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On Infrared Intensities of Spinel, $MgAl_2O_4$

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In spinel ($MgAl_2O_4$), the strongest infrared band at 485 cm^{-1} shows less LO–TO splitting than the medium band at 670 cm^{-1}. This unexpected relationship is explained in terms of the vibrational coupling of these TO modes. A new manner for evaluating the LO mode is proposed.

O'Horo et al.[1] and Grimes et al.[2] have obtained the infrared spectra of spinel from the Kramers–Kronig transformation of Wang and Zanzucchi's reflectivity data.[3] They have found four infrared bands at 670, 485, 428, and 305 cm^{-1}, which are denoted here by ν_6, ν_7, ν_8, and ν_9, respectively. These bands are assigned to the T_{1u} TO modes on the basis of the space group $Fd3m$,[1,4,5] although some authors have assigned them on the basis of the space group $F43m$.[2,6] The infrared spectra in the polycrystalline state[4,7] have also been reported. Grimes et al.[2] have found two LO modes at 855 and 630 cm^{-1}, which are associated with ν_6 and ν_7 TO modes, respectively. Hence, the LO–TO splittings of ν_6 and ν_7 are 185 and 145 cm^{-1}, respectively. On the other hand, the infrared intensity of ν_7 is considerably stronger than that of ν_6. The relationship between the LO–TO splittings and the infrared intensities is contradictory to the expectation that the LO–TO splitting results are due to the infrared intensity.[8,9] In the present study, this unexpected finding will be discussed on the basis of a normal coordinate analysis and an infrared intensity analysis.

An infrared intensity analysis of lattice modes has rarely been reported, as far as we know, although many studies[10] on the Raman intensity have been reported. Hence, we are interested in the infrared intensity analysis, especially in terms of the present system because of the problems related to the infrared intensity, as described above.

Spinel belongs to the space group $Fd3m \equiv O_h^7$ with $z = 2$ in the Bravais unit cell.[5] The lattice constant is: $a = 8.081$ Å.[5] The fundamentals reported[1,2,5] are shown in Table 1. The valence force field with some interaction constants was used for the short-range potential functions. The long-range Coulomb potential function was derived on the basis of the rigid ion model, and the F matrix for the LO modes was simultaneously constructed for the wave vector along the z direction. The short-range force constants used are given in Table 2, where K and H mean the stretching and bending force constants, respectively, and I is the interaction constant. The effective ionic charges[5] have been reported as: $Z_{Mg} = 0.60$ e, $Z_{Al} = 1.92$ e, and $Z_O = -1.11$ e. They were used in the present calculation. The calculated wavenumbers and the force constants are given in Tables 1 and 2, respectively.

Table 1. Observed and Calculated Wavenumbers (cm^{-1}) of Spinel

		Obs.[a]	Calcd
A_{1g}		772	773
E_g		410	418
T_{2g}		671	658
		492	477
		311	312
T_{1u} (TO)	ν_6	670	669
	ν_7	485	490
	ν_8	428	436
	ν_9	305	302
T_{1u} (LO)	ν_6	855	871
	ν_7	630	610
	ν_8	428	436
	ν_9	309	305

a) From Ref. 5.

Table 2. Values of Short-Range Force Constants[a] and Bond Lengths

	Force constant	r/Å
K(Mg–O)	169.0	1.93
K(Al–O)	150.0	1.92
K(Al···O)	6.0	3.38
K(Mg···Al)	−8.0	3.35
K(Mg···Mg)	14.0	3.50
K(O···O)	18.3	2.58
K(O···O)	20.4	2.86
K(O···O)	−15.7	3.13
H(OMgO)	13.5	
I(AlO, AlO)	8.6	84.1[b]
I(AlO, AlO)	−26.2	95.9[b]
I(AlO, AlO)	−1.0	180.0[b]
I(MgO, MgO)	54.2	

a) K and I in $N\,m^{-1}$ and H in 10^{-20} $N\,m\,rad^{-2}$. b) Angles of str.–str. in degree.

The infrared intensity of the i-th mode is calculated as

$$I_i \propto (\partial\mu/\partial Q_i)^2 = \left|\sum_j (\partial\mu/\partial x_j)(\partial x_j/\partial Q_i)\right|^2 = \left|\sum_j e_j l_{ji}\right|^2, \quad (1)$$

where μ and Q are the dipole moment and the normal coordinate, respectively, and x_j is the Cartesian displacement coordinate of the j-th atom and l_{ji} is the element of L_x matrix defined by $X = L_x Q$.

Because of the ionic crystal, the infrared intensity results largely arose from the displacement of ions, as given by Eq. 1. Hence, we calculated the intensity using Eq. 1, neglecting the other terms.[11,12] Some sets of short-range force constants were examined in order to achieve agreement between the observed and calculated intensities. Nevertheless, the agreement between the observed and calculated wavenumbers is some-

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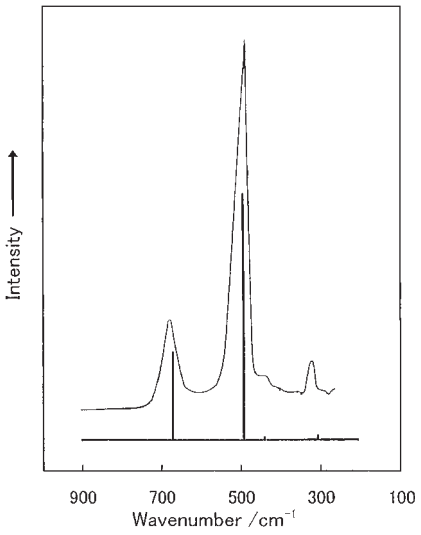

Fig. 1. The observed infrared spectrum[1] (with permission from Elsevier) and calculated line intensities.

what poor, as seen in Table 1. However, since we only used 13 force constants, neglecting many effective non-bonded ones, the agreement between the observed and calculated wavenumbers may be satisfactory.

