength) related to an infrared-active phonon mode is proportional to the induced polarization. It is plausible to expect that with respect to their absorption coefficients, the A_1 and E_1 ($P6_3cm$) modes with infrared active A_{1u} or E_{1u} counterparts in $P6_3/mmc$ will be stronger than the A_1 and E_1 modes with infrared-inactive A_{1g} or E_{1g} counterparts in $P6_3/mmc$. We note here that the LO-TO splitting depends linearly on the mode's oscillator strength and these infrared-active modes characterized by large LO-TO splittings (oscillator strengths) will give rise to stronger infrared

TABLE IV. Experimental and calculated values of the Raman and infrared mode frequencies (in cm^{-1}) in hexagonal YMnO₃ [space group $P6_3mc(C_{6v}^3)$] and description of the atomic displacements. *x*, *y*, and *z* mean the directions of the displacements of the atoms. In the last column are given the symmetries of the corresponding modes in the $P6_3/mmc$ structure (see Table V).

Mode symmetry	Expt. Raman	IR	Calc. TO LO	Direction and sign of largest atomic displacements	Corresponding modes in $P6_3/mmc$
$\overline{A_1}$	148		147 147	+z(Y1) - z(Y2)	
A_1	190		204 216	rot. $_{x,y}$ (MnO ₅)	
A_1	257	265	222 269	+z(Y1,Y2) -z(Mn)	A_{2u}
A_1	297		299 301	x(Mn), z(O3)	
A_1		398	388 398	+z(O3) - z(O4) + x, y(O2) - x, y(O1)	
A_1	433	428	423 467	+z(O4,O3) -z(Mn)	A_{2u}
A_1	459		492 496	+x, y(O1,O2) -x, y(Mn)	
A_1		612	588 601	+z(O1,O2) -z(Mn)	A_{2u}
A_1	681		662 662	+z(O1) -z(O2)	A_{1g}
E_1			117 118	+x,y(Mn,O3,O4) -x,y(Y1,Y2)	E_{1u}
E_1			147 149	+x, y(Y1) -x, y(Y2)	
E_1			158 158	+x,y(Y2) -x,y(Y1)	
E_1		211	212 231	+x, y(01, 02) -x, y(Y1, Y2)	
E_1		238	233 245	<i>x</i> , <i>y</i> (Mn,O3), <i>z</i> (O1,O2)	
E_1		281	250 337	+x, y(01, 02) -x, y(03)	E_{1u}
E_1		308	353 367	+x, y(01, 02, 03) -x, y(04, Mn)	
E_1	376		390 403	+x, y(O1) -x, y(O2)	
E_1	408		410 415	+x, y(O1) -x, y(O2)	E_{1g}
E_1		457	459 477	+x, y(O4,O3) -x, y(O2,O1,Mn)	
E_1		491	492 527	+x, y(04, 03, 01, 02) -x, y(Mn)	E_{1u}
E_1			559 559	x, y(O4)	
E_1		596	586 589	<i>x</i> , <i>y</i> (O3)	
E_1	632		635 635	x, y(O3) - x, y(O4)	
E_2			71	x, y(Y1,Y2,Mn)	E_{2u}
E_2			108	+x, y(Mn,O3,O4) -x, y(Y1,Y2)	E_{2g}
E_2	135		136	+x,y(Y1) -x,y(Y2)	
E_2			161	+x,y(Y2) -x,y(Y1)	
E_2	~ 215		212	+x, y(O2,Mn) -x, y(O1,O3)	E_{2u}
E_2			241	<i>z</i> (Mn,O2,O1)	
E_2			245	<i>z</i> (Mn,O1,O2)	
E_2	302		336	+z(O2) - z(O1), x, y(O4)	
E_2			382	+x, y(01, 02, 04, 03) -x, y(Mn)	E_{2g}
E_2			407	+x, y(01,04) -x, y(02,Mn)	
E_2			458	+x,y(O4) -x,y(O1,Mn)	E_{2g}
E_2			515	+x,y(04,03) +x,y(01,02)	
E_2			557	x, y(O4)	
E_2			580	<i>x</i> , <i>y</i> (O4,O3)	
E_2			638	<i>x</i> , <i>y</i> (O3,O4)	

absorption bands. Further, an assignment of the experimentally observed phonon lines to definite atomic motions can be done by comparison with calculations of lattice dynamics for the $P6_3cm$ and $P6_3/mmc$ structures and accounting for the considerations given above.

