



## Full Paper

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## Long wavelength optical phonon frequencies for mixed chromite spinels

### Abstract

A detailed study of long wavelength optical phonon frequencies for mixed chromite spinels  $\text{CdCr}_2\text{Se}_{4(1-y)}\text{S}_y$ ,  $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$ ,  $\text{Cd}_{1-x}\text{Zn}_x\text{Cr}_2\text{Se}_4$  and  $\text{Hg}_x\text{Zn}_{1-x}\text{Cr}_2\text{Se}_4$  are presented using rigid-ion model. In this model, the short-range part is evaluated by the expansion of potential energy in the harmonic approximation using Taylor's expansion and the long-range part is evaluated by screened Coulomb potential. Using the above proposed model, we have calculated the composition dependent zone-centre optical phonon frequencies for mixed chromite spinels. We have found an overall good agreement between experimental and theoretical results. We have also found that the ionicity of spinel structure compounds decreases as  $\text{CdCr}_2\text{X}_4 > \text{ZnCr}_2\text{X}_4 > \text{HgCr}_2\text{Se}_4$ , (X = S and Se) and sulphide spinels are more ionic than the selenide spinels.

### Key Words

Zone-centre; Mixed spinel; One-mode; Short-range; Long-range.

## INTRODUCTION

In the few decades, various studies of electrical, magnetic and vibrational properties of mixed spinel compounds are of great interest in theoretical and experimental point of view<sup>[1-3]</sup>. The infrared absorption and Raman scattering of mixed crystals are of three distinct types of compositional vibrations of phonon frequencies as one-mode, two-mode and partly two-mode behaviour. In the case of one-mode behaviour, one set of phonon frequencies varies with the concentration of the component. In the case of two-mode behaviour, two sets of phonon frequencies are observed to occur at the frequencies at the frequencies close to those of end members and in the case of partly two-mode behaviour, two sets of phonon frequencies are observed only over certain composition range and one-set of phonon frequencies over remaining composition<sup>[4,5]</sup>. The spinel type mixed compounds exhibits all the three types, one, two and partly two-mode, behaviours among four infrared active modes<sup>[6,7]</sup>.

The study of long-wavelength optical behaviour of mixed system with many atoms in the unit cell is important for understanding the disorder effect in matter<sup>[8,9]</sup>.

These lattice imperfections have a large effect on most of the physical properties, mostly the lattice dynamics of the crystal lattice. This in turn affects its various vibrational properties. The addition of small impurities may destroy the translational symmetry of the unperturbed perfect crystal in addition to slightly changing its lattice modes and hence the presence of small impurity may make a periodic solid spectroscopically interesting and informative.

In recent years, many works has been done on different types of mode behaviour in binary, ternary and quaternary types of mixed systems but not work has been done on the phonon modes on the mixed system having spinel structure. Wakamura et al.<sup>[10,11]</sup> explained the compositional dependence of the vibrational modes of  $\text{Hg}_x\text{Zn}_{1-x}\text{Cr}_2\text{Se}_4$  and  $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$  mixed spinel systems, which include basic units in which the force parameters and atomic masses of the substituted atoms varying monotonically with the composition are taken into consideration. Watanabe et al.<sup>[12]</sup> used the short-range force constant model, given by Bruesch and Ambrogio<sup>[13]</sup>, to explain the lattice vibrations of  $\text{Cd}(\text{In}_{1-x}\text{Cr}_x)_2\text{S}_4$  mixed spinel systems. Gupta et al.<sup>[14,15]</sup> have calculated the zone-centre phonon frequencies for  $\text{Cd}_{1-x}\text{Zn}_x\text{Cr}_2\text{S}_4$  and  $\text{CdCr}_2\text{Se}_{4(1-y)}\text{S}_y$  mixed spinels using

