Correlation between magnetic properties and electronic transport in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ below room temperature

Correlation between magnetic properties and electronic transport in $LaCr_{0.5}Ga_{0.5}O_3$ below room temperature

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Abstract

In order to study variations in the transport and magnetic properties due to Ga doping into $LaCrO_3$, ac and dc measurements were carried out on $LaCr_{0.5}Ga_{0.5}O_3$ along with magnetic measurements. This oxide compound exhibits the hopping conduction of adiabatic small polarons in the paramagnetic region with a hopping energy of $W_H \simeq 0.28$ eV, which is larger than the 0.20 eV in $LaCrO_3$. The dissociation energy required to free a small polaron from a bound state is $W_O \simeq 0.06$ eV. The activation energy for the bulk conduction is nearly equal to $W_H + W_O/2$. The Néel temperature T_N in $LaCr_{0.5}Ga_{0.5}O_3$ is ~90 K, which is considerably lower than the $T_N \simeq 300$ K in $LaCrO_3$. These results are discussed in terms of the variation in the hybridization of Cr 3d–O 2p orbitals by Ga doping. A decrease of the on-site Coulombic interaction U due to Ga doping plays an important role in the hybridization of $LaCr_{0.5}Ga_{0.5}O_3$.

1. Introduction

Since the 1950s many studies have been carried out concerning the structure, magnetic properties and electronic transport in transition metal oxides with strongly correlated electron systems. These characteristics are related directly to localized 3d electrons on the transition metal ions and they correlate very closely with each other. In particular, the electronic transport properties of perovskite oxides containing heavy hybridization of 3d–O 2p orbital are of interest because the character of the electronic carriers strongly depends on the hybridization, and a magnetic interaction between localized spins on 3d transition metals through oxygen ions plays an important role in their magnetic properties, i.e. superexchange interaction. These are issues which should be elucidated experimentally.

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Perovskite $LaCrO_3$ is one such transition metal oxide. This oxide is antiferromagnetic below its Néel temperature of $T_N \simeq 300$ K, and exhibits adiabatic polaronic conduction in the paramagnetic region above T_N [1, 2]. Karim *et al* have elucidated the electronic transport mechanism at $T > T_N$ by measurement of the electronic conductivity and thermoelectric power, and reported that $LaCrO_3$ is a p-type insulator and the activation energy required for electronic conduction in the paramagnetic region is 0.19 eV [3]. Most of the other literature has also reported an activation energy of around 0.20 eV [4, 5]. Goodenough suggested that Cr ions show half-filled t_{2g} above the O 2p level in $LaCrO_3$, which contains a molecular orbital caused by Cr 3d–O 2p hybridization [6]. According to an optical study [7], $LaCrO_3$ is a charge transfer $(C–T)$ type insulator and the ground state of Cr^{3+} with the $3d^3$ configuration is $t_{2g\uparrow}^3$, i.e. a high spin configuration of $S = 3/2$, where S is the resultant spin. The high spin state of Cr^{3+} is also reported in magnetic studies [1–3].

When the density of 3d electrons in $LaCrO_3$ is diluted, it is of great interest to investigate how its magnetic properties and electronic transport properties change. Since the electronic structure of Ga^{3+} is $3d^{10}$, Ga^{3+} is a non-magnetic ion and hence Ga^{3+}-doping for Cr^{3+} dilutes the density of 3d electrons in $LaCrO_3$. Due to the $3d^{10}$ configuration, however, it would seem to be difficult for Ga^{3+} ions to contribute to electronic conduction and magnetic ordering in Ga-doped $LaCrO_3$. Therefore, not only the electronic transport properties but also the magnetic properties are expected to change as a result of Ga doping because the number of Cr^{3+} ions dominating these properties decreases.

