Elastic and Thermal Properties of La$_{1-x}$Sr$_x$MnO$_3$ Manganites.

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Abstract. The elastic and thermal properties of perovskite manganites La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.165, 0.185, 0.20, 0.40, 0.80, 0.90, 1.0) have been studied as a function of temperature (1K $\leq$ T $\leq$ 300K) by means of Atoms in Molecules (AIM) theory and a Modified Rigid Ion Model (MRIM) respectively. The specific heat values ($C_v$) and the Debye temperatures obtained by us from the lattice contributions are in reasonably good agreement with the available experimental data for some concentrations (x) of La$_{1-x}$Sr$_x$MnO$_3$. In addition, the results on the Bulk Modulus ($B_T$), cohesive energy ($\phi$), molecular force constant ($f$), Reststrahlen frequency ($\nu_o$) and Grüneisen parameter ($\gamma$) are also analysed.

1. Introduction
Mixed valence manganites with the perovskite structure $R_{1-x}A_x$MnO$_3$ (where, e.g., $R$=La, Nd, Pr; ...and $A$=Ba, Ca, Sr, Pb) have attracted a large proportion of researcher from varied fields because of their interesting physical properties such as phase coexistence, metal-insulator transitions, colossal magnetoresistance effect and other multiferroic properties. [1] These properties makes these systems promising for magnetic sensor and reading head device applications. A number of works has been devoted to study the interplay between structure and transport properties of these manganese perovskites [2-4]. The magnetic, electronic and structural phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ is well established for all the values of concentration (x) [5]. The two end members of the compounds, La$_{1-x}$Sr$_x$MnO$_3$, are LaMnO$_3$ and SrMnO$_3$ and they are pseudocubic and hexagonal anti-ferromagnetic insulators respectively [6]. But La$_{1-x}$Sr$_x$MnO$_3$ compounds exists in orthorhombic, rhombohedral, tetragonal structures and can either be an antiferromagnetic insulator, ferromagnetic metal/insulator or paramagnetic insulator with very interesting physical properties.

The reason lies in the strong electron-phonon interactions in these materials. The strong coupling between the electron and the lattice phonons brings about a large change in the physical properties of these compounds by a small change in the chemical composition. The one-electron bandwidth also depends substantially on the electron–phonon coupling effects coming from the long range cooperative Jahn–Teller (JT) distortion of MnO$_6$ octahedra. Such effects are pronounced in the optimally doped manganites with the orthorhombic crystal structure of the $Pnma$ symmetry ($r_A < 1.22$ Å) and strongly reduced for those with the rhombohedral structure of the $R\bar{3}c$ symmetry ($r_A > 1.22$ Å) [7]. The presence of smaller cations (Sr$^{2+}$) at A-site does manifest itself as increasing tilts of the MnO$_6$ octahedra (the GdFeO$_3$-type distortion), which increase the orthorhombic splitting of the unit-

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cell dimensions compared with the cubic perovskite-type cell. The effect of decreasing A-site cation radius size on elastic and thermal properties in La$_{1-x}$Sr$_x$MnO$_3$ orthorhombic series in analyzed in the present work. We have used Modified Rigid Ion Model (MRIM) to study the thermal properties of La$_{1-x}$Sr$_x$MnO$_3$ perovskite manganites. The essentials of the MRIM formalism and the results obtained from its application are presented in the subsequent sections.

\begin{equation}
\phi = -\frac{e^2}{2} \sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} - \sum_{kk'} C_{kk} r_{kk}^{-6} \\
+ \sum_{i} \left[ n_i b_i \beta_i^{kk'} \exp\left(\frac{(r_{ik} + r_{k'i})}{\rho_i}\right) \right] \\
+ \sum_{i} \left[ n_i' b_i^{kk'} \exp\left(\frac{(r_{ik}' - r_{kk})}{\rho_i'}\right) \right]
\end{equation}

Here, first term is attractive long range coulomb interactions energy. The second term represents the contributions of van der Waal’s (vdW) attraction for the dipole-dipole interaction and is determined by using the Slater- Kirkwood Variational (SKV) method [8]. The third term is overlap repulsive energy represented by the Hafemeister-Flygare-type (HF) [9] interaction extended up to the second neighbour. $b_i$ and $\rho_i$ are the hardness and range parameters for the $i^{th}$ cation-anion pair ($i = 1, 2$) respectively and $\beta_i^{kk'}$ is the Pauling coefficient [10] All other terms have usual meaning as defined in our earlier papers[11-16].

