Lattice dynamical calculations of spinel structure compounds

A K Kushwaha, Girija Shankar & S S Kushwaha
Department of Physics, Bundelkhand University, Jhansi 284 128
E-mail: akkphys_bu@yahoo.com

Received 10 August 2005; revised 15 February 2006; accepted 28 February 2006

Lattice dynamical calculations have been performed for normal spinel structure compounds using the proposed theoretical model. In this model, the dynamical matrix is split into two parts: (i) the short range part is evaluated by using Taylor’s expansion of the crystal potential energy in the harmonic approximation and (ii) the long range part is evaluated on the basis of screened Coulomb potential. This model is applied to study the zone centre (\(\Gamma=0\)) phonon frequencies of sulphide spinels MCr2S4 (M= Mn, Fe, Cd). The significant outcome of the present work is that (i) the tetrahedral M-S force constants are smaller than the respective octahedral (Cr-S) ones, (ii) the bending force constants are negligible, and (iii) the effective dynamical charges of the bivalent metal ions are nearly zero. The zone-center phonon frequencies, thus calculated using these parameters are found to be in very good agreement with the observed results.

Keywords: Spinel structure, Lattice dynamics, Octahedral, Zone center, Phonons

IPC Code: C30B

1 Introduction

Lattice dynamical calculation is one of the important tools in understanding the thermodynamical, structural, bonding and numerous other solid state properties. Consequently, the lattice dynamical calculation of various compounds has been widely studied by experimental techniques. The experimental techniques have quite precise information about the vibration of phonons. Phonons being one of the elementary excitations of solids provide complete information about the interatomic forces in solids. The interatomic forces are of paramount importance as their study leads to an understanding of bonding and structural properties of the compounds. All the properties depend upon constituent atoms of the crystal and can be obtained with the help of theoretical models of lattice dynamical calculations.

Among the ternary chalcogenides \(\text{A}^{II}\text{B}^{III}\text{C}_4\), spinel type compounds are of considerable experimental and theoretical interest. Thus, magnetic and electric properties, structural features, such as structure maps and cation distributions with regard to the tetrahedral and octahedral sites and vibrational behaviour in terms of bonding, ionicity and carrier concentration have been studied thoroughly in the last five decades\(^{1,6}\). The spinel structure compounds have numerous applications such as in the preparation of high frequency core materials and in geophysics. Their bonding and stability properties requires significant attention due to their phase transformation into an olivine structure, an important part of earth mental. In recent years lattice dynamical calculations have been done by Lutz et al\(^{7}\). using short-range model (SRM), rigid-ion model (RIM) and polarizable ion model (PIM). Gupta et al\(^{8}\). have studied the zone-center phonon frequencies of spinel structure compounds using a short-range model. Recently Pascal et al\(^{9}\). performed ab-initio calculation of infrared and Raman phonon modes for \(\text{MgAl}_2\text{O}_4\) using the density function theory\(^{10}\).

In the present work, we have developed a theoretical model to study the zone-center (\(\Gamma=0\)) phonon frequencies of normal sulphide spinels MCr2S4 (Mn, Fe, Cd). In the present model, the dynamical matrix is split into two parts (ii) the short-range part and (ii) the long-range part. The short-range part is evaluated by using Taylor’s expansion of crystal potential energy and the long-range part is evaluated using screened Coulomb potential.

2 Theory

2.1 Crystal Structure and Symmetry

The crystal structure of spinel \(\text{AB}_2\text{C}_4\) classified as \(\text{HI}_1\) space group \(\text{O}_{6}^{7}\) (Fd3m), consists of a slightly distorted cubic close packed arrangement of C-ions with the A and B-ions occupy \(1/2\) of the octahedral and \(1/8\) of the tetrahedral sites\(^{11}\), respectively (normal
spinel). An inverse spinel in which one half of the
b-ions occupies the tetrahedral sites and the other half
of B-ions and the A-ions occupy the octahedral sites.

