

## QUANTUM EFFECTS IN SEMICONDUCTORS AND DIELECTRICS

### Transport properties of cobaltites containing holmium

Yu. N. Chiang<sup>a)</sup>

*B. I. Verkin Institute for Low-Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, pr. Lenina 47, Kharkov 61103, Ukraine*

V. F. Khirnyĭ

*Institute of Single Crystals of the Center for Science and Technology "Institute of Single Crystals" of the National Academy of Sciences of Ukraine, pr. Lenina 60, Kharkov 61072, Ukraine*

O. G. Shevchenko

*B. I. Verkin Institute for Low-Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, pr. Lenina 47, Kharkov 61103, Ukraine*

A. A. Kozlovskii, A. V. Semenov, V. M. Puzikov, and T. G. Deĭneka

*Institute of Single Crystals of the Center for Science and Technology "Institute of Single Crystals" of the National Academy of Sciences of Ukraine, pr. Lenina 60, Kharkov 61072, Ukraine*

(Submitted April 29, 2008; revised May 20, 2008)

Fiz. Nizk. Temp. **34**, 1197–1202 (November 2008)

The temperature and magnetic field dependences of the electric resistance of ceramic samples  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  and  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  at temperatures ranging from room to liquid-nitrogen temperature and magnetic fields to 7 kOe, applied perpendicular to the direction of current transport, are studied. Electric conduction in these samples is of the semiconductor type, and the magnetoresistance in a narrow temperature interval and comparable fields changed sign, ranging from  $-50$  to  $+120\%$ . A nonlinear dependence of the resistance of the samples on the magnitude of the transport current for weak currents and high sensitivity of the resistance to a weak magnetic field are observed. Analysis of the data shows a magnetic contribution (the presence of low-spin ( $S=1$ ) states  $t_{2g}^5e_g^1$  or high-spin ( $S=2$ ) states  $t_{2g}^4e_g^2$  of the  $\text{Co}^{3+}$  ions) to the mechanism of interelectronic correlations under conditions of percolation conductivity of the systems investigated. The corresponding activation energies are estimated.

© 2008 American Institute of Physics. [DOI: [10.1063/1.3009593](https://doi.org/10.1063/1.3009593)]

### I. INTRODUCTION

Extensive investigations of perovskite-like transition-metal oxides and compounds based on them have shown that these are systems with strong interelectronic correlation, which is the main determinant of the electronic properties. It has been established that correlation factors such as the charge, spin, and orbital symmetry of the electrons in the atoms of these compounds produce a great diversity of states which depend on the character of a magnetic and electrostatic interactions. Neglecting HTSC, of the systems under study the most common systems with interelectronic correlations are manganites (perovskites  $\text{MnO}_3$ ) and cobaltites (perovskites  $\text{CoO}_3$ ) doped with molybdenum, including with the substitution of the latter by alkaline-earth elements Ba, Ca, and Sr. The interest in these systems is explained by their high sensitivity to factors which correlate ferromagnetic and electronic states, and their capability of exhibiting unique electronic properties, such as gigantic and colossal magnetoresistance.<sup>1–3</sup> However, the nature of such changes, just as the mechanism of the correlation between electrons, and perovskite-like compounds has still not been adequately studied. In this connection it is desirable to extend the investigations to compounds with different degrees of influence of

the factors which are responsible for the state of the electrons. In the present work the conductivity of cobaltites in which the electronic orbitals of Ho and Sr are such factors are studied. The combination of these elements in different concentrations as dopants of the perovskite  $\text{CoO}_3$  is interesting because of the possibility of substantially changing the state of the Co-3d and O-3p electrons.<sup>4–6</sup> It is known that Hund's intra-atomic energy in the Co/O octahedra of the cobaltites is of the same order of magnitude as the crystal field energies, and as a result the  $\text{Co}^{3+}$  ions, generally speaking, can occupy different spin states ranging from low-spin (LS)  $t_{2g}^6e_g^0$  ( $S=0$ ) to high-spin (HS)  $t_{2g}^4e_g^2$  ( $S=2$ ) and including intermediate spin (IS)  $t_{2g}^5e_g^1$ ,<sup>7</sup> depending on the type and concentration of the rare-earth dopants. For example, in the compound  $\text{LaCoO}_3$ , which is a nonmagnetic dielectric at normal pressure and low temperatures, a transition from the ground low-spin into the paramagnetic state, corresponding to a transition of the  $\text{Co}^{3+}$  ions from the LS into the IS state, occurs as a result of the thermal excitation of the cobalt ions. For partial substitution of  $\text{Sr}^{2+}$  ions for  $\text{La}^{3+}$  ions in the compound  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $x > 18\%$ ) semiconducting samples passed from the paramagnetic into the ferromagnetic state with metallic conductivity.<sup>8</sup> It is believed that the change of

