Lattice dynamics of manganites $RMnO_3$ ($R =$ Sm, Eu or Gd): instabilities and coexistence of orthorhombic and hexagonal phases

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Abstract. The lattice dynamical and allied properties of the multiferroic manganites SmMnO$_3$, EuMnO$_3$ and GdMnO$_3$ were investigated in this work by means of a shell model with transferable pairwise interionic interaction potential. This shell-model potential is able to reproduce the available crystal structure and phonon frequencies. A zone center imaginary $A_u$ mode is observed in these lattice dynamics calculations that indicates metastability of the perovskite phase. Comparison of the Gibbs free energies in the orthorhombic and hexagonal phases points to the possible coexistence of the two phases of these manganites under ambient conditions.

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1. Introduction

It is well known that multiferroic materials possess any two or all three states of ferroelectricity, ferromagnetism and ferroelasticity occurring in the same phase and, hence, they are of great technological and fundamental importance. The recent discovery of large magnetoelectric effects [1] in the rare-earth manganites ($RMnO_3$) has kindled interest among investigators in understanding the complex relationships between lattice distortion, magnetism, dielectric and transport properties of undoped $RMnO_3$. With respect to structure, these manganites have been grouped into the hexagonal phase ($P6_3cm$) with $R (= Ho, Er, Tm, Yb, Lu or Y)$ [2] having smaller ionic radius ($r_R$) and the orthorhombic structure ($Pnma$) with $R (= La, Pr, Nd, Sm, Eu, Gd, Tb or Dy)$ [3] having larger $r_R$. However, it is well known that the compounds in the first group can also be formed in a metastable perovskite $Pnma$ phase by high-pressure synthesis, by soft chemistry synthesis or by epitaxy. On the other hand, some compounds of the second group could be synthesized [4]–[6] in a metastable hexagonal phase by epitaxial stabilization. The present work is devoted to a theoretical study of these multiferroic manganites, and through a host of computations of the Gibbs free energies and thermodynamic properties for these manganites, we intend to provide a microscopic basis for the metastability and phase competition between these two structures.

The crystal structure of $RMnO_3$ ($R = Sm, Eu or Gd$) has been studied previously using x-ray and neutron diffraction techniques [7]–[9]. The perovskite structure has a lower unit cell volume compared to the hexagonal phase. For hexagonal $RMnO_3$ ($R = Sm, Eu or Gd$), only the lattice parameters obtained through x-ray diffraction experiments on thin films are known. All three orthomanganites exhibit a Jahn–Teller distorted orthorhombic structure and show sharp peaks in the specific heat due to various magnetic transitions. A wealth of experimental data is available on these manganites; therefore it seems essential to theoretically understand their physical properties, like crystal structure, Raman and infrared frequencies, specific heat, elastic constants, phonon density of states (PDOS) and phonon dispersion curves.

Raman techniques [10] have been successfully employed to investigate the phonon excitations in various orthorhombic $RMnO_3$ compounds ($R = Sm, Eu or Gd$) of the manganite family. Recently, the lattice dynamical studies of the parent member LaMnO$_3$ have been...
reported [11] using a seven-parameter shell model [12]–[14] based on an interatomic potential that consists of the long-range Coulomb and the short-range interaction terms. Earlier calculations on other manganite materials have used more complex lattice dynamical models [15]–[19], whereas we have used a simpler shell model with a smaller number of parameters [11]. Previously, a modified rigid ion model has been used to elucidate the cohesive, thermal and thermodynamic properties of doped and undoped perovskite manganites [20, 21].

We have computed the phonon dispersion curves (PDCs) for the orthorhombic \( R\text{MnO}_3 \) (\( R \) = Sm, Eu or Gd) along three major symmetry (\( \Sigma, \Delta \) and \( \Lambda \)) directions. The method of computation is presented in section 2.