The main purpose of the present study is to investigate variations in the electronic transport and magnetic properties due to Ga doping of $LaCrO_3$, and to elucidate the reasons for such variations. From this point of view, these properties of $LaCr_{0.5}Ga_{0.5}O_3$ have been investigated in the present study. The 50% Ga-doped $LaCrO_3$ compound is an appropriate starting composition for the present purpose, as for such heavy doping it is expected that almost all experimental methods can recognize any anomalies caused by the doping. In most transition metal oxides, the majority carrier is a small polaron of a 3d carrier that is created by strong electron–phonon interactions between the localized 3d carrier and neighbouring ions, and hopping of the small polaron dominates the electronic conduction, i.e. the polaronic conduction [8]. Therefore, the transport properties are very sensitive to the 3d electronic structures of transition metal ions. In Ga-doped $LaCrO_3$, the electronic transport properties are also expected to depend on the 3d configuration of Cr^{3+}. Therefore, in $LaCr_{0.5}Ga_{0.5}O_3$, electronic transport and magnetic properties must correlate strongly with one another.

As for polaronic conduction, there is also an experimental advantage—alternating current (ac) measurements are possible for polaronic conduction and the results obtained by the ac method provide very important knowledge about polaronic conduction which direct current (dc) measurements cannot disclose [8]. The activation energy of polaronic conduction consists of the polaron hopping energy and the dissociation energy required to free a small polaron from a bound state due to a potential difference [8, 9]. In principle, these energy values are to be obtained separately in the ac measurements [8, 10, 11]. Since these energy values are the important parameters which reveal the reasons for the variations in the transport and magnetic properties due to Ga doping, the ac and dc measurements were carried out on $LaCr_{0.5}Ga_{0.5}O_3$ as functions of temperature in the range of 77 K to room temperature along with the magnetic measurements.

2. Experimental details

$LaCr_{0.5}Ga_{0.5}O_3$ powder was prepared by a conventional ceramic technique using La_2O_3, Cr_2O_3 and Ga_2O_3 as the starting materials. The mixture was calcined at 1200 °C twice with

intermediate grinding, and then the calcined powder was pressed into pellet specimens. The final sintering process for the pellet specimens was 1450 °C for 12 h. The powder Cu Kα x-ray diffraction (XRD) technique measured the specimen and examined a single-phase compound with an orthorhombic perovskite structure at room temperature. There was no ordering of different cations such as ordered-double perovskites, though Ga ions occupy just 50% of the perovskite B sites instead of Cr ions in the present XRD measurement. The XRD peaks could be indexed as the *Pnma* space group with lattice constants of $a = 5.483(2)$, $b = 7.764(2)$ and $c = 5.517(1)$ Å. These values are close to those of LaCrO$_3$ [1, 2] because they have almost the same ionic sizes of 0.615 Å for Cr^{3+} and 0.62 Å for Ga^{3+} [12].

Gold was evaporated on the polished surfaces of the specimen as the electrodes for the measurements of four-probe dc conductivity. The ac measurements were carried out in a manner similar to that in previous reports [10, 11, 13, 14], using an Agilent 4294A precision impedance analyser with a frequency range of 100 Hz–1 MHz below room temperature. Details of the dc method are described elsewhere [10, 11, 14]. Every measurement was performed as a function of temperature over the range of 77 K to room temperature in the heating run. The magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS), with a magnetic field of 1 T in the temperature range of 10–400 K.

3. Results

3.1. Electronic conduction

In polaron transport theory, the conductivity due to the hopping of adiabatic small polarons has the form of $\sigma T = A \exp(-E/k_B T)$ [8, 9, 15, 16], where A is the pre-exponential factor proportional to the density of electronic carriers, E is the activation energy required for polaronic conduction and k_B is the Boltzmann constant. Based upon the polaron transport theory, figure 1 shows the Arrhenius plot of $\sigma_{dc} T$ for LaCr$_{0.5}$Ga$_{0.5}$O$_3$, where σ_{dc} is the four-probe dc conductivity. The valuable data for the present analysis could be obtained at $T > 110$ K because the remarkably large resistance at low temperatures exceeded the limitation of the present four-probe dc method. There is a linear Arrhenius relation with $E_{dc} = 0.34 \pm 0.01$ eV, where the subscript dc represents the parameter for dc conduction. In this temperature region, LaCr$_{0.5}$Ga$_{0.5}$O$_3$ is paramagnetic, as will be described later.

