LATTICE VIBRATIONS OF MIXED CHROMITE SPINELS

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ABSTRACT

In the present paper, we have study the of zone-centre phonon modes of mixed chromite spinels using a proposed theoretical model. In this model, we have calculated the three bond stretching, three bond-bending interactions and three effective dynamical charges. Using the above calculated model parameters, we have calculated the composition dependent zone-centre phonon modes for mixed chromite spinelsCdCr2Se4(1-x)S4x, Zn1-xCdxCr2S4, CdxZn1-xCr2Se4 and HgxZn1-xCr2Se4. We find good agreement with the experimental and theoretical results available in the literature.

***Keywords**:* zone-centre, Raman, infrared, spinels

INTRODUCTION

Solid solutions are the mixtures of different pure compounds, where the mixing occurs within the crystal lattice. Spinel structure compounds forms a complete set of solid solutions with random distribution of the metal atoms on the two metal lattice sites. The vibrational spectra of mixed spinel structure compounds show one-mode behaviour, two-mode behaviour, i.e., the respective phonon modes split into two components and partially two-mode behaviour.

The study of zone-centre phonons for the mixed chromite spinels are studied from last four decades[1-4] but these all calculations are based on the crude models. Gupta et al[5, 6]have calculated the zone-centre phonon frequencies for $Cd_{1-x}Zn_xCr_2S_4$ and $CdCr_2Se_{4(1-y)}S_{4y}$ mixed spinels using de-Launay type angular force constant model. Recently, Sinha et al[7] have calculated the optical phonons for chromite spinels $Cu_{1-x}Mg_xCr_2O_4$. In these calculations they have calculated the interatomic interactions upto third nearest neighbours. Kringeet al[8] have measured the zone centre phonon frequencies for the mixed spinel $CoCr_{2-x}In_{2x}S_4$.

Wei et al[9] have studied the zone-centre Raman phonons for $LiNi_xMn_{2-x}O_4$ and find out the structural properties. Modi et al[10] have calculated the elastic properties of ferrite spinel $Zn_xCu_{1-x}Fe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) using zone-centre infrared modes and Bhatu et al[11] have studied the structural and elastic properties of $Li_{0.5(1-x)}Ni_xFe_{2.5-0.5x}O_4$ (x = 0.0 – 1.0) by infrared spectroscopic measurement. But all thesespinels are the inversec spinel structure.

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In the present work, two different types of mixed spinel compounds are studied. $Zn_{1-x}Cd_xCr_2S_4$, $Cd_xZn_{1-x}Cr_2Se_4$ and $Hg_xZn_{1-x}Cr_2Se_4$was studied first because hecation substitution is relatively simple. Only the tetrahedral divalent cation is being substituted by the other divalent cations. The second mixed spinel compound is $CdCr_2Se_{4(1-x)}S_{4x}$. This compound involves the substitution one anion by the other anion.

Crystal Structure and Potential Model

The physical, electronic, and chemical properties of a material totally depends upon the arrangement of atoms into molecules or crystal lattices. The spinel class of compounds, AB_2X_4, where A and B represent differing cations and X is anions, belongs to space group Fd3m (O_h^7). The spinel structure compound contains 8 molecules within the unit cell and hence it contains total 56 atoms but only 14 atoms are necessary to construct the simplest primitive cell. Group theoretical analysis shows that there are only 17 fundamental lattice vibration modes[12-13] (zone-centre phonon modes) exists. These fundamental modes are expressed as

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

Here A_{1g}, E_g and F_{2g} modes and F_{1u}modes are Raman and infrared-active modes respectively. F_{1g}, and A_{2u}, E_u and F_{2u} are Raman and infrared-inactive modes respectively.

