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Exchange interaction in LaCoO₃ between cobalt ions Co³⁺ in different spin states

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The values and signs of the contributions to the superexchange interaction of Co³⁺ ions in LaCoO₃ in different spin states, namely, the superexchange of a pair of ions in the intermediate (IS) state and the superexchange of a pair of ions, one of which is in the intermediate state and the other in the high-spin (HS) state, are studied. For this purpose, virtual electron-hole pairs produced in the course of superexchange (the so-called exchange loops) have been studied within the framework of a multiband generalization of the Hubbard model. It is shown that the cobalt ions in the intermediate state are ordered ferromagnetically, while a pair of ions in different HS and IS states makes an AFM contribution to the superexchange.

Keywords: superexchange interaction, magnetic structure, Hubbard model, projection operator method, exchange loop.

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1. Introduction

Unusual properties of undoped LaCoO₃ with Co³⁺ ions in the low-spin (LS) state ¹A₁ and thermally induced spin states ³T₁ and ⁵T₂ are of great interest [1–3]. In the experiment, two blurred transitions are observed: from the diamagnetic to the paramagnetic state at T₃ ≈ 120 K and the dielectric-metal transition with a further increase in temperature to T_{IM} ≈ 530 K [4–7]. The LS-state existing at low temperatures is characterized by zero spin on the Co³⁺ ion and the absence of magnetic moments in the bulk sample. In this state, the LaCoO₃ crystal is a non-magnetic dielectric [8]. The magnetic contributions detected at temperatures below 35 K are associated with the presence of impurities [6] and crystal lattice [2,9] defects. An increase in temperature to 100 K leads to a transition to a paramagnetic state. There are many works linking this transition with the occupation of medium-spin (IS) [10–15] and high-spin (HS) [16–21] states, but it is still not clear which of them are responsible for paramagnetism. At the same time, the energy of IS-states is much higher, and their thermal occupation is unlikely, and HS-states can be populated at finite temperatures or with optical excitation [22]. The study of the dependence of magnetization on temperature leads to the conclusion that there is an antiferromagnetic (AFM) exchange interaction [16]. However, there is experimental evidence of the presence of ferromagnetic order in polycrystalline samples [23], on the surface of single crystals [24] and in thin films LaCoO₃ with a stretchable substrate [25–31].

The magnetic structure of the deformed LaCoO₃ was considered in [32] using density functional theory. It

has been shown that during stretching, competition arises between the ferromagnetic (FM) exchange between the nearest neighbors (the so-called *nn*-bonds) and a stronger AFM interaction between the second neighbors. The study of thin films LaCoO₃ by numerical simulation [33] has shown that the ferromagnetic ordering in such films is due to effective super-exchange interactions between atoms in HS-states, each of which can be considered as a connected pair of two IS-excitons making virtual jumps to neighboring nodes. These fluctuations mediate HS–HS interactions beyond the *nn*-connections.

In the study [8], the interatomic exchange interaction between HS-states in LaCoO₃ was investigated within the framework of a multielectronic approach that allows us to represent the complete exchange interaction as the sum of partial contributions from all the main and excited cation terms [34–36]. This approach is a generalization of the projection operator method for computing the Anderson super-exchange interaction [37]. As a result, an expression was derived for the super-exchange interaction between two Co³⁺ ions in excited HS-states, which has the form of the sum of FM and AFM contributions, and the resulting magnitude and sign of the super-exchange depend on the relationship between the intra-atomic Hund interaction *J_H* and the effective Hubbard parameter *U_{eff}* [8]. The question of the magnitude and sign of the exchange interaction between Co³⁺ ions in IS-states has not been considered. In this paper, we generalized the results of [8] to the exchange interaction in LaCoO₃ between cobalt ions Co³⁺ in IS-states, as well as to the inhomogeneous case when one of the interacting ions are in the IS- state, and the other — is in the HS-state.

