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Vibrational, Elastic Properties and Sound Velocities of $ZnAl_2S_4$ Spinel

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Abstract. Nine parameter rigid-ion model is used to calculate the zone-centre phonon frequencies, elastic properties, sound velocities along symmetry directions and Debye temperature for $ZnAl_2S_4$ spinel. We have also calculated the interatomic interactions upto third nearest neighbours. The main outcomes of present calculations are that the tetrahedral bonding is stronger in comparison to the octahedral bonding. We have compared our calculated results with the previously available experimental and theoretical data.

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1 Introduction

A large group of compounds with chemical formula AB_2X_4 crystallizes as spinel structure. In the spinel structure A atoms are occupied by the tetrahedral sides and the B atoms are occupied by the octahedral sides. Compounds having spinel structure are wide band gap semiconductor and, hence, these compounds found more attention by the theoretical and experimental researchers.

$ZnAl_2S_4$ belongs to the family of spinel structure and the studies of this compound are scare. Very recently, Yang et al. [1] have been calculated the lattice dynamical, elastic and thermodynamic properties of $ZnAl_2S_4$ using first principles method by VASP code [2-4] and CASTEP code [5]. Brik et al. [6] have also used the CASTEP code [5] to calculated the electronic optical and elastic properties by density functional theory. Yang et al. [1] and Brik et al. [6] describe electron–ion interactions by the full potential frozen-core projector augmented wave [7] method, and the exchange-correlation is treated within the generalized gradient approximation (GGA) [8,9] of Perdew-Burke-Ernzerhof (PBE) [10]. The ultrasoft pseudopotentials are used for all elements and the GGA with PBE functional is employed for the exchange correlation of electrons. Haddou et

al. [11] have calculated the structural, elastic, electronic, optical, and thermodynamic properties of $ZnAl_2S_4$ compound using density functional theory using full-potential linearized augmented plane wave plus local orbitals method [12,13] as implemented in Wien2K code [14].

In the present paper, we have studied the zone-center phonon properties, elastic properties, sound velocities and Debye temperature for $ZnAl_2S_4$ using a proposed nine parameter (three bond-stretching, three-bond bending and three effective dynamical charges) rigid-ion model.

2 Crystal Structure and Potential Model

The spinel $ZnAl_2S_4$ belongs to space group $Fd\bar{3}m$, a cubic lattice consisting of 8 molecules within the unit cell. Because of the large number of atoms within the spinel unit cell, it is common to identify sub-units within the spinel unit cell. A tetrahedral unit, ZnO_4 is comprised of the Zn at the center of a cube and four sulphur atoms in the nonadjacent corners. The octahedral unit consists of Al atom surrounded by six sulphur atoms, two along each dimensional axis, to form a AlS_6 octahedron. The tetrahedra within the spinel lattice are isolated from one another while octahedral units share a single edge. Two sulphur atoms are shared between adjacent octahedra. The primitive cell of $ZnAl_2S_4$ spinel contains only 14 atoms. The group theoretical analysis shows following normal modes of symmetries for spinel

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

The (R) and (IR) identify Raman- and infrared-active vibrational species, respectively.

The potential energy Φ of the compounds possessing the spinel structure can be expressed as [15]

$$\Phi = \varphi^{\mathrm{N}} + \varphi^{\mathrm{C}}\,, \quad (2)$$

where superscripts N and C refer to the non-Coulomb and Coulomb parts respectively.

The secular determinant is given by

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

where $kk' = 1, 2, \ldots, s$ label the ions per unit cell. $\mathbf{q}$ denotes the wave-vector whose allowed values range over the first Brillouin zone. α and $\beta = x, y, z$ designate the coordinate axes and δ is the usual Kronecker delta symbol. m_k is the mass of the ion k^{th} in the l^{th} cell. The elements of the dynamical matrix are

defined as,

$$D_{\alpha\beta}(\mathbf{q}kk') = \sum_{l'} \frac{1}{\sqrt{m_k m_k}} \varphi_{\alpha\beta}(lk, l'k') \exp[i\mathbf{q}\mathbf{r}^{\circ}(lk, l'k')], \tag{4}$$

where $\mathbf{r}^{\circ}(lk, l'k') = \mathbf{r}^{\circ}(l'k') - \mathbf{r}^{\circ}(lk)$. As usual $\varphi_{\alpha\beta}(lk, l'k')$ denote the coupling parameters between ions (lk) and $(l'k')$.