In a ceramic specimen, the dc conductivity involves the bulk conductivity and the boundary conductivity. Generally, the boundary resistance is large, particularly at low temperatures. Since the boundary resistance often interferes with the elucidation of the electronic transport properties in oxides, it is necessary to extract only the bulk resistance from the measured resistance. Complex-plane impedance analysis, which is one of the ac methods, certainly meets such a requirement because this analysis method distinguishes the bulk resistance from other resistances [8, 11, 17–20]. The inset of figure 1 displays a typical complex-plane impedance spectrum for LaCr$_{0.5}$Ga$_{0.5}$O$_3$ at 170 K. The spectroscopy comprises the highest-frequency semicircular arc corresponding to the bulk conduction, and the intermediate-frequency semicircle stemming from the conduction across the grain boundaries. In figure 1, $\log(\sigma_b T)$ is also plotted against $1/T$, where σ_b is the bulk conductivity obtained from the impedance spectroscopy at each temperature. Then, σ_b shows the Arrhenius relation with $E_b = 0.30 \pm 0.02$ eV in the paramagnetic region, where E_b is the activation energy required for the bulk conduction. The magnitude of E_b is somewhat lower than E_{dc}. This is due to the exclusion of the boundary contribution at low temperatures. Therefore, the data obtained from the bulk conduction, σ_b and E_b, are appropriate for the properties of LaCr$_{0.5}$Ga$_{0.5}$O$_3$ rather than σ_{dc} and E_{dc}. Moreover, σ_{dc} maintains the Arrhenius relation down to about 110 K, below which the present four-probe measurement is impossible, while σ_b deviates from the relation at about
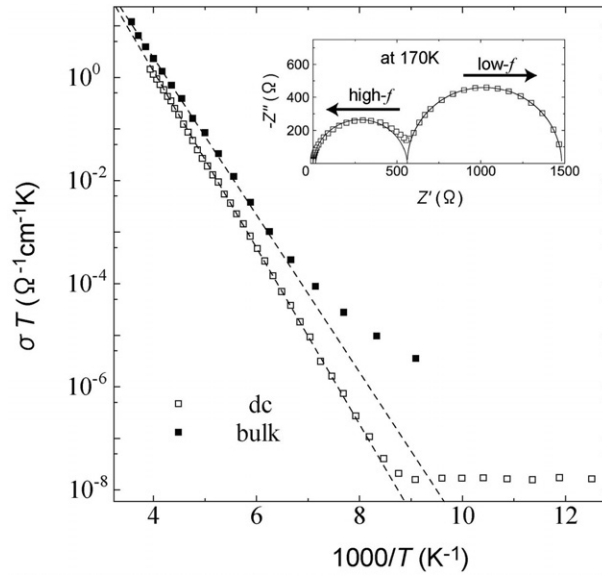
Figure 1. The Arrhenius relations of σT and $1/T$ for $LaCr_{0.5}Ga_{0.5}O_3$. The open squares show dc conductivities. The solid squares show the bulk conductivities obtained by the impedance analyses. Inset: the complex-impedance spectra at 170 K, where Z' and Z'' represent the real and imaginary parts of the total impedance at each applied frequency. The solid semicircular arcs are guides to the eye. The highest resistance value of the highest-frequency arc corresponds to the bulk conduction. The labels high-f and low-f indicate high and low frequencies.

T_O at which there is a magnetic anomaly, as will be described later. Such a difference may also be due to the exclusion because in ceramics generally the grain boundary involves no magnetic ordering.

3.2. Dielectric relaxation

As shown in previous works [8, 10, 11, 13, 14, 21], the hopping motion of small polarons involves a dielectric relaxation process which provides important knowledge about the polaron dynamics. Figure 2 plots the dielectric loss factor ε'' against the applied frequency f as a parametric function of temperature at 10 K increments for $LaCr_{0.5}Ga_{0.5}O_3$. The impedance spectra could be obtained in the range of 200–280 K, although the measurements were carried out in the range of 77 K to room temperature. In this temperature region, $LaCr_{0.5}Ga_{0.5}O_3$ is surely paramagnetic, as mentioned above. At each temperature, the spectrum involves a dielectric relaxation process possessing the maximum dielectric loss factor ε''_{max} at the resonance frequency $f_{\varepsilon''_{max}}$. As the temperature increases, the magnitude of the maximum loss factor and the resonance frequency regularly increase, like the dielectric relaxation processes caused by the hopping of small polarons in other transition metal oxides. The emergence of such a dielectric relaxation process certainly ensures that the hopping conduction of small polarons takes place in $LaCr_{0.5}Ga_{0.5}O_3$ [8, 10, 11, 13, 14, 21].