The calculated line intensities are given with the observed spectrum[1] in Fig. 1. Their agreement indicates that the LO–TO splittings and the infrared intensities have been reasonably analyzed, despite, however, the remaining problem described above. As is well-known, the LO–TO splitting is given by the relation[8]

$$\nu_l^2 = \nu_t^2 + (\partial\mu/\partial Q)^2/(\pi V), \tag{2}$$

where ν_l and ν_t are the frequencies of the LO and TO modes, respectively, and V is the volume of the Bravais unit cell. Although Eq. 2 predicts that the stronger the infrared intensity is, the larger the LO–TO splitting will be, the true LO modes may result from further coupling with some other mode, for example with ν_6 and ν_7, as

$$\begin{vmatrix} \nu_{6l'}^2 - \nu^2 & (\partial\mu/\partial Q_6)(\partial\mu/\partial Q_7)/(\pi V) \\ sym. & \nu_{7l'}^2 - \nu^2 \end{vmatrix} = 0, \tag{3}$$

where $\nu_{l'}^2$ is given by Eq. 2. The values of $\partial\mu/\partial Q_6$ and $\partial\mu/\partial Q_7$ are 205 and 346 esu $g^{-1/2}$, respectively. From Eq. 2 $\nu_{6l'}$ and $\nu_{7l'}$ are calculated to be 750 and 746 cm^{-1}, respectively. The wavenumbers of the LO modes calculated from Eq. 3 are 866 and 607 cm^{-1}. That is, the LO modes calculated by Eq. 3 coincide well with the observed ones. This indicates that, since the basis functions of Eq. 3 are Q_{6t} and Q_{7t}, the eigen states are given by their linear combinations as $Q_{6t} + Q_{7t}$ and $Q_{6t} - Q_{7t}$ for 855 and 630 cm^{-1}, respectively, by reference to the relation of $\nu_{6l'} \approx \nu_{7l'}$. This is also supported by the vibrational modes, as shown in Fig. 2. That is, the additive and subtractive modes of the Q_{6t} and Q_{7t} given in Fig. 2c correspond well to those given in Fig. 2a, except for the direction of the displacements. It should be noted that the LO modes in Fig. 2a belong to the A_1 species on the basis of the C_{4v} symmetry,[13] whereas the LO modes in Fig. 2c belong to the T_{1u} species in the O_h symmetry.

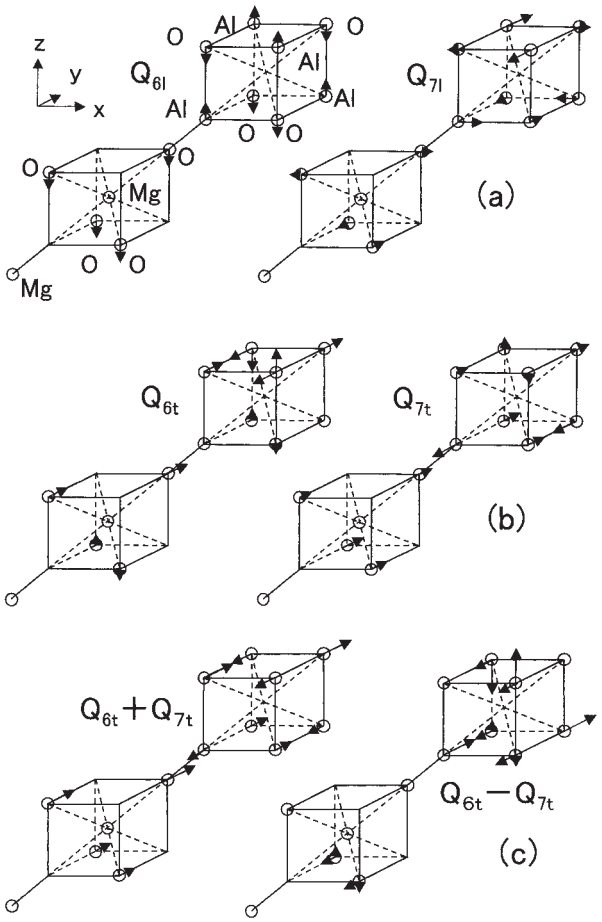

Fig. 2. Vibrational modes of Q_6 and Q_7. (a) LO modes from the normal coordinate analysis. (b) TO modes with displacements mainly along the y axis. (c) The additive and subtractive modes of Q_{6t} and Q_{7t}.

In the present analysis, the problem of the unexpected relationship between the LO–TO splitting and the infrared intensity is settled. This is the first time to clarify that LO modes can be evaluated from TO modes and their infrared intensities without a vibrational analysis.

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