



Lattice dynamical calculations for selenide spinels

A K Kushwaha* and S S Kushwaha

Department of Physics, K N Government P.G. College, Gyanpur, Bhadohi-221 304, Uttar Pradesh, India

E-mail : akkphys_bu@yahoo.com

Received 14 July 2006, accepted 1 December 2006

Abstract : The infrared and Raman phonon modes in the normal cubic $M\text{Cr}_2\text{Se}_4$ ($M = \text{Hg}, \text{Zn}$ and Cd) spinels are calculated at the first Brillouin zone-centre using rigid-ion model. The interatomic interaction between Cr-Se dominates over the other interatomic interactions. The tetrahedral $M\text{Se}_4$ units are less ionic than the octahedral CrSe_6 groupings. Good agreement is found with the available experimental infrared and Raman spectra for chromium selenide spinels

Keywords : Selenide spinel, lattice dynamics, infrared and Raman phonon modes.

PACS No. : 63.20.-e

1. Introduction

Contrary to collective bonding features, such as cohesive energies, enthalpies of formation, band structures *etc.*, determination of the strengths of individual bonds in solids is not straightforward. One of the few procedures suitable is lattice dynamical calculations. The spinel structure is one of the most important and most comprehensive studies of all structure types. It is observed that wide band gaps in these structures offer attractive photo electronic and optical applications [1]. Studies of spinels also have numerous applications in geophysics and magnetism [2, 3]. For instance, the spinel transition of olivine, which is a major constituent of Earth's mantle, is widely accepted as the origin of the near 410 km seismic discontinuity [4]. The ferromagnetic properties of some spinels are also of great importance in the solid-state chemistry.

Detailed analysis of the vibrational spectra of spinels is complicated by order/disorder phenomena that occur in these structures. In order to get more detailed information on bonding, structure, and dynamics of the spinel structure, lattice dynamical calculations should be a valuable tool. Such calculations, which are performed since the early seventies [5-12], are mostly based on relatively crude models and suffer from lack of complete experimental infrared and Raman data. Thus apart from rigid-ion model (RIM) calculations

* Corresponding Author

[9, 13], simple short-range models (SRM) [14] were used. Furthermore, most calculations were performed on the basis of the ideal spinel structure neglecting the structure parameter μ of the real crystal structure.

Recently *ab-initio* calculations have been performed to calculate the Raman and infra-red-phonon modes at the zone-centre by Pascal and Gervais [15] and Wijs *et al* [16] for MgAl_2O_4 and by Fang *et al* [17] for cubic Si_3N_4 .

In the present paper, we have carried out an improved treatment of the lattice dynamical calculations of the spinel type MCr_2Se_4 ($M = \text{Hg, Zn, Cd}$) by employing rigid-ion model and compare our results with the experimental and other theoretical results available in the literature.

2. Crystal structure and potential model

The compounds under discussion are so-called normal spinels. It is commonly accepted that normal spinels exhibits a cubic structure, with space group $\text{Fd}3\text{m}(O_h^7)$ and 56 atoms per unit cell. Fourfold-(special 8a Wyckoff position) and eightfold-(special 16d Wyckoff position) coordinated cationic sites are located in an oxygen (general 32e Wyckoff position) close-packed pseudo-face-centred-cubic sublattice. To complete the description of the anion position, an additional parameter, u and generally known as the internal parameter, is introduced. In most spinels, u lies between 0.24 and 0.275 if the origin of the unit cell is taken at the centre of inversion. For a particular value $u = 0.25$, the anions form an exactly cubic close-packed lattice and define a regular tetrahedron and octahedron with the cation as centre.

Only two formula units are present in the primitive unit cell, leading to 42 normal modes. In addition to three acoustic modes of F_{1u} symmetry, 39 optic modes are distributed among the following symmetries at the Brillouin zone-centre [18-20] as

$$\Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g} + 4F_{1u} + 2F_{2u} \quad (1)$$

There are five Raman active ($A_{1g}, E_g, 3F_{2g}$) and four infrared active ($4F_{1u}$) modes and rest are Raman inactive (F_{1g}) and infrared inactive ($2A_{2u}, 2E_u$ and $2F_{2u}$) modes.