Usually the dielectric relaxation process stemming from the polaronic conduction is approximately described by the Debye theory [8, 22, 23]. At a temperature T, then, the resonance frequency has the form of $f_{\varepsilon''_{max}} \propto \exp(-W_H/k_B T)$, where W_H is the hopping energy of a small polaron. On the other hand, the magnitude of the maximum dielectric loss factor ε''_{max} is theoretically proportional to the number of hopping carriers: $\varepsilon''_{max} \propto \exp(-W_O/2k_B T)/T$
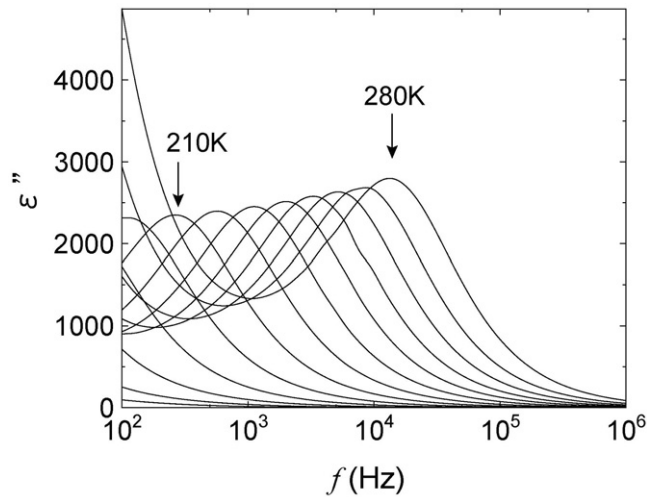
Figure 2. Frequency dependences of the dielectric loss factor ε'' at several temperatures between 210 and 280 K for $LaCr_{0.5}Ga_{0.5}O_3$.
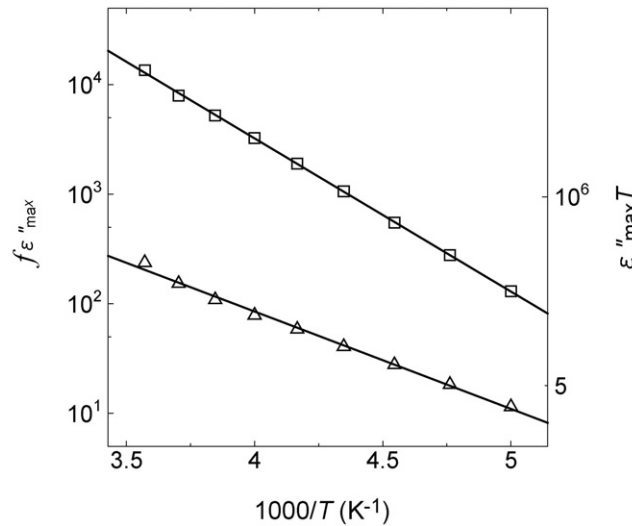

Figure 3. The Arrhenius relation between $f_{\varepsilon''_{max}}$ (square) and $1/T$, and the Arrhenius relation between $\varepsilon''_{max}T$ and $1/T$ (triangle).

in the adiabatic polaronic conduction, where W_O is the dissociation energy to free a small polaron from a bound state due to a potential difference [8, 9, 11]. Figure 3 presents the Arrhenius plots of $f_{\varepsilon''_{max}}$ and $\varepsilon''_{max}T$. The Arrhenius relations estimate $W_H = 0.28 \pm 0.01$ eV and $W_O = 0.06 \pm 0.02$ eV. Consequently, the activation energy required for the hopping conduction of small polarons in $LaCr_{0.5}Ga_{0.5}O_3$ is $(W_H + W_O/2) = 0.31 \pm 0.02$ eV, which is in good agreement with the activation energy for the bulk conduction, $E_b = 0.30 \pm 0.02$ eV. Such a good coincidence of these energy values implies that an adiabatic small polaron is the majority carrier responsible for the electronic conduction and hopping dominates the electronic transports in the paramagnetic region of $LaCr_{0.5}Ga_{0.5}O_3$.