The model parameters, hardness ($b$) and range ($\rho$) parameters are determined from the equilibrium condition:

\begin{equation}
\left[d\phi/dr\right]_{r_0} = 0 \quad \text{and} \quad B = 1/9Kr_0\left[d^2\phi/dr^2\right]_{r_0} = r_0
\end{equation}

where $K$ is the crystal-structure-dependent constant, $r_0$ is the equilibrium nearest neighbour distance of the basic perovskite cell and B is the bulk modulus. The cohesive energy for La$_{1-x}$Sr$_x$MnO$_3$ is calculated using equation (1) and other thermal properties such as the molecular force constant ($f$), Reststrahlen frequency ($\nu_o$), Debye temperature ($\theta_D$), Grüneisen parameter ($\gamma$) and specific heat ($C_v$)
are computed using the expression given in our previous papers [14-16]. The AIM (Atoms in Molecules) theory [17] is the used to determine the bulk modulus for the rare earth magnates and it decides the equilibrium conditions of the lattice (2) in our model. AIM theory emphasizes the partitioning of static thermodynamic properties in condensed systems into atomic or group contributions. So, we considered that the molar volume \( V \) can be written as the sum over atomic volumes \( (V_i) \) such that atomic volumes fill up the entire space of the lattice within the given structure and space symmetry of these manganites. AIM theory state that inverse of bulk modulus is simple weighted average of atomic compressibility.

\[
\kappa = \sum_i f_i \kappa_i \quad \text{and} \quad \frac{1}{B} = \sum_i \frac{f_i}{B_i} \quad \text{where} \quad f_i = \frac{V_i}{V}
\]  

(3)

Here \( f_i \) is the fractional volume occupancy due to quantum subsystem \( i \) in a unit formula volume, \( B \) is bulk modulus of the compound and \( K \) its compressibility. Here, we have considered oxygen atoms as the bulkiest and most compressible and its local compressibility varies according to the varying cation volumes and their relative occupying factor \( f_i \) on the lines of Pendas et al. [17]. We have computed the bulk modulus using eqn. (3) on the basis of AIM theory and in the low temperature analysis the MnO\(_6\) octahedral are considered to be undistorted and perfect. The values obtained by us are represented as LT bulk modulus in Table 1. Within the perovskite structure Re\(^{3+}\) occupies the centre of dodecahedron of oxygen. But due to orthorhombic deformation of the lattice, the coordination number of Re\(^{3+}\) reduces to 9, as three oxygen atoms remain essentially non-bonded. For the rhombohedral structure of La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_6\) the coordination number for A-site is taken to be 12. Now, if in this environment the Re\(^{3+}\) is substituted by a smaller cation (Sr\(^{2+}\)), the dodecahedron of oxygen will try to collapse towards the central Sr\(^{2+}\) cation and in turn the Mn-O-Mn angle will buckle. If we investigate the rare earth manganites La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\) where the A-site cation radius reduce with increasing doping concentration of Sr\(^{2+}\), the buckling of Mn-O-Mn angle progressively increases which leads to increased distortions of the lattice. As the A-site cation radius decrease the structure progressively deviates from the quasicubic to orthorhombic and a decrease in the unit cell volume can be observed. This decrease in cell volume corresponds to increase in bulk modulus of the compound. So, the effect of decreasing superexchange angle Mn-O-Mn (<\(\theta^\circ\)) from its ideal value of 180° for cubic perovskite (or increasing tilt angle (<\(\theta^\circ\)) of the MnO\(_6\) octahedra around pseudocubic direction [111]), is to increase the bulk modulus of the compound. It can now be visualized that the buckling of the Mn-O-Mn angle due to substitution of smaller cation at the A-site can substantially increase the bulk modulus of the compound as the tilting of the octahedral with the decreasing cation size at the A-site will fills the unit cell volume effectively. The fact is evident from our results depicted in Table 1. When we consider the doping at the A-site in LaMnO\(_3\) compounds then the local compressibility of impurities with respect to host ions are governed by the size difference and tuned by the formal charge mismatch between host and guest cations. We considered the effect of charge and size mismatch along with the octahedral distortions due to Jahn-Teller effect on the bulk modulus of the compounds. These factors will determine the change in the unit cell volume which in turn will change the global bulk modulus of the compound. The expression for the high temperature bulk modulus is

