Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Effect of Electrostatic Interaction and Its Relation to Lithium Intercalation in $LiTi_2O_4$ Spinel Oxides

H. C. Gupta [a] & Neelima Rani [b]

[a] Physics Department, Indian Institute of Technology, Hauz Khas, New Delhi, 110016, India

[b] Physics Department, Maitreyi College, Bapu Dham Complex, New Delhi, 110021, India

Version of record first published: 04 Oct 2006

To cite this article: H. C. Gupta & Neelima Rani (1998): Effect of Electrostatic Interaction and Its Relation to Lithium Intercalation in $LiTi_2O_4$ Spinel Oxides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 89-94

To link to this article: http://dx.doi.org/10.1080/10587259808042371

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 89–94
Reprints available directly from the publisher
Photocopying permitted by license only

Effect of Electrostatic Interaction and Its Relation to Lithium Intercalation in $LiTi_2O_4$ Spinel Oxides

H.C.GUPTA[a] and NEELIMA RANI[b]
[a]Physics Department, Indian Institute of Technology, Hauz Khas, New Delhi-110016, India;
[b]Physics Department, Maitreyi College, Bapu Dham Complex, New Delhi-110021, India

Abstract The phonons in superconducting oxide spinel $LiTi_2O_4$ are investigated using a short range force constant model (Model I) and a modified rigid ion model (Model II), including the long range Coulomb electrostatic interaction. The phonons, in which lithium atoms are involved, have been identified and their relation to the long range Coulomb interaction discussed.

Keywords phonons, spinel oxides, electrostatic interaction

INTRODUCTION

Recently, the oxide spinel $LiTi_2O_4$ has been studied extensively[1-6] from the point of view of superconductivity mechanism. For investigating the phenomenon of the superconductivity mechanism, the study of the phonons in $LiTi_2O_4$ is quite important. Experimentally, only the Raman measurements are available in case of $Li_{1+x}Ti_{2-x}O_4$[7], whereas theoretically the semi-empirical treatment[5] and the first principles study[6] of the lattice dynamics of $LiTi_2O_4$ have been

made. The semi-empirical method values[5] obtained by taking account of effective long range interatomic forces caused by the electron-phonon interaction did not provide satisfactory agreement in case of Raman modes. Because of the involvement of the ionic character, we will like to study in this paper, the phonons in $LiTi_2O_4$ with and without the long range Coulomb electrostatic interaction. Model I for phonon calculation will consider only the short range forces upto the third nearest neighbour whereas model II for phonons will include the long range Coulomb electrostatic interaction in addition to the short range force constants. The potential energy distributions in both these models will be discussed in case of active Raman and infrared modes. The effect of the electrostatic interaction, specially on the lithium involved force constants, will be investigated.

THEORY

$LiTi_2O_4$ is a normal spinel, with space group Fd3m. Group theoretical treatment of the optical zone centre phonon modes yields

$$\tilde{a} = A_{1g}+E_g+F_{1g}+3F_{2g}+2A_{2u}+2E_u+4F_{1u}+2F_{2u}$$

with Raman active modes of the species $A_{1g}, E_g, F_{1g}, F_{2g}$ and infrared active modes of the species F_{1u}.

The lattice dynamical calculations were carried out according to the Wilson-GF matrix method on the basis of cartesian symmetry coordinates[8]. The dynamical matrix is

$$D = M F M$$

where M is a diagonal matrix specifying the masses of the atom involved. The force constant matrix F for model I involves the short range force constants upto third neighbour whereas for model II, the long range Coulomb forces are also included alongwith the short range force constants.

It has been observed that the Raman A_{1g} and E_g modes depend only on X-ion in AB_2X_4 spinels[9,10], and hence, from the study of Raman modes of other oxide spinels[9,10], it has been inferred that for $Li_{1+x}Ti_{2-x}O_4$, the A_{1g} and E_g mode should have a value of 628 cm^{-1} and 429 cm^{-1} respectively. The other observed Raman frequencies[7] 494 cm^{-1} and 339 cm^{-1} correspond to F_{2g} modes. In this study, we have not used the angular force constants based on our earlier investigations of inverse spinels[11]. Hence, one can obtain the values of three central force constants $Á_1$, $Á_2$, $Á_3$ corresponding to the first three nearest neighbours by using the expressions of the A_{1g} and E_g modes against their experimental values and deciding about the value of one of the three force constants $Á_1$, $Á_2$, $Á_3$. The analytical expressions for A_{1g} and E_g modes are given by Gupta etal.[12].

$m_x w^2 = Á_1 + Á_2 + 8Á_3$ (1) A_{1g} mode

$m_x w^2 = Á_2 + 2Á_3$ (2) E_g mode

The value of the X-X force constant $Á_3$ has been taken to be 0.2 N/cm, based on the earlier studies of oxide spinel[9,10] and the semi-empirical treatment of Oda et al.[5]. Using this value of $Á_3$, the value of A_{1g} as 628 cm^{-1} and the value of E_g as 429 cm^{-1}, the interatomic force constants $Á_1$ and $Á_2$ are evaluated as 0.8 N/cm and 1.35 N/cm respectively. Also, in our analysis, the B-B interaction is taken as equal to $Á_3$, since the X-X and the B-B distances are the same. For model II, the force constant $Á_1$ is found to be equal to 0.5 N/cm. Also based on the work of Zwinscher and Lutz[13] for spinels, the effective charges of $LiTi_2O_4$ have been estimated as Z_{Li} =0.4, Z_{Ti} =1.0 and Z_O =-0.6.

