Magnetic properties of lanthanum manganite and valence equilibria of manganese

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Abstract

The paramagnetic susceptibility of lanthanum manganite has been measured over a wide temperature range (100–1073 K). On the basis of the thermodynamic equilibria between the various manganese ions with different valence and spin states and the magnetic interactions between the various manganese ions, a semiempirical formula has been proposed to calculate the paramagnetic susceptibilities of lanthanum manganite at different temperatures. The results indicate that most of the discrepancies between the calculated and experimental reciprocal susceptibilities of lanthanum manganite are less than 10% and that the relative contents of the various manganese ions in lanthanum manganite vary with temperature. The relative content of the trivalent manganese ion with a high spin state is dominant over the whole temperature range, while the relative content of the tetravalent manganese ion with a high spin state decreases monotonously with increasing temperature. At 300 K the calculated relative content of the tetravalent manganese ion in lanthanum manganite is about 34%, which is in good agreement with the experimental result (30%). There are some divalent manganese ions present in lanthanum manganite from low temperature to high temperature. The ratio of the relative contents of the tetravalent and divalent manganese ions in the compound varies with temperature. Above 750 K the relative content of the tetravalent manganese ion is less than that of the divalent manganese ion. The variation in the electrical resistivity of lanthanum manganite with temperature has also been interpreted reasonably.

1. Introduction

A number of rare earth–transition metal oxides with the perovskite-type structure have been studied extensively. It has been found that these mixed oxides can possess various functional properties such as catalytic activity, superconductivity and special electrical or magnetic properties.

Since the 1950s lanthanum manganite and its related mixed crystals with $AMnO_3$ (A $\equiv$ Ca, Sr, Ba) and $LaMO_3$ (M $\equiv$ Co, Fe, Cr) have been prepared and various chemical and physical properties, especially magnetic properties and the magnetic superexchange interaction between the magnetic metal ions in these compounds, have been studied [1–8].

It is known that the effect of the valence and spin states of the various metal ions on the magnetic, electrical and catalytic properties of the compounds is very significant [9, 10]. Therefore determination of the relative contents of the various metal ions with different valence and spin states in these compounds at different temperatures will be very interesting and necessary for understanding or interpreting why or how various properties of these compounds vary with temperature. However, little research on the relative contents of the various magnetic metal ions with different valence and spin states in the compounds has been published.

In this paper we first propose a semiempirical formula to describe the relationship between the paramagnetic susceptibility and the relative contents of the various manganese ions in lanthanum manganite at different temperature based on the thermodynamic equilibria between the various manganese ions and the superexchange interactions between the various manganese ions at different temperatures. We then derive various thermodynamic parameters from the experimental paramagnetic susceptibilities of lanthanum manganite at different temperatures by the semiempirical formula. Finally, we calculate the relative contents of the trivalent, tetravalent and divalent manganese ions in lanthanum manganite at different temperatures. From these calculated results various experimental phenomena such as the variation in the electrical resistivity of lanthanum manganite with temperature can also be interpreted reasonably.

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2. Experimental details

The lanthanum manganite is prepared by the thermal decomposition of the lanthanum citrate complex. All the chemicals used in the experiments are analytical reagent grade. The freshly prepared citrate complex of lanthanum and manganese is first decomposed by slow heating and kept at 870 K for about 1 h. The resultant powder is pressed into pellets and fired in air at 1220 K for 6 h. The content of the tetravalent manganese ion in the sample has been determined by a standard chemical procedure and the analytical result indicates that the composition of the compound is LaMnO$_{3+\lambda}$ ($\lambda = 0.15$). Thus the relative content of the tetravalent manganese ion in lanthanum manganite is about 30%.

The results of powder X-ray diffraction of the sample show that the compound is a single-phase material with a hexagonal perovskite structure. The lattice parameters calculated from the powder X-ray diffraction pattern are $a = 0.5516$ nm and $c = 1.3323$ nm. These results are very close to the published lattice parameters $a = 0.5523$ nm and $c = 1.3324$ nm for LaMnO$_{3.15}$ [11].