In the present paper, we have used the nine parameter rigid-ion model proposed by Kushwahaet al[14] and calculated the compositional dependent zone-centre phonon frequencies for the mixedchromitespinels. In

this model, the potential energy for the spinel structure compounds is expressed as

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

where N represents the non-Coulombic short-range interactions and C represents the long-range Coulombic interactions, respectively.The secular determinant is given by

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

where$kk' = 1, 2,..$ s, label the ions per unit cell. **q** denotes the wave-vector whose allowed values range over the first Brillouin zone, α and β = x,y,z designate the coordinate axes and δ is the usual Kronecker delta symbol.

For simplicity the dynamical matrix can be expressed in terms dimensionless frequency tensor $T_{\alpha\beta}(\mathbf{q},kk')$ as

$$D_{\alpha\beta}(q,kk') = \frac{e^2}{V}(m_k m_{k'})^{-1/2} T_{\alpha\beta}(q,kk') \quad ...(4)$$

$$D_{\alpha\beta}(q,kk') = \frac{e^2}{V}(m_k m_{k'})^{-1/2}\left[T^N_{\alpha\beta}(q,kk') + T^C_{\alpha\beta}(q,kk')\right] \quad ...(5)$$

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

The potential energy ϕ^N for the short-range non-Coulombic interactions can be written as

$$\phi^N = \sum_{lmn}\left[\frac{1}{r}\left(\frac{d\phi^N}{dr}\right)_{|r|=|r_k|}\left\{r^\circ_{lmn}(S_{lmn}-S_\circ)+\frac{1}{2}|S_{lmn}-S_\circ|^2\right\} + \frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi^N}{dr}\right)\right\}_{|r|=|r_k|}\left\{r^\circ_{lmn}.(S_{lmn}-S_\circ)\right\}^2\right] \quad ...(6)$$

where$\mathbf{S_0}$ and $\mathbf{S_{lmn}}$ are the displacements of the central ion and its first neighbour ions from their normal positions, r_{lmn} represents the position coordinates of neighbouring ions in equilibrium. l, m, n, represent the direction cosines of the line joining the central ion and a nearest neighbour. $|\mathbf{r_k}|$ is the nearest neighbour distance.

In the present work, let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ^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 ϕ^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. In this paper, we have considered the interatomic interactions up to third nearest neighbours.

For the long-range Coulombic interaction, i.e., for ϕ^C, have been calculated by the Ewald's method given in the literature[14, 15]

RESULTS

In the present paper, let A_1 A_2 and A_3 are the three bond-stretching interactions between the ions A and S (Se), Cr and S (Se) and S-S (Se-Se) respectively and let B_1 B_2 and B_3 are the three bond-bending interactions between the ions A and S (Se), Cr and S (Se) and S-S (Se-Se) respectively.

Since the spinel structure compounds contain 14 atoms per unit cell therefore we get dynamical matrix of the order of (42 x 42). We have solve the dynamical matrix at zone-centre and get analytical expressions for all the different fundamental modes. Using the experimental values of Raman active modes A_{1g}, E_g and infrared active modes F_{1u}[1-3, 16, 17] at zone-centre, we have calculated 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[14.] 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.

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$CdCr_2Se_{4(1-x)}S_{4x}$, $Zn_{1-x}Cd_xCr_2S_4$, $Cd_xZn_{1-x}Cr_2Se_4$ and $Hg_xZn_{1-x}Cr_2Se_4$ at different compositions (0<x<1) are evaluated, using Vegard's law[18] and the force parameters of the end members of the corresponding mixed spinel. Then the zone-centre phonon frequencies for mixed spinel 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 different compositions and listed in Tables-2, 3, 4 1nd 5 respectively

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

Table-1: The calculated values of force constants (kdynes/cm) and effective dynamical charges for $ZnCr_2S_4$, $CdCr_2S_4$,$ZnCr_2Se_4$, $HgCr_2Se_4$ and $CdCr_2Se_4$