short range force constant model. Recently, Sinha et al<sup>[16]</sup> have calculated the optical phonons for chromite spinels  $\text{Cu}_{1-x}\text{Mg}_x\text{Cr}_2\text{O}_4$  and Krings et al.<sup>[7]</sup> have measured the zone-centre phonon frequencies for the mixed spinel  $\text{CoCr}_{2-x}\text{In}_x\text{S}_4$  and they found that the highest energy phonon mode exhibits one-mode behaviour whereas three low energy phonons reveals two-mode behaviour. All the above theoretical models are based on the crude model and hence we have proposed a theoretical model in which the dynamical matrix is split into two parts such as the short-range part and the long-range part. The short-range part is evaluated by using Taylor expansion of the potential energy of the spinel structure compounds in the harmonic approximation.

### CRYSTAL STRUCTURE AND POTENTIAL MODEL

The crystal structure of spinel  $\text{AB}_2\text{C}_4$  classified as  $\text{HI}_1$  space group  $\text{O}_h^7$  (Fd3m), and consist of a slightly distorted cubic close packed arrangement of C-ions with the A and B-ions occupy  $\frac{1}{2}$  of the octahedral and  $\frac{1}{8}$  of the tetrahedral sites, respectively (normal spinel)<sup>[17]</sup>. The primitive rhombohedral unit cell contains two formula units, i.e., 14 atoms per unit cell. Group theoretical treatment of the optical zone-centre ( $\Gamma = 0$ ) phonon modes are known to be resolved into 17 fundamental lattice vibration modes<sup>[18-20]</sup>. The representation of these modes at zero wave-vectors is expressed as

$$\Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g} + 5F_{1u} + 2F_{2u} \quad (1)$$

Here  $A_{1g}$ ,  $E_g$  and  $3F_{2g}$  modes are Raman-active and  $F_{1u}$  modes are infrared-active modes. In the  $5F_{1u}$  modes, one mode with frequency zero is translation mode, and the other four modes are observed in the infrared region. There is one Raman-inactive mode,  $F_{1g}$ , while  $2A_{2u}$ ,  $2E_u$  and  $2F_{2u}$  are infrared-inactive modes.

The lattice dynamical method is carried out by using the rigid-ion model proposed by Kushwaha et al<sup>[21,22]</sup>. In this model the potential energy of the spinel structure compounds is expressed as the summation of short-range non-Coulombic and long-range Coulombic interactions as

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

where N and C refers to the short-range non-Coulombic and long-range Coulombic interactions, respectively.

The secular determinant is given by

$$|D(\mathbf{q}, \mathbf{kk}') - \omega^2 \delta_{\alpha\beta} \delta_{\mathbf{kk}'}| = 0 \quad (3)$$

where  $\mathbf{kk}' = 1, 2, \dots, s$ , label the ions per unit cell.  $\mathbf{q}$  denotes the wave-vector whose allowed values range over the first Brillouin zone,  $\alpha$  and  $\beta = x, y, z$  designate the coordinate axes and  $\delta$  is the usual Kronecker delta symbol.

It is convenient to express the dynamical matrix in

terms dimensionless frequency tensor  $T_{\alpha}(\mathbf{q}, \mathbf{kk}')$  according to the equation:

$$D_{\alpha\beta}(\mathbf{q}, \mathbf{kk}') = \frac{e^2}{V} (\mathbf{m}_k \mathbf{m}_{k'})^{-1/2} T_{\alpha\beta}(\mathbf{q}, \mathbf{kk}') \quad (4)$$

Where  $V$  is the volume of the unit cell and  $e$  is the electronic charge.