2. Lattice dynamics computations

The interatomic potential of the shell model employed in the calculations is expressed as [11]–[14]

\[
V(r) = \left\{ \frac{e^2}{4\pi\varepsilon_0} \right\} \frac{Z(k)Z(k')}{r} + a \exp \left\{ -b r \left( R(k) + R(k') \right) \right\},
\]

where \( a = 1822 \text{ eV} \) and \( b = 12.364 \text{ eV} \). \( Z(k) \) and \( R(k) \) are the effective ionic charge and radius parameters associated with atom \( k \). The effect of polarizability of the oxygen ions in this model has been included by considering a massless shell (charge \( Y(O) = -1.8e \)) and shell-core force constant \( K(O) = 183 \text{ eV} \text{ Å}^{-2} \).

For the orthomanganites, the shell-model parameters are evaluated in such a way that the forces on each atom and the internal stresses in the crystal vanish and they reproduce the crystal structure close to that observed by the diffraction experiments at zero pressure. The crystal structure of orthorhombic \( R\text{MnO}_3 \) (\( R \) = Sm, Eu or Gd) has been calculated by minimizing the Gibbs free energy with respect to the structural parameters. Group-theoretical analysis for the orthorhombic perovskite manganites gives the classification of the phonon modes at the zone center (\( \Gamma \)) point and along the \( \Sigma, \Delta \) and \( \Lambda \) directions as [11]

\[
\begin{align*}
\Gamma &: 7A_g^1 + 7B_{2g}^1 + 5B_{1g}^1 + 5B_{3g}^1 + 10B_{1u} + 10B_{3u} + 8A_u + 8B_{2u}, \\
\Sigma &: 17\Sigma_1 + 13\Sigma_2 + 13\Sigma_3 + 17\Sigma_4, \\
\Delta &: 15\Delta_1 + 15\Delta_2 + 15\Delta_3 + 15\Delta_4, \\
\Lambda &: 17\Lambda_1 + 13\Lambda_2 + 13\Lambda_3 + 17\Lambda_4.
\end{align*}
\]

The optimized potential yields the long-wavelength phonon modes close to their measured values. Out of the 60 \( \Gamma \)-point phonon modes, 24 \( (7A_g^1 + 5B_{1g} + 7B_{2g} + 5B_{3g}) \) are Raman active, 25 \( (9B_{1u} + 7B_{2u} + 9B_{3u}) \) are infrared active, 8 \( (8A_u) \) are optically inactive and 3 \( (B_{1u} + B_{2u} + B_{3u}) \) are acoustic modes. For the computation of the PDCs, the equilibrium structure and the interatomic potential expressed by equation (1) along with the symmetry vectors obtained through the group theoretical analysis for \( Pnma \) space group [11] have been employed to diagonalize the dynamical matrix along the three high-symmetry directions and to classify the phonon frequencies obtained into their irreducible representations. The procedures adopted to compute the PDOS and allied thermodynamic properties like specific heat are discussed elsewhere [11]–[14], [22, 23] in detail. The results of the computations (performed using the DISPR [14] program, developed at BARC) are presented and discussed below.
Table 1. The potential parameters for $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) using the shell model in the lattice dynamical calculations.

|       | Sm   | Eu   | Gd   | Mn   | O    |
|-------|------|------|------|------|------|
| $Z(k)$ (e) | 2.75 | 2.75 | 2.75 | 1.00 | −1.25|
| $R(k)$ (Å)  | 2.06 | 2.04 | 2.037| 1.07 | 1.71 |

3. Results and discussion

The optimized parameters for orthorhombic $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) thus obtained are listed in table 1.

3.1. Crystal structure

The multiferroic perovskite manganites $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) (with space group $Pnma$) have an orthorhombic structure with four formula units per unit cell [7, 9]. The computed cell parameters, atomic coordinates and strain parameter ($s = 2(a − c)/(a + c)$) of orthorhombic $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) are shown in table 2 and are also compared with available experimental data [8, 9].