The lattice dynamical calculations are carried out by using the rigid-ion model proposed by Kushwaha *et al* [21]. In this model the potential energy of the spinel structure compounds are expressed as the summation of short-range non-Coulombic part and long-rang Coulombic part as

$$\phi = \phi^N + \phi^C. \quad (2)$$

In view of eq. (2), It is convenient to express the dynamical matrix in terms of dimensionless frequency tensor $T_{\alpha\beta}(q, kk')$,

$$D_{\alpha\beta}(q, kk') = \frac{e^2}{V} (m_k m_{k'})^{-1/2} T_{\alpha\beta}(q, kk'), \quad (3)$$

where V is the volume of the unit cell, e is the electronic charge. m_k and $m_{k'}$ are the masses of the atoms involved, kk' denote the number of atoms per unit cell, and α and

β represent the coordinate axis x, y, and z and the frequency tensor $T_{\alpha\beta}(q, kk')$ is given as the sum of two contributions:

$$T_{\alpha\beta}(q, kk') = T_{\alpha\beta}^N(q, kk') + T_{\alpha\beta}^C(q, kk'). \quad (4)$$

In the present investigation, a rigid-ion model [21] has been applied to study the zone-centre phonons of selenide spinels $M\text{Cr}_2\text{Se}_4$ ($M = \text{Hg}, \text{Zn}, \text{and Cd}$). The set of analytical expressions are obtained by solving the dynamical matrix at the zone-centre. In these expressions, A_1 , A_2 and A_3 are bond-stretching force constants for the interatomic interactions M-Se, Cr-Se and Se-Se, respectively, whereas B_1 , B_2 and B_3 are the corresponding bond-bending force constants.

3. Results and discussion

By using the analytical expressions A_{10} , E_{10} and F_{10} , and the corresponding measured phonon frequencies [5, 22-24] at the zone-centre, the bond stretching and bond-bending force constants are evaluated for the first three neighbours. These force constants are listed in Table 1.

Table 1. The value of force constants (kdynes/cm) and effective dynamical charges for HgCr_2Se_4 , ZnCr_2Se_4 and CdCr_2Se_4

Force parameters	$A_{10}, \text{Cr}_2\text{Se}_4$	ZnCr_2Se_4	CdCr_2Se_4
A_1	54.14	66.77	49.74
B_1	1.44	2.54	2.93
A_2	78.23	74.14	74.41
B_2	4.12	4.73	4.75
A_3	14.70	12.66	14.33
B_3	1.61	1.92	1.08
Z_A	0.00	0.00	0.00
Z_B	0.88	0.92	0.86
Z_C	0.44	0.46	0.43

To evaluate the effective dynamical charges, we have used the equation derived by Scott [22], for ternary compounds $A_{n_A}B_{n_B}C_{n_C}$, given as

$$4\pi c^2 \sum_j (\omega_{LQj}^2 - \omega_{TQj}^2) = \frac{4\pi}{V} \left[\frac{n_A (Z_A^* \theta)^2}{m_A} + \frac{n_B (Z_B^* \theta)^2}{m_B} + \frac{n_C (Z_C^* \theta)^2}{m_C} \right] \quad (5)$$

where c =speed of light. n_A , n_B and n_C are stoichiometric coefficients and the condition of charge neutrality in a unit cell is given as

$$n_A Z_A^* + n_B Z_B^* + n_C Z_C^* = 0. \quad (6)$$

In order to determine three unknowns Z_A^*, Z_B^*, Z_C^* from the eqs. (5) and (6), we have follow the method proposed by Gervais [23]. These charges are given in Table 1.

Using above force parameters, we have calculated the zone-centre phonon frequencies of selenide spinels given in Table 2 (for HgCr_2Se_4), Table 3 (for ZnCr_2Se_4) and Table 4 (for CdCr_2Se_4) along with the available experimental and theoretical results in the literature.

