Lattice dynamical study of optical modes in Tl₂Mn₂O₇ and In₂Mn₂O₇ pyrochlores

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The Raman and IR spectra and force field have been investigated for $A_2Mn_2O_7$ (A = Tl,In) by means of a short-range force constant model which includes four stretching and four bending force constants. Unusual spectral and force field changes are observed and analyzed. The stretching force constant Mn-O and A-O' are found to be relatively higher than those of other pyrochlore oxides of the $A_2Mn_2O_7$ family, while the remaining force constant values are significantly smaller, especially for $Tl_2Mn_2O_7$. This trend may be due to strong hybridization of the Tl (6s) orbital with O (2p) and Mn (3d). The assignment of all the modes has been proposed and potential energy distribution is also reported. The evaluated frequencies are close to the available observed infrared and Raman frequencies, giving further support to the present assignments.

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I. INTRODUCTION

The discovery of colossal magnetoresistance (CMR) in manganese oxides has generated much interest in both basic research and possible applications.¹⁻⁶ CMR effects in perovskite (namely, $La_{1-r}Sr_rMnO_3$) and pyrochlore (namely, Tl₂Mn₂O₇) manganese oxides are found in the vicinity of a metal-insulator transition and a ferromagnetic ordering transition, although the origin of the CMR behavior in both families of compounds is very different. In perovskites, the CMR behavior is explained within the framework of the doubleexchange (DE) model. The Jahn-Teller distortion and a strong electron-phonon coupling also play an important role in perovskites.⁷ On the contrary, the pyrochlore ferromagnetism ($T_{\rm C}$ =120 K) is a consequence of superexchange interactions between Mn4+ magnetic moments, whereas the metallic behavior of Tl₂Mn₂O₇ originates from the hybridization among Tl (6s), O (2p), and Mn (3d),^{8,9} which is probably at the very origin of the magnetotransport properties of this peculiar pyrochlore.

At room temperature, most $A_2B_2O_7$ pyrochlores exhibit a face-centered-cubic structure belonging to the space group $(Fd3m, O_h^7)$, No. 227; the primitive cell contains two formula units. The pyrochlore $A_2B_2O_6O'$ structure (Fig. 1) may be considered as interpenetrating networks of B_2O_6 and A_2O' , although the latter is not essential for the stability of the structure.¹⁰ The B_2O_6 sublattice is formed by BO_6 octahedra sharing corners, with B-O-B angles close to 135°. Manganese pyrochlores of stoichiometry $A_2Mn_2O_7$ have been described for trivalent A cations such as rare earths, In, and Tl. The transport and magnetic properties dramatically depend upon the nature of the A cation. All compounds exhibit ferromagnetic interactions, with Curie temperatures around 15 K (for instance, Y₂Mn₂O₇ or Lu₂Mn₂O₇), excepting Tl₂Mn₂O₇ and In₂Mn₂O₇, which exhibit much higher $T_{\rm C}$'s of 120 K. Moreover, only the Tl₂Mn₂O₇ pyrochlore exhibit semimetallic conductivity and CMR properties.⁸ These differential properties have been explained as a result of a strong hybridization between the Tl (6*s*), O (2*p*), and Mn (3*d*) orbitals. It is plausible to expect that the different nature of the chemical bond in these oxides will also influence the phonon spectra, and hence a study of phonons is undertaken in the present work for A_2 Mn₂O₇ (A = In,Tl).

In fact, very interesting information about the physics of these materials can be learned through light scattering and absorption experiments. Raman and IR spectroscopy can give insight to the dynamical processes caused by phonons, charge carriers, and spins that may effect the magnetoresistance process. The force field is also one of the important physical factors, which reflects the electronic structure of the bond and its variations with the bond environment. In terms of total amount of research devoted so far to the pyrochlore materials, surprisingly little work appears to have been done on the spectroscopic studies and lattice dynamics of these compounds.^{11,12} In particular, available information about the assignment of the observation to specific modes of vibrational and force field study is still lacking. Motivated by this situation, we thought it pertinent to study the Raman and IR spectra and force field of A_2 Mn₂O₇ (Tl, In). The assignment of all vibrational modes has been made. The results are also



FIG. 1. $A_2B_2O_7$ cubic pyrochlore structure with BO_6 octahedra and A_2O' chains.