It is seen from table 2 that our calculated results are in fairly good agreement with the corresponding experimental data [8, 9]. The calculated lattice parameters ($a$, $b$ and $c$) differ by only 0.7% on average from the experimentally observed data [8, 9] for $RMnO_3$ ($R = \text{Sm, Eu or Gd}$). The calculated values of unit cell volume ($V$) have also shown good agreement with experimental data. The decreasing trend of $V$ with decreasing order of ionic radius ($r_R$) exhibited by both the experimental and our calculated results is similar, as can be seen from table 2.

It is obvious from these satisfactory predictions that our shell-model calculations are capable of reproducing the crystal structures of orthorhombic $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) manganites.

3.2. Elastic constants

The longitudinal acoustic wave velocities as computed from the slopes of the acoustic phonon branches for $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) are shown in table 3. These compare well with the available experimental data [24] at 130 K. We have also calculated the elastic constants for these materials through a computation of the acoustic wave velocities along different symmetry directions and listed them in table 3. These calculated values could not be compared due to a lack of experimental data on them.

3.3. Raman and infrared spectra

In table 4, we present the calculated Raman frequencies for orthorhombic $RMnO_3$ ($R = \text{Sm, Eu or Gd}$) and compare them with the available experimental data [10, 25]. A comparison of experimental data with the results obtained from other shell-model computations performed by Iliev et al [10] shows that the average deviation of the calculated Raman frequencies is 11.8%,
Table 2. Comparison of the experimental data [8, 9] (at 295 K) with calculated structural parameters (at 0 K) and calculated isotropic displacement parameter $B$ (at 300 K) for orthorhombic $RMnO_3$ ($R = \text{Sm, Eu or Gd}$). For the space group $Pnma$, $(\text{Sm, Eu, Gd})$ Mn, O1 and O2 atoms are located at $(x, 0.25, z)$, $(0, 0, 0)$, $(x, 0.25, z)$ and $(x, y, z)$, respectively, and their symmetry equivalent positions.

|                | SmMnO$_3$  | Expt [8] | Calc. | EuMnO$_3$ | Expt [9] | Calc. | GdMnO$_3$ | Expt [8] | Calc. |
|----------------|------------|---------|-------|------------|---------|-------|------------|---------|-------|
| $a$ (Å)        | 5.862      | 5.884   |       | 5.8361(16) | 5.849   |       | 5.866      | 5.836   |       |
| $b$ (Å)        | 7.477      | 7.468   |       | 7.4618(23) | 7.458   |       | 7.431      | 7.478   |       |
| $c$ (Å)        | 5.362      | 5.265   |       | 5.3437(16) | 5.244   |       | 5.318      | 5.243   |       |
| $V$ (Å$^3$)    | 235.01     | 231.3   |       | 232.708(12)| 228.8   |       | 231.77     | 228.8   |       |
| $s$            | 0.089      | 0.111   |       | 0.088      | 0.109   |       | 0.098      | 0.107   |       |
| $R$ ($= \text{Sm, Eu or Gd}$) |                 |         |       |                 |         |       |                 |         |       |
| $x$            | 0.0759     | 0.094   |       | 0.0774      | 0.094   |       | 0.0807     | 0.093   |       |
| $z$            | 0.985      | 0.985   |       | 0.9848     | 0.984   |       | 0.9384     | 0.983   |       |
| $B$ (Å$^2$)    | 0.34       | 0.38    |       | 0.47(5)    | 0.35    |       | 0.23       | 0.26    |       |
| Mn             |             |         |       |             |         |       |             |         |       |
| $B$ (Å$^2$)    | 0.32       | 0.37    |       | 0.23(9)    | 0.33    |       | 0.15       | 0.27    |       |
| O1             |             |         |       |             |         |       |             |         |       |
| $x$            | 0.473      | 0.446   |       | 0.4714     | 0.445   |       | 0.471      | 0.444   |       |
| $z$            | 0.097      | 0.129   |       | 0.0974     | 0.131   |       | 0.103      | 0.134   |       |
| $B$ (Å$^2$)    | 0.48       | 0.60    |       | 0.56(8)    | 0.63    |       | 0.28       | 0.62    |       |
| O2             |             |         |       |             |         |       |             |         |       |
| $x$            | 0.3241     | 0.330   |       | 0.3247     | 0.330   |       | 0.3246     | 0.329   |       |
| $y$            | 0.0485     | 0.065   |       | 0.0485     | 0.066   |       | 0.0508     | 0.067   |       |
| $z$            | 0.7076     | 0.686   |       | 0.7055     | 0.686   |       | 0.7057     | 0.687   |       |
| $B$ (Å$^2$)    | 0.42       | 0.48    |       | 0.60(4)    | 0.47    |       | 0.29       | 0.43    |       |