Figure 1 shows a portion of the normal spinel
structure. The primitive rhombohedral unit cell
contains two formula units. The 14 atoms, which form
the basis of the structure, are depicted and numbered.
Table 1 contains the equilibrium coordinate of these
14 atoms referred to the cubic system (x, y, z) of
Fig. 1. A complete representation of the spinel
structure is shown in Fig. 2.

The reduction of 3×14=42 dimensional
representation into the irreducible lattice vibration
mode at zero wave vector (Γ=0) is known to be
resolved into 17 fundamental lattice vibration modes.
The representation of these modes at zero wave
vectors is expressed as:

\[ \Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g} + 5F_{1u} + 2F_{2u} \] …(1)

where \( A_{1g}, E_g \) and \( 3F_{2g} \) modes are Raman active and
\( F_{1u} \) modes are infrared active modes. In the \( 5F_{1u} \)
modes, one mode is translation mode, frequency of
which is zero 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. Figs (3 and 4) show
vibrations of Raman and Infrared active modes,
respectively.

2.2 Potential Model

The potential energy \( \Phi \) of the compounds
possessing the spinel structure is expressed as:

\[ \Phi = \phi^N + \phi^C + \phi^I + \phi^M \] …(2)

where superscripts N and C refer to the non-
Coulombic and Coulombic parts respectively. I and M
stand for contributions corresponding to dipole
interaction and macroscopic field, respectively.

---

Table 1—Equilibrium coordinates \( a_x, a_y, a_z \) of the 14 atoms which form the basis of the primitive unit cell,
\( a \) is the cubic lattice parameter, the structure parameter \( u \) defines the position of the anion.
The numbering of the atoms and coordinate system is shown in Fig. 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>( a_x )</th>
<th>( a_y )</th>
<th>( a_z )</th>
<th>Atom</th>
<th>( a_x )</th>
<th>( a_y )</th>
<th>( a_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>(1/2−u)a</td>
<td>ua</td>
<td>(1/2−u)a</td>
</tr>
<tr>
<td>2</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>9</td>
<td>(1/2−u)a</td>
<td>(1/2−u)a</td>
<td>ua</td>
</tr>
<tr>
<td>3</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>10</td>
<td>ua</td>
<td>(1/2−u)a</td>
<td>(1/2−u)a</td>
</tr>
<tr>
<td>4</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>11</td>
<td>(5/8)a</td>
<td>(5/8)a</td>
<td>(5/8)a</td>
</tr>
<tr>
<td>5</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>(u−1/4)a</td>
<td>12</td>
<td>(5/8)a</td>
<td>(3/8)a</td>
<td>(3/8)a</td>
</tr>
<tr>
<td>6</td>
<td>(1/4)a</td>
<td>(1/4)a</td>
<td>(1/4)a</td>
<td>13</td>
<td>(3/8)a</td>
<td>(3/8)a</td>
<td>(5/8)a</td>
</tr>
<tr>
<td>7</td>
<td>ua</td>
<td>ua</td>
<td>ua</td>
<td>14</td>
<td>(3/8)a</td>
<td>(5/8)a</td>
<td>(3/8)a</td>
</tr>
</tbody>
</table>

---
The secular determinant is given by

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

where $kk' = 1, 2, \ldots \ldots s$ labeling the ions per unit cell. $q$ denotes the wave vector whose allowed values range over the first Brillouin zone. $\alpha$ and $\beta = x, y, z$ designating the coordinate axes and $\delta$ is the usual Kronecker delta symbol. $m_k$ is the mass of the ion $k$ in the $l$th cell. The elements of the dynamical matrix are defined as,

$$D_{\alpha \beta}(q, kk') = \sum m_k m_{k'} \phi_{\alpha \beta}(lk,l'k') \exp[iq \cdot r_{l'(l'k')}(lk)] \quad \cdots (4)$$

where $r_{l'(l'k')}(lk) = r_{l'(l'k')} - r_{lk}$. As usual $\phi_{\alpha \beta}(lk, l'k')$ denotes the coupling parameters between ions $(lk)$ and $(l'k')$.

