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Specific heat and Thermodynamics of Titanate Perovskite Materials

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Abstract
Specific heat and thermodynamical properties of the $LaTiO_{3+\delta/2}$ have been investigated for the first time using extended rigid ion model (ERIM). With the increase of nominal hole doping δ, the system undergoes a phase change from an insulating phase to a metallic phase at $\delta_c^{IM} = 0.05$ and the low-temperature antiferromagnetic phase disappears at $\delta_c^{mag} = 0.08$. $LaTiO_{3+\delta/2}$ has been suggested to have promising scientific and technological applications. Our computed specific heat results follow the same trends of variation with corresponding experimental data. The values of specific heats also increase with temperature. The theoretically computed thermodynamical properties of $LaTiO_{3+\delta/2}$ compound are in good agreement with the available experimental results.
Keywords: Thermodynamical properties, Perovskites, Specific heat, Debye temperature, Cohesive energy

1 Introduction

Recently metal-insulator transitions (MIT) in 3d-transition metal ternary oxide systems have been intensively investigated in order to clarify the anomalous properties of correlated electrons[1]. One of the most prototypical systems is the perovskite-type one, from the mineral perovskite $LaTiO_3$. The perfect perovskite structure is an extremely simple one with the chemical formula ABO_3, where A is a monovalent, divalent or trivalent alkaline- or rare-earth element and B is a pentavalent, tetravalent or trivalent transition-metal element such as Ti or Mn. One of the advantages in studying this particular class of titanate lies in its relatively simple electronic and lattice features; namely, in a stoichiometric compound $LaTiO_3$ a relevant electron is only single 3d electron per each Ti site,whose network forms a simple, approximately cubic, lattice[1-3]. These materials are at the focus of scientific research due to their potential technological applications[4]. Orbital degrees of freedom, in addition to spin, charge, and lattice structure, are gaining increasing interest in current solid-state physics. That is, in manganites the question of orbital order plays a key role in the understanding of electronic properties such as the colossal magnetoresistant effect. In the orthorhombic perovskite $LaMnO_3$ (Mn^{3+}:$3d^4$) one finds a different scenario. Here the e_g band is occupied by one electron, the degeneracy is lifted by the Jahn-Teller (JT) effect, and the orbitals are ordered. $LaTiO_3$ is an antiferromagnetic $3d^1$ Mott-Hubbard insulator with a Neel temperature of $T_N =$ 146 K. It has degenerate t_{2g} orbitals. The role of the orbital degrees of freedom in this system is still unclear[5-8]. With the increase of nominal hole doping δ, the system undergoes a phase change from an insulating phase to a metallic phase at $\delta_c^{IM} = 0.05$ and the low-temperature antiferromagnetic phase disappears at $\delta_c^{mag} = 0.08$. It is found that our computed results on thermodynamic properties such as cohesive and thermal properties of $LaTiO_{3+\delta/2}$ using ERIM after improving modified rigid ion model (MRIM) developed recently by Renu Choithrani *et al*[9-11] and applied successfully on pure and doped perovskite manganites and multiferroic materials are closer to the available experimental values. Perovskite-type titanate system, $LaTiO_{3+\delta/2}$ is known to be a canonical system for the filling-controlled insulator-metal transition and has widely been studied by transport, thermodynamic and spectroscopic measurements, as well as theoretically. $LaTiO_{3+\delta/2}$ have been suggested to have promising scientific and technological applications. Our computed specific heat results follow the same trends of variation with corresponding experimental data by Y. Taguchi *et al*[2].

2 Formalism of extended rigid ion model ERIM

The author has recently developed an extended rigid ion model (ERIM) by incorporating the long-range (LR) Coulomb attraction, the short-range (SR) Hafemeister–Flygare (HF) type overlap repulsion effective up to the second neighbour ions, the van der Waals (vdW) attraction due to the dipole–dipole (d–d) and dipole–quadrupole (d–q) interactions and zero point energy (ZPE) effects in the framework of modified rigid ion model (MRIM) developed earlier by us[9-11].

