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Structural and phonon dynamical properties of perovskite manganites: (Tb, Dy, Ho)MnO_3

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ABSTRACT

A shell model has been used to study the structure, phonon dynamics and phase coexistence of perovskite manganites $RMnO_3$ (R=Tb, Dy, Ho). The calculated crystal structure, Raman and IR frequencies and specific heats are found to be in good agreement with the available experimental data. The phonon density of states, elastic constants, elastic stiffness, shear constants and phonon dispersion curves have been computed for these manganites. A zone center imaginary A_u mode is revealed in these phonon dispersion curves, which indicates the occurrence of the metastability of the perovskite phase. The Gibbs free energy values calculated as a function of temperature and pressure for $RMnO_3$ in the orthorhombic phase, when compared with those of the hexagonal phase, reveal the possibility of coexistence of these two phases in the present multiferroic manganites under ambient conditions.

1. Introduction

Multiferroic perovskite manganites have attracted immense interest in recent years due to their magnetoelectric phenomena and several potential technological applications [1–3]. The discovery of ferroelectricity in $TbMnO_3$ has been reported by Kimura et al. [4], where the effect of spin frustration causes sinusoidal antiferromagnetic ordering. They have found gigantic magnetoelectric and magnetocapacitance effects in $TbMnO_3$, which can be attributed to switching of the electric polarization induced by magnetic fields as observed by Kimura et al. [4]. The magnetic structure of the paraelectric and ferroelectric phases of $TbMnO_3$ has been determined by Kenzelmann et al. [5]. They have shown that the paraelectric, magnetically incommensurate phase has sinusoidally modulated collinear magnetic order that does not break inversion symmetry whereas the ferroelectric phase has noncollinear incommensurate magnetic order described by two irreducible representations, which explicitly breaks inversion symmetry and thus gives rise to electric polarization. The strong coupling between the magnetic order and polarization-order parameters in $TbMnO_3$ suggests that the ferroelectricity might be induced by the incommensurate magnetism [6].

Carron et al. [7] have experimentally studied the Raman phonons as a function of the rare earth ions and temperature for the orthorhombic (o-)$RMnO_3$ (R=Pr, Nd, Eu, Tb, Dy, Ho) manganites. They have correlated the frequencies of the three most intense modes of these orthorhombic compounds with some structural parameters like Mn–O bond distances, octahedral tilt angle and Jahn–Teller distortion. Later on, the polarized Raman spectra for a series of o-$RMnO_3$ (R=Pr, Nd, Eu, Gd, Tb, Dy, Ho) have been observed by Iliev et al. [8], where they have assigned the observed frequencies as well as studied the basic distortions responsible for the mode activation. Their study shows that the variation of lattice distortion with radius of the rare earth atoms affects significantly both the phonon frequencies and the shape of some of the Raman modes. The Raman frequencies have also been investigated by Laverdiere et al. [9] and Kumar et al. [10] for A_g and B_{2g} modes in $TbMnO_3$. Currently, the infrared (IR) spectral frequencies have been measured by Schmidt et al. [11] and Kumar et al. [12] for $TbMnO_3$. For these reasons, the aim of the present paper is to thoroughly investigate the phonon dynamical properties of the present system of manganites.

The crystal structure of o-$RMnO_3$ (R=Tb, Dy, Ho) exhibits distorted perovskite structure with space group *Pnma* at room temperature [8,13,14]. Their magnetic structures have also been studied by means of both X-ray diffraction (XRD) [15] and neutron diffraction [16] measurements. The magnetization of $TbMnO_3$ shows two sharp peaks around 27 and 42 K. In case of $HoMnO_3$, there are magnetic transitions below 60 K as are observed by Tachibana et al. [17] and Munoz et al. [18]; a sharp peak around $T_N \sim 40$ K marks antiferromagnetic (AF) transition into the incommensurate (IC) phase, additional anomaly is observed at $T'_N \sim 5$–15 K and this feature is ascribed to a lock-in-transition to the E-type structure.

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A modified rigid ion model (MRIM) has been recently developed by some of us [19] to elucidate the cohesive, thermal and thermodynamic properties of the pure and doped perovskite manganites, probably for the first time. Also, the lattice dynamical studies of (Sm, Eu, Gd)MnO_3 [20], $LaMnO_3$ [21] and $YMnO_3$ [22] have been performed by using a seven parameter shell model [23–25] based on a transferable interatomic potential.

In the process of development of new physics, an important input is the fundamental understanding of the phonon dynamical and thermodynamical properties in terms of the microscopic structure and dynamics. Therefore, it seems important to apply the shell model [20] for describing the phonon dynamical and related properties of the multiferroic manganites $RMnO_3$ (R=Tb, Dy, Ho) such as the crystal structure, phonon density of states, phonon dispersion curves, Raman and IR frequencies, elastic constants, elastic stiffness, shear constants, Debye temperature, specific heat and phase coexistence. The symmetry vectors obtained through the group-theoretical analysis for *Pnma* space group at the zone center (Γ) point and along the high symmetry directions have been employed to classify the phonon frequencies obtained into their irreducible representations.

The present study has shown an interesting and informative effort made in this field. The essential formalism of the shell model has been described in the following section.