Table 3. The longitudinal acoustic wave velocities $V_1$ (m s$^{-1}$) and elastic constants (GPa) of $RMnO_3$ ($R = \text{Sm, Eu or Gd}$).

|                | SmMnO$_3$ | Expt [24] (T = 130 K) | Calculated (T = 0 K) | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ |
|----------------|-----------|-----------------------|----------------------|----------|----------|----------|----------|----------|----------|
| SmMnO$_3$      | 4812      | 5100                  | 157                  | 159      | 190      | 52       | 72       | 75       |          |
| EuMnO$_3$      | 3325      | 4798                  | 165                  | 154      | 194      | 50       | 73       | 76       |          |
| GdMnO$_3$      | 4255      | 4721                  | 166                  | 143      | 198      | 45       | 74       | 76       |          |

whereas our present model gives this value as 7%. Also, Iliev et al [10] have used a much more complex shell model with 20 parameters, while our shell model has only seven parameters. A good comparison of the Raman modes emphasizes the conjecture that ionic interactions play a significant role in describing the vibrational properties of this system of manganites.
Table 4. Comparison of the calculated and experimental [10, 25] Raman-active phonon frequencies (cm\(^{-1}\)) for orthorhombic \(RMnO_3\) \((R = \text{Sm, Eu or Gd})\) (1 meV = 8.059 cm\(^{-1}\) = 0.242 THz).

| Raman data | SmMnO\(_3\) | EuMnO\(_3\) | GdMnO\(_3\) |
|------------|-------------|-------------|-------------|
| \(A_g\)    | Calculated  | Expt [25]   | Expt [10]   | Calculated  | Expt [25]   | Expt [10]   | Calculated  | Expt [10]   |
|            | 111         | –           | –           | 110         | –           | –           | 110         | –           |
|            | 149         | –           | –           | 149         | –           | –           | 147         | –           |
|            | 232         | 237         | –           | 234         | 263         | –           | 235         | 276         |
|            | 267         | 286         | 266         | 270         | 307         | –           | 269         | 310         |
|            | 332         | 355         | 353         | 334         | 367         | 361         | 332         | 371         |
|            | 435         | 479         | 477         | 441         | 484         | 479         | 443         | 486         |
|            | 503         | 496         | 496         | 505         | 503         | 501         | 508         | 506         |
| \(B_{2g}\) | Calculated  | –           | –           | 103         | –           | –           | 101         | –           |
|            | 202         | –           | –           | 202         | 287         | –           | 200         | –           |
|            | 282         | 291         | –           | 284         | 308         | –           | 285         | –           |
|            | 341         | 324         | –           | 345         | 326         | 324         | 349         | 329         |
|            | 489         | 460         | 461         | 494         | 466         | 465         | 496         | 469         |
|            | 514         | 511         | 513         | 519         | 520         | 518         | 519         | 525         |
|            | 564         | 606         | 607         | 567         | 608         | 610         | 570         | 612         |
| \(B_{1g}\) | Calculated  | –           | –           | 138         | –           | –           | 131         | –           |
|            | 202         | –           | –           | 204         | –           | –           | 203         | –           |
|            | 265         | –           | –           | 265         | –           | –           | 265         | –           |
|            | 291         | –           | –           | 295         | –           | –           | 291         | –           |
|            | 524         | –           | –           | 527         | –           | –           | 524         | –           |
| \(B_{3g}\) | Calculated  | –           | –           | 110         | –           | –           | 105         | –           |
|            | 241         | –           | –           | 245         | –           | –           | 243         | –           |
|            | 283         | –           | –           | 284         | –           | –           | 282         | –           |
|            | 448         | –           | –           | 451         | –           | –           | 450         | –           |
|            | 500         | –           | –           | 502         | –           | –           | 500         | –           |