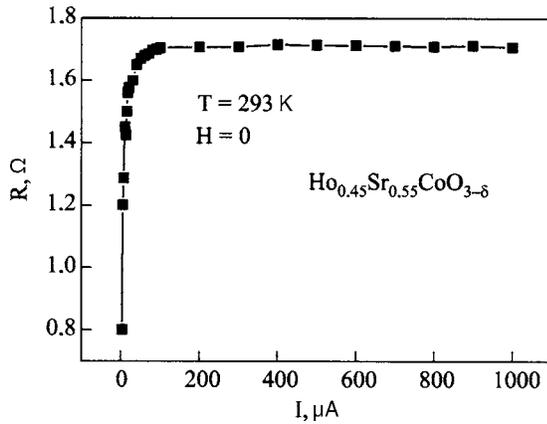


FIG. 1. Typical dependence of the resistance of prepared samples  $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  on the magnitude of the dc transport current.

the spin state of the cobalt ions is closely associated with a change of their valence from 3+ to 4+ as a result of a transition of one  $d$  electron into an unoccupied level near the top of the valence band under the influence of the exchange interaction between  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions. In the present work the properties of the system  $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  are studied. As expected, on account of the presence of holmium in this system most cobalt ions are in the low-spin state, the energy of the high-spin state being no more than 0.08 eV higher.<sup>9</sup> In contrast to the lighter elements in orthorhombic perovskites, Ho possesses the smallest ionic radius, which intensifies the polyhedral distortions of the “lattice” of cobalt octahedra and makes such distortions more temperature dependent. For example, it is known that such distortions can behave non-monotonically, alternately decreasing and increasing, reflecting the non-systematic change of the spin state of the transition-element ions as temperature systematically increases from room temperature to  $\sim 1000$  K.<sup>9</sup>

## II. RESULTS AND DISCUSSION

The transport properties of the ceramic samples  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  ( $x=0.45$ ) and  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  ( $x=0.55$ ) were investigated. The samples were prepared using the standard solid-phase synthesis technology.<sup>10</sup> The samples were  $0.25 \times 0.55 \times 2.5$  cm rectangular parallelepipeds. A four-probe method with dc current was used to measure resistance in a stabilization regime and with the total error of the temperature reading less than 10%.

### A. Conduction in the absence of a magnetic field

Figure 1 displays for all experimental samples the typical dependence of their resistance on the magnitude of the transport current. For low currents this relation deviates from Ohm’s law. Evidently, such a nonlinear effect, manifested as an increase of the resistance along a certain direction on the line of potential probes with increasing current (electric bias  $eV$ ), is possible only for percolation type conduction in samples with cluster structure and tunneling conduction of branched chains of potential barriers between clusters or with electronic phase separation, which can result in macroscopic nonuniformities and mixed percolation-type conduction.<sup>11</sup> It is evident in Fig. 1 that a region of ohmic conduction is

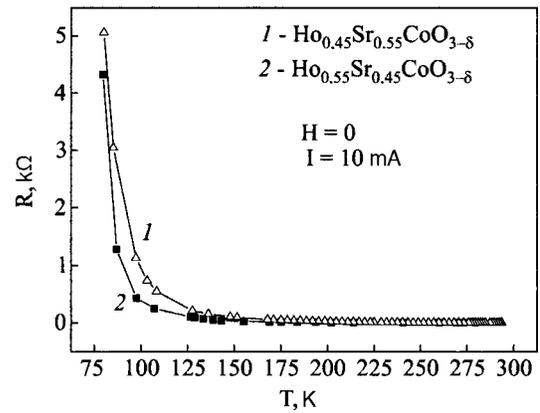


FIG. 2. Temperature dependences of the resistance of the ceramic samples  $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ .

realized for currents above approximately  $100 \mu\text{A}$ , which can be regarded as corresponding to the percolation threshold in our materials. In what follows, we shall discuss the results obtained above the percolation threshold.