\[
B_T = \frac{K_S B_0 \cos \omega \exp(n \sigma^2 / r_0^{2.5})}{\exp(\Delta_{JT}) \sigma_C}
\]  

(4)

Where \( K_S \) is the spin-order-dependent constant of proportionality, \( B_0 \) is the low temperature bulk modulus for undistorted structure calculated on the basis of AIM theory, \( \sigma^2 \) is the cation size variance at A-site, \( n \) is the coordination number of A-site cation and \( r_0 = (V/\sigma)^{1/3} \), where \( V \) is the unit formula volume) is the simple perovskite cell parameter, \( \sigma_C \) is the charge mismatch, \( \Delta_{JT} \) is JT distortion of MnO\(_6\) octahedra and \( \cos \omega \) is the effect of buckling of Mn-O-Mn angle. The expression for calculating the various distortion factors are given in our previous paper [14]. The high temperature value of bulk
modulus of the distorted structure is presented in Table 1. It can be observed from the Table 1 that distortions change the low temperature bulk modulus $B_0$ by a factor of approximately 2 to 3 in insulating paramagnetic phase. The bulk modulus of these compounds is higher in paramagnetic phase due to linearly increasing lattice distortions in this phase compared to spin-ordered phase. The results thus obtained are presented and discussed below.

### Table 1. The A-site cation radius, tolerance factor and model parameters for orthorhombic ($x=0.165-0.90$ except $x=0.40$), rhombohedral ($x=0.40$) $La_{1-x}Sr_xMnO_3$ compounds and hexagonal $SrMnO_3$ at low temperatures and high temperature bulk modulus in paramagnetic insulating phase above $T_N/T_C$

| Doping concentration $x$ | $r_A$ (Å) | Tolerance factor $t$ | $b_1 \times 10^{19}$ (J) | $b_2 \times 10^{19}$ (J) | $\rho_1$ (Å) | $\rho_2$ (Å) | Low Temp. Bulk Modulus in GPa | High Temp. Bulk Modulus in GPa |
|-------------------------|-----------|----------------------|--------------------------|--------------------------|--------------|--------------|-----------------------------|-----------------------------|
| 0.165                   | 1.2101    | 0.911                | 0.288                    | 0.493                    | 0.938        | 1.239        | 126.5$^{a}$                | 179.4$^{a}$                |
| 0.185                   | 1.2093    | 0.910                | 0.279                    | 0.482                    | 0.892        | 1.216        | 132.1$^{a}$                | 172.9$^{a}$                |
| 0.200                   | 1.2088    | 0.912                | 0.274                    | 0.476                    | 0.863        | 1.201        | 134.2$^{a}$                | 171.7$^{a}$                |
| 0.400                   | 1.3056    | 0.957                | 0.862                    | 1.220                    | 0.250        | 0.475        | 137.0$^{b}$                | 298.7$^{b}$                |
| 0.700                   | 1.1908    | 0.933                | 0.249                    | 0.448                    | 0.774        | 1.180        | 161.4$^{b}$                | 193.6$^{b}$                |
| 0.800                   | 1.1872    | 0.937                | 0.262                    | 0.470                    | 0.867        | 1.249        | 155.1$^{b}$                | 216.9$^{b}$                |
| 0.900                   | 1.1836    | 0.941                | 0.274                    | 0.491                    | 0.956        | 1.309        | 146.2$^{b}$                | 282.6$^{b}$                |
| 1.000                   | 1.1800    | 0.945                | 0.431                    | 0.643                    | 2.297        | 1.651        | 121.2$^{d}$                | 269.9$^{d}$                |