Species	Frequencies (cm^{-1})					
	0.0	0.2	0.4	0.6	0.8	1.0
A_{1g}	395	395	394	393	391	392
E_g	216	225	232	241	249	253
$F_{2g}(1)$	364	361	356	352	350	349
$F_{2g}(2)$	290	288	287	286	283	281
$F_{2g}(3)$	125	121	118	113	108	95
$F_{1u}(1)(TO)$	389	386	385	384	382	380
$F_{1u}(1)(exp)$	387	387	389	385	382	378
$F_{1u}(2)$	341	337	332	328	325	324
$F_{1u}(2)(exp)$	336	334	332	328	324	321
$F_{1u}(3)$	245	244	242	241	241	240
$F_{1u}(3)(exp)$	247	245	244	242	241	239
$F_{1u}(4)$	113	110	105	102	98	95
$F_{1u}(4)(exp)$	114	113	114	114	114	114
$F_{1u}(1)(LO)$	406	403	401	398	397	396
$F_{1u}(1)(exp)$	403	402	401	397	395	391
$F_{1u}(2)$	365	361	358	355	353	351
$F_{1u}(2)(exp)$	361	358	357	356	353	350
$F_{1u}(3)$	246	245	243	241	240	239
$F_{1u}(3)(exp)$	249	248	246	244	242	241
$F_{1u}(4)$	118	115	108	102	98	96
$F_{1u}(4)(exp)$	116	116	117	117	115	115
$A_{2u}(1)$	457	452	443	436	429	426
$A_{2u}(2)$	275	285	295	312	317	327
$E_u(1)$	377	371	367	362	359	356
$E_u(2)$	150	142	136	128	121	116
F_{1g}	257	254	251	249	247	243
$F_{2u}(1)$	332	331	329	328	328	326
$F_{2u}(2)$	169	161	153	142	138	128

Table-2: Experimental [1, 2] and calculated zone center phonon frequencies (cm^{-1}) of $Zn_{1-x}Cd_xCr_2S_4$

Species	Frequencies (cm^{-1})					
	0.0	0.2	0.4	0.6	0.8	1.0
A_{1g}	235	256	278	309	348	392
E_g	152	171	186	205	231	253
$F_{2g}(1)$	223	246	289	305	326	348
$F_{2g}(2)$	172	196	212	235	254	281
$F_{2g}(3)$	86	89	91	92	94	95
$F_{1u}(1)(TO)$	289	298	307	322	343	380
$F_{1u}(1)(exp)$	288					380
$F_{1u}(2)$	266	275	289	295	310	324
$F_{1u}(2)(exp)$	267					324
$F_{1u}(3)$	183	197	208	215	228	240
$F_{1u}(3)(exp)$	188	186	191	206	232	239
$F_{1u}(4)$	78	81	86	89	93	95
$F_{1u}(4)(exp)$	75	76	83	83	92	96
$F_{1u}(1)(LO)$	295	304	326	342	369	392
$F_{1u}(1)(exp)$	293					392
$F_{1u}(2)$	282	296	305	321	339	351
$F_{1u}(2)(exp)$	281					348
$F_{1u}(3)$	185	196	208	215	235	239
$F_{1u}(3)(exp)$	188					242
$F_{1u}(4)$	88	91	93	94	96	100
$F_{1u}(4)(exp)$	77					98
$A_{2u}(1)$	466	452	439	432	429	426
$A_{2u}(2)$	280	291	302	315	322	335
$E_u(1)$	406	402	311	318	325	356
$E_u(2)$	210	212	213	215	216	218
F_{1g}	156	175	191	205	221	243
$F_{2u}(1)$	380	369	351	341	332	326
$F_{2u}(2)$	136	134	132	130	129	128

Table-3: Experimental [1, 19] and calculated zone center phonon frequencies (cm^{-1}) of $CdCr_2Se_{4(1-x)}S_{4x}$