Table 2. Experimental [24-26] and calculated zone-centre phonon frequencies of HgCr_2Se_4 along with the results of Lauwers [5]

Species	Frequencies (cm ⁻¹)		
	Experimental	Calculated	Lauwers <i>et al</i>
A_{1g}	237	239	220
E_g	157	154	158
$F_{2g}(1)$	210	215	207
$F_{2g}(2)$	168	164	176
$F_{2g}(3)$	65	69	69
$F_{1u}(1)(\text{TO})$	286	285	310
$F_{1u}(2)$	268	273	242
$F_{1u}(3)$	169	174	197
$F_{1u}(4)$	55	60	76
$F_{1u}(1)\text{LO}$	291	293	311
$F_{1u}(2)$	282	284	255
$F_{1u}(3)$	172	171	197
$F_{1u}(4)$	58	64	78
$A_{2u}(1)$		475	
$A_{2u}(2)$		281	
$E_u(1)$		416	
$E_u(2)$		150	
F_{1g}		157	
$F_{2u}(1)$		388	
$F_{2u}(2)$		141	

Table 3. Experimental [24] and calculated zone-centre phonon frequencies of ZnCr_2Se_4 along with the results of Lauwers [5]

Species	Frequencies (cm ⁻¹)		
	Experimental	Calculated	Lauwers <i>et al</i>
A_{1g}	240	241	235
E_g	152	150	153
$F_{2g}(1)$	230	229	230
$F_{2g}(2)$	182	185	186

Table 3. (contd.)

$F_{2g}(3)$	112	115	101
$F_{1u}(1)(TO)$	297	302	296
$F_{1u}(2)$	274	275	266
$F_{1u}(3)$	198	197	211
$F_{1u}(4)$	85	88	88
$F_{1u}(1)LO$	302	304	298
$F_{1u}(2)$	288	291	286
$F_{1u}(3)$	201	201	211
$F_{1u}(4)$	87	90	90
$A_{2u}(1)$		462	
$A_{2u}(2)$		283	
$E_u(1)$		406	
$E_u(2)$		202	
F_{1g}		152	
$F_{2u}(1)$		379	
$F_{2u}(2)$		133	

Table 4. Experimental [5,24] and calculated zone-centre phonon frequencies of $CdCr_2Se_4$ along with the results of Lauwers [5].

Species	Frequencies (cm^{-1})		Lauwers and Herman[9]
	Experimental	Calculated	
A_{1g}	237	336	226
E_g	154	152	152
$F_{2g}(1)$	225	226	218
$F_{2g}(2)$	169	168	178
$F_{2g}(3)$	84	85	92
$F_{1u}(1)(TO)$	288	290	299
$F_{1u}(2)$	267	266	253
$F_{1u}(3)$	186	189	207
$F_{1u}(4)$	75	75	86
$F_{1u}(1)LO$	293	294	299
$F_{1u}(2)$	281	285	277
$F_{1u}(3)$	188	195	207
$F_{1u}(4)$	77	79	89
$A_{2u}(1)$		466	

Table 4. (contd.)

$A_{2u}(2)$	280
$E_u(1)$	409
$E_u(2)$	207
F_{1g}	154
$F_{2u}(1)$	380
$F_{2u}(2)$	136

Results as obtained on the basis of the lattice dynamical calculations we may draw the following conclusions:

(i) The stretching force constant A_2 (CrSe₆ octahedron) is larger than A_1 (ZnSe₄ tetrahedron), *i.e.*, second neighbour interaction is stronger than the first neighbour interaction, whereas the bending force constants are negligible.

(ii) The effective dynamical charges of bivalent metal ions are nearly zero.

Model parameter calculations showed that the force constants A_1 and A_2 greatly depend upon the distances between M-Se and Cr-Se ions. The model calculations also shows that the octahedral bonding is stronger than tetrahedral bonding, the reason being that the bonding between Cr-Se ions is more ionic than the bonding between M-Se ions. This is also conformed from the values of effective ionic charges. Altogether, the ionicity of sulphide spinels [21] is larger than those of the corresponding selenide spinels, as it is expected from common chemical sense.