In view of Eq. (3), the dynamical matrix $D(q, kk')$ is constructed from four constituents

$$D(q, kk') = D^N + D^C + D^I + D^M \quad \cdots (5)$$

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

$$F^C = -ZQZ \quad \cdots (6)$$

where $Z$ is a diagonal matrix specifying the effective dynamical charges $z_k$. The matrix elements of $Z$ are given by

$$Z_{\alpha \beta kk'} = \delta_{\alpha \beta} \delta_{kk'} z_k \quad \cdots (7)$$

Likewise the elements of $Q$ are expressed as:

$$Q = Q_{\alpha \beta kk'}(q) - \delta_{kk'} \sum (z_{k''}/z_k) Q_{\alpha \beta kk''}(0) \quad \cdots (8)$$

where $Q$ is the Coulombic coefficient matrix, representing the long-range electrostatic interaction.

The third term $F^I$, the Coulombic interaction part resulting from the induced dipole interactions through the electronic polarizability is expressed by the following equation
\[ F^i = -ZQRQZ \]  \quad \ldots (9)  

where  
\[ R = (I - AQ)^{-1} A \]  

\[ I_{\alpha\beta k k'} = \delta_{\alpha\beta} \delta_{kk'} \]  \quad \ldots (10)  

\[ A_{\alpha\beta k k'} = \delta_{kk'} \alpha_{\alpha k} \]  \quad \ldots (10)  

\[ \alpha_k \] being the electronic polarizability tensor of the \( k \)th ion. The last term, i.e., macroscopic field part is given by the equation:  
\[ F^M = ZSYSZ \]  \quad \ldots (11)  

where  
\[ S = I + QR \]  \quad \ldots (12)  

\[ Y_{\alpha\beta k k'} = \left\{ (P + j\rho)^{-1} \right\}_{\alpha\beta} \]  \quad \ldots (12)  

\[ \Gamma_{\alpha\beta} = \delta_{\alpha\beta} \]  

\[ \rho_{\alpha\beta} = \sum_{kk} R_{\alpha\beta k k} \]  

\[ f_{\alpha\beta} = \frac{4\pi q_{\alpha} q_{\beta}}{V} \left| q \right|^2 \]  

\[ V \] is the unit cell volume and tilde denotes the transposed matrix.

It has been observed that the contributions due to the third term, i.e., the Coulomb interaction part resulting from the induced dipole interactions is not of importance so far as our studies are concerned because electronic polarizability giving rise to such interaction is insignificant. Also contributions of the last term (the macroscopic field part) are negligibly smaller in comparison with the non-Coulombic and Coulombic parts in the zone-center frequency calculations for spinel structure. In view of these observations, our model essentially reduces to the rigid ion model incorporating the short-range non-Coulombic and Coulombic interactions. We shall obtain matrix elements \( D_{\alpha\beta}(q,kk') \) for such interactions. It is convenient to express the dynamical matrix in terms dimensionless frequency tensor \( T_{\alpha\beta}(q,kk') \) according to  
\[ D_{\alpha\beta}(q,kk') = \frac{e^2}{V} (m_k m_k')^{-1/2} T_{\alpha\beta}(q,kk') \]  \quad \ldots (13)  

In our model, the frequency tensor 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 \ldots (14)  

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 Eqs 13 and 14 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 \( ^7 \) \( \text{Oh} \) from the set of independent matrix elements.

### 2.3 Short-range Non-Coulombic Interaction

For the non-Coulombic interaction, potential energy of the spinel structure \( \phi^N \) using Taylor’s series can be written as,

\[
\phi^N = \sum_{l m n} \left[ \frac{1}{r} \left( \frac{d\phi^N}{dr} \right)_{\| r \|} \right] t_{l m n}^\alpha (S_{l m n} - S_\alpha) + \frac{1}{2} \left| S_{l m n} - S_\alpha \right|^2 \\
+ \frac{1}{2} \left[ \frac{1}{r} \left( \frac{1}{r} \frac{d\phi^N}{dr} \right)_{\| r \|} \right] t_{l m n}^\alpha (S_{l m n} - S_\alpha) \]  \quad \ldots (15)  

where \( S_\alpha \) and \( S_{l m n} \) are the displacements of the central ion and its first neighbour ions from their normal positions, \( t_{l m n}^\alpha \) represents the position coordinates of neighbouring ions in equilibrium. \( l, m, n \), represent the direction cosines of the line joining the central ion and the nearest neighbours. \( \left| r_i \right| \) is the nearest neighbour distance.