The framework of ERIM is derived from the following interionic interaction potential:

$$\phi_{ERIM} = \phi_{MRIM} + \phi_{ZPE} \qquad (I)$$

Where, ϕ_{MRIM} potential (by Renu Choithrani *et al*[9]) is given by

$$\phi_{MRIM} = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} + \left[\begin{array}{l} n b_1 \beta_{kk'} \exp\{(r_k + r_{k'} - r_{kk'})/\rho_1\} + \\ \frac{n'}{2} b_2 \left[\beta_{kk} \exp\{(2r_k - r_{kk})/\rho_2\} + \beta_{k'k'} \exp\{(2r_{k'} - r_{k'k'})/\rho_2\}\right] \end{array}\right]$$
$$- \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} \quad (1)$$

and $\phi_{ZPE} = (9/8)\, N\, K_B \theta_D$ (2)

The symbols involved equations (1) and (2) are the same as those defined in our earlier papers[11]. Here, k (k′) denote the positive (negative) ions and the sum is taken over all the ions (kk′).

In Eq. (1), the first term represents the long-range Coulomb attraction, the second and third terms are the short-range Hafemeister-Flygare[12] type repulsion operating upto the second neighbour ions. The fourth and fifth terms in it are the vdW attraction energies due to the dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions with $c_{kk'}$ and $d_{kk'}$ as the corresponding vdW coefficients. The values of these coefficients are estimated by using the following expressions:

$$c_{kk'} = (3e^2 \alpha_k \alpha_{k'} / 2m)\ [(\alpha_k/N_k)^{1/2} + (\alpha_{k'}/N_{k'})^{1/2}]^{-1} \quad (3)$$

$$d_{kk'} = (27e^2 \alpha_k \alpha_{k'} / 8m)\ [(\alpha_k/N_k)^{1/2} + (\alpha_{k'}/N_{k'})^{1/2}]^2$$
$$[(\alpha_k/N_k)^{1/2} + 20/3(\alpha_k\alpha_{k'}/N_kN_{k'})(\alpha_{k'}/N_{k'})]^{-1} \quad (4)$$

derived from the Slater-Kirkwood Variational (SKV) method[13]. Here, m and e are the mass and charge of electrons, respectively. $\alpha_k(\alpha_{k'})$ are the polarizabilities of k(k′) ions ; N_k ($N_{k'}$) are the effective number of electrons responsible for the polarization of k(k′) ions.

The values of $c_{kk'}$ and $d_{kk'}$ are evaluated using the Eqs. (3) and (4) and following the procedure prescribed by us[9-11]. ERIM has been developed and applied by the author, probably for the first time, to describe the transport properties of the perovskite materials. The specific heat, model parameters and the transport properties such as cohesive and thermal properties of $LaTiO_{3+\delta/2}$ compound using their expressions given in our earlier papers[9-11]. The computed results thus obtained are presented and discussed below.

3 Result and discussion

The input data for different compositions (δ) are obtained from the Vegards law[14] using the experimental data[1-3, 5-8] reported for the parent members and thermodynamic relations on the lines of refs.[9-11]. Using these input data and the vdW coefficients ($c_{kk'}$ and $d_{kk'}$) calculated from the SKV method[13], the model parameters (ρ_1, b_1 and ρ_2, b_2) have been evaluated for different compositions (δ = 0.01, 0.04, 0.06, 0.08, and 0.16) and temperatures ($T^2 \leq 50\ K^2$) for $LaTiO_{3+\delta/2}$ and listed them in Table 1. The model parameters (ρ and b) have shown decreasing trend with increasing composition, indicating the decrease in the strength of these perovskite-type titanate systems. Using the model parameters (ρ and b), the values of cohesive energy (ϕ) for $LaTiO_{3+\delta/2}$ have been computed to test the validity of our model. It is found from Table 1 that the magnitude of the cohesive energy decreases from ϕ = -142.71 eV (for δ = 0.01) to -141.87 eV (for δ = 0.16). Also, the computed values of cohesive energy at all given compositions are in good agreement with the available measured data for the parent member $LaMnO_3$[15] of the manganite family. The negative values of the cohesive energy indicate the stability of the compound. The values of Restrahalen frequencies from δ = 0.01 to 0.16 shows conformity with the experimental value (υ_0 = 10.764 THz) available only at 300 K[16] for $LaTiO_3$. It is also noticed from Table 1 that the higher values of Debye temperatures indicate the presence of higher phonon frequencies in these materials. The calculated values of Debye temperatures of $LaTiO_{3+\delta/2}$ (δ = 0.01, 0.04, 0.06, 0.08, and 0.16) are found to lie in the range 501.761-500.362 K, which is closer to the reported value of θ_D (= 516.6 K)[16] for $LaTiO_3$ and also comparable to the range (300-550 K)[9-11] often found in perovskite materials. The computed values of Grüneisen parameter (γ) is decreasing slightly on varying composition δ = 0.01 to 0.16 and its value lies in between 2 and 3 as reported by Dia *et al*[17]. The specific heat curve of Perovskite-type titanate system, $LaTiO_{3+\delta/2}$ (δ = 0.01, 0.04, 0.06, 0.08, and 0.16) obtained using ERIM is in good agreement with the experimental curve[2] (see Fig. 1). It is interesting to note from Fig.1 that both the calculated and experimental specific heats increase linearly with temperature indicating the display of phononic contributions (~T^3) in $LaTiO_{3+\delta/2}$. Further, the values of specific heat increase rapidly with the increase of δ from 0.01 to 0.08 whereas decreases from 0.08 to 0.16. This critical behavior is due to the antiferromagnetic instability that has been investigated for the filling controlled insulator-metal transition system, $LaTiO_{3+\delta/2}$, by transport and specific heat measurements[2]. It is noticed that electronic specific heat coefficient takes a maximum value (≈17 mJ/mol.K^2) at δ = 0.08 and is reduced in the antiferromagnetically ordered phase observed by Taguchi *et al*[2].