$^{a}$ ref.[23], $^{b}$ ref. [24], $^{c}$ ref. [25], $^{d}$ ref. [22]

3. Results and Discussions

3.1 Model Parameters

The unit cell parameters $(a, b, c)$ in the space group $Pnma$ are taken from the reference [5, 25-31, 38] and we have converted the orthorhombic structure into a cubic structure by converting lattice constants $a, b, c$ of the orthorhombic structure into the simple cubic perovskite lattice parameter $(r_0)$ for the present compound. The first term of equation (1) was calculated by using a computer programme in terms of $Mn$-$Mn$ $(r_0)$ interionic distance of simple cubic perovskite cell. LaMnO$_3$ has five atoms in the asymmetric unit with La and O occupying the crystallographic sites $4(c)$, except for one oxygen atom which is at general position $8(d)$ and Mn is at $4(a)$ position. For the space group $Pnma$ $La/Sr$, Mn, O$_1$, O$_2$ atoms are located at $(x, 0.25, z)$, $(0, 0, 0)$, $(x, 0.25, z)$ and $(x, y, z)$. Whereas in cubic unit cell of side $r_0$ the general location of the atoms can be assigned as $(0.5, 0.5, 0.5)$, $(0, 0, 0)$, $(0.5, 0, 0)$ and $(0, 0.5, 0)$ for $La/Sr$, Mn, O$_1$ and O$_2$ atoms respectively. To convert the orthorhombic cell with cell sides $a, b, c$, along $x, y, z$ axis respectively to simple cubic unit cell of side $r_0$, we use the following relations

$$r_0 = \left( \frac{a^2 + b^2 + c^2}{3} \right)^{1/2} \quad (5)$$

Further the distance between ion pairs are written in terms of $r_0$ as

$$d_{Mn-O_1} = r_0 \left[2(m^2 + 0.5)^2 + 2n^2 + 4p^2 \right]^{1/2} \quad (6)$$

$$d_{Mn-Mn} = r_0 \left[2m^2 + 2n^2 + 4p^2 \right]^{1/2} \quad (7)$$

Where $m, n, p$ are positive integers taking values from 0 to 50 with unit steps successively and $a, b, c$ are related to simple cubic cell side length $r_0$ by equation (5). Similarly all others distance for the ion
pairs Mn-O, Mn-O, Mn-La/Sr, Mn-Mn, La/Sr-O, La/Sr-O, La/Sr-O in terms of \( r_0 \) are used to calculate the lattice cohesive energy term. This calculated value of \( r_0 \) is used in deciding the equilibrium condition of the lattice (2) The values of input data like the calculated simple cubic perovskite lattice cell parameter (\( r_0 \)) and other interionic distances taken from refs. [5, 25-31, 38] are used for the evaluation of model parameters (\( b_1, \rho_1 \)) and (\( b_2, \rho_2 \)) corresponding to the ionic pairs \( Mn^{3+}/Mn^{4+}-O^{2-} \) and \( La^{3+}/Sr^{2+}-O^{2-} \) respectively for different composition \( x \) (0.165 ≤ \( x \) ≤ 0.9) and temperature (10K ≤ \( T \) ≤ 300K) of Sr-doped \( LaMnO_3 \). The vdW coefficients \( C_{kk'} \) were calculated using SKV method [8] for the present manganites. The values of model parameters (\( b_1, b_2, \rho_1 \) and \( \rho_2 \)) for various compositions (\( x \)) of \( La_{1-x}Sr_xMnO_3 \) are listed in Table 1.