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

\[
\frac{e^2}{V} A_k = \left. \frac{d\phi^N}{dr^2} \right|_{\| r \|} 
\]  \quad \ldots (16)  

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

\[
\frac{e^2}{V} B_k = \left. \frac{1}{r} \frac{d\phi^N}{dr} \right|_{\| r \|} 
\]  \quad \ldots (17)
where \( k = 1, 2, 3 \) for first, second and third neighbours.

2.4 Long-range Interaction Part

For the Coulomb part, i.e., for \( \Phi^C \), the Coulombic contribution of all quantities has been calculated from the equation based on the Ewald’s method \(^1\).

The potential function for the Coulombic part can be written as:

\[
\Phi^C_{kk}(r) = \frac{(Z_k e)(Z_k e)}{|r|} \quad \ldots (18)
\]

where \( r = r^0(l,k) - r^0(l,k) \), \( Z_k e \) and \( Z_k e \) are charges on the \( k^\text{th} \) and \( k^\text{th} \) ions.

2.5 Effective Dynamical Charges

According to Scott \(^13\) for ternary compound \( A_n B_m C_{2n} \), the effective charge is independent of high frequency dielectric constant as:

\[
4\pi e^2 \sum_j (\omega^2_\text{LO} - \omega^2_\text{TO}) = \frac{4\pi}{V} \left[ \frac{n_A(Z_A^* e)^2}{m_A} + \frac{n_B(Z_B^* e)^2}{m_B} + \frac{n_C(Z_C^* e)^2}{m_C} \right] \quad \ldots (19)
\]

where \( c \) is the velocity of light, \( V \) the volume of the unit cell. \( n_A, n_B \) and \( n_C \) are stoichiometric coefficients and \( m_A, m_B, m_C \) are the atomic masses. Summation over \( j \) extends over all infrared modes. \( Z_A^* e \), \( Z_B^* e \) and \( Z_C^* e \) are effective charges on ions A, B and C respectively. It may be tentatively be assumed that same kind of atoms in a unit cell have a same value of charges \( Z^* e \) and the condition of charge neutrality in a unit cell is written as:

\[
n_A Z_A^* + n_B Z_B^* + n_C Z_C^* = 0 \quad \ldots (20)
\]

In order to determine these unknown \( Z_A^* \), \( Z_B^* \) or \( Z_C^* \) from two Eqs (19 and 20), we use an assumed value of \( Z_A^* \) following Gervais \(^14,15\) method which imposes a restriction on the magnitude of \( Z_A^* \) by the connection that the value in the square root which is included in the equation by combining Eqs (19) and (20) must be positive.

3 Results and Discussion

The force constants obtained in Table 2 reveal that the potential of the spinel structure is mainly controlled by Cr-S (\( A_2 \) octahedron) and M-S (\( A_1 \) tetrahedron) stretching whereas the bending forces are negligible. It is found that in the case of chromium sulphide spinel (Table 3), second neighbour interaction (\( A_2 \), between Cr-S ions) dominates over the first neighbour interaction (\( A_1 \) between M-S ions) The reason being that the bonding between Cr-S ions is octahedral (ionic) whereas the bonding between M-S ions is tetrahedral (covalent) in nature. Further, the octahedral bonding is stronger than tetrahedral bonding. The effective dynamical charges of bivalent metals on the tetrahedral sites are nearly zero.