Table1- Model Parameters and Thermodynamic Parameters of $LaTiO_{3+\delta/2}$

Model Parameters					Thermodynamic Parameters			
δ	Ti-O ρ_1 (Å)	Ti-O $b_1(10^{-12}$ erg)	La-O ρ_2 (Å)	La-O $b_2(10^{-12}$ erg)	ϕ (eV)	υ_0 (THz)	Θ_D (K)	γ
0.01	0.5701	0.9978	0.7376	0.6470	-142.71	10.459	501.761	2.89
0.04	0.5598	0.9861	0.7198	0.6317	-142.09	10.438	500.752	2.85
0.06	0.5379	0.9614	0.7125	0.6205	-141.96	10.433	500.514	2.81
0.08	0.5146	0.9237	0.7019	0.6198	-141.79	10.427	500.210	2.78
0.16	0.5262	0.9425	0.7072	0.6201	-141.87 (141.81)[15]	10.430 (10.764)[16]	500.362 (516.6)[16]	2.80 (2-3)[17]

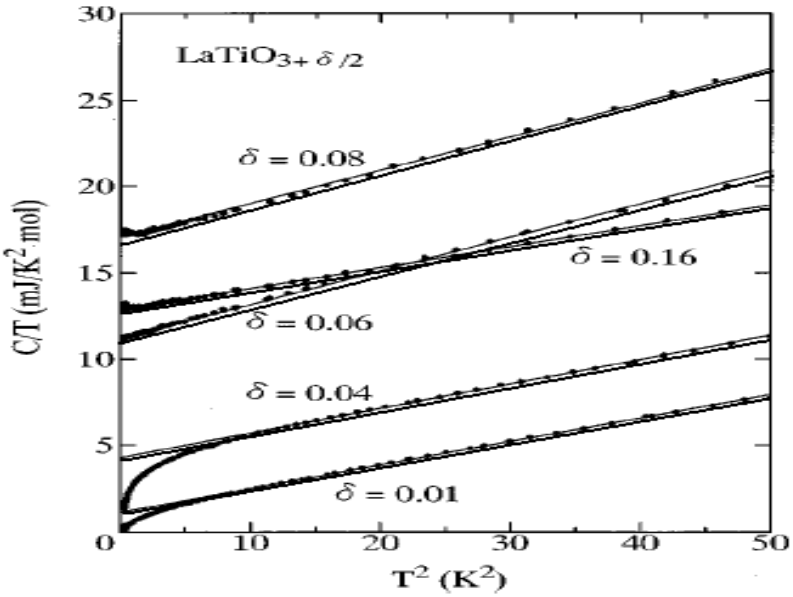

Fig. 1 The variations of specific heat with temperature for $LaTiO_{3+\delta/2,}$ where the solid lines and lines with circles are the present model calculation and experimental data[2], respectively.

4 Conclusions

The systematic trend of variations of thermodynamic properties and the closer agreement with the available experimental data on specific heats reveal the suitability and appropriateness of ERIM for the $LaTiO_{3+\delta/2}$ materials. Some of the results are, probably, being reported for the first time and hence our comment on their reliability are restricted until the report of experimental data on them. Presently, these values are of academic interest and they can serve as guide to the experimental workers in future.

It may be concluded that ERIM is effectively useful model for the unified and comprehensive study of the perovskite materials, because the beauty of our potential lies in satisfactory explanation of the variety of physical properties (such as cohesive, thermal, elastic, thermodynamic) with same success[9-11] for the multiferroics, manganites and other perovskite materials.

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