JOURNAL OF SOLID STATE CHEMISTRY 113, 215–220 (1994)

BRIEF COMMUNICATION

Valence State Equilibria between Cobalt and Manganese Ions and Magnetic Properties of $LaCo_{0.9}Mn_{0.1}O_3$

Y. Q. Jia

Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China

S. T. Liu

Dalian Institute of Chemical Physics, Academia Sinica, Dalian 116011, China

and

Y. Wu

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, China

Received September 8, 1993; in revised form January 25, 1994; accepted February 4, 1994

According to the thermodynamic equilibria between the low spin state Co^{III} ($t_{2g}^6e_g^0$) ion and the high spin state Co^{3+} ($t_{2g}^4e_g^2$) ion and between the cobalt and manganese ions with different valence state and spin state, an approximate semiempirical formula has been proposed to calculate the magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ in a wide temperature range (100–1200 K). The results show that the calculated susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ are very close to the experimental susceptibilities, and the relative errors are smaller than 5%, except in a few cases. In $LaCo_{0.9}Mn_{0.1}O_3$ there may exist the low spin state Co^{III} ion, the high spin state Co^{3+} and Co^{2+} ions, and the high spin state Mn^{3+} and Mn^{4+} ions at different temperatures. The content of the low spin state Co^{III} ion has been predominant in $LaCo_{0.9}Mn_{0.1}O_3$ in the whole temperature range, and decreases gradually with increasing temperature. At lower temperatures, the content of the Mn^{4+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ is larger than that of the Mn^{3+} ion; however, at higher temperatures, the manganese ion is mainly trivalent. The calculated results are in good agreement with some experimental results; for example, the effective paramagnetic moment of the compound agrees with the paramagnetic Curie point of the compound. The temperature dependence of the electric resistivity of $LaCo_{0.9}Mn_{0.1}O_3$ has also been predicted.

INTRODUCTION

A large number of rare earth–transition metal oxides with perovskite-type structure have been synthesized and studied because of their having specially physical or chemical properties, such as catalytic activity and electric and magnetic properties. Some systematic research on the magnetic and electric properties of some rare earth–transition metal oxides have been published (1–6). Although the effect of the valence state and the spin state of metal ions on the catalytic, electric, and magnetic properties of the compound is very significant, little attention has been paid to the relationships between the relative content of various metal ions with different valence states and spin states and the physical or chemical properties of the compound.

At any temperature some thermodynamic equilibria must exist between various metal ions with different spin states and valence states in any compound, especially when the chemical reaction happens in the solid state compound. Therefore, based on possible thermodynamic equilibria between various cobalt ions and maganese ions due to thermal excitation of the diamagnetic Co^{III} ion or due to the oxidation–reduction reaction and the deoxidation of the compound at high temperatures, a semiempirical formula has been proposed to calculate the magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ over a wide temperature range (100–1200 K). In the calculations some superexchange interactions between the main components in the compound have also been considered. The results indicate that the calculated magnetic susceptibilities are in good agreement with the experimental results, and most of the relative errors are smaller than 5%. The other calculated magnetic parameters are also satisfactory. The possible variation of the resistivity of $LaCo_{0.9}Mn_{0.1}O_3$ with temperature can be predicted.