In this model, the frequency tensor is given as the sum of the contributions of short-range non-Coulombic and long-range Coulombic interactions as

$$D_{\alpha\beta}(\mathbf{q}, \mathbf{kk}') = \frac{e^2}{V} (\mathbf{m}_k \mathbf{m}_{k'})^{-1/2} [T_{\alpha\beta}^N(\mathbf{q}, \mathbf{kk}') + T_{\alpha\beta}^C(\mathbf{q}, \mathbf{kk}')] \quad (5)$$

For the short-range non-Coulombic interaction, the potential energy of the spinel structure  $\phi^S$  using Taylor's series can be expressed as

$$\begin{aligned} \phi^N = \sum_{lmn} \left[ \frac{1}{r} \left( \frac{d\phi^N}{dr} \right) \right]_{|r|=|r_k|} & \left\{ \mathbf{r}_{lmn} \cdot (\mathbf{S}_{lmn} - \mathbf{S}_0) + \frac{1}{2} |\mathbf{S}_{lmn} - \mathbf{S}_0|^2 \right\} \\ & + \frac{1}{2} \left[ \frac{1}{r} \frac{d}{dr} \left( \frac{1}{r} \frac{d\phi^N}{dr} \right) \right]_{|r|=|r_k|} \left\{ \mathbf{r}_{lmn} \cdot (\mathbf{S}_{lmn} - \mathbf{S}_0) \right\}^2 \end{aligned} \quad (6)$$

where  $\mathbf{S}_0$  and  $\mathbf{S}_{lmn}$  are the displacements of the central ion and its first neighbor ions from their normal positions,  $r_{lmn}$  represents the position coordinates of neighboring ions in equilibrium.  $l, m, n$ , represent the direction cosines of the line joining the central ion and a nearest neighbor.  $|r_k|$  is the nearest neighbor distance.

In our work we have considered the non-Coulombic interaction between central ion and its three nearest neighbors. Let  $A_k$  be the bond-stretching force constant defined by the second derivative of the potential energy  $\phi^N$

$$\frac{e^2}{V} A_k = \frac{d^2 \phi^N}{dr^2} \Big|_{|r|=|r_k|} \quad (7)$$

The bond-bending force constant  $B_k$  is expressed as the first derivative of the potential energy  $\phi^N$

$$\frac{e^2}{V} B_k = \frac{1}{r} \frac{d\phi^N}{dr} \Big|_{|r|=|r_k|} \quad (8)$$

Here  $k = 1, 2, 3$  for first, second and third neighbor.

For the long-range Coulombic interaction, i.e., for  $\phi^C$ , have been calculated by the Ewald's method<sup>[23]</sup>.

### RESULTS

In the present paper, let  $A_1$  and  $B_1$  represent the bond-stretching and bond-bending force constants between A and S (Se) type of ions respectively,  $A_2$  and  $B_2$  represent similar force constants between Cr and S (Se) types of ions and  $A_3$  and  $B_3$  correspond to bond-stretching and bond-bending force constants between S-S (Se-Se) types of ions.

The dynamical matrix of the order of (42 x 42) is obtained by using the methodology of rigid-ion model. When we solve it at the zone-centre, we get analytical expressions for all the different fundamental modes of the spinel structure compounds. Using the experimental values of  $A_{lg}$ ,  $E_g$  and  $F_{lu}$  [24-29] as input data, we have calculated the three bond-stretching ( $A_1$ ,  $A_2$  and  $A_3$ ) and three bond-bending ( $B_1$ ,  $B_2$  and  $B_3$ ) force constants. The effective dynamical charges are evaluated by TO-LO splitting [21,22]. These calculated force parameters for  $ZnCr_2S_4$ ,  $CdCr_2S_4$ ,  $ZnCr_2Se_4$ ,  $HgCr_2Se_4$  and  $CdCr_2Se_4$  are listed in TABLE 1.