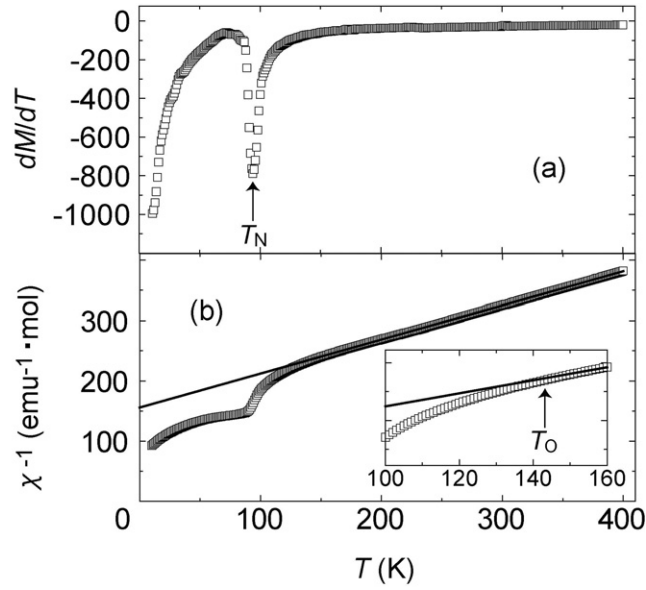**Figure 4.** (a) Temperature dependences of dM/dT; the arrow indicates the Néel temperature T_N. (b) χ^{-1} versus T; the straight line represents the Curie–Weiss law, which holds above T_O (the inset).

In most insulators where band conduction dominates electronic transport, the energy W_O included in the polaronic conduction corresponds to the band gap between the conduction and valence bands E_g in intrinsic insulators, or to the ionization energy of donors or acceptors ΔE in the extrinsic case. In these insulators, therefore, the main part of the activation energy required for electronic conduction results from either E_g or ΔE. In transition metal oxides with narrow conduction bands and small transfer integrals, however, the dominant component of the activation energy is the hopping energy. In fact, the hopping energy is generally more than 90% of the activation energy.

4. Discussion

4.1. Magnetic properties

Figure 4 presents temperature dependences of dM/dT (a) and χ^{-1} (b), where M is magnetization and χ is susceptibility. The dM/dT curve involves the sharp depression at $T \simeq 94$ K, which corresponds to the Néel temperature T_N. Since T_N is about 300 K in LaCrO$_3$ [1, 2], T_N in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ is lower than LaCrO$_3$ by more than 200 K. Curie–Weiss behaviour is observed at $T > T_O \simeq 144$ K as shown in figure 4, where T_O is determined as the temperature at which χ^{-1} deviates from the Curie–Weiss law. LaCr$_{0.5}$Ga$_{0.5}$O$_3$ is surely paramagnetic at $T > T_O$, though the deviation at T_O may be due to any magnetic interaction. The deviation of σ_b as shown in figure 1 may also be due to the magnetic interaction and the temperature T_O may be affected by the distribution of non-magnetic Ga^{3+}. The Curie–Weiss behaviour also estimates the effective magnetic moment per Cr ion at the perovskite B site in LaCr$_{0.5}$Ga$_{0.5}$O$_3$, $\mu_{eff} = 3.76$ μ_B, where μ_B is the Bohr magneton. This effective magnetic moment indicates that the Cr ion shows a trivalent and high spin configuration, $t^3_{2g\uparrow}$, in LaCr$_{0.5}$Ga$_{0.5}$O$_3$, because the magnetic moment estimated in this way is very close to the

theoretical value, i.e. $\mu_{\mathrm{eff}} = g\sqrt{(S(S+1))} = 3.87\ \mu_{\mathrm{B}}$ when $g = 2$ and $S = 3/2$. Therefore it is reasonably accepted that the electronic structure of Cr^{3+} hardly changes even if Ga^{3+} ions occupy 50% of the perovskite B sites instead of Cr^{3+}. As a result, the antiferromagnetic coupling between Cr^{3+} ions due to superexchange interaction via O^{2-} is surely expected to work effectively in $LaCr_{0.5}Ga_{0.5}O_3$. The low T_N observed in $LaCr_{0.5}Ga_{0.5}O_3$ is mainly caused by the decrease in Cr^{3+}–O^{2-}–Cr^{3+} couplings due to Ga doping.