0022-4596/94 $6.00

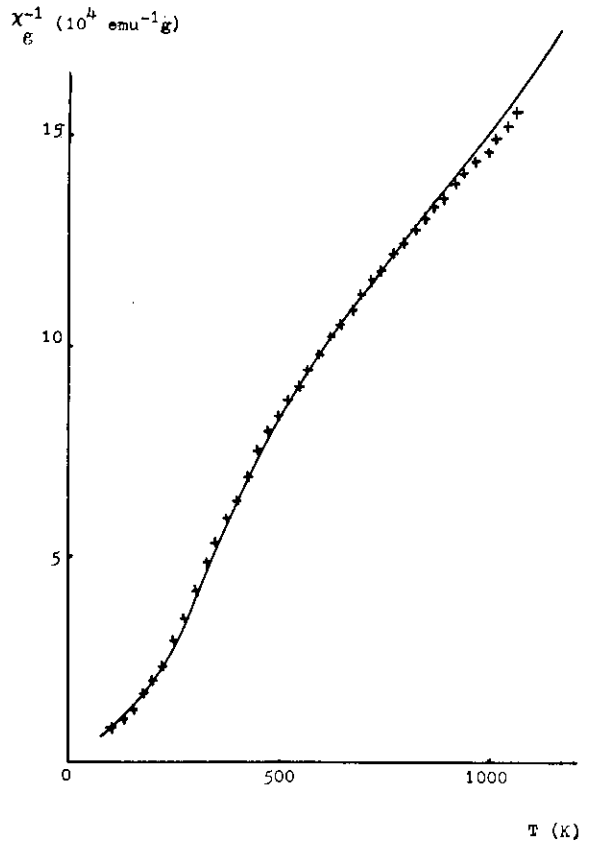

FIGURE 1

EXPERIMENTAL

$LaCo_{0.9}Mn_{0.1}O_3$ is prepared by the thermal decomposition of the citrate complexes of lanthanum, cobalt, and manganese. All the chemicals used in the experiments are of analytical reagent grade. The freshly prepared citrate complex of lanthanum, cobalt, and manganese in a 1:0.9:0.1 stoichiometric ratio is decomposed by slow heating and kept at 870 K for about 1 hr, and the resultant powder is pressed into pellets and fired in air at 1230 K for 6 hr.

The results of the powder X-ray diffraction of the sample show that the compound is a single-phase material with a rhombohedral structure. The calculated lattice parameters are $a = 0.5448$ and $c = 1.3114$ nm, respectively. The magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ have been measured over the temperature range 100–1073 K with a MB-2 automatic recording balance. The curve of the inverse magnetic susceptibility per gram of $LaCo_{0.9}Mn_{0.1}O_3$ vs temperature is shown in Fig. 1.

CALCULATIONS AND RESULTS

In $LaCoO_3$ the diamagnetic trivalent Co^{III} ($t_{2g}^6 e_g^0$) is the ground state at 0 K and the formation of the paramagnetic trivalent Co^{3+} ($t_{2g}^4 e_g^2$) is due to the thermal excitation of the diamagnetic Co^{III} ion; therefore, there must be the thermodynamic equilibrium (6, 7)

$$Co^{III} \rightleftharpoons Co^{3+} \quad \text{and} \quad \frac{X(Co^{3+})}{X(Co^{III})} = e^{-E/kT}, \qquad [1]$$

where $X(Co^{III})$ and $X(Co^{3+})$ are the relative content of the low spin state Co^{III} ion and the high spin state Co^{3+} ion in $LaCo_{0.9}Mn_{0.1}O_3$, respectively; E is the activation energy from the ground state to the excited state; k is the Boltzmann constant, and T is the absolute temperature.

In the La–Co–Mn–O system, there may exist an oxidation–reduction reaction

$$Co^{III,3+} + Mn^{3+} \rightleftharpoons Co^{2+} + Mn^{4+}.$$

At any temperature, the above reaction can have a thermodynamic equilibrium

$$\frac{X(Co^{2+}) \cdot X(Mn^{4+})}{X(Co^{III,3+}) \cdot X(Mn^{3+})} = K_1, \qquad [2]$$

where K_1 is the equilibrium constant for the reaction.