**Table 2** Cohesive and thermal properties of orthorhombic, rhombohedral \( La_{1-x}Sr_xMnO_3 \) and hexagonal \( SrMnO_3 \) at low temperatures and Debye temperature (HT) above \( T_N/T_C \)

| Doping concentration x | \( \Phi \) (eV) (MRIM) | \( \Phi \) (eV) (Kapustinskii equation) | \( f \) (N/m) | \( \nu \) (THz) | \( \theta_0 \) (K) | \( \theta_0 \) (K) | \( \gamma \) |
|------------------------|----------------------|--------------------------------------|--------------|--------------|----------------|----------------|------|
| 0.165                  | -142.6               | -142.0                               | 25.1         | 8.2          | 391.3          | 466.0          | 2.57 |
|                        | -139.7,-140.5 \(^a\) |                                      |              | 8.58 \(^b\) | 390 \(^c\)    |                |      |
| 0.185                  | -143.7               | -142.8                               | 26.2         | 8.4          | 400.6          | 458.3          | 2.62 |
|                        |                      |                                      |              |              | 395,402 \(^e\) |                |      |
| 0.200                  | -144.1               | -143.4                               | 26.8         | 8.5          | 405.2          | 457.4          | 2.66 |
|                        |                      |                                      |              |              | 423 \(^i\)    |                |      |
| 0.400                  | -146.5               | -144.6                               | 27.4         | 8.7          | 418.9          | 618.5          | 2.67 |
|                        |                      |                                      |              |              | 435 \(^a\)    |                |      |
| 0.700                  | -153.2               | -148.2                               | 31.8         | 9.7          | 466.6          | 511.0          | 2.82 |
| 0.800                  | -153.8               | -147.4                               | 30.3         | 9.6          | 460.6          | 545.6          | 2.69 |
|                        |                      |                                      |              |              | 473 \(^g\)    |                |      |
| 0.900                  | -153.8               | -146.6                               | 28.5         | 9.5          | 452.8          | 629.4          | 2.58 |
| 1.000                  | -155.9               | -150.0                               | 19.9         | 8.0          | 382.4          | 570.7          | 1.71 |

\(^a\)ref [18, 19], \(^b\)ref [32], \(^c\)ref. [34], \(^d\)ref [33], \(^e\)ref. [36], \(^i\)ref. [35], \(^g\)ref. [37]
3.2 Cohesive properties.
We calculated the cohesive energy of La$_{1-x}$Sr$_x$MnO$_3$ compounds using equation (1) and reported them in Table 2. The negative values of cohesive energy show that the compounds are stable below room temperature. The experimental values of cohesive energy for the La$_{1-x}$Sr$_x$MnO$_3$ compounds are not available but our calculated values are close to the reported value -139.70eV[18] and -140.6eV[19] for La$\equiv$MnO$_3$. Recently, Madelung energy of BaBiO$_3$ with perovskite structure is reported to be around -165eV (first term of our equation 1) [20]. It can be inferred from the results of cohesive energy (Table 2) that the stability of La$_{1-x}$Sr$_x$MnO$_3$ compounds increases with the higher Sr$^{2+}$ content. Further, to ascertain the validity of the modified RIM we have used the generalized Kapustinskii equation to calculate the lattice energy of these perovskites and the results (table II) are found to be close to the MRIM results (average deviation being less than 3%). Kapustinskii equation [21] for the lattice energies of crystals with multiple ions is given as

$$U / Kmol^{-1} = -\frac{1213.9}{<r>} \left( 1 - \frac{\rho}{<r>} \right) \sum_k n_k z_k^2$$

where $<r>$ = weighted mean cation-anion radius sum (using Goldschmidt radii) and $\rho$ is taken as the average value of our model parameters $\rho_1$ and $\rho_2$. $t$ is the number of type of ions in the formula unit each of number $n_k$ and charge $z_k$.

3.3 Bulk Modulus
The bulk moduli calculated on the basis of AIM theory [17] are found to be in good agreement with the available experimental data. Perovskite SrMnO$_3$ exists in cubic and hexagonal form and bulk modulus in low temperature hexagonal form is reported to be 121 GPa [22] and our result for hexagonal form is 121.2GPa. Our calculated value of 126.5GPa for the low temperature bulk modulus of La$_{0.83}$Sr$_{0.165}$MnO$_3$ in the spin ordered state (ferromagnetic/ antiferromagnetic) is close to reported value of 125 GPa at 300K for La$_{0.875}$Sr$_{0.125}$MnO$_3$ of Hazama et al. [23]. Also the reported value of La$_{0.8}$Sr$_{0.2}$MnO$_3$ in rhombohedral structure is 176.2 GPa at 310K [24] and the value of La$_{0.7}$Sr$_{0.3}$MnO$_3$ is 167 GPa as reported by Kozenko et al. [25], these are close to our high temperature (paramagnetic phase) bulk modulus of 172.9 GPa for x=0.185 and 171.6GPa for x=0.20 respectively (table 1).