TABLE I. Factor group analysis for the zone-center vibrational modes of pyrochlore $A_2B_2O_6O'$.

Ion	Number of equivalent positions (Wyckoff notation)	Site group symmetry	Irreducible representations			
A	16(<i>c</i>)	D_{3d}	$A_{2\mu} \oplus E_{\mu} \oplus 2F_{1\mu} \oplus F_{2\mu}$			
В	16(<i>d</i>)	D_{3d}	$A_{2u} \oplus E_u \oplus 2F_{1u} \oplus F_{2u}$			
0	48(f)	C_{2v}	$A_{1g} \oplus E_g \oplus 2F_{1g} \oplus 3F_{2g} \oplus A_{2u}$			
			$\oplus E_u \oplus 3F_{1u} \oplus 2F_{2u}$			
0′	8(<i>a</i>)	T_d	$F_{1u} \oplus F_{2g}$			
Total			$\Gamma = A_{1g} \oplus E_g \oplus 2F_{1g} \oplus 4F_{2g} \oplus 3A_{2u}$			
			$\oplus 3E_u \oplus 8F_{1u} \oplus 4F_{2u}$			
Acoustic			$\Gamma_{\rm ac} = F_{1u}$			
Raman			$\Gamma_R = A_{1g} \oplus E_g \oplus 4F_{2g}$			
Infrared			$\Gamma_{\rm IR} = 7F_{1u}$			

compared and discussed with other $A_2Mn_2O_7$ (A = Y,Dy, Er,Yb) and different pyrochlore oxides.^{13–16}

II. EXPERIMENTAL AND THEORY

The elaboration of $In_2Mn_2O_7$ pyrochlore required previous preparation of a very reactive precursor, obtained by wet-chemistry techniques. A mixture of In_2O_3 and $MnCO_3$ was dissolved in citric and nitric acid; the solution was slowly evaporated, leading to an organic resin which was dried at 120 °C and slowly decomposed at temperatures up to 600 °C in order to eliminate all the organic materials and nitrates. This precursor powder was thoroughly ground with KClO₄ (30% in weight), put into a gold capsule (8 mm diameter, 10 mm length), sealed, and placed in a cylindrical graphite heater. The reaction was carried out in a pistoncylinder press at a pressure of 2 GPa at 1000 °C for 60 min. Then the material was quenched to room temperature and the pressure was subsequently released. The raw product, ob-



FIG. 2. Raman spectra of A_2 Mn₂O₇ (A = Y,In,Dy,Er,Yb,Tl) pyrochlore.



FIG. 3. Infrared spectra of the $A_2Mn_2O_7$ (A = Y,Dy,Er,Yb,In,Tl) pyrochlores. The inset shows far-IR spectra of $A_2Mn_2O_7$ (A = Dy,Tl).

tained as a dense, homogeneous pellet, was ground and washed in water, in order to dissolve KCl coming from the decomposition of KClO₄; then, the powder sample was dried in air at 150 °C for 1 h. The preparation of $Tl_2Mn_2O_7$ was performed by solid-state reaction from Tl_2O_3 and MnO_2 , ground together and put into a gold capsule. The high-pressure reaction conditions were the same described for the $In_2Mn_2O_7$ compound.

Raman measurements were done in a Raman spectrometer with an Olympus microscope, a Jobin-Yvon HR 460 monochromator and a N₂-cooled charge-coupled device (CCD). All spectra were obtained at room temperature, exciting with the 514.5-nm line of a Spectra Physics Ar-Kr laser and Super-Notch Plus filter (Kaiser Optical Systems) to suppress the Rayleigh scattering. The IR spectra (50–4000 cm⁻¹) were recorded from KBr and polyethylene pellets in an IR BRUKER-IFS66v/S spectrophotometer.

The normal coordinate analysis treatment was carried out according to the Shimanaouchi method¹⁷ based on the Wilson *GF* method. A short-range force constant model (SR-FCM) was chosen. In the *GF* matrix method, the eigenvalue equation is given by $|FG-E\lambda|=0$, where the *F* matrix con-

tains force constants that describe the vibrational potential energy of system. The *G* matrix involves the mass number and certain spatial relationship of the atoms, thus bringing the kinetic energies into the equation. *E* is the unit matrix of the same dimension of *F* and *G*, and λ is defined by λ $=4\pi^2c^2\nu^2$. The force constant matrix includes valence forces between nearest neighbors Mn-O, *A*-O', *A*-O and repulsive forces between nearest neighbors O-O' and angle bending forces between O-Mn-O, O-Mn-O, O-*A*-O', and O-*A*-O. These eight force constants are optimized to give the best fit of observed Raman and infrared wave numbers.