In addition, many of rare earth–transition metal oxides will have deoxidation reactions at higher temperatures. Because the relative content of the cobalt ion is much larger than that of the manganese ion in $LaCo_{0.9}Mn_{0.1}O_3$, the following deoxidation reaction will be considered,

$$Co^{III,3+} + \tfrac{1}{2}O^{2-}(\text{lat.}) \rightleftharpoons Co^{2+} + \tfrac{1}{4}O_2 + V_O,$$

where O^{2-}(lat.) is the oxygen atom in the lattice and V_O is the oxygen vacancy in the lattice. When the oxygen partial pressure of the atmosphere about $LaCo_{0.9}Mn_{0.1}O_3$ is constant, the above deoxidation reaction can reach a thermodynamic equilibrium state at a certain temperature,

$$\frac{X(Co^{2+})}{X(Co^{III,3+})} = K_2, \qquad [3]$$

where K_2 is the equilibrium constant of the deoxidation reaction. Here the effect of the relative content of the oxygen atom in the lattice, of the concentration of the oxygen vacancy in the lattice, and of the oxygen partial pressure on the deoxidation reaction equilibrium have been included in the equilibrium constant K_2.

In a wide temperature range, the temperature dependence of the reaction equilibrium constant can be described approximately by a general function (8),

$$\ln K_i = -\frac{\Delta H_i}{RT} + a_i \frac{\ln T}{R} + b_i \frac{T}{2R} + c_i \frac{T^2}{6R} + d_i, \qquad [4]$$

where R is the gas constant; T is the absolute temperature; and ΔH_i, a_i, b_i, c_i, and d_i are constant for a reaction

system. Therefore, the relative content of the Co^{III}, Co^{3+}, Co^{2+}, Mn^{3+}, and Mn^{4+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ at any temperature can be determined from the formulas [1]–[3],

$$X(Co^{III}) = \frac{A}{(1 + e^{-E/kT}) \cdot (1 + K_2)}$$

$$X(Co^{3+}) = \frac{Ae^{-E/kT}}{(1 + e^{-E/kT}) \cdot (1 + K_2)}$$

$$X(Co^{2+}) = \frac{AK_2}{1 + K_2} \qquad [5]$$

$$X(Mn^{3+}) = \frac{BK_2}{K_1 + K_2}$$

$$X(Mn^{4+}) = \frac{BK_1}{K_1 + K_2},$$

where A and B are the total content of the cobalt and the manganese in $LaCo_{0.9}Mn_{0.1}O_3$. Here $A = 0.9$ and $B = 0.1$, respectively.

Because each magnetic metal ion can contribute to the paramagnetic moment of the molecule, we can have (9, 10)

$$M^2 = m_1^2 \cdot X(Co^{III}) + m_2^2 \cdot X(Co^{3+}) + m_3^2 \cdot X(Co^{2+}) + m_4^2 \cdot X(Mn^{3+}) + m_5^2 \cdot X(Mn^{4+}), \qquad [6]$$

where M is called the *apparent magnetic moment* of the $LaCo_{0.9}Mn_{0.1}O_3$ molecule, and m_1, m_2, m_3, m_4, and m_5 are the effective magnetic moments of the Co^{III}, Co^{3+}, Co^{2+}, Mn^{3+}, and Mn^{4+} ions in the compound, respectively.

The dependence of the magnetic susceptibility of $La Co_{0.9}Mn_{0.1}O_3$ on temperature may obey the Curie–Weiss law; therefore, superexchange magnetic interactions between the metal ions in the compound must be considered in the calculation of the susceptibility. According to a similar method, we propose the following semiempirical formula to approximate the magnetic susceptibility of $La Co_{0.9}Mn_{0.1}O_3$ at any temperature (7, 10),

$$\chi = \frac{(N/3k) \cdot \mu_B^2 \cdot M^2}{T - T_\theta}, \qquad [7]$$

where N is the Avogadro constant; k is the Boltzmann constant; T is the absolute temperature; μ_B is the Bohr magneton; and M is the apparent magnetic moment of the $LaCo_{0.9}Mn_{0.1}O_3$ molecule. Here (9, 10)

$$T_\theta = \theta_1 X(Co^{III})^2 + \theta_2 X(Co^{3+})^2 + 2\theta_3 X(Co^{III})X(Co^{3+}) + 2\theta_4 X(Co^{III})X(Mn^{3+}), \qquad [8]$$

where θ_1 is the superexchange magnetic interaction parameter for Co^{III}–O–Co^{III}; θ_2 for Co^{3+}–O–Co^{3+}; θ_3 for Co^{III}–O–Co^{3+}; and θ_4 for Co^{III}–O–Mn^{3+}. These parameters θ_i have been considered to be constant over the whole temperature range.