The paramagnetic susceptibilities of the sample have been measured over the temperature range 77–1073 K using an MB-2 automatic recording balance. The curve of the inverse magnetic susceptibility per gram of lanthanum manganite vs. temperature is shown in Fig. 1.

3. Calculations and results

LaMnO$_{3+\lambda}$ and LaMnO$_{3+\lambda}$-based perovskites have been found to exhibit a wide range of oxidative (excess of oxygen) and reductive (oxygen deficiency) non-stoichiometry [8]. Therefore lanthanum manganite with an
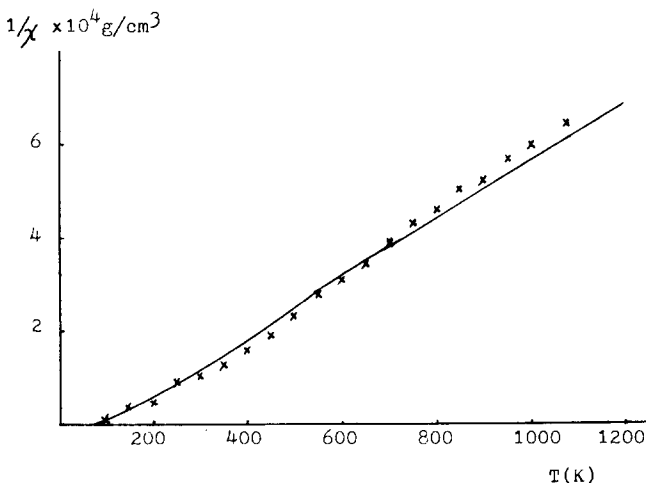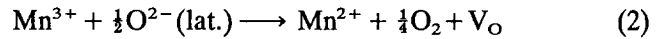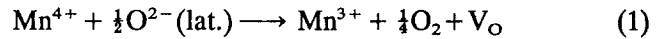

Fig. 1. Variation in inverse magnetic susceptibility per gram of lanthanum manganite with temperature: ×, experimental values; ——, calculated curve.

excess of oxygen will lose some oxygen atoms in the lattice with increasing temperature. In this case there may exist the reactions

$$\text{Mn}^{4+} + \tfrac{1}{2}\text{O}^{2-}\text{(lat.)} \longrightarrow \text{Mn}^{3+} + \tfrac{1}{4}\text{O}_2 + \text{V}_\text{O} \qquad (1)$$

$$\text{Mn}^{3+} + \tfrac{1}{2}\text{O}^{2-}\text{(lat.)} \longrightarrow \text{Mn}^{2+} + \tfrac{1}{4}\text{O}_2 + \text{V}_\text{O} \qquad (2)$$

where O^{2-}(lat.) is an oxygen atom in the lattice and V_O is an oxygen atom vacancy in the lattice. When the oxygen partial pressure of the atmosphere surrounding the lanthanum manganite is constant, the above reactions can reach a thermodynamic equilibrium state at a certain temperature. The relationship between the relative contents of the various manganese ions with different valence states in the compound can be described by the thermodynamic equilibrium constants

$$\frac{X(\text{Mn}^{3+})}{X(\text{Mn}^{4+})} = K_1, \qquad \frac{X(\text{Mn}^{2+})}{X(\text{Mn}^{3+})} = K_2 \qquad (3)$$

where the relative content of oxygen atoms in the lattice, the concentration of oxygen atom vacancies in the lattice and the oxygen partial pressure of the atmosphere surrounding the compound are considered to be constant at a certain temperature and their effects on the reaction equilibrium have been included in the constants K_i. However, the thermodynamic equilibrium constant depends on the temperature of the reaction system. Over a wide temperature range the variation in the reaction equilibrium constant with temperature can be described approximately by the general function [12]

$$\ln K = -\frac{\Delta H}{RT} + a\frac{\ln T}{R} + b\frac{T}{2R} + c\frac{T^2}{6R} + d \qquad (4)$$