<table>
<thead>
<tr>
<th>Force parameters</th>
<th>MnCr(_2)S(_4)</th>
<th>FeCr(_2)S(_4)</th>
<th>CdCr(_2)S(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>88.21</td>
<td>86.48</td>
<td>46.96</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>12.82</td>
<td>2.76</td>
<td>1.50</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>94.08</td>
<td>95.80</td>
<td>80.95</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1.96</td>
<td>2.08</td>
<td>1.69</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>18.95</td>
<td>8.24</td>
<td>18.25</td>
</tr>
<tr>
<td>( B_3 )</td>
<td>0.29</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>( Z_a )</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( Z_b )</td>
<td>0.64</td>
<td>0.98</td>
<td>0.62</td>
</tr>
<tr>
<td>( Z_c )</td>
<td>0.32</td>
<td>0.49</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 2:—Value of force constants (kDynes/cm) and effective dynamical charges

<table>
<thead>
<tr>
<th>Species</th>
<th>MnCr(_2)S(_4)</th>
<th>FeCr(_2)S(_4)</th>
<th>CdCr(_2)S(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>378</td>
<td>379</td>
<td>379</td>
</tr>
<tr>
<td>( E_g )</td>
<td>251</td>
<td>249</td>
<td>247</td>
</tr>
<tr>
<td>( F_{2g}(1) )</td>
<td>346</td>
<td>347</td>
<td>348</td>
</tr>
<tr>
<td>( F_{2g}(2) )</td>
<td>382</td>
<td>279</td>
<td>277</td>
</tr>
<tr>
<td>( F_{2g}(3) )</td>
<td>108</td>
<td>108</td>
<td>108</td>
</tr>
<tr>
<td>( F_{3g}(1)(\text{TO}) )</td>
<td>381</td>
<td>383</td>
<td>385</td>
</tr>
<tr>
<td>( F_{3g}(2) )</td>
<td>322</td>
<td>324</td>
<td>322</td>
</tr>
<tr>
<td>( F_{3g}(3) )</td>
<td>262</td>
<td>257</td>
<td>258</td>
</tr>
<tr>
<td>( F_{3g}(4) )</td>
<td>121</td>
<td>123</td>
<td>126</td>
</tr>
<tr>
<td>( F_{3g}(1)(\text{LO}) )</td>
<td>397</td>
<td>398</td>
<td>391</td>
</tr>
<tr>
<td>( F_{3g}(2) )</td>
<td>342</td>
<td>342</td>
<td>344</td>
</tr>
<tr>
<td>( F_{3g}(3) )</td>
<td>263</td>
<td>261</td>
<td>259</td>
</tr>
<tr>
<td>( F_{3g}(4) )</td>
<td>122</td>
<td>124</td>
<td>126</td>
</tr>
</tbody>
</table>

Table 3:—Observed \(^{12,14}\) and calculated zone-centre phonon frequencies of MnCr\(_2\)S\(_4\), FeCr\(_2\)S\(_4\) and CdCr\(_2\)S\(_4\) along with the results of Lutz et al. \(^7\).

KUSHWAHA et al.: LATTICE DYNAMICAL CALCULATIONS
In the case of Raman active modes, value of \( A_{1g} \) and \( E_g \) modes differ by 0.3-0.8 and 0.8-1.2% respectively from their experimental values. The values of \( F_{2g}(1), F_{2g}(2) \) and \( F_{2g}(3) \) modes have been found to deviate by 0.3-1.1, 0.4-1.9 and 1.7-5.9% from their corresponding experimental values. Similarly calculated values of the infrared active modes for \( F_{1u}(1) \) differ by 0.3-0.8% and 0.3-0.7% from their measured values for TO and LO polarizations. Also the infrared modes for \( F_{1u}(2), F_{1u}(3) \) and \( F_{1u}(4) \) for TO and LO polarizations differ from their corresponding experimental values by 0.3-1.5, 0.4-0.8 and 2.1-3.5% for TO polarization and 0.3-1.1, 0.8-1.2 and 0.8-2.0% for LO polarization for these spinels.

### References