2. Shell model computations

The interatomic potential of the present shell model [20] consists of the long-range Coulomb and the short-range interactions and employs the effective ionic charge and effective radius, associated with the atoms, as the adjustable parameters. The effect of polarizability of the oxygen ions in this model has been included by considering a massless shell with charge Y linked to the core of the ions by harmonic interactions with a shell–core force constant K. The knowledge of the interatomic interactions in these materials is important to understand various crystal and phonon dynamical properties of the multiferroic manganites in the fundamental and technological researches.

The shell model parameters have been 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 neutron diffraction experiments. These computations are performed using the DISPR [24] program. The optimized parameters for $RMnO_3$ (R=Tb, Dy, Ho) thus obtained are listed in Table 1. The phonon dispersion curves (PDCs) for the orthorhombic phase have been computed using the equilibrium structure at the minimum of the potential energy.

The phonon density of states are given by [20–23]

$$g(\omega)=N\int_{BZ}\sum\delta[\omega-\omega_j(q)]d\mathbf{q} \tag{1}$$

with N as a normalization constant such that $\int g(\omega)d\omega=1$ and $g(\omega)d\omega$ is the ratio of the number of eigenstates in the frequency interval $(\omega, \omega+d\omega)$ to the total number of eigenstates. Here, $\omega_j(q)$ is the phonon frequency of jth normal mode of the wave vector $\mathbf{q}$.

Table 1
The potential parameters obtained for $RMnO_3$ (R=Tb, Dy, Ho) using the shell model.

	Tb	Dy	Ho	Mn	O
Z(k) (e)	2.75	2.75	2.75	1.00	−1.25
R(k) (Å)	2.0171	2.016	2.00	1.07	1.71
Y(O)=−1.8e					
K(O)=183 eV Å^{-2}					

These density of states have been used to evaluate the specific heat at constant volume [20–23] at different temperatures (T).

$$C_v(T)=k_B\int\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{(\hbar\omega/k_BT)}}{[e^{(\hbar\omega/k_BT)}-1]^2}g(w)d\omega. \tag{2}$$

here, k_B and h are the Boltzmann and Planck constants, respectively. The definition of other symbols and the procedure adopted to compute these lattice dynamical properties are prescribed in detail elsewhere [20–23].

The group-theoretical analysis performed for the perovskite manganites shows that the phonon modes at the zone center point (Γ) may be classified as [20–23] $7A_g+7B_{2g}+5B_{1g}+5B_{3g}+10B_{1u}+10B_{3u}+8A_u+8B_{2u}$. Out of these 60 phonon modes, 24($7A_g+5B_{1g}+7B_{2g}+5B_{3g}$) are Raman active, 25 ($9B_{1u}+7B_{2u}+9B_{3u}$) are infrared (IR) active, 8 ($8A_u$) are silent, and 3 ($B_{1u}+B_{2u}+B_{3u}$) are acoustic modes. The following group-theoretical classification has been obtained along the three high symmetry directions:

$$\begin{aligned}&\textstyle\sum:\ 17\sum_1+13\sum_2+13\sum_3+17\sum_4\\&\Delta:\ 15\Delta_1+15\Delta_2+15\Delta_3+15\Delta_4\\&\Lambda:\ 17\Lambda_1+13\Lambda_2+13\Lambda_3+17\Lambda_4\end{aligned} \tag{3}$$

The dynamical matrix corresponding to the present interatomic potential [20] has been diagonalized along these symmetry directions and the normal modes have been classified into different representations to obtain the phonon dispersion curves in $RMnO_3$ (R=Tb, Dy, Ho). The computed results are presented and discussed below.

3. Results and discussion

3.1. Crystal structure

The DISPR program [24] (developed at BARC) has been used to compute the optimized potential parameters and the atomic coordinates, which are listed in Tables 1 and 2, respectively. These parameters yield nearly vanishing forces on any atom. The values of these parameters have been used to compute the eigenvalues of the dynamical matrix corresponding to the present shell model.

The acquaintance for the nature of interatomic interactions in solids is of paramount importance as it leads to explain their vibrational, thermodynamical, elastic, cohesive and numerous other physical properties. The understanding of many physical properties of materials is predictable with the knowledge of their crystal structure. Thus, the crystal structure of o-$RMnO_3$ (R=Tb, Dy, Ho) has been calculated by minimizing the Gibbs free energy with respect to the structural parameters. The multiferroic perovskite manganites $RMnO_3$ (R=Tb, Dy, Ho) (with space group *Pnma*) have an orthorhombic structure with four formula units per unit cell [13,14]. It has five atoms in the asymmetric unit with R and O occupying the crystallographic sites 4(c), except for one oxygen atom, which is at the general position 8(d) and Mn is at the 4(a) position.

The values of the calculated lattice parameters (a, b, c), atomic coordinates (x, y, z), unit cell volumes (V) and strain parameters ($s(=2(a-c)/(a+c))$ are listed in Table 2 for the orthorhombic manganites $RMnO_3$ (R=Tb, Dy, Ho) and compared with the available experimental neutron diffraction data [13,14]. It is noticed from this table that our calculated results are in fairly good agreement with their corresponding experimental data [13,14]. The calculated lattice parameters (a, b, c) have been found to differ only by 0.8% on an average from the experimentally observed data [13,14] for these $RMnO_3$. The calculated values of the unit cell volumes (V) are also in good agreement with their experimental data [13,14]. The decreasing trend of V with