Species	Frequencies (cm^{-1})					
	0.0	0.2	0.4	0.6	0.8	1.0
A_{1g}	241					239
E_g	150					154
$F_{2g}(1)$	229	225	223	221	218	215
$F_{2g}(2)$	185	179	177	170	167	164
$F_{2g}(3)$	115	104	195	87	78	69
$F_{1u}(1)(TO)$	302	293	288	286	285	285
$F_{1u}(1)(exp)$	297					286
$F_{1u}(2)$	275	273	270	267	265	266
$F_{1u}(2)(exp)$	274					268
$F_{1u}(3)$	197	190	183	178	174	174
$F_{1u}(3)(exp)$	198					169
$F_{1u}(4)$	88	80	71	67	63	60
$F_{1u}(4)(exp)$	85					55
$F_{1u}(1)(LO)$	305	300	298	294	293	229
$F_{1u}(1)(exp)$	302					291
$F_{1u}(2)$	291	289	287	286	285	284
$F_{1u}(2)(exp)$	288					282
$F_{1u}(3)$	201	196	189	183	178	171
$F_{1u}(3)(exp)$	201					172
$F_{1u}(4)$	90	85	78	72	67	64
$F_{1u}(4)(exp)$	87					58
$A_{2u}(1)$	462	467	469	472	474	475
$A_{2u}(2)$	283	283	282	282	281	281
$E_u(1)$	406	409	411	412	413	416
$E_u(2)$	202	192	186	175	163	150
F_{1g}	152	152	154	155	156	157
$F_{2u}(1)$	397	395	392	390	389	388
$F_{2u}(2)$	133	135	138	139	139	141

Table-4: Experimental [1, 2] and calculated zone center phonon frequencies (cm^{-1}) of $Hg_xZn_{1-x}Cr_2Se_4$

Species	Frequencies (cm^{-1})					
	0.0	0.2	0.4	0.6	0.8	1.0
A_{1g}	241	241	240	239	238	336
E_g	150	150	151	151	152	152
$F_{2g}(1)$	229	229	228	228	226	226
$F_{2g}(2)$	185	182	178	178	172	168
$F_{2g}(3)$	115	111	104	96	92	85
$F_{1u}(1)(TO)$	300	294	292	288	290	290
$F_{1u}(1)(exp)$	297					288
$F_{1u}(2)$	275	270	270	269	276	266
$F_{1u}(2)(exp)$	274					267
$F_{1u}(3)$	197	194	191	187	186	189
$F_{1u}(3)(exp)$	198					186
$F_{1u}(4)$	88	84	81	77	76	75
$F_{1u}(4)(exp)$	85					75
$F_{1u}(1)(LO)$	304	301	299	297	296	294
$F_{1u}(1)(exp)$	302					293
$F_{1u}(2)$	291	285	284	283	282	285
$F_{1u}(2)(exp)$	288					281
$F_{1u}(3)$	201	199	197	196	195	195
$F_{1u}(3)(exp)$	201					188
$F_{1u}(4)$	90	87	85	82	81	79
$F_{1u}(4)(exp)$						
$A_{2u}(1)$	462	462	463	464	464	466
$A_{2u}(2)$	283	283	281	281	280	280
$E_u(1)$	406	406	407	408	408	409
$E_u(2)$	202	204	204	205	207	207
F_{1g}	152	152	153	154	154	154
$F_{2u}(1)$	379	379	380	380	382	380
$F_{2u}(2)$	133	134	136	136	138	136

Table-5: Experimental [1, 2] and calculated zone center phonon frequencies (cm^{-1}) of $Cd_xZn_{1-x}Cr_2Se_4$

CONCLUSIONS

In the present paper, we have calculated zone centre phonon frequencies for the mixed chromite spinels$CdCr_2Se_{4(1-x)}S_{4x}$, $Zn_{1-x}Cd_xCr_2S_4$, $Cd_xZn_{1-x}Cr_2Se_4$ and $Hg_xZn_{1-x}Cr_2Se_4$ using nine parameter rigid ion model. We find an overall good agreement with the previously available experimental and theoretical results.

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