Figure 2 displays the typical curves of the temperature dependences of the electric resistance of samples with the indicated values of  $x$  in zero magnetic field at current 10 mA. They qualitatively correspond to an Arrhenius function, i.e. in general, their character corresponds to exponential semiconductor behavior.

However, a detailed analysis of these dependences reveals important features which can be conveniently analyzed using a logarithmic representation of the curves. In Fig. 3 the curves  $R(T)$  are plotted in the coordinates  $\ln R(T^{-1})$ .

It is evident that in this representation the curves exhibit nonlinearity and sensitivity to the dopant concentration, and they cannot be described by a single universal Arrhenius function with exponent  $\sim T^{-1}$ , as in the case of ideal semiconductor systems with intrinsic conductivity. Attempts to describe the conduction in the experimental compounds by universal exponentials with exponents  $\sim T^{-n}$  ( $n < 1$ ), taking account of the presence of strong nonuniformity (noncrystallinity) which gives rise to localization effects, likewise were

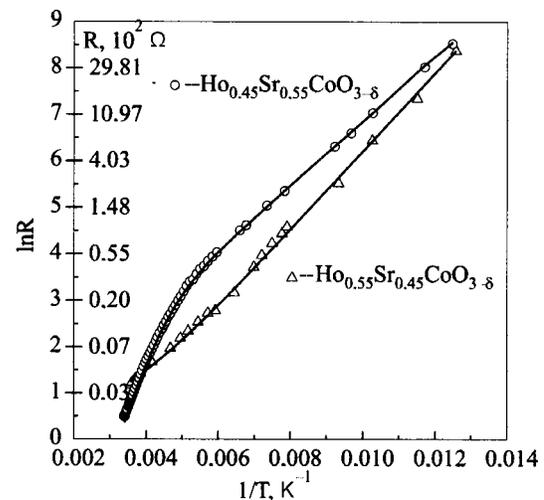


FIG. 3. Experimental dependences of the resistance of samples in logarithmic units on the reciprocal of the temperature (points). Solid lines—description using the expression (2) (see text for explanation).

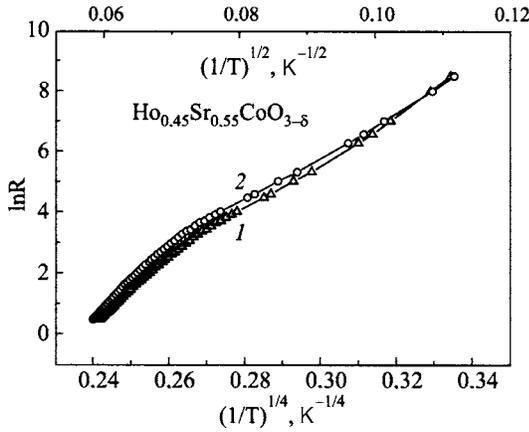


FIG. 4. Experimental temperature dependences of the resistance of samples in logarithmic units in the following representations: 1) polaron conductivity (curve 1, triangles); 2) hopping conductivity (Mott's relation), curve 2 (circles).

unsuccessful. This follows from Fig. 4 where the same values of  $\ln R(T)$  as in Fig. 3 are presented as a function of  $\sim T^{-n}$  with  $n=1/4$  (hopping conduction with a variable hopping length,<sup>12</sup> polaron conduction<sup>13</sup>) and  $n=1/2$  (hopping conduction in the presence of correlation and flow through<sup>14</sup>).

Comparing the curves in Figs. 3 and 4 we conclude that the Arrhenius relation corresponding to the conduction of semiconductor matrices describes very accurately the behavior of the conduction of our samples only at low temperatures (see linear sections of the curves in Fig. 3). The remaining conduction mechanisms of those indicated did not describe the conduction, not only as a whole but also in individual temperature intervals; this is indicated by the absence of the linear sections on the curves presented in Fig. 4 in the temperature coordinates corresponding to these mechanisms.