TABLE 1

Parameters for Calculation of the Relative Content of Various Cobalt and Manganese Ions and Parameters for the Magnetic Interactions between Some Cobalt and Manganese Ions in $LaCo_{0.9}Mn_{0.1}O_3$ in the Temperature Range 100–1200 K

Parameters for activation energy E and equilibrium constant K_i	Superexchange interaction parameters θ_i
$E = 0.0058$ eV	
$\Delta H_1 = 2196.32$ J/K · mol	$\theta_1 = 275.6$ K
$a_1 = 0.294$ J/K · mol	$\theta_2 = 926.1$ K
$b_1 = 0.122$ J/K² · mol	$\theta_3 = -234.2$ K
$c_1 = -3.48\ 10^{-3}$ J/K³ · mol	$\theta_4 = -1669.1$ K
$d_1 = -0.0254$	
$\Delta H_2 = 1415.84$ J/K · mol	
$a_2 = -1.829$ J/K · mol	
$b_2 = -0.146$ J/K² · mol	
$c_2 = -1.45\ 10^{-4}$ J/K³ · mol	
$d_2 = -0.391$	

We can obtain the values of all the parameters in the formulas [1]–[8] through fitting to the experimentally measured magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ in the temperature range 100–1073 K by means of the formula [7]. The obtained parameters have been listed in Table 1. From these parameters, the equilibrium constants K_1 and K_2 can be calculated using the formula [4]. Then the relative contents of all the cobalt and manganese ions with different valence states and spin states in $LaCo_{0.9}Mn_{0.1}O_3$ can be evaluated at any temperature using the formula [5]. The variation of the relative contents of various cobalt and manganese ions in $LaCo_{0.9}Mn_{0.1}O_3$ with temperature are shown in Figs. 2 and 3, respectively. In addition, the variation with temperature of the logarithm of the ratio of the relative content of the Mn^{4+} ion to that of the Co^{2+} ion in the compound is shown in Fig. 4. For comparison, the curve of the calculated inverse magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ in the temperature range 100–1200 K is also shown in Fig. 1.

DISCUSSION

As Fig. 1 shows, the calculated inverse magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ in a wide temperature range are very close to the experimental results. Most of the relative errors between the calculated $1/\chi$ and the experimental $1/\chi$ are less than 5%.

From Table 1, we find that the calculated activation energy E from the diamagnetic low spin Co^{III} in the ground state to the paramagnetic high spin Co^{3+} in the excited state is about 0.006 eV. This is slightly smaller than the values other authors have suggested, $E = 0.01$ eV and

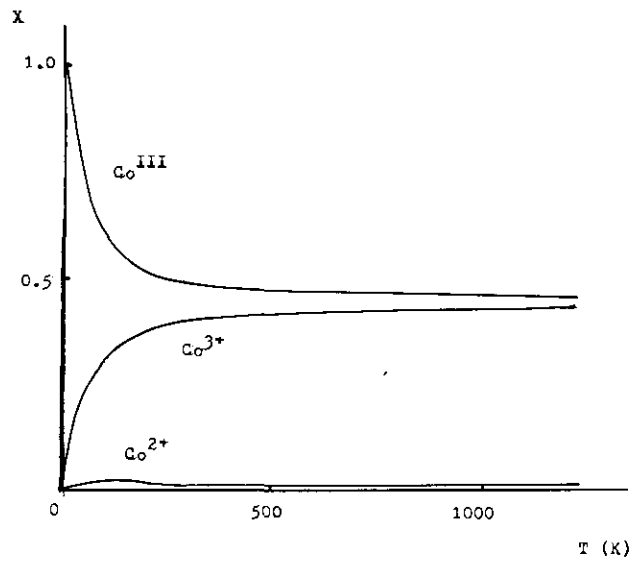

FIGURE 2

0.02 eV, for the activation energy from Co^{III} to Co^{3+} in $LaCoO_3$ (2, 11). This may be because the two compounds are different from each other and the activation energies of same thermal excitation process in different hosts will be different.