In view of equation (3), the dynamical matrix $D(\mathbf{q}, kk')$ is constructed from two constituents

$$D(\mathbf{q}, kk') = D^{\mathrm{N}} + D^{\mathrm{C}}\,. \tag{5}$$

The first term D^N of the dynamical matrix is the non-Coulomb interaction part, which is introduced to simulate the contributions from short-range non-Coulomb interaction to the potential energy. The second term is the Coulomb interaction part due to undeformable ion interactions, and we can write it in conventional matrix form as

$$F^{\mathrm{C}} = -\mathbf{ZQZ}\ , \tag{6}$$

where $\mathbf{Z}$ is a diagonal matrix specifying the effective dynamical charges z_k.

In view of these observations our model essentially reduces to the rigid-ion model incorporating the short-range non-Coulomb and Coulomb interactions. We shall obtain matrix elements $D_{\alpha\beta}(\mathbf{q}, kk')$ for such interactions. It is convenient to express the dynamical matrix in terms dimensionless frequency tensor $T_{\alpha\beta}(\mathbf{q}, kk')$ according to

$$D_{\alpha\beta}(q, kk') = \frac{e^2}{V}(m_k m_{k'})^{-1/2} T_{\alpha\beta}(q, kk')\,, \tag{7}$$

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

In our model, the frequency tensor is given as the sum of normal (N) and Coulomb (C) contributions

$$T_{\alpha\beta}(q, kk') = T^{\mathrm{N}}_{\alpha\beta}(q, kk') + T^{\mathrm{C}}_{\alpha\beta}(q, kk')\,. \tag{8}$$

As the dynamical matrix in spinels is of the rank 42 and is symmetric in both type of indices ($\alpha\beta$ and kk', each of two tensors in (8) has $6 \times 105 = 630$ independent components. At zero wave-vector most of these become equal and can be obtained by means of symmetry operations of the space group O_h^7 from the set of independent matrix.

For the short-range non-Coulomb interaction, the potential energy of the spinel structure φ^{N} using Taylor's series can be expressed as,

$$\varphi^{\mathrm{N}} = \sum_{lmn} \Big[\frac{1}{r}\Big(\frac{d\varphi^{\mathrm{N}}}{dr}\Big)_{|r|=|r_k|} \Big\{r^{\circ}_{lmn}(S_{lmn} - S_{\circ}) + \frac{1}{2}|S_{lmn} - S_{\circ}|^2\Big\} + \frac{1}{2}\Big\{\frac{1}{r}\frac{d}{dr}\Big(\frac{1}{r}\frac{d\varphi^{\mathrm{N}}}{dr}\Big)\Big\}_{|r|=|r_k|} \{r^{\circ}_{lmn}(S_{lmn} - S_{\circ})\}^2\Big], \tag{9}$$

where $S_\circ$ and 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. $|\mathbf{r}_k|$ is the nearest neighbor distance.

In the present paper, we have considered the non-Coulomb 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 φ^{N}

$$\frac{e^2}{V}A_k = \frac{d^2\varphi^{\mathrm{N}}}{dr^2}\Big|_{|r|=|r_k|}. \tag{10}$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy φ^{N}

$$\frac{e^2}{V}B_k = \frac{1}{r}\,\frac{d\varphi^{\mathrm{N}}}{dr}\Big|_{|r|=|r_k|}. \tag{11}$$

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

For the Coulomb part, i.e., for φ^{C}, the Coulomb contribution of all quantities has been calculated from the equation based on the Ewald's method [16]. The potential function for the Coulomb part can be written as

$$\varphi^{\mathrm{C}}_{kk'}(r) = \frac{(Z_k e)(Z_{k'} e)}{|r|}, \tag{12}$$

where $\mathbf{r} = \mathbf{r}^\circ(l', k') - \mathbf{r}^\circ(l, k)$, $Z_k e$ and $Z_{k'} e$ are charges on the k-th and k'-th ions.

3 Results and Discussions

We have considered, A_1, A_2 and A_3 are the bond-stretching and B_1, B_2 and B_3 are the bond-bending interactions between Zn–S, Al–S and S–S, respectively.

Table 1. The value of force constants (kdynes/cm) and effective dynamical charges for $ZnAl_2S_4$ spinel

Force parameters	Internal coordinates	Present calculation
A_1	Zn–S	115.38
B_1	Zn–S	9.98
A_2	Al–S	46.28
B_2	Al–S	5.71
A_3	S–S	11.27
B_3	S–S	2.56
Z_{Zn}		1.41
Z_{Al}		1.72
Z_S		-1.21

The dynamical matrix of the order of (42×42) is obtained by using the methodology of rigid-ion model. When we solve it at the zone-center, we get analytical expressions for all the different fundamental modes of the spinel structure compounds. Using experimental values of Raman modes $\mathrm{A_{1g}}$ and $\mathrm{E_g}$ and the infrared mode $\mathrm{F_{1u}}$, we have calculated the above interatomic interactions and listed in Table 1.