It follows from Fig. 3 that for  $T > 125$  K in  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  and  $T > 173$  K in  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  the linear dependence of the function  $\ln R(T)$  on the parameter  $1/T$  breaks down. This means that there exist at least two parallel temperature-dependent conduction channels, which itself indicates a large-scale phase separation of the system and percolation conduction. We know that the phase separation is characteristic not only for magnetically ordered phases but also for the paramagnetic state.<sup>15</sup> In our measurements of the magnetic susceptibility no ferromagnetic regions were found for our experimental samples. Apparently, the absence of a ferromagnetic phase is due to the weakness of the exchange interaction in our compounds,<sup>16</sup> which is additionally confirmed by the essentially pure semiconductor behavior of the resistance at low temperatures in the range  $1/T > 0.006$  (Fig. 3).

The model with two conduction channels presumes that the conductivity  $\sigma$  can be represented as a sum of the conductivities of two parallel branches

$$\sigma = \sigma_1 + \sigma_2 = \sigma_{\infty 1} F_1 + \sigma_{\infty 2} F_2, \quad (1)$$

where  $F_1$  and  $F_2$  are functions describing independent contributions of the high-spin states in the narrow hole band and states in the conduction band of the semiconductor matrix.

TABLE I. Computed values of the activation energies for the samples  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  and  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  (see Eq. (2)).

$x$	$R_{\infty} \Omega$	$\Delta_1, \text{K}$	$\Delta_2, \text{K}$	$m$
0.45	$0.105 \pm 2\%$	$2500 \pm 0.05\%$	$844 \pm 0.5\%$	0.005
0.55	$0.95 \pm 0.5\%$	$2500 \pm 0.05\%$	$690 \pm 0.7\%$	0.005

Since  $\sigma \rightarrow \sigma_{\infty}$  as  $T \rightarrow \infty$ , we shall represent the distribution of the contributions as

$$\sigma = m \sigma_{\infty} F_1 + (1 - m) \sigma_{\infty} F_2,$$

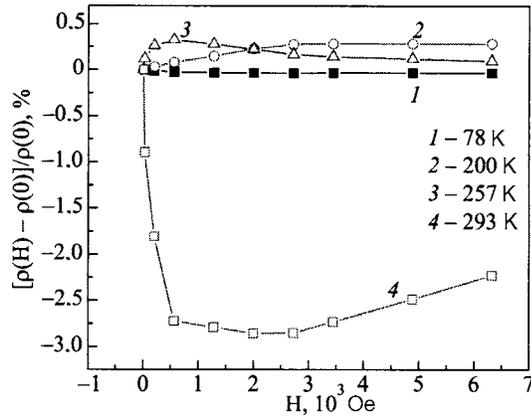
where  $m$  is the  $\sigma_1$  fraction and  $(1 - m)$  the  $\sigma_2$  fraction. Correspondingly, the total resistance of the samples can be written in the form

$$R = R_{\infty} [m F_1 + (1 - m) F_2]; \quad R_{\infty} = \sigma_{\infty}^{-1} (L/S) \quad (2)$$

( $L$  and  $S$  are, respectively, the length and cross-section of the sample). For  $F_1$  we chose the well-known expression for the conductivity proportional to the concentration of Co ions which are thermally excited in the high-spin state:<sup>5</sup>  $F_1 = v / [v + \exp(\Delta_1/T)]$  ( $\Delta_1$  is the spin gap in the spectrum of LS and HS ionic states;  $v=15$  is the multiplicity of the HS states);  $F_2$  is the standard Arrhenius relation for the conductivity of a gap semiconductor:  $F_2 = \exp(-\Delta_2/T)$ . Table I gives, together with the error of the description of the experiment, the values obtained for the adjustable parameters by using the expression (2) with the indicated functions  $F_1$  and  $F_2$  to describe the behavior of the conductivity of the samples of our experimental compounds.

The (relative) errors indicated in Table I are the deviations of the quantities from the indicated values, which keep the computed curves at any point within the limits of the measurement error ( $\sim 10\%$ ). The smallness of these values shows that the model chosen for the conductivity describes quite accurately the real temperature behavior of the resistance of the samples of the experimental compound. It is interesting that the value of  $\Delta_1$  in them is three times larger than the gap between the LS and HS electronic states in cobaltites with other dopants.<sup>9</sup> This makes it possible to give the following explanation for the existence of a contribution, which is small (see Fig. 3,  $T > 150$  K) but fundamentally important, to the conductivity that is associated with the presence of hopping conduction between cobalt ions which are present in different spin states in the experimental compound.