where R is the gas constant, T is the absolute temperature and ΔH, a, b, c and d are constant for a particular reaction system. Therefore at a certain temperature the relative contents of the tetravalent, trivalent and divalent manganese ions in lanthanum manganite can be obtained approximately by the formulae

$$X(\text{Mn}^{4+}) = \frac{1}{1 + K_1 + K_1 K_2} \qquad (5)$$

$$X(\text{Mn}^{3+}) = \frac{K_1}{1 + K_1 + K_1 K_2} \qquad (6)$$

$$X(\text{Mn}^{2+}) = \frac{K_1 K_2}{1 + K_1 + K_1 K_2} \qquad (7)$$

where

$$K_i = \exp\left(-\frac{\Delta H_i}{RT} + a_i\frac{\ln T}{R} + b_i\frac{T}{2R} + c_i\frac{T^2}{6R} + d_i\right)$$

Each manganese ion with a spin $S \neq 0$ in the crystal will make a contribution to the paramagnetic moment

of the lanthanum manganite molecule, in which case we have the formula

$$M^2 = m_1^2 X(Mn^{4+}) + m_2^2 X(Mn^{3+}) + m_3^2 X(Mn^{2+}) \qquad (8)$$

where M is the "apparent magnetic moment" of the lanthanum manganite molecule, m_1, m_2 and m_3 are the effective magnetic moments of the tetravalent, trivalent and divalent manganese ions respectively and $X(Mn^{4+})$, $X(Mn^{3+})$ and $X(Mn^{2+})$ are the relative contents of the tetravalent, trivalent and divalent manganese ions in lanthanum manganite respectively.

The dependence of the magnetic susceptibility of lanthanum manganite on temperature will obey the Curie–Weiss law over most intervals of temperature from 100 to 1200 K, except for a small interval around the phase transition temperature. For the superexchange interaction between the various manganese ions in lanthanum manganite and related mixed compounds, the parameters describing the magnetic interaction can be expressed as θ_1 for $Mn^{4+}-O-Mn^{4+}$, θ_2 for $Mn^{3+}-O-Mn^{3+}$, θ_3 for $Mn^{2+}-O-Mn^{2+}$, θ_4 for $Mn^{4+}-O-Mn^{3+}$, θ_5 for $Mn^{4+}-O-Mn^{2+}$ and θ_6 for $Mn^{3+}-O-Mn^{2+}$. If the parameters θ_i ($i = 1-6$) can be considered as constant, T_θ of lanthanum manganite may be evaluated approximately by the formula [3, 13]

$$T_\theta = T_{\theta_1} + T_{\theta_2} + T_{\theta_3} + T_{\theta_4} + T_{\theta_5} + T_{\theta_6}$$

or

$$T_\theta = \theta_1 X(Mn^{4+})^2 + \theta_2 X(Mn^{3+})^2 + \theta_3 X(Mn^{2+})^2$$
$$+ 2\theta_4 X(Mn^{4+})X(Mn^{3+}) + 2\theta_5 X(Mn^{4+})X(Mn^{2+})$$
$$+ 2\theta_6 X(Mn^{3+})X(Mn^{2+}) \qquad (9)$$

On the basis of the above results we can propose a semiempirical formula to calculate approximately the paramagnetic susceptibilities of lanthanum manganite at different temperatures:

$$\chi = \frac{(N/3k)\mu_B^2 M^2}{T - T_\theta} \qquad (10)$$

where N is the Avogadro constant, k is the Boltzmann constant, T is the absolute temperature and μ_B is the Bohr magneton.

We can obtain the values of all the parameters in eqns. (5)–(10) by fitting to the experimental measured paramagnetic susceptibilities of lanthanum manganite at different temperatures using eqn. (10). The parameters obtained are listed in Table 1. From these parameters the equilibrium constants K_1 and K_2 can be calculated. Then the relative contents of the tetravalent, trivalent and divalent manganese ions in lanthanum manganite at different temperatures can be evaluated by eqns. (5)–(7). The variations in the calculated relative contents of the various manganese ions in lanthanum manganite with temperature are shown in Fig. 2. In

addition, the variation in the logarithm of the ratio of the relative contents of the tetravalent and divalent manganese ions in lanthanum manganite with temperature is shown in Fig. 3. For comparison, the curve of the calculated inverse magnetic susceptibility of lanthanum manganite in the temperature range 100–1200 K is also shown in Fig. 1.