Despite the high spin configuration, the effective magnetic moment of Cr ions in $LaCr_{0.5}Ga_{0.5}O_3$ is slightly smaller than that in $LaCrO_3$, i.e. $\mu_{\mathrm{eff}} = 4.19\ \mu_{\mathrm{B}}$ [3]. According to LSDA + U calculation [24], the effective magnetic moment in $LaCrO_3$ is very sensitive to change of the on-site Coulomb interaction U, and the magnetic moment increases with U. This calculation also suggests that the hybridized Cr 3d–O 2p orbital below the Fermi level occurs due to $U > 0$ and then the occupied Cr $t_{2g\uparrow}$ levels shifts to a lower energy region with an increase in U. These suggestions may anticipate that the occupied Cr $t_{2g\uparrow}$ levels in $LaCr_{0.5}Ga_{0.5}O_3$ are in an energy region higher than that in $LaCrO_3$. Then, the electrons occupying the Cr $t_{2g\uparrow}$ levels in the higher energy region weakly hybridize with O 2p at most because there is an energy gap between $t_{2g\uparrow}$ and O 2p when $U = 0$. The light hybridization of the Cr 3d–O 2p orbital may relate to the displacement of O^{2-}. There is a possibility that the O^{2-} of Cr^{3+}–O^{2-}–Ga^{3+} bonds displaces to Ga^{3+} rather than to Cr^{3+} when the electronegativity of Cr is smaller than that of Ga. In practice, the electronegativities are 1.66 and 1.81 for Cr and Ga, respectively, in the Pauling scale. Then the degree of hybridization of Cr 3d–O 2p in $LaCr_{0.5}Ga_{0.5}O_3$ is weaker than that in $LaCrO_3$. In $LaCr_{0.5}Ga_{0.5}O_3$, such light hybridization weakens the superexchange interaction of Cr^{3+}–O^{2-}–Cr^{3+} as compared with $LaCrO_3$, and, as a result, the magnetic interaction is much suppressed. Consequently, the considerable reduction of T_N in $LaCr_{0.5}Ga_{0.5}O_3$ is a logically proper sequence.

4.2. Electronic transport properties

According to optical measurements [7], $LaCrO_3$ is a C–T type Mott insulator with a C–T gap of approximately 2 eV, which is very large as compared to the activation energy required for polaronic conduction. The LSDA + U calculation also backs up the optical results [24]. However, the activation energy required for p-type electronic conduction in $LaCrO_3$ is $E \simeq 0.20$ eV, which is very small compared to the C–T gap [3–5]. These facts indicate that the majority carrier responsible for p-type conduction in $LaCrO_3$ must be the holes doped at energy levels below the Fermi level. According to Webb *et al*, in fact, the inherent structural defects included in $LaCrO_3$ create Cr^{4+} identical to the defects made in Sr-doped $LaCrO_3$ [25]. Moreover, in a perovskite-type oxide represented by ABO_3, the BO_3 portion is a stoichiometric ReO_3 structure whereas the A site may easily be deficient [26]. This is experimentally verified in $LaFeO_3$ which exhibits p-type conduction with a low activation energy and variations in the electronic properties caused by lanthanum vacancies resulting from a slight deviation from unity in the La/Fe ratio [14, 27–29]. Though a small number of Cr^{4+} ions must be created in $LaCrO_3$, the p-type carrier has a remarkable O 2p-character because of the heavily hybridized Cr 3d–O 2p orbital [6, 7, 24]. The experimental results obtained in the present study are likely to suggest that a similar speculation holds in $LaCr_{0.5}Ga_{0.5}O_3$, but the degree of hybridization is rather different from $LaCrO_3$. The argument about the reduction of the effective magnetic moment mentioned above accepts the light hybridization of the Cr 3d–O 2p orbital in $LaCr_{0.5}Ga_{0.5}O_3$. Therefore, Ga doping into $LaCrO_3$ changes the nature of Cr 3d–O 2p hybridization and, as a result, in the p-type carrier in $LaCr_{0.5}Ga_{0.5}O_3$ 3d character is enhanced rather than O 2p character as compared with $LaCrO_3$. As described before, W_H is 0.28 eV in $LaCr_{0.5}Ga_{0.5}O_3$ whereas the activation energy for the dc conduction in $LaCrO_3$