We must point out that the parameters ΔH_1 and ΔH_2 are integration constants and not the standard reaction heat of the above reactions (8). In addition, the effects of the relative content of the oxygen atom in the lattice, of the concentration of the oxygen vacancy in the lattice, and of the oxygen partial pressure have been included in the equilibrium constant. Therefore, these parameters may possess slightly different values for $LaCo_{0.9}Mn_{0.1}O_3$ with different crystal defects.

Because $\Delta G_T^\circ = -RT \ln K_T$, we can also evaluate the free energy for the oxidation–reduction reaction between the cobalt and manganese ions and for the deoxidation reaction of the compound at 300 and 600 K, respectively. The calculated results are $\Delta G^\circ_{300\ K} = 12.743$ kJ/mol and $\Delta G^\circ_{600\ K} = 41.866$ kJ/mol for the deoxidation reaction of the compound and $\Delta G^\circ_{300\ K} = 11.927$ kJ/mol and $\Delta G^\circ_{600\ K} = 104.515$ kJ/mol for the oxidation–reduction reaction between the cobalt and manganese ions. Because these ΔG_T° are positive, we can conclude that at lower temperatures the main reaction in $LaCo_{0.9}Mn_{0.1}O_3$ may be the oxidation–reduction reaction between the cobalt and manganese ions, since its ΔG_T° is slightly smaller than that of the deoxidation reaction of the compound. At higher temperature the main reaction in $LaCo_{0.9}Mn_{0.1}O_3$ may be the deoxidation reaction of the compound, because its ΔG_T° is much smaller than that of the oxidation–reduction reaction between the cobalt and manganese ions.

As Figs. 2 and 3 show, the relative contents of all the cobalt and manganese ions in $LaCo_{0.9}Mn_{0.1}O_3$ vary with temperature. The relative content of the Co^{III} ion and the Co^{3+} ion decreases and increases rapidly with increasing temperature below 300 K. This is because some cobalt ions go from a low spin state to a high spin state due to thermal excitation. When temperature is above 500 K, the relative content of both the Co^{III} ion and the Co^{3+} ion will reach a constant value. However, the diamagnetic low spin state Co^{III} ion has been the main component in $LaCo_{0.9}Mn_{0.1}O_3$ in the whole temperature range 100–1200 K. The relative content of the Co^{2+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ has been smaller, and has a maximum at about 200 K. Because this maximum corresponds to the maximum of the relative content of the Mn^{4+} ion or the minimum of the relative content of the Mn^{3+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ at 200 K, we can consider that these Co^{2+} ions may be mainly from the oxidation–reduction reaction between the trivalent cobalt ions and the trivalent manganese ions in the compound. But when the temperature is above 500 K, the relative content of the Co^{2+} ion will reach a small constant value; this may be because the deoxidation reaction of $LaCo_{0.9}Mn_{0.1}O_3$ is slower and smaller. As Fig. 3 shows, when the temperature is below 500 K, the variation of the relative content of both the Mn^{3+} ion and the Mn^{4+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ with temperature is very large. When temperature is above 500 K, the relative content of the Mn^{4+} ion is very small and ignorable. However, at higher temperatures the manganese ions are mainly in the trivalent state. The above results may be reasonable, because the Co^{2+} ions produced due to the high temperature deoxidation reaction of the compound can reduce Mn^{4+} ions to Mn^{3+} ions, so that the high temperature deoxidation reaction will suppress the oxidation–reduction reaction between the trivalent cobalt and the trivalent manganese ions in $LaCo_{0.9}Mn_{0.1}O_3$.