One obvious difference of holmium-doped cobaltites from cobaltites doped with other rare earths is the very small ionic radius of Ho and therefore stronger coulomb interaction along the Co-O line than in cobaltites doped with, for example, lanthanum, whose ionic radius is almost 1.5 times greater. As a result, the  $[t_{2g} - e_g]$  gap  $\Delta_1$  in the energy spectrum of Co-3d electrons will be much larger in the first case than in the second case. It is reasonable to suppose that for comparable concentrations of the second dopant, strontium, activating the HS  $\text{Co}^{3+}$  ions, specifically, the  $\text{Co}^{4+}$  ( $t_{2g}^4 e_g^2$ ) ions,<sup>17</sup> the density of hole states which are realized by a double exchange interaction between  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions cannot be large because of the substantial activation energy of high-spin ionic states with a large  $[t_{2g} - e_g]$  gap. The nor-

FIG. 5. Magnetoresistance of the sample  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$ .

malized number  $F_1$  of thermally excited  $\text{Co}^{3+}$  ions varies for  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  from  $F_1 = 4 \cdot 10^{-8}$  (for  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  from  $1 \cdot 10^{-5}$ ) on heating from temperature  $T_e \approx 150$  K, taken as the temperature of the transition into the paramagnetic state and the onset of a double exchange interaction, to  $F_1 = 3.7 \cdot 10^{-2}$  at  $T \sim 300$  K. The concentration  $n_h$  of holes participating in the double exchange interaction can be obtained from the expression<sup>18</sup>

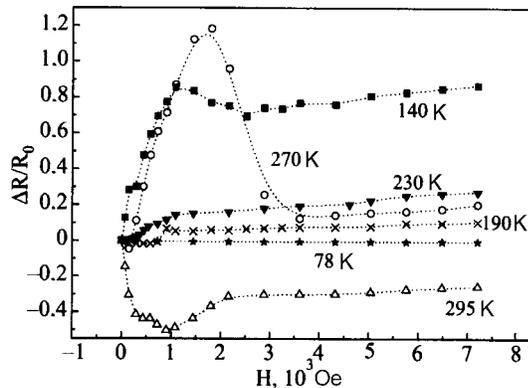
$$k_B T_C = n_h \xi \Delta_1, \quad (3)$$

where  $\xi$  is the number of nearest-neighbor oxygen ions. The hole concentration  $n_h = 0.98$  at% for  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  and 1.2 at% for  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ .

### III. MAGNETORESISTANCE

In an external magnetic field  $H$  the conductivity of ceramic samples  $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  with the experimental Sr concentration exhibits a specific behavior which is even seen in weak fields. Figures 5 and 6 display the magnetoresistance (MR) of the samples as the ratio  $\Delta R/R_0 = [\rho(H) - \rho(0)]/\rho(0)$  as a function of the magnetic field intensity. It is evident that the most characteristic features of MR, such as the sign change and the large values of the MR, appear primarily in weak fields (up to 1 kOe) and at quite high temperatures (not lower than approximately 150 K).

All this indicates that the electronic phase state of the experimental compounds depends strongly on their magnetic state, whose structure is determined by the character of the

FIG. 6. Magnetoresistance of the sample  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ .

spin ordering. The latter is established by, as shown, for example, by an analysis of the system  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ , the competition between the antiferromagnetic interaction (between localized  $t_{2g}$  states) and the ferromagnetic interaction (hopping type between  $e_g$  states).<sup>19</sup> The room-temperature effects, where the imposition of a magnetic field of only 1 kOe results in the appearance of negative magnetoresistance, i.e. switching on of a mechanism for scattering of electrons by magnetic (spin) disorder, are most striking. This shows that a magnetic structure of ferromagnetic clusters with magnetic moments (spins) which are randomly oriented in the absence of a magnetic field, is present in our samples. However, the paramagnetic character of the magnetic susceptibility observed in our samples apparently indicates that the volume occupied by such clusters is small. The capability of this spin structure to rearrange itself even in a weak field shows that it is magnetically unstable. This is also confirmed by the high sensitivity of the magnetic structure to the charge ordering of the system. Thus, as the Sr dopant concentration decreases by 10%, the negative MR at  $T \approx 295$  K changes by an order of magnitude, from -3% (Fig. 5) to -50% (Fig. 6). As temperature decreases by 20–30 K, the MR changes sign, becoming positive and reaching +120%, and it practically vanishes at  $T = 78$  K (Fig. 6). The nature of this effect is not completely understood, and we hope that it can be elucidated by studying the thermo-emf.