In the case of Raman active modes, value of A_{1g} mode differs by 0.4-0.8% and that of E_g mode differs by 1.3-1.9% from their respective experimental values. Values of $F_{2g}(1)$, $F_{2g}(2)$ and $F_{2g}(3)$ modes show deviations of the order of 0.4-2.4%, 0.6-2.4% and 1.2-6.1% from their corresponding observed values in the case of all selenide spinels. In the case of infrared active modes, values of $F_{1u}(1)$, $F_{1u}(2)$, $F_{1u}(3)$ and $F_{1u}(4)$ modes differ by amounts 0.4-1.7%, 0.4-1.9%, 0.5-3.1% and 0-9.1% from their respective measured values for transverse optic polarization and by amounts 0.3-0.7%, 0.7-1.4%, 0.0-3.7% and 2.6-10.3% for longitudinal optic polarizations.

References

- [1] N Ueda, T Omata, N Hikuma, K Ueda, H Miquchi, T Hashimoto and H Kawazoe *Phys. Re. Lett.* **61** 1954 (1992)
- [2] H W H Green *Geophys. Res.* **11** 817 (1984)
- [3] W Schiessl *et al.*, *Phys. Rev.* **B53** 9143 (1996)
- [4] A E Ringwood and A Major *Phys. Earth Planet. Inter.* **3** 89 (1970)
- [5] P Bruesch and F D'Ambrogio *Phys Stat. Sol. (b)* **50** 513 (1972)
- [6] H D Lutz and H Haeuseler *Ber. Bunsenges, Phys. Chem.* **79** 604 (1975)
- [7] H Shimizu, Y Ohbayashi, K Yamamoto and K Abe *J. Phys. Soc. Japan* **38** 750 (1975)
- [8] S I Boldish and W B White *Rare Earths Mod. Sci. Technol.* **13th** 607 (1978)

- [9] H A Lauwers and M A Herman *J. Phys. Chem. Solids* **41** 223 (1980)
- [10] M A Aldzhanov, A M Aliev, R K Veliev, K K Mamedov, M A Mekhtiev and V Ya Shteinshtreiber *Phys. Stat. Sol. (b)* **115**, K75 (1983)
- [11] M Wakki *Jpn. J. Phys. (Part 1)* **24** 1471 (1985)
- [12] K Wakamura, H Iwatani and K Takarabe *J. Phys. Chem. Solids* **48** 857 (1987)
- [13] M E Striefler and G R Barsch *J. Phys. Chem. Solids* **48** 57 (1987)
- [14] H C Gupta, M M Sinha, K B Chand and Balram *Phys. Chem. Solids* **53** 775 (1992)
- [15] T Pascal and F Gervais *J. Phys. C* **14** 3543 (2002)
- [16] G A de Wijs, C M Fang, G Kresse and G de With *Phys. Rev.* **B65** 094305 (2002)
- [17] C M Fang, G A de Wijs, H T Hintzen and G de With *J. Appl. Phys.* **93** 5175 (2003)
- [18] W B White and B A De Angelis *Spectrochim Acta* **23A** 985 (1967)
- [19] H D Lutz *Z Naturforsch* **24a** 1417 (1969)
- [20] A Chopelas and A M Hofmeister *Phys. Chem. Minerals* **1** 1861 (1991)
- [21] A K Kushwaha, Girija Shankar and S S Kushwaha *Indian J. Pure Appl. Phys.* **44** 385 (2006)
- [22] K Wakamura, T Arai and K Kudo *J. Phys. Soc. Jpn.* **40** 1118 (1976)
- [23] M N Iliev, E Anastassakis and T Arai *Phys. Stat. Solidi (b)* **86** 717 (1978)
- [24] M N Iliev, G Gutherod and H Pink *Solid State Commun.* **27** 863 (1978)
- [25] J F Scott *Phys. Rev.* **34** 1360 (1971)
- [26] F Gervais *Solid State Comm.* **18** 181 (1976)