To check the effective magnetic moments of the cobalt and manganese ions with different spin state and valence state in $LaCo_{0.9}Mn_{0.1}O_3$, we have used different values

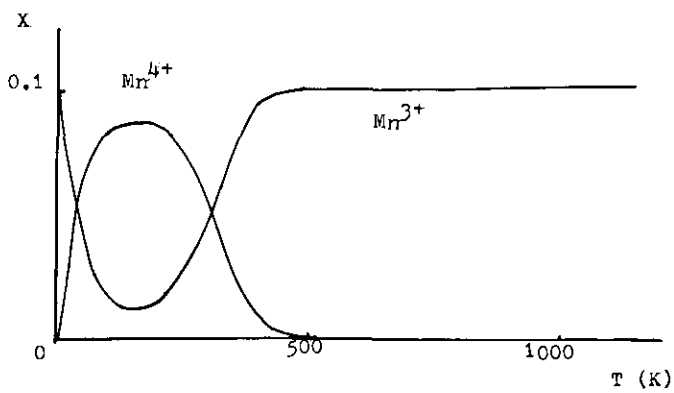

FIGURE 3

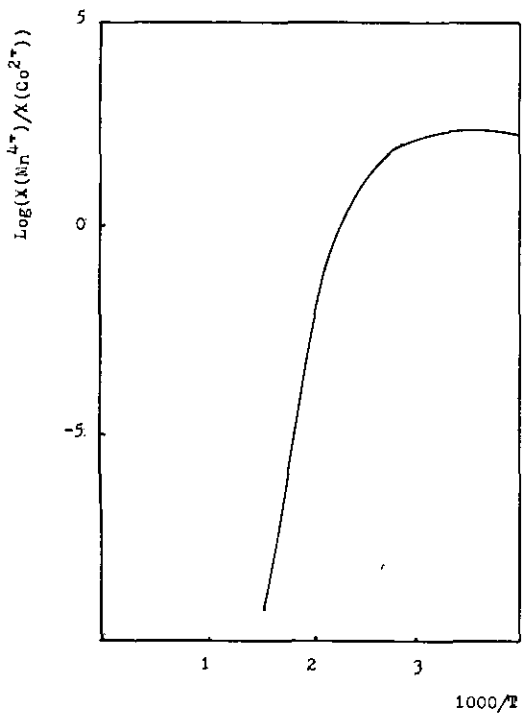

FIGURE 4

for the effective magnetic moments of the trivalent cobalt, the divalent cobalt, the trivalent manganese, and the tetravalent manganese ions in the calculations for the magnetic susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$. We have found that only when $m_1 = 0.0$ for the Co^{III} ion, $m_2 = 5.0\ \mu_B$ for the Co^{3+} ion, $m_3 = 3.8\ \mu_B$ for the Co^{2+} ion, $m_4 = 5.0\ \mu_B$ for the Mn^{3+} ion, and $m_5 = 3.9\ \mu_B$ for the Mn^{4+} ion, respectively, the satisfactory results can be obtained. These effective magnetic moments are close to those of the corresponding free ions: $m_1 = 0\ \mu_B$, $m_2 = 4.9\ \mu_B$, $m_3 = 3.87\ \mu_B$, $m_4 = 4.9\ \mu_B$, and $m_5 = 3.87\ \mu_B$, respectively.