4. Discussion

From Fig. 1 it can be seen that the calculated inverse magnetic susceptibilities of lanthanum manganite are very close to the experimental results over a wide temperature range (100–1200 K). Generally the relative errors between the calculated and experimental $1/\chi$ values are less than 10%. This indicates that the calculated results are reliable and acceptable.

We note that in both the calculated and experimental curves of $1/\chi$ vs. T there is a slight but appreciable break at about 700 K. This is in agreement with the reported experimental results [3].

All the parameters needed for calculation of the equilibrium constants K_1 and K_2 of the oxidation–reduction reaction of the manganese ions in lanthanum manganite are listed in Table 1. We must point out that the parameters ΔH_1 and ΔH_2 are not equal to the standard heats of reaction of the above reactions. This is because the relative content of oxygen atoms in the lattice, the concentration of oxygen atom vacancies in the lattice and the oxygen partial pressure of the atmosphere surrounding the lanthanum manganite have been included in the values of the equilibrium constants K_1 and K_2. In addition, we must emphasize that these parameters may possess slightly different values for lanthanum manganite with different original contents of the various manganese ions and with different crystal defects. However, we can also assume that the effect of the relative content of oxygen atoms in the lattice, the concentration of oxygen atom vacancies in the lattice and the oxygen partial pressure of the atmosphere surrounding the compound on the above two reactions may be the same. If this is so, the fact that ΔH_2 is much larger than ΔH_1 may imply that the tetravalent manganese ion is reduced to the trivalent manganese ion much more easily than the trivalent manganese ion is reduced to the divalent manganese ion in lanthanum manganite, especially at low temperature. Because the effect of the oxygen partial pressure has been included in the equilibrium constant, it can be expected that the effect of the oxygen partial pressure of the atmosphere surrounding the compound on the reaction $Mn^{4+} \rightarrow Mn^{3+}$ will be much larger than that on the reaction $Mn^{3+} \rightarrow Mn^{2+}$. As Fig. 2 shows, at low temperature the main components in the lanthanum manganite are the Mn^{3+} and Mn^{4+} ions; hence we can expect that the oxygen partial pressure will have a more

TABLE 1. Parameters for calculation of relative contents of various manganese ions and parameters of magnetic interactions between various manganese ions in lanthanum manganite

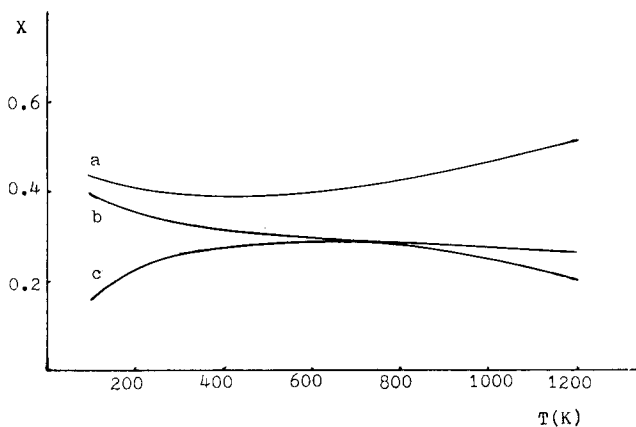| Parameters for equilibrium constants K_i		Superexchange interaction parameters θ_i
$\Delta H_1 = 38.46$ J K^{-1} mol^{-1}	$\Delta H_2 = 910.74$ J K^{-1} mol^{-1}	$\theta_1 = -23.24$ K
$a_1 = 0.0988$ J K^{-1} mol^{-1}	$a_2 = 0.141$ J K^{-1} mol^{-1}	$\theta_2 = 672.41$ K
$b_1 = -4 \times 10^{-3}$ J K^{-2} mol^{-1}	$b_2 = -9.95 \times 10^{-3}$ J K^{-2} mol^{-1}	$\theta_3 = 416.88$ K
$c_1 = 3.43 \times 10^{-5}$ J K^{-3} mol^{-1}	$c_2 = -2.017 \times 10^{-6}$ J K^{-3} mol^{-1}	$\theta_4 = -408.98$ K
$d_1 = 0.0815$	$d_2 = 0.147$	$\theta_5 = -356.19$ K
		$\theta_6 = 949.22$ K