3.4 Thermal Properties
Using the simple perovskite lattice cell parameter ($r_0$) and the model parameters ($b_1$, $b_2$, $\rho_1$, $\rho_2$) for the desired compositions (x) (table 1) the thermal properties at different temperatures and concentrations (0.165≤x≤0.90) were calculated and are reported in table 2. The restrahlen frequency of these compounds is close to reported value of 8.58THz for LaMnO$_3$ [32]. The Grüneisen parameter is within the reported limit of 2-3 [33]. In the observed doping range Debye temperature increase and the lattice specific heat decrease with increasing Sr$^{2+}$ doping (x). The similar anomalous softening of the lattice is observed by Okuda et al.[34] over the doping region 0.1<x<0.4 but we observed this trend over a wider region of doping 0.165≤x≤0.90. Table 2 indicates that for La$_{1-x}$Sr$_x$MnO$_3$ system the calculated values using MRIM are near the available experimental values [34-37]. The Debye temperature of these compounds below $T_N$ is found to be different from the stable room temperature paramagnetic phase values. The results indicate that spin ordered phase is less distorted and the compressibility is more compared to the paramagnetic phase of these doped compounds.

3.5 Specific Heat
The specific heat for La$_{1-x}$Sr$_x$MnO$_3$ perovskite manganite is calculated in the 1K≤T≤300K temperature. At very low temperatures the temperature dependence of specific heat is [3,34]

$$C = \gamma T + \beta T^3 + \delta T^{3/2}$$

(9)

here first term is electronic contribution, second term is lattice contribution, which has been calculated by using a MRIM, and third term is ferromagnetic spin wave contribution. We have
added the experimentally reported electronic specific heat and calculated ferromagnetic spin wave contribution term to our lattice specific heat term according to doping concentration (x) and the resulted values (Figure.1, 2) have reasonably good match with the available experimental values [35, 37-38]. It can be observed for figure 1(a) that higher order lattice terms are expected to contribute above 6K. The thermodynamic properties reported here at other doping concentration can work as guide to experimental workers.