Figure 1 shows the computed infrared frequencies \((9B_{1u} + 7B_{2u} + 9B_{3u})\) along with the LO–TO splitting; the figure also shows the experimental data [26] available only for GdMnO\(_3\). The optically inactive \((A_u)\) modes for each of the three manganites are also shown in the figure.

3.4. Phonon density of states

The total PDOS has been computed and the results are depicted in figure 2 for the orthomanganites \(RMnO_3\) \((R = \text{Sm, Eu or Gd})\). The total PDOS spans the spectral range up to 80 meV. Also, it has shown broad structures in the 10–50 meV range with peaks around 15, 25, 32 and 38 meV. The partial density of states of individual atoms (Sm/Eu/Gd), Mn, O1 and O2 have also been computed and shown in figure 2. It is seen from these that (Eu/Sm/Gd) atoms generally contribute up to 30 meV. The Mn atoms too contribute mainly up to 30 meV with a few broad peaks. It is interesting to also note, in figure 2, that the peaks around 65 and 72 meV in the total PDOS can be attributed to the oxygen ions alone.
Figure 1. Calculated long-wavelength (infrared active (LO—squares; TO—circles) and silent (upright triangles)) phonon frequencies and mode assignments. Experimental data (inverted triangles) [26] are available only for GdMnO$_3$. These data are to be compared with the calculated phonon frequencies corresponding to B$_{1u}$ (TO). The B$_{1u}$, B$_{2u}$ and B$_{3u}$ modes are infrared active, while the A$_u$ modes are silent (1 meV = 8.059 cm$^{-1}$ = 0.242 THz).
3.5. Specific heat

The calculated density of states has been used to evaluate the specific heat at constant volume ($C_V$) as a function of temperature. The values of the specific heat for orthorhombic $RMnO_3$ ($R =$ Sm, Eu or Gd) up to the temperature range of 1000 K are displayed in figure 3. They are compared with the respective available experimental data [27] in the figure. Our results have

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Figure 3. Computed specific heat (solid line) at constant volume of SmMnO$_3$, EuMnO$_3$ and GdMnO$_3$ as a function of temperature and its comparison with the experimental values (shown as □; [27]).
followed a trend more or less similar to that exhibited by the experimental curve. The peaks observed in the experimental specific heat curves are not found in our calculated results; this might be due to the exclusion of magnetic interactions from the specific heat in our model calculations.

3.6. Phonon dispersion curves

The PDCs for (Sm, Eu, Gd)MnO$_3$ along the three high-symmetry directions $\Sigma$, $\Delta$ and $\Lambda$ in the Brillouin zone have been computed using the present shell model and DISPR program \cite{14}. The

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Computed phonon-dispersion curves for SmMnO$_3$ along the high-symmetry $\Sigma$, $\Delta$ and $\Lambda$ directions. Group-theoretical representations are indicated on top of the figure. $\Gamma$ is the Brillouin zone center and X, Y and Z are the zone boundary points (1 meV = 8.059 cm$^{-1}$ = 0.242 THz).}
\end{figure*}