Fig. 2. Variation in relative contents of tetravalent, trivalent and divalent manganese ions in lanthanum manganite with temperature: a, Mn^{3+}; b, Mn^{4+}; c, Mn^{2+}.
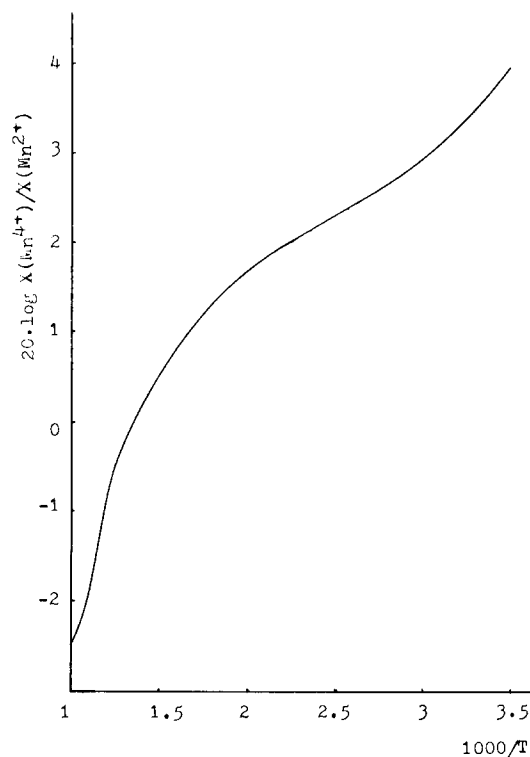
Fig. 3. Variation in logarithm of ratio of relative contents of tetravalent and divalent manganese ions in lanthanum manganite with reciprocal temperature.

significant effect on the properties of the compound, which depend mainly on the relative content of the tetravalent manganese ion at low temperature. On the other hand, at high temperature the main components in the lanthanum manganite are the Mn^{3+} and Mn^{2+} ions; hence we can expect that the oxygen partial pressure will have small effect on the properties of the compound, which depend mainly on the relative content of the divalent manganese ion at high temperature. This conclusion is supported by some experimental results [14]. This may also be why the oxygen partial pressure of the atmosphere surrounding the lanthanum manganite can have a very significant effect on the electrical properties of lanthanum manganite at low temperature but no appreciable effect at high temperature [14].

From Fig. 2 we can see that the relative content of the trivalent manganese ion is dominant in lanthanum manganite over the whole temperature range. The relative content of the tetravalent manganese ion decreases gradually with increasing temperature. We have also found that the calculated relative content of the tetravalent manganese ion in lanthanum manganite is 33.7% at 300 K. This is very close to the experimentally determined relative content of the tetravalent manganese ion in the sample (30%). However, it is un-

expected that there exist some divalent manganese ions in lanthanum manganite even at low temperature. The variation in the relative content of the divalent manganese ion with temperature is not monotonous. Below 400 K the relative content of the divalent manganese ion increases rapidly with increasing temperature, while above 400 K it reaches a constant value. We feel it is possible that there exist some divalent manganese ions in lanthanum manganite with an oxygen excess or deficiency or with other crystal defects. We can perhaps assume that an excess of oxygen in lanthanum manganite may not be necessary for the presence of the tetravalent manganese ion. The existence of the tetravalent manganese ion in lanthanum manganite may not only be due to the existence of an oxygen excess in the com-