We have noted that the magnetic interaction parameter θ_4 for Co^{III}–O–Mn^{3+} possesses a larger absolute value. This stronger interaction in the Co^{III}–O–Mn^{3+} may be related to the special electronic configuration of both the Co^{III} ion and the Mn^{3+} ion because the manganese ion can very easily go from an electronic configuration $t_{2g}^3e_g^1$ to an electronic configuration $t_{2g}^3e_g^2$, in which the manganese ion possesses a stabler configuration with a half-filled shell, when an electron transfers from the cobalt ion to the manganese ion through the bridge Co^{III}–O–Mn^{3+}. Simultaneously, in the above process, the cobalt ion will go from an electronic configuration $t_{2g}^6e_g^0$ to an electronic configuration $t_{2g}^5e_g^0$, in which the cobalt ion also possesses a stabler configuration with a half-filled shell.

M, the apparent magnetic moment of $LaCo_{0.9}Mn_{0.1}O_3$ molecule, corresponds to the effective paramagnetic moment of the compound. Jonker has given the effective paramagnetic moment of $LaCoO_3$–$LaMnO_3$ solid state solutions calculated from $1/\chi$–T measurements (2). From Fig. 5 of Jonker, we can evaluate the effective paramagnetic moment of $LaCo_{0.9}Mn_{0.1}O_3$ as about 3.3 μ_B at low temperatures and about 3.8 μ_B at high temperatures. Our calculated M is between 3.2 μ_B and 3.7 μ_B from 100 to 1200 K. This is in good agreement with the results of Jonker. From the figure of the paramagnetic Curie point in the $LaCoO_3$–$LaMnO_3$ solid state solution, we can also find that the paramagnetic Curie point of $LaCo_{0.9}Mn_{0.1}O_3$ extrapolated from the low-temperature measurement and from the high-temperature measurement is about −80 K and 0 K, respectively (2). Our calculated T_θ is about −20 K from 300 K to 1200 K. We must emphasize that the M and T_θ of any compound are related to the composition of the compound, especially to the valence states and spin states of various metal ions, as well as the oxygen defect in the compound. Because the relative content of various metal ions with different spin states and valence states varies with temperature in $LaCo_{0.9}Mn_{0.1}O_3$, we can give only some approximate values for the above results.

The $LaCoO_3$ and the Mn-doped $LaCoO_3$ is a p-type semiconductor. From the calculated relative content of various metal ions in $LaCo_{0.9}Mn_{0.1}O_3$, we may predict the variation of the electric resistivity of the compound with temperature. We can assume that in both the deoxidation reaction and the oxidation–reduction reaction between the cobalt and manganese ions in $LaCo_{0.9}Mn_{0.1}O_3$, when a Co^{III} or Co^{3+} ion gains an electron, the Co^{III} or Co^{3+} ion will become a Co^{2+} ion; similarly, when a Mn^{3+} ion loses an electron, the Mn^{3+} ion will become a Mn^{4+} ion, and that the electrons in these processes may belong to the valence band of the compound. Because in the oxidation–reduction reaction between the cobalt and manganese ions in $LaCo_{0.9}Mn_{0.1}O_3$ the trivalent cobalt ion cannot directly gain the electron from the manganese ion and the trivalent manganese ion cannot directly give the electron to the cobalt ion, any electron transfer between the cobalt and manganese ions must pass through the oxygen bridge Co^{III}–O–Mn^{3+}. In most of the transition metal oxides, the oxygen atom will bond with the metal atoms and form a valence band. Therefore, when a trivalent cobalt ion becomes a divalent cobalt ion, an electron in the valence band will transfer to the cobalt ion, whereas, when a divalent cobalt ion becomes a trivalent cobalt ion, an electron will transfer from the cobalt ion to the valence band. When the valence band loses an electron, a hole will be formed in the valence band. Thus, the formation of a Co^{2+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ will imply the generation of a hole in the valence band of the compound. Similarly, when a trivalent manganese ion loses an electron and becomes a tetravalent manganese ion, the electron lost by the manganese ion will return to the valence band and annihilate a hole in the valence band. Therefore, we can