Table IV shows that consistent with our expectations most of the experimentally observed Raman lines do correspond to modes of small or zero LO-TO splitting, while the pronounced lines in the infrared absorption rather correspond to calculated modes of large LO-TO splitting. The $P6_3mc - P6_3/mmc$ counterparts can be found by looking for modes of similar atomic displacement shapes and close calculated wave numbers in Tables IV and V. The last column of Table IV indicates which of the $P6_3cm$ modes correspond to Raman- or infrared-active modes in the parent $P6_3/mmc$ structure. In Table V are indicated the modes with atomic displacements typical for a free AB_5 bipyramidal unit.¹³ The latter assignment could be helpful for interpretation of Raman and infrared spectra of rare-earth alluminates and gallates (with YAIO₃-type structure, see Ref.

TABLE V. Calculated values of the Raman- and infrared-active mode frequencies (in cm⁻¹) in hexagonal YMnO₃ [space group $P6_3/mmc(D_{6h}^4)$] and a description of the atomic displacements. x, y, and z mean the directions of the displacements of the atoms. In the last column are given the notations for corresponding vibrations in a free AB_5 molecule as described in Ref. 13.

Mode symmetry	Calc. TO LO	Direction and sign of largest atomic displacements	Normal modes in free $AB_5(\nu_i)$
$\frac{1}{A_{1g}}$	666	z(O _{ap})	ν ₂
A_{2u}	170 270	$+z(\mathbf{Y}) -z(\mathbf{Mn},\mathbf{O}_{pl}, \mathbf{O}_{ap})$	
A_{2u}	389 439	$+z(O_{pl}) -z(Mn)$	$ u_4$
A_{2u}	594 605	$+z(O_{ap})^{T}$ - $z(Mn,O_{pl})$	ν_3
E_{1g}	402	$x, y(O_{ap})$	
E_{1u}	121 121	$+x,y(Mn,O_{pl}) -x,y (Y,O_{ap})$	
E_{1u}	239 383	$+x, y(O_{ap})-x, y(Y,Mn,O_{pl})$	ν_7
E_{1u}	496 545	$+x,y(O_{pl})-x,y(Mn)$	ν_5
E_{2g}	107	$x, y(Mn, O_{pl})$	
E_{2g}°	395	$+x, y(O_{ap}) -x, y(O_{pl}, Mn)$	
E_{2g}	498	$+x, y(O_{pl}) -x, y(Mn, O_{ap})$	
E_{2u}	83	$x, y(\mathbf{Y}, \mathbf{O}_{ap})$	
E _{2u}	244	$x, y(O_{ap}) - x, y(Y)$	

14), isostructural to the YMnO₃ high-temperature phase.

The A_1 Raman line at 681 cm⁻¹, which is dominant in the zz and xx spectra, corresponds to the single $P6_3/mmc$ Raman-active mode of A_{1g} symmetry. The main atomic motions involved are stretching vibrations of O(1) and O(2) atoms along the c direction. Note that the zero LO-TO splitting of this mode is also experimentally confirmed as no difference in the line position in the zz(TO) and xx(LO) is detectable. The E_1 line corresponding to the E_{1g} $P6_3/mmc$ mode [O(1),O(2) vibrations in the ab planes] is at 408 cm⁻¹ and is the strongest one in the zx Raman spectrum. As to the E_2 counterparts of the three $E_{2g} P6_3/mmc$ modes, they seem to be of very low intensity and could not be detected in the xy and xx spectra.

The Raman lines of A_1 symmetry at 148 cm⁻¹ and of E_2 symmetry at 135 cm⁻¹ also deserve special mention because, although they are the strongest ones after the 681 cm⁻¹ line, their appearance does not follow from direct comparison of the $P6_3cm$ and $P6_3/mmc$ Γ -point modes. Actually, as indicated in Table IV, these modes involve motions of mainly Y(1) and Y(2) atoms along the *c* axis and in the *ab* plane, respectively. The corresponding modes in the $P6_3/mmc$ structure are zone-boundary modes.

Given that the symmetry of the infrared absorption lines is not known, the assignment given in Table IV for some of them is only tentative. This is particularly the case for the

³F. Moussa, M. Hennion, J. Rodriguez-Carvajal, H. Moudden, L.

lines at 265, 281, and 308 cm⁻¹, which differ in wave numbers by +16, +11, and -15 %, respectively, from the values obtained in calculations of lattice dynamics.

VI. CONCLUSIONS

In conclusion, Raman and infrared spectra of the hexagonal ferroelectric YMnO₃ were analyzed in close comparison with results of lattice-dynamical calculations for the noncentrosymmetrical $P6_3cm$ and centrosymmetrical $P6_3/mmc$ structures. The satisfactory agreement between experimentally measured and calculated phonon wave numbers allowed us to assign most of the observed lines to definite phonon modes.

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