DISCUSSION

Using the short range force constants as described above for model I, the calculated

phonon at the zone centre are given in Table-1

Table-1 Zone centre phonon frequencies (cm^{-1}) in case of $LiTi_2O_4$

Mode	Raman Results[7]	Present Calculations Model I	Model II	Renormalized phonon frequency as calculated by Oda etal.[5]
A_{1g}	628.0	628.0	619.3	548.1
E_g	429.0	429.0	420.6	337.2
F_{2g}		652.4	599.5	687.3
	494.0	542.4	495.5	516.4
	339.0	344.2	344.3	288.5
F_{1u}	(TO)	668.3	554.7	696.3
		508.6	478.4	506.4
		424.9	393.2	389.2
		210.3	269.6	289.0
		0.0	0.0	0.0
F_{1u}	(LO)		589.1	
			540.2	
			393.2	
			270.5	
			0.0	

alongwith the observed Raman measurements[7] and the phonons as calculated semi-empirically by Oda et al.[5].Also given in Table-1 are the calculated values of phonons for model II where the electrostatic interaction has been accounted by incorporating the dynamical effective charges in addition to the short range force constants. One can observe that the present results are better than those of Oda et al.[5] for both the models. One possible reason of discrepancy in case of Oda et al.[5] can be a very large interatomic force constant Ti-Ti value of 0.8 N/cm.

When we compare the results of phonons for model I with model II, it is observed that there is almost no splitting between the transverse optical (TO) and the longitudinal

optical (LO) modes for the lower frequencies but there is a large splitting between TO and LO modes for the higher frequencies. One can observe that except the lithium involved force constants, all other force constants remain the same which implies that the effect of the incorporation of the electrostatic interaction is directly related to the lithium involved force constants.

Table-2 Potential energy distribution (%) of the zone centre phonons of $LiTi_2O_4$ (LRFC = long range coulomb forces)

Mode	Force constant	Model I	Model II	Mode	Force constant	Model I	Model II (TO)	Model II (LO)
A_{1g}	Li-O	21	14	$F_{1u}(1)$	Li-O	60	64	65
	Ti-O	36	37		Ti-O	31	30	29
	O-O	43	44		Ti-Ti		2	2
	LRFC		5		O-O	9		
					LRFC		4	4
E_g	Ti-O	77	81	$F_{1u}(2)$	Li-O	6	16	3
	O-O	23	24		Ti-O	86	93	80
	LRFC		-5		Ti-Ti	2	1	2
					O-O	6	1	17
					LRFC		-11	-2
$F_{2g}(1)$	Li-O	69	69	$F_{1u}(3)$	Li-O	32	26	1
	Ti-O	19	38		Ti-O	63	70	56
	O-O	12	11		Ti-Ti	3	2	
	LRFC		-18		O-O	2	19	4
					LRFC		-17	9
$F_{2g}(2)$	Li-O	8	2	$F_{1u}(4)$	Li-O	1	1	1
	Ti-O	45	40		Ti-O	4	5	6
	O-O	47	47		Ti-Ti	40	25	26
	LRFC		11		O-O	55	30	29
					LRFC		39	38
$F_{2g}(3)$	Li-O	23	34					
	Ti-O	59	42					
	O-O	18	13					
	LRFC		11					

From Table-2, it can be observed that due to

the incorporation of long range Coulomb forces (LRFC), it is the lithium involved force constant potential energy density which is generally more affected. If we compare the degree of ionicities as investigated by Zwinscher and Lutz[13], then we observe that $LiTi_2O_4$ spinel is more ionic than sulphides and selenides spinels but less ionic than other oxide spinels like $ZnCr_2O_4$. This indicates the decrease of the electrostatic repulsion by the intercalation of lithium ion in $LiTi_2O_4$.

References

[1] J.M.Heintz, M. Drillon, R.Kuentzler, Y.Dossman, J.P.Kappler, O.Durmeyer and F.Gautier, Z. Phys. B. 76, 303 (1989)
[2] T.Ekino and J.Akimitsu, PhysicaB 165-166, 1599 (1990)
[3] F.Gompf, B.Renker and H.Mutka, PhysicaB, 180-181, 459 (1992)
[4] T.Oda, M.Shirai, N.Suzuku and K.Motizuki, Journal of Superconductivity 7, 555(1994)
[5] T.Oda. M.Shirai, N.Suzuki and K.Motizuki, J.Phys. Condens. Matter 6, 6997 (1994)
[6] T.Oda, M.Shirai, N.Suzuki and K.Motizuki, Physica B 219-220, 451 (1996)
[7] D.Z.Liu, W.Hayes, M.Kurmoo, M.Dalton and C.Chen, Physica C 235-240, 1203 (1994)
[8] T.Shimanouchi, M.Tsuiboi and T.Miyazawa, J.Chem.Phys. 35,1597(1961)
[9] H.C.Gupta, M.M.Sinha, Balram and B.B.Tripathi, J.Solid State Chemistry 102, 315 (1991)
[10] H.C.Gupta, M.M.Sinha, Balram and B.B.Tripathi, Physica B192, 343 (1993)
[11] H.C.Gupta and Balram, J. Phys. Soc. Japan 64, 142 (1995)
[12] H.C.Gupta, A.Parashar, V.B.Gupta and B.B.Tripathi, Phys. Stat. Solidi 160b, K19 (1990)
[13] J.Zwinscher and H.D.Lutz, J.Alloys. Compounds 219, 103 (1995)