consider that the concentration of holes in the valence band will be inversely proportional to the relative content of the Mn^{4+} ion and proportional to that of the Co^{2+} ion in $LaCo_{0.9}Mn_{0.1}O_3$. However, the electric resistivity of the compound is inversely proportional to the concentration of the hole in the valence band. In Fig. 4, we have given the variation of the logarithm of the ratio of the relative content of the Mn^{4+} ion to that of the Co^{2+} ion in $LaCo_{0.9}Mn_{0.1}O_3$ with temperature in the range 250–650 K. We have found that the temperature variation of the logarithm of $X(Mn^{4+})/X(Co^{2+})$ in $LaCo_{0.9}Mn_{0.1}O_3$ is very similar to the temperature variation of log ρ of $LaCo_{0.9}Fe_{0.1}O_3$. This is understandable, because the behavior of the manganese ion in $LaCo_{0.9}Mn_{0.1}O_3$ is very similar to that of the ferric ion in $LaCo_{0.9}Mn_{0.1}O_3$.

CONCLUSIONS

Based on the thermal excitation equilibrium between the low spin state Co^{III} and the high spin state Co^{3+}, on the oxidation–reduction reaction equilibrium in La $Co_{0.9}Mn_{0.1}O_3$, as well as on the magnetic interactions between the main components in the compound, a semiempirical formula has been proposed to calculate the susceptibilities of $LaCo_{0.9}Mn_{0.1}O_3$ at different temperatures. The calculated $1/\chi$ is very close to the experimental $1/\chi$ in a wide temperature range, 100–1200 K. The results indicate that at lower temperatures the main reaction in $LaCo_{0.9}Mn_{0.1}O_3$ may be the oxidation–reduction reaction between the cobalt and manganese ions; however, at higher temperatures the main reaction in the compound will be the deoxidation reaction. The cobalt ion in La $Co_{0.9}Mn_{0.1}O_3$ is mainly in the low spin state Co^{III} $(t_{2g}^6 e_g^2)$ or the high spin state Co^{3+} $(t_{2g}^4 e_g^2)$, and the manganese ion is mainly in the high spin state Mn^{3+} $(t_{2g}^3 e_g^1)$. The generation and the annihilation of the hole in the valence band of the compound may correspond to the formation of the Co^{2+} ion and the Mn^{4+} ion in $LaCo_{0.9}Mn_{0.1}O_3$. From the variation of the logarithm of $X(Mn^{4+})/X(Co^{2+})$ with temperature, the temperature dependence of the electric resistivity of $LaCo_{0.9}Mn_{0.1}O_3$ may be predicted.

REFERENCES

1. J. B. Goodenough, *Phys. Rev.* **164,** 755 (1968).
2. G. H. Jonker, *J. Appl. Phys.* **37,** 1424 (1966).
3. O. Parakash, P. Ganguly, G. R. Rao, C. N. R. Rao, D. S. Rajoria, and V. G. Bhide, *Mater. Res. Bull.* **9,** 1173 (1974).
4. G. H. Jonker, *Physica* **22,** 707 (1956).
5. G. V. S. Rao, B. M. Wanklyn, and C. N. R. Rao, *J. Phys. Chem. Solids* **32,** 345 (1971).
6. P. M. Raccah and J. B. Goodenough, *Phys. Rev.* **155,** 932 (1967).
7. S. T. Liu, Y. Wu, and Y. Q. Jia, *J. Alloys Comp.* **200,** 171 (1993).
8. W. J. Moore, "Basic Physical Chemistry," Prentice–Hall, Englewood Cliffs, NJ 1983.
9. H. Taguchi, M. Shimada, and M. Koizumi, *J. Solid State Chem.* **40,** 42 (1981).
10. S. T. Liu, Y. Wu, and Y. Q. Jia, *J. Alloys Comp.* **197,** 91 (1993).
11. V. G. Bhide, D. S. Rajoria, C. R. Rao, and C. N. R. Rao, *Phys. Rev. B* **6,** 1021 (1972).
12. C. N. R. Rao, O. Parkash, and P. Ganguly, *J. Solid State Chem.* **15,** 186 (1975).