pound. It may also be caused by the existence of some divalent manganese ions created by lattice defects, lattice distortion or other electron transfer processes, e.g. valence fluctuation, which often occurs in compounds of metals with different valence states, because the deficiency of cation charge in the compound caused by the presence of some divalent manganese ions can cancel the excess of cation charge in the compound caused by the presence of the tetravalent manganese ions. Besides, the presence of both tetravalent and divalent manganese ions can lead to lattice distortion in lanthanum manganite owing to the significant differences between the crystal radii of the tetravalent, trivalent and divalent manganese ions [15] and between the chemical bondings of the various manganese ions with different electronic configurations and nearest oxygen atoms. Therefore we can consider that the tetravalent and divalent manganese ions may be created by different mechanisms. For convenience, the tetravalent and divalent manganese ions caused by an excess or deficiency of oxygen and by lattice defects or distortion are called the static component, while those caused by various dynamic processes, e.g. the valence fluctuation process, the electron transfer process or the superexchange process $Mn^{3+}-O-Mn^{3+} \rightleftharpoons Mn^{4+}-O-Mn^{2+}$, are called the dynamic component. Generally the static components of both the tetravalent and divalent manganese ions can be determined by a standard chemical procedure but the dynamic components cannot be determined by any chemical method. However, in the above calculations the paramagnetic susceptibility of lanthanum manganite has been related to all the components (static and dynamic) of the manganese ions in the compound, so that the calculated relative contents of both the tetravalent and divalent manganese ions will be the total contents composed of the static and dynamic components. Thus the calculated relative content of the divalent manganese ion appears somewhat larger than expected. In practice the relative content of the divalent manganese ion associated with the static component, e.g. from the deoxidation reaction of lanthanum manganite, will not be very large when the dynamic component is subtracted from the total content of the divalent manganese ion.

The superexchange interactions between the magnetic metal ions in various rare earth–transition metal oxides have been calculated by several approximate methods [3, 13]. Similarly, we have also performed such calculations for lanthanum manganite. The calculated results are given in Table 1. The parameters $\theta_1-\theta_6$ obtained seem to be reasonable and acceptable. However, we must point out that the parameters θ_i will be constant only when the composition of the compound is constant and no phase transition occurs over the whole temperature range. For lanthanum manganite, not only

will the composition of the compound, e.g. the relative contents of the various manganese ions, vary with temperature, but also a phase transition can occur at about 700 K. Therefore the values of the parameters θ_i calculated here are approximate, though the calculation method is reasonable. The calculated T_θ is positive with a value in the approximate range 130–300 K. We have also noted that the calculated T_θ is negative when the temperature is below 50 K.

As mentioned above, a phase transition can occur in lanthanum manganite at about 700 K [3, 14, 16]. The phase transition can cause changes in both the symmetry about the metal ion and the relative distances between the ions in the lattice. These changes will affect the overlaps between the valence orbitals of the atoms in the compound and will thus result in variations in the chemical bondings and the superexchange interactions between the ions in the compound [16]. Therefore the phase transition can affect the values of the parameters θ_i. However, we consider that the effect of the phase transition on the oxidation–reduction reaction in the solid state compound may not be very large, so the effect of the phase transition on the relative contents of the various manganese ions may be very small. Hence the variation in the relative contents of the various manganese ions with temperature may still be reasonable even though the effect of the phase transition is not considered in the calculation.

To check the spin states of the various manganese ions in lanthanum manganite, we have used different values for the effective magnetic moments of these ions. We have found that the most satisfactory results can be obtained when the $m_1 = 3.9$ μ_B, $m_2 = 5.0$ μ_B and $m_3 = 5.7$ μ_B. These values are very close to the effective magnetic moments of the tetravalent manganese ion with a high spin state ($m = 3.87$ μ_B), the trivalent manganese ion with a high spin state ($m = 4.9$ μ_B) and the divalent manganese ion with a high spin state ($m = 5.9$ μ_B) respectively. This indicates that all the manganese ions in lanthanum manganite are in a high spin state. The calculated "apparent magnetic moment" of the lanthanum manganite molecule is in the range 4.8–5.1 μ_B over the whole temperature range. This is very close to the effective magnetic moment of lanthanum manganite published by others [3].