is around 0.20 eV. Since polaronic conduction is expected to take place in LaCrO$_3$ [1–3], the hopping energy must be very close in value to the dc activation energy as well as in LaCr$_{0.5}$Ga$_{0.5}$O$_3$. Therefore the difference in the hopping energy of LaCr$_{0.5}$Ga$_{0.5}$O$_3$ and LaCrO$_3$ is approximately 0.08 eV.

As for the hopping energy, there is the relationship of $W_H = W_P/2 - t$, where W_P is the polaron binding energy and $2t$ is the conduction bandwidth [8, 9]. Accordingly, the higher hopping energy in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ than in LaCrO$_3$ is ascribed to either an increase in the polaron binding energy or to a decrease in the conduction bandwidth by Ga doping, or both. If we assume that W_p is nearly independent of Ga doping, we have the relation $2t_{CG} \simeq 2t_C - 0.16$ eV, where $2t_{CG}$ and $2t_C$ are the conduction bandwidths of LaCr$_{0.5}$Ga$_{0.5}$O$_3$ and LaCrO$_3$, respectively. This relationship indicates that the conduction band in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ is surely narrower than that in LaCrO$_3$, as expected. In such a case, however, the bandwidth in LaCrO$_3$ is more than 0.16 eV, which seems contrary to the narrow conduction bands peculiar to 3d carriers. Therefore, the contribution of the bandwidth to the overall change should be relatively small. This speculation suggests some contribution of the polaron binding energy to the difference in the hopping energy of LaCr$_{0.5}$Ga$_{0.5}$O$_3$ and LaCrO$_3$. By referring to the previous calculations about the energy values of small polarons based upon the Anderson attractive potential of a polaron [30–33], it is expected that the magnitude of the electron–phonon-coupling constant between the localized 3d carrier on a Cr ion and the neighbouring Ga^{3+} is larger than the coupling constant between the 3d carrier and the neighbouring Cr^{3+}. When a coupling constant is large, the polaron binding energy can be large [31–33]. Probably, the fact that the hopping energy in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ is higher than in LaCrO$_3$ results from both a reduction of the bandwidth and an increase in the polaron binding energy due to Ga doping. Then there is the possibility that the hopping energy increases monotonically with the level of Ga doping.

5. Conclusion

The electronic transport and magnetic properties of LaCr$_{0.5}$Ga$_{0.5}$O$_3$ have been elucidated experimentally. The electronic conduction in the paramagnetic region below room temperature is mainly described in terms of the polaronic conduction of small polarons of 3d holes. The activation energy for polaronic conduction is 0.31 ± 0.02 eV, which is the sum of the hopping energy of 0.28 ± 0.01 eV and half of the dissociation energy required to free a small polaron from a bound state, $(0.06 \pm 0.02)/2$ eV. The conduction band in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ mainly involves a Cr t$_{2g}$ orbital and a O 2p orbital that are weakly hybridized. Such light hybridization narrows the conduction band and yields strongly localized holes as the majority carrier. This is mainly responsible for the small polaron hopping conduction with a high hopping energy and a low dissociation energy. Furthermore, the light hybridization of the Cr 3d–O 2p orbital in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ brings about a Néel temperature considerably lower than that of LaCrO$_3$. Therefore, the transport properties and the magnetic properties in LaCr$_{0.5}$Ga$_{0.5}$O$_3$ correlate very closely with each other.

Acknowledgments

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