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{The computed phonon-dispersion curves for EuMnO$_3$ along the high-symmetry $\Sigma$, $\Delta$ and $\Lambda$ directions. Group-theoretical representations are indicated on top of the figure. $\Gamma$ is the Brillouin zone center and X, Y and Z are the zone boundary points (1 meV = 8.059 cm$^{-1}$ = 0.242 THz).}
\end{figure*}
Figure 6. The computed phonon-dispersion curves for GdMnO$_3$ along the high-symmetry $\Sigma$, $\Delta$ and $\Lambda$ directions. Group-theoretical representations are indicated on top of the figure. $\Gamma$ is the Brillouin zone center and X, Y and Z are the zone boundary points (1 meV = 8.059 cm$^{-1}$ = 0.242 THz).

computed PDCs are depicted in figures 4–6. The modes belonging to different representations are plotted separately (shown as dashed lines) in the same figures. With 20 atoms in the unit cell, the PDCs have 60 phonon branches along each symmetry direction. At the zone boundary points X, Y and Z, the branches are degenerate in pairs due to the high symmetry at these points. It is interesting to note that the PDCs along the $\Sigma_2$, $\Delta_2$ and $\Lambda_2$ directions have exhibited some imaginary frequency values in all three, SmMnO$_3$, EuMnO$_3$ and GdMnO$_3$. These features of soft modes indicate the occurrence of phase transformations in SmMnO$_3$, EuMnO$_3$ and GdMnO$_3$ manganites. In particular, it is noted that for o-RMnO$_3$, one $A_u$ mode at the $\Gamma$ point is not a stable mode. This is a clear indication of the metastability of the orthorhombic phase of RMnO$_3$. In the computations, dynamic stability sets in on application of pressure. On transferring the shell-model parameters to the known [4]–[6] hexagonal structure (for the atomic coordinates, we used those known [28] for hexagonal DyMnO$_3$), forces on the atoms are nearly zero, but dynamical instability exists. The volume change ($\sim$9%) in going from the orthorhombic to the hexagonal phase is reproduced in the computations. Comparison of the Gibbs free energy for the two phases (figures 7 and 8) shows that the energy difference is of the order of less than 2 kJ mol$^{-1}$, under ambient conditions, and hence coexistence is very much possible.

4. Conclusion

In summary, we have reported here our investigation of the lattice dynamical and thermodynamic properties of RMnO$_3$ ($R$ = Sm, Eu or Gd) perovskites and their hexagonal polymorphs employing a transferable shell-model potential. For the orthorhombic manganites, our calculated crystal structure parameters, Raman frequencies and infrared frequencies are found to be in good agreement with the available experimental data. The transferable

$^5$ The contribution of the imaginary frequencies (which constitute less than 1% of the total) to the phonon density of states has not been considered.
shell-model potential reproduces the change in volume when going from the perovskite to the hexagonal phase. The Gibbs free energies are within 2 kJ mole$^{-1}$, which is in accord with thermodynamic estimation [28]. The existence of imaginary modes points to inherent instability in both perovskite and hexagonal phases. On the basis of our results, it may be concluded that the present shell model is suitable and appropriate for the description of the lattice dynamical and related properties of $R\text{MnO}_3$ ($R =$ Sm, Eu or Gd) manganites.

**Figure 7.** Calculated Gibbs free energy (including vibrational contribution) for the orthorhombic and hexagonal phases of $R\text{MnO}_3$ ($R =$ Sm, Eu or Gd) as a function of temperature.
Figure 8. Calculated Gibbs free energy for the orthorhombic and hexagonal phases of $R\text{MnO}_3$ ($R =$ Sm, Eu or Gd) as a function of pressure. The solid (orthorhombic phase) and dashed (hexagonal phase) lines are just guides to the eye.
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References