TABLE 1 : The value of force constants (kdynes/cm) and effective dynamical charges for  $ZnCr_2S_4$ ,  $CdCr_2S_4$ ,  $ZnCr_2Se_4$ ,  $HgCr_2Se_4$  and  $CdCr_2Se_4$

Force parameters	$ZnCr_2S_4$	$CdCr_2S_4$	$ZnCr_2Se_4$	$HgCr_2Se_4$	$CdCr_2Se_4$
$A_1$	70.80	46.96	66.77	54.14	49.74
$B_1$	2.60	1.50	2.54	1.44	2.93
$A_2$	88.47	90.95	74.14	78.23	74.41
$B_2$	2.49	1.96	4.73	4.12	4.75
$A_3$	11.99	18.25	12.66	14.70	14.33
$B_3$	0.36	0.31	1.92	1.61	1.08
$Z_A$	0.00	0.00	0.00	0.00	0.00
$Z_B$	0.66	0.62	0.92	0.88	0.86
$Z_C$	0.33	0.31	0.46	0.44	0.43

The mixed spinel resulted into two spinel compounds at composition  $x=0$  and  $x=1$ . These are called end members of the mixed spinel. The force parameters and masses of the mixed spinels at different compositions ( $0 < x < 1$ ) are evaluated, using Vegard's law [30], for  $CdCr_2Se_{4(1-x)}S_{4x}$

$$A(x) = (1-x)A_{(CdCr_2Se_4)} + xA_{(CdCr_2S_4)}$$

$$m(x) = (1-x)m_{(Se)} + xm_{(S)}$$

and for  $Zn_{1-x}Cd_xCr_2S_4$ ,  $Cd_xZn_{1-x}Cr_2Se_4$  and  $Hg_xZn_{1-x}Cr_2Se_4$

$$A(x) = (1-x)A_{(ZnCr_2(S)Se_4)} + xA_{(CdCr_2S(Se)4)}$$

$$m(x) = (1-x)m_{((S)Se)} + xm_{((S)S)}$$

Using above relations and with the help of force parameters of the end members of the corresponding mixed spinel compounds, the force parameters and the masses for mixed compounds  $CdCr_2Se_{4(1-x)}S_{4x}$ ,  $Zn_{1-x}Cd_xCr_2S_4$ ,  $Cd_xZn_{1-x}Cr_2Se_4$  and  $Hg_xZn_{1-x}Cr_2Se_4$  are calculated for different compositions. Then the optical phonon frequencies for above mixed spinel compounds are calculated at the zone-center at different compositions. Results are shown in Figures 1, 2, 3 and 4 along with the available experimental results, which exhibit an overall good agreement for all values of composition. It is clear from the figures that there is one set of optical phonon frequencies for whole composition range, i.e., one mode behavior.