III. RESULTS AND DISCUSSION

The group-theoretical analysis for optical and acoustical modes from the correlation method¹⁸ and taking account the symmetry conditions are listed in Table I: we have

$$\Gamma = A_{1g} + E_g + 2F_{1g} + 4F_{2g} + 3A_{2u} + 3E_u + 8F_{1u} + 4F_{2u}.$$

Out of these 26 normal modes, only A_{1g} , E_g , $4F_{2g}$, are Raman active, $7F_{1u}$ are infrared active, and one F_{1u} acoustical. All seven F_{1u} modes and six Raman-active modes are

TABLE II. Definition of internal coordinates and force field (in N cm ⁻¹)) for A_2 Mn ₂ O ₇ ($A = Y$, In, Dy, Er,
Yb, Tl). The values for Y, Dy, Er, and Yb have been taken from Ref. 16.	

Internal coordinates		Force constant (N cm ⁻¹)					
		Y ₂ Mn ₂ O ₇	Dy ₂ Mn ₂ O ₇	$Er_2Mn_2O_7$	Yb ₂ Mn ₂ O ₇	In ₂ Mn ₂ O ₇	Tl ₂ Mn ₂ O ₇
<i>K</i> 1	Mn-O	0.776	0.878	0.787	0.734	0.843	1.027
K2	A-O'	0.227	0.317	0.348	0.306	0.369	0.873
<i>K</i> 3	A-O	0.096	0.186	0.192	0.194	0.234	0.088
<i>K</i> 4	O-O'					0.045	0.026
H5	O-Mn-O	0.274	0.276	0.282	0.263	0.331	0.168
H6	O-Mn-O	0.376	0.343	0.361	0.383	0.248	0.402
H7	O-A-O	0.073	0.031	0.046	0.074		0.05
H8	O-A-O'	0.246	0.212	0.208	0.208	0.148	0.09

observed in most cases. The Raman and infrared spectra of A_2 Mn₂O₇ (Tl, In) are shown in Figs. 2 and 3, respectively. For comparison, the spectra of other manganese pyrochlores are also displayed.¹⁶ The A_{1g} (totally symmetric mode) is readily assigned as it gives rise to a strong polarized line.¹² The observed A_{1g} and F_{2g}^1 are least for Tl₂Mn₂O₇ compared to other manganese pyrochlores. The most striking feature of the $Tl_2Mn_2O_7$ spectra is that, in general, the frequencies are lower than those observed for other pyrochlores, but some frequencies are increased in $\text{Tl}_2\text{Mn}_2\text{O}_7$ like F_{1u}^1 and F_{1u}^2 . The F_{1u}^2 and F_{1u}^3 modes become quite distinct as the mass increases. The lower-range frequencies F_{1u}^5 , F_{1u}^6 , and F_{1u}^7 are almost the same for both In and Tl compounds, though the higher-range frequencies of $In_2Mn_2O_7$ are comparable to those of other manganese pyrochlores.¹⁸ The bands are assigned to symmetry species by comparing the previously published study of pyrochlore oxides.^{13–16,19} The extra band around 700 cm⁻¹ is observed in all Raman spectra presented in this work and has been assigned as an overtone.^{20,21}

TABLE III. Comparison of calculated and experimental values of phonon wave numbers (in cm^{-1}) near the Brillouin zone center at room temperature.