It has been found that there is a rather sharp jump near 720 K in the dependence of the electrical resistivity of lanthanum manganite on temperature [6]. Because the electrical resistivity of a semiconductor is inversely proportional to the concentration of carriers and since lanthanum manganite is a p-type semiconductor, its electrical resistivity will mainly be inversely proportional to the concentration of holes in the compound. We consider that there must be a certain relationship between the relative contents of the various manganese ions and the concentration of holes in lanthanum man-

ganite. First we can assume that all the manganese ions in a stoichiometric lanthanum manganite sample without any lattice defects will be trivalent. However, if there is an excess of oxygen atoms in the compound, these excess of oxygen atoms will remove some valence electrons from the trivalent manganese ions, leading to the formation of tetravalent manganese ions via the reaction $Mn^{3+} - e^- \rightarrow Mn^{4+}$. On the other hand, if there is a deficiency of oxygen atoms in the compound, some valence electrons which the oxygen atoms have obtained from the manganese atoms will return to the trivalent manganese ions; hence some trivalent manganese ions will become divalent manganese ions via the reaction $Mn^{3+} + e^- \rightarrow Mn^{2+}$. Therefore we can consider that when stoichiometric lanthanum manganite gets an excess of oxygen atoms, some trivalent manganese ions will become tetravalent manganese ions, whereas when it loses some oxygen atoms in the lattice, some trivalent manganese ions will become divalent manganese ions. Generally in metal oxides the oxygen atoms will bond with the metal atoms to form the valence bands of the solid state compound. Thus we can also assume that the electron which the trivalent manganese ion gains in the process $Mn^{3+} + e^- \rightarrow Mn^{2+}$ may be an electron from the valence band. If this is so, when a trivalent manganese ion removes an electron from the valence band, simultaneously a hole in the valence band will be formed. Similarly, when a trivalent manganese ion loses an electron to the valence band, simultaneously a hole in the valence band will be annihilated. Therefore the concentration of holes in the valence band of lanthanum manganite will be proportional to the relative content of the divalent manganese ion and inversely proportional to the relative content of the tetravalent manganese ion in the compound. In this case we can assume that the electrical resistivity of lanthanum manganite will be proportional to the ratio of the relative contents of the tetravalent and divalent manganese ions in lanthanum manganite. The variation in the logarithm of this ratio with temperature in the range 286–1000 K is shown in Fig. 3. We find that there is a sharp jump near 750 K in the curve of $\log[X(Mn^{4+})/X(Mn^{2+})]$ vs. $1000/T$ as there is in the experimental curve of $\log \Omega$ vs. $1000/T$ [6], which demonstrates that the above calculations and assumptions may be reasonable. Besides, generally a phase transition process can be identified by a break or sharp variation in the curve of $\log \Omega$ vs. $1/T$. As Fig. 3 shows, the sharp variation in the curve of $\log[X(Mn^{4+})/X(Mn^{2+})]$ vs. $1000/T$ occurs at about 730–760 K, which

is in agreement with the temperature region of the phase transition in lanthanum manganite.

5. Conclusions

Thermodynamic equilibria exist between the various manganese ions in lanthanum manganite. A semiempirical formula can be used to calculate the paramagnetic susceptibilities of lanthanum manganite at different temperatures between 100 and 1200 K. The calculated $1/\chi$ is close to the experimental $1/\chi$ over a wide temperature range. The relative contents of the tetravalent, trivalent and divalent manganese ions in lanthanum manganite vary with temperature. The relative content of the trivalent manganese ion is dominant, while the relative content of the tetravalent manganese ion decreases monotonously with increasing temperature. There are also some divalent manganese ions in lanthanum manganite. All the manganese ions in lanthanum manganite are in a high spin state. Some assumptions about the possibilities of the presence of the divalent and tetravalent manganese ions in lanthanum manganite due to different mechanisms have also been given and discussed. A possible interpretation of the sharp variation in the curve of $\log \Omega$ vs. $1000/T$ has been given.

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