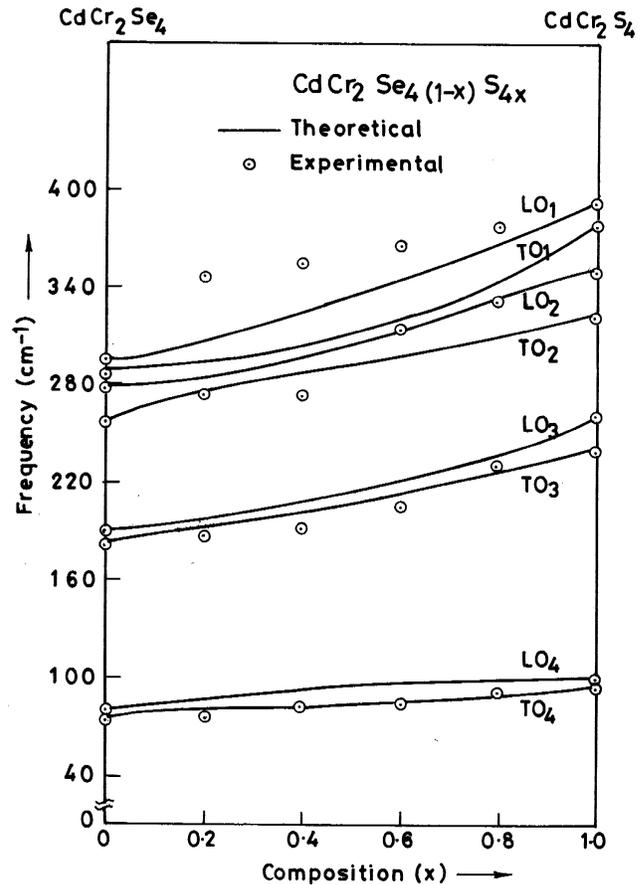


Figure 1 : One-mode behaviour of  $CdCr_2Se_{4(1-x)}S_{4x}$

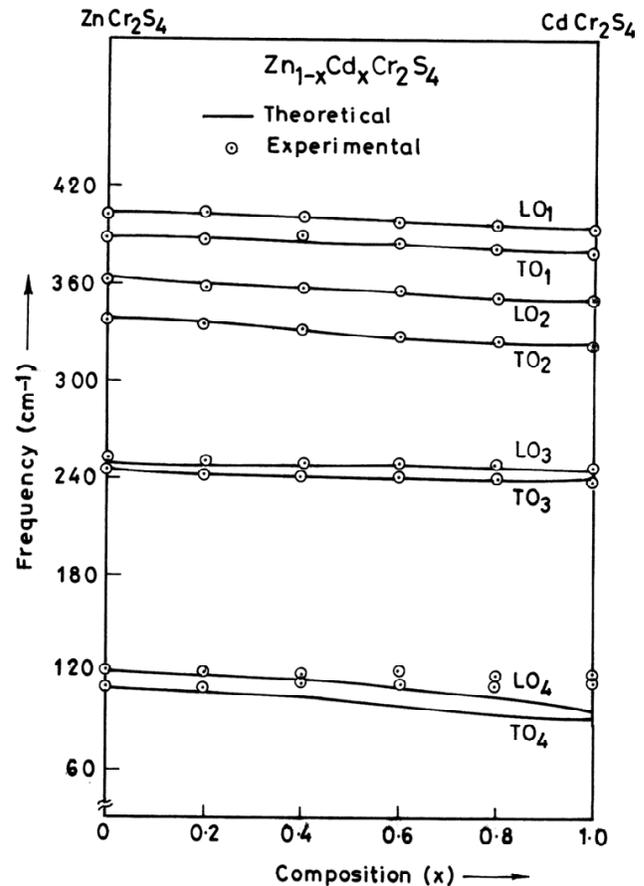


Figure 2 : One-mode behaviour of  $Zn_{1-x}Cd_xCr_2S_4$

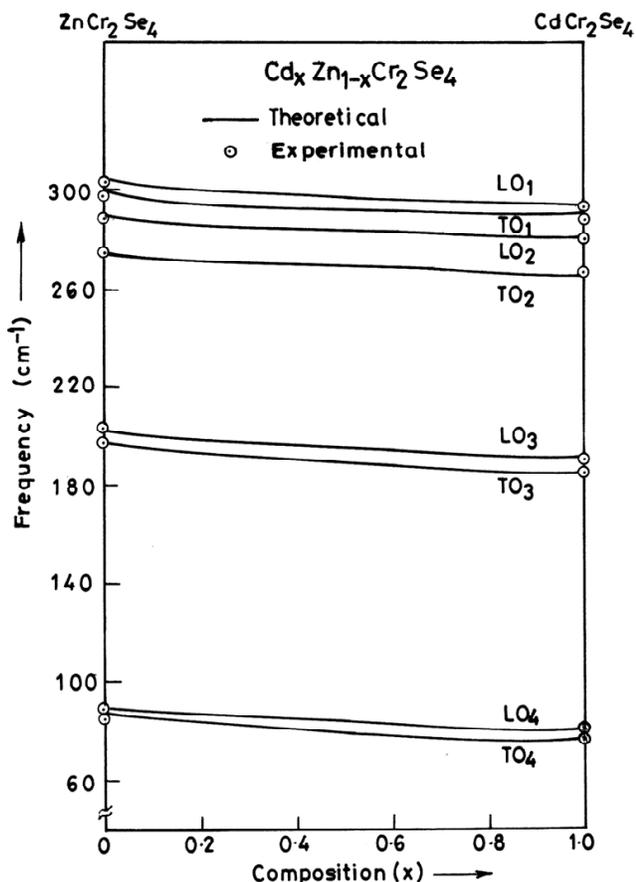


Figure 3 : One-mode behaviour of  $Cd_x Zn_{1-x} Cr_2 Se_4$

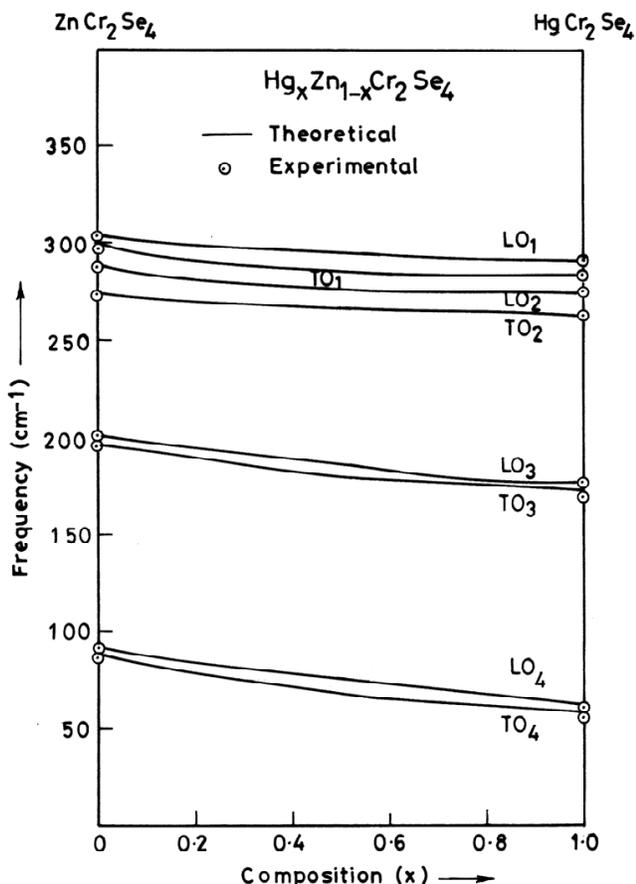


Figure 4 : One-mode behaviour of  $Hg_x Zn_{1-x} Cr_2 Se_4$

DISCUSSIONS

Figure 1 shows that the LO/TO splitting in  $CdCr_2Se_4$  is less and is increases as we move from  $CdCr_2Se_4$  to  $CdCr_2S_4$  with composition. This means that LO/TO splitting increases when Se is replaced by S and hence we conclude that the ionicity of the spinel structure compounds increases when Se is replaced by S, i.e.,  $CdCr_2S_4$  is more ionic in comparison to  $CdCr_2Se_4$ . Similarly, Figures 2 and 3 shows that the LO/TO splitting increases as we move from  $ZnCr_2X_4$  to  $CdCr_2X_4$  ( $X = S$  and  $Se$ ) for sulphide and selenide spinels both with the concentration of metal ions and Figure 4 shows that LO/TO splitting also increases with the concentration of metal ions from  $ZnCr_2Se_4$  to  $HgCr_2Se_4$ . Therefore, we conclude that the  $CdCr_2X_4$  is more ionic than  $ZnCr_2X_4$  and  $ZnCr_2Se_4$  is more ionic than  $HgCr_2Se_4$ , i.e., the ionicity of sulphide and selenide spinels decreases as  $CdCr_2X_4 > ZnCr_2X_4 > HgCr_2Se_4$ , where  $X = S$  and  $Se$  and sulphide spinels are more ionic than selenide spinels.

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