### IV. CONCLUSION

The temperature and magnetic field dependences of the electric resistance of the ceramic samples  $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_{3-\delta}$  and  $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$  at temperatures ranging from room temperature to liquid-nitrogen temperature and magnetic fields up to 7 kOe applied perpendicular to the direction of the transport current were investigated. The electric conductivity of the samples in general is of a semiconductor character, and for weak currents it is a nonlinear function of the magnitude of the current. It undergoes radical changes in some temperature range even in weak magnetic fields. This results in changes of the magnetoresistance from -50% to +120%. No single mechanism of hopping conduction describes the temperature behavior of the conductivity within the experimental temperature interval. Analysis of the data obtained shows that a magnetic contribution (the presence of low-spin states  $t_{2g}^5 e_g^1$  or high-spin states  $t_{2g}^4 e_g^2$  of  $\text{Co}^{3+}$  ions) appears in the correlation between electrons when a substantial spin gap is present together with percolation transport. Estimates of the corresponding activation energies were presented.

<sup>a)</sup>E-mail: chiang@ilt.kharkov.ua

<sup>1</sup>S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).

<sup>2</sup>S. A. Kivelson, E. Fradkin, and V. J. Emery, Nature (London) **393**, 550 (1998).

<sup>3</sup>M. McCormack, S. Jin, T. H. Tiefel, R. M. Fleming, O. M. Phillips, and R. Ramesh, Appl. Phys. Lett. **64**, 3045 (1994).

<sup>4</sup>L. A. Nekrasov, S. V. Streltsov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. B **68**, 235113 (2003).

- <sup>5</sup>K. Asai, O. Yokokura, N. Nishimori, H. Chou, J. M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima, and K. Kohn, *Phys. Rev. B* **50**, 3025 (1994).
- <sup>6</sup>S. G. Ovchinnikov and Yu. S. Orlov, *Zh. Eksp. Teor. Fiz.* **131**, 485 (2007).
- <sup>7</sup>J. B. Goodenough, in *Progress in Solid State Chemistry*, edited by H. Reiss, Pergamon, New York, Vol. 5 (1971).
- <sup>8</sup>J. Wu and C. Leighton, *Phys. Rev. B* **67**, 174408 (2003).
- <sup>9</sup>X. Liu and C. T. Prewitt, *J. Phys. Chem. Solids* **52**, 441 (1991).
- <sup>10</sup>A. A. Kozlovskii, V. P. Khirniĭ, T. G. Deĭnika, O. V. Semenov, and V. M. Puzikov, *Nanosistemy, nanomaterialy, nanotekhnologii* **5**, 609 (2007).
- <sup>11</sup>K. I. Kugel', A. L. Rakhmanov, A. O. Sboĭchikoc, M. Yu. Kagan, I. V. Brodskii, and A. V. Klaptsov, *Zh. Eksp. Teor. Fiz.* **125**, 648 (2004).
- <sup>12</sup>N. F. Mott, *Metal-Insulator Transitions*, Taylor and Francis, London (1990).
- <sup>13</sup>M. I. Klinger, *J. Phys. C* **9**, 3955 (1976).
- <sup>14</sup>B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer, New York (1984).
- <sup>15</sup>M. Yu. Kagan and K. I. Kugel', *Usp. Fiz. Nauk* **171**, 577 (2001).
- <sup>16</sup>J. B. Goodenough, *Phys. Rev.* **117**, 1442 (1960).
- <sup>17</sup>A. Chainani, M. Mathew, and D. D. Sarma, *Phys. Rev. B* **46**, 9976 (1992).
- <sup>18</sup>R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri, T. V. Ramakrishnan, R. Mahesh, N. Rangavittal, and C. N. R. Rao, *Phys. Rev. B* **53**, 3348 (1996).
- <sup>19</sup>C. H. Chen, S. W. Cheong, and A. S. Cooper, *Phys. Rev. Lett.* **71**, 2461 (1993).

Translated by M. E. Alferieff