	In ₂ M	n ₂ O ₇	$Tl_2Mn_2O_7$		
	Calculated	Observed ^a	Calculated	Observed ^a	
A_{1g}	511.3	510	490.9	489	
E_g	344.1	346	317.3	327	
F_{2g}^{1}	547.1	548	523.5	512	
$F_{2g}^{2^{\circ}}$	442.1	428	495.0		
$F_{2g}^{3^{\circ}}$	365.1		412.2	392	
$F_{2q}^{\overline{4}^{\circ}}$	303.0	292	296.6	289	
$F_{1u}^{\overline{1}^{\circ}}$	535.7	542	589.0	595	
F_{1u}^{2}	483.5	482	492.8	512	
F_{1u}^{3}	436.9		436.1	454	
F_{1u}^{4}	347.4	336	389.1		
F_{1u}^{5}	266.9	280	288.3	275	
F_{1u}^{6}	144.0	140	123.1	125	
F_{1u}^{7u}	131.0		97.0	98	

^aThis work.

The eight internal coordinate sets introduced in the force field calculations and their definition are given in Table II. The refined force constants are also reported in Table II. The comparison between the observed and calculated wave numbers is given in Table III. A satisfactory fit (average error of 5% between observed and calculated wavenumbers) was obtained with four stretching and four bending force constants. As the octahedra $Mn-O_6$ is the backbone of the pyrochlore structure, a similar trend is observed in calculated force constants. The most dominating force constants belonging to the octahedra are found to be K1, H5, and H6. Here K1 and K2 values are the largest for Tl₂Mn₂O₇ among all the pyrochlore oxides until studied now. Further, K1, K2, and H6 force constants increase as A changes from a rare earth (Y, Dy, Er, Yb) to Tl, whereas the other force constants decrease. This trend may be due to the hybridization among Tl (6s), O (2p), and Mn (3d) orbitals, accounting for an strengthening of the Mn-O and Tl-O chemical bonds. For other manganese pyrochlores, a very slight change is observed in these force constants from Y to Yb pyrochlores. Although the experimental Raman and infrared wave numbers also do not exhibit any systematic variation when A changes from Y to Yb, a general trend is observed along the series, leading to a decrease in the force constant with an increase in bond length.



FIG. 4. Potential energy distribution (PED) of Raman-active modes for $Tl_2Mn_2O_7$.



FIG. 5. Potential energy distribution (PED) of IR-active modes for $Tl_2Mn_2O_7$.

Comparing the obtained force constants from the earlier studied pyrochlore oxides,^{12,16,17} it has been observed that in BO₆ octahedra (B = Mn, Ti, Hf, Sn), Mn cations are more tightly bound to oxygens than Ti, Hf, and Sn in titanates, hafnates, and stannates. In manganates $A_2Mn_2O_7$, the stretching force constant (K1) has the largest value observed for any pyrochlore oxides.

The potential energy distribution (PED), which gives important information to understand the energy localization of the active modes, has a similar trend for both Tl and In compounds as shown in Figs. 4 and 5. From the PED, it is

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observed that A_{1g} and F_{2g}^1 modes are due to the bending of Mn-O₆ octahedra. Similarly, F_{2g}^2 and F_{2g}^3 are mainly due to the stretching of Mn-O and A-O' bonds, respectively. Hence the increase in frequency can be correlated well with the increase in stretching force constants K1 and K2. From the PED, it is obvious that F_{1u}^1 has the most dominating force constant K1, and as the measured frequency is highest among all the manganates, the highest value of K1 for $Tl_2Mn_2O_7$ is justified. F_{1u}^2 and F_{1u}^3 have important contributions from H5 and K2, respectively. Also, F_{1u}^5 is due to the stretching vibration of A-MnO₆ and F_{1u}^6 and F_{1u}^7 are mainly influenced by the bending vibrations of AO_6O' polyhedra. This is the reason behind why F_{1u}^6 and F_{1u}^7 frequencies differ more than other frequencies when A changes from Y to lanthanide elements. For mangantes pyrochlores, it is also observed that the three bending force constants have important contribution in the PED (H5, H6, and H8), but earlier studied titanates, hafnates, and stannates do not display much contribution from H8.

IV. CONCLUSION

We have applied the SRFC model involving various stretching and bending force constants to evaluate the Raman and IR wave numbers in the case of $Tl_2Mn_2O_7$ and $In_2Mn_2O_7$. The force constant values suggest that due to hybridization of different states Tl (6*s*), O (2*p*), and Mn (3*d*) force constants *K*1, *K*2, and *H*6 dominate in the force field while others decrease. The calculated IR and Raman modes exhibit a satisfactory agreement with the experimental observation, and an assignment of these frequencies to species modes has been established.

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