[1] Kimura T, Lawes G, Goto T, Tokura Y and Ramirez A P 2005 Phys. Rev. B 71 224425
[2] Yakel H L, Koehler W C, Bertaut E F and Forrat E F 1963 Acta Crystallogr. 16 957
[3] Gilleo M A 1957 Acta Crystallogr. 10 161
[4] Lee D, Lee J H, Murugavel P, Jang S Y, Noh T W, Jo Y, Jung M H, Ko Y D and Chung J S 2007 Appl. Phys. Lett. 90 182504
[5] Bosak A A, Dubourdieu C, Senator J P, Gorbenko O Y and Kaul A R 2002 J. Mater. Chem. 12 800
[6] Balasubramanian K R, Havelia S, Salvador J F, Zheng H and Mitchell J F 2007 Appl. Phys. Lett. 91 232901
[7] Moussa F, Hennion M, Rodriguez-Carvajal J, Moudden H, Pinsard I and Revcolevschi A 1996 Phys. Rev. B 54 15149
[8] Mori T, Kamegashira N, Aoki K, Shishido T and Fukuda T 2002 Mater. Lett. 54 238
[9] Dabrowski B, Kolesnik S, Baszczuk A, Chmaissem O, Maxwell T and Mais J 2005 J. Solid State Chem. 178 629
[10] Iliev M N, Abrashev M V, Laverdierie J, Jandl S, Gospodinov M M, Wang Y Q and Sun Y Y 2006 Phys. Rev. B 73 064302
[11] Rini E G, Rao M N, Chaplot S L, Gaur N K and Singh R K 2007 Phys. Rev. B 75 214301
[12] Rao M N, Chaplot S L, Choudhury N, Rao K R, Azuah R T, Montfrooij W T and Bennington S M 1999 Phys. Rev. B 60 12061
[13] Chaplot S L, Choudhury N, Ghose S, Rao M N, Mittal R and Goel P 2002 Eur. J. Mineral. 14 291
[14] Chaplot S L Bhabha Atomic Research Centre, External Report No. BARC-972 unpublished
[15] Nikiforov A E and Popov S E 2001 Phys. Solid State 43 1132
[16] Smirnova I S 1999 Physica B 262 247
[17] Iliev M N, Lee H G, Popov V N, Abrashev M V, Hamed A, Meng R L and Chu C W 1997 Phys. Rev. B 56 2488
   Iliev M N, Abrashev M V, Lee H-G, Popov V N, Sun Y Y, Thomsen C, Meng R L and Chu C W 1998 Phys. Rev. B 57 2872
[18] Popov V N 1995 J. Phys.: Condens. Matter 7 1625
[19] Granado E et al 1998 Phys. Rev. B 58 11435
[20] Choithrani R, Gaur N K and Singh R K 2008 Solid State Commun. 147 103
[21] Choithrani R, Gaur N K and Singh R K 2008 Solid State Commun. 145 308
[22] Choithrani R and Gaur N K 2008 J. Magn. Magn. Mater. 320 612
[23] Choithrani R and Gaur N K 2008 J. Magn. Magn. Mater. 320 3384
[24] Rao K R, Chaplot S L, Choudhury N, Ghose S, Hastings J M, Corliss L M and Price D L 1998 Phys. Chem. Miner. 16 83
[25] Choudhury N, Chaplot S L and Rao K R 1989 Phys. Chem. Miner. 16 599
[26] Lalitha G and Venugopal Reddy P 2008 J. Magn. Magn. Mater. 320 754
[27] Laverdierie J, Jandl S, Mukhin A A and Ivanov V V 2006 Eur. Phys. J. B 54 67
[28] Pimenov A, Rudolf T, Mayr F, LoiDl A, Mukhin A A and Balbashov A M 2006 Phys. Rev. B 74 100403
[29] Kimura T, Ishihara S, Shintani H, Arima T, Takahashi K T, Izhizaka K and Tokura Y 2003 Phys. Rev. B 68 060403
[30] Graboy I E, Bosak A A, Gorbenko O Y, Kaul A R, Dubourdieu C, Senator J-P, Svetchnikov V L and Zandbergen H W 2003 Chem. Mater. 15 2632

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