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References
[1] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R and Chen L H 1994 Science 264 413-5; Fontcuberta J Feb 1999 Physics world. p 33-9; Millis A J 1999 Nature 392 147-52.
[2] Tokura Y (ed) 2000 “Colossal Magnetoresistive Oxides” (Gordon and Breach Publishers, London).
[3] Salamon M B and Jaime M 2001 Rev Mod Phys 73 583-628
[4] Ju H L, Kwon C, Li Q et al. 1994 Appl Phys Lett 65 2108
[5] Mitchell J F., Argyriou D N, Potter C D, Hinks D G, Jorgensen J D and Bader S D 1996 Phys Rev B 54 6172; Hemberger J, Krimme A, Kurz T, Nidda H-A K von., Ivanov V Yu. 2002 Phys Rev B 66 094410-7; Chmaissem O, Dabrowski B, Kolesnik S, 2003 Phys Rev B 67 094431-44.
[6] Wollan E D and Koehler W C 1955 Phys Rev 100 545-63.
[7] Mira J, Rivas J, Hueso L E, Rivadulla F, Quintela M A L, Rodrıguez M A S and Ramos C A 2001 Phys Rev B 65 024418
[8] Slater J C, Kirkwood J G 1931 Phys Rev 37 682-97
[9] Hafemiester D W and Flygare W H 1965 J Chem Phys 43 795-800.
[10] Pauling L 1945 Nature of the Chemical Bond (Cornell University Press, New York)
[11] Rini E G, Rao M N, Chaplot S L, Gaur N K, Singh R K 2007 Phys Rev B 75 214301(1-7)
[12] Gaur N K, Choithrani R and Srivastava Archana 2008 Solid State Commun 145 308-11
[13] Kaur N, Mohan R, Gaur N K and Singh R K 2007 J Phys Chem Solids 68 2247-51
[14] Srivastava Archana and Gaur N K. 2009 J Phys: Condens Matter 21 096001-14
[15] Srivastava A, Gaur N K, Kaur N and Singh R K 2008 J Magn. & Magn. Mater 320 2596-601; Srivastava A, Gaur N K, 2009 J Magn. & Magn. Mater. (in press).
[16] Srivastava A and Gaur N K 2008 AIP conf series 1004 334; Srivastava A and Gaur N K 2008 Indian J of Pure & Appl Phys 46 451-3; Srivastava A, Gaur N K 2009 Indian J Phys 83 1-10
[17] Pendas A M, Costales A, Blanco M A, Recio J M and Luana V 2000 Phys Rev B 62 13970-8
[18] Kovalyev N N, Gavartin J L, Shluger A L and Stoneham A M 2002 Physica B 312-313 734-6
[19] DeSouza R A, Islam M S, Boris A V and Ivers-Tiffe E 1999 J Mater Chem 9 1621-7
[20] Hase I, Yanagisawa T 2007 Phys Rev B 76 174103(1-4)
[21] Glasser Leslie 1995 Inorg. Chem. 34 4935-6
[22] Rune Søndenå, Ravindran P, Stolen S, Grande T and Hanfland M 2006 Phys Rev B 74 144102
[23] Hazama H, Nemoto Y, Goto T, Asamitsu A, Tokura Y 2000 Physica B 281-282 447
[24] Darling T W, Migliori A, Moskopoulo E G, Trugman S A 1998 Phys Rev B 57 5093
[25] Kozlenko D P, Goncharenko I N and Savenko B N 2004 J Phys: Condens Matter 16 6755–62
[26] Asamitsu A, Moritomo Y, Kumai R, Tomioka Y and Tokura Y 1996 Phys Rev B 54 1716
[27] De Leon-Guevara A M, Berthet P, Berthon J, Millot F et al 1997 Phys Rev B 56 6031-5
[28] Dabrowski B, Xiong X, Bukowski Z et al 1999 Phys Rev B 60 7006
[29] Machida A, Moritomo Y, Ohyama K, Okamoto S, Ishihara S, Maekawa S and Nakamura A 2000 Phys Rev B 62 80
[30] Mayr F, Hartinger Ch and Loidl A 2005 *Phys Rev* B 72 024425; Moritomo Y, Akimoto T et al 1998 *Phys Rev* B 58 5544

[31] Uhlenbruck S, Teipen R, Klingeler R, Büchner B, Friedt O, Hücker M, Kierspel H, Niemöller T, Pintsard L, Revcolevschi A and Gross R 1999 *Phys Rev Lett* 82 185

[32] Fedorov I, Lorenzana J, Dore P, De Marzi G, Maselli P, Calvani P, Cheong S-W, Koval S and Migoni R 1999 *Phys. Rev.* B 60 11875-8

[33] Radaelli P G and Cheong S-W 2002 *Phys. Rev.* B 66 094408(1-9)

[34] Okuda T, Asamitsu A, Tomioka Y, Kimura T, Taguchi Y and Tokura Y 1999 *Phys Rev Lett* 81 3203-6.

[35] Michalopoulou A, Syskakis E and Papastaikoudis C 2001 *J Phys: Condens Matter* 13 11615–21

[36] Michalopoulou A, Syskakis E and Papastaikoudis C 2003 *J Phys: Condens Matter* 15 7763–76

[37] Bindu R, Maiti K, Rawat R and Khalid S 2008 *Appl Phys Lett* 92 121906

[38] Szewczyk A, Gutowska M, Dabrowski B, Plackowski T, Danilova N P and Gaidukov Yu P 2005 *Phys Rev* B 71 224432