The interatomic interactions up to third nearest neighbours for $ZnAl_2S_4$ (Table 1) shows that the first neighbour interaction (Zn–S, tetrahedral) is stronger than the second neighbour interactions (Al–S, octahedral). This shows that the tetrahedral bonding is more ionic than that of the octahedral bonding.

Using the above calculated force parameters and analytical expressions for all the different fundamental modes at zone centre, we have calculated zone-centre Raman and infrared active and inactive phonon modes and listed in Table 2, along with the available experimental [17] and theoretical results [1] in the literature for $ZnAl_2S_4$ spinel.

Table 2. Observed [16] and calculated [1] zone-centre phonon frequencies for $ZnAl_2S_4$ spinel

Species	Frequencies [cm^{-1}]		
	Observed	Calculated	Yang et al
A_{1g}	350	350	437
E_g	133	132	229
$F_{2g}(1)$	224	223	135
$F_{2g}(2)$	282	284	301
$F_{2g}(3)$	415	416	374
$F_{1u}(1)$ TO	69.3	68	136
$F_{1u}(2)$	163.9	161	296
$F_{1u}(3)$	344.2	345	335
$F_{1u}(4)$	445.7	448	395
$F_{1u}(1)$ LO	76.9	74	137
$F_{1u}(2)$	188.6	188	309
$F_{1u}(3)$	397.3	400	342
$F_{1u}(4)$	480.0	482	470
$A_{2u}(1)$		398	400
$A_{2u}(2)$		430	427
$E_u(1)$		215	217
$E_u(2)$		344	341
F_{1g}		214	211
$F_{2u}(1)$		161	164
$F_{2u}(2)$		282	280

We have also calculated the three elastic constants C_{11}, C_{12} and C_{44} for $ZnAl_2S_4$ spinel by using the methodology given in the literature [18] and listed in Table 4. The calculated elastic constants verifies the mechanical stability condi-

tions given by

$$(C_{11} - C_{12}) > 0, \quad C_{12} < B < C_{11}, \quad (C_{11} + 2C_{12}) > 0, \quad C_{44} > 0 \quad (13)$$

Using these calculated elastic constants, we have also calculated the mechanical properties, sound velocities and Debye temperature for $ZnAl_2S_4$ spinel and listed in Tables 3 and 4 along with their previously theoretical [1,6,11] results in the literature. The experimental data are not available in the literature for comparison.

Table 3. Calculated elastic constants C_{11}, C_{12} and C_{44} [GPa], bulk modulus B [GPa], compressibility coefficient K [GPa^{-1}], shear modulus G [GPa], Young's modulus Y [GPa], Poisson's ratio σ, anisotropy factor and compared to other workers [1,6,11] of $ZnAl_2S_4$ spinel

	C_{11}	C_{12}	C_{44}	B	G	B/G	K	Y	σ	A
Present	153	56	48	88	48	1.83	1.13×10^{-3}	122	0.58	0.99
Cal. [11]	151	58	47	89	47	1.90		119	0.28	1.0
Cal[a] [1]	120	68	65	85	45	1.89		115	0.2749	2.4499
Cal[b] [1]	120	65	64	84	45	1.85		115	0.2710	2.3432
Cal. [6]	112	51	60	71	46	1.56		81	0.3114	1.9367

[a]VASP; [b]CASTEP

Table 4. Elastic wave velocities (in m/s) for different propagation directions and Debye temperature (Θ_D in K) for $ZnAl_2S_4$ spinel

Compound	$v_L^{[100]}$	$v_T^{[100]}$	$v_l^{[110]}$	$v_t^{[110]}$	$v_{t\perp}^{[110]}$	$v_{v_{l'}}^{[111]}$	$v_{v_{t'}}^{[111]}$	V_L	V_T	V_m	Θ_D
Present	4890	2789	4972	2789	2804	4969	2799	5891	3112	3789	601
Cal. [11]											575
Cal. [6]								6342	3728	4133	944

Now, we compare the results of $ZnAlS_4$ with the results of $ZnAl_2O_4$ [19]. We can draw following conclusions:

1. $ZnAl_2S_4$ is less ionic in comparison to $ZnAl_2O_4$ which is obvious and hence we can see that the phonon modes of $ZnAl_2S_4$ having less frequencies in comparison to the phonon frequencies of $ZnAl_2O_4$.
2. The elastic constants, bulk modulus and hence compressibility of $ZnAl_2S_4$ is less in comparison to $ZnAl_2O_4$.

4 Conclusions

In the present paper, we have calculated the interatomic interactions for $ZnAl_2S_4$ spinel up to third nearest neighbours using nine parameter rigid-ion model. We

have also calculated, zone-centre phonon frequencies, elastic constants, mechanical properties, sound velocities in high symmetry directions and Debye temperature. We have also compare the results of $ZnAl_2S_4$ and $ZnAl_2O_4$.

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