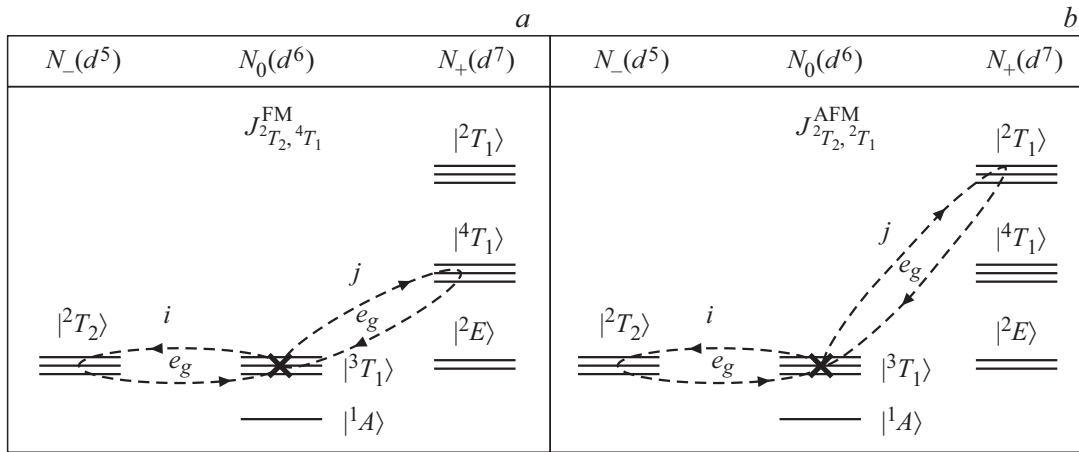


Figure 1. Scheme of neutral, hole and electron terms of Co^{3+} ions. Two exchange loops $J_{2T_2, 4T_1}^{FM}$ (a) and $J_{2T_2, 2T_1}^{AFM}$ (b), giving the main contribution to the super-exchange interaction for IS-states in LaCoO_3 .

2. Exchange interaction in LaCoO_3 between cobalt ions Co^{3+} in intermediate IS-state

The calculation of super-exchange interaction is based on a multi-band generalization of the Hubbard model. With the help of a unitary transformation, a second-order perturbation theory is constructed, where interatomic jumps of electrons of an interband nature are distinguished, giving an expression of the super-exchange Hamiltonian [34–37]. This is done using the projection operator method developed in [37] for the Hubbard single-band model and generalized to the case of an arbitrary spectrum of virtual excitations [34–36]. In the standard Hubbard model with one electron per atom, the super-exchange interaction is formed as a result of the birth and subsequent destruction of virtual electron-hole pairs. At the initial moment, two ions are in the configuration d^1 (let us call them electroneutral). As a result of the birth of an electron-hole pair, virtual hole terms d^0 and electronic terms d^2 appear. In the multi-band case, the principle is the same, but the neutral ion d^n with the number of electrons $n_0 = 6$ for Co^{3+} , as well as the hole c $n_h = n_0 - 1$ and the electron d^{n+1} with $n_e = n_0 + 1$ can be in various multiplet states. The representation of the X-Hubbard operators makes it possible to analyze partial contributions to the exchange from various neutral ion terms, both basic and excited. The resulting Hamiltonian of the super-exchange interaction

$$\hat{H}_S = - \sum_{i \neq j} J_{ij}^{tot} \left(\hat{S}_{i n_0} \hat{S}_{j n_0} - \frac{1}{4} \hat{n}_{i n_0}^{(h)} \hat{n}_{j n_0}^{(e)} \right), \quad (1)$$

where J_{ij}^{tot} — full node pair exchange, $\hat{S}_{i n_0}$ — spin operator on i -m node, $\hat{n}_{i n_0}^{(h,e)}$ — quasiparticle number operators for hole (h) and electron (e) terms, is the sum of contributions from all ground and excited states, each of which can be graphically represented as a virtual electron-hole pair or a so-called exchange loop [38]. The sign of

each contribution is determined by the ratio of the spins $S(d^{n+1})$ and $S(d^{n-1})$ of the electron and hole terms if $S(d^{n-1}) = S(d^{n+1})$, then the interaction is antiferromagnetic. When $S(d^{n-1}) = S(d^{n+1}) \pm 1$, then a ferromagnetic exchange is formed. The main contribution to the super-exchange IS of states in LaCoO_3 is given by two exchange loops of the opposite sign, shown in Fig. 1.

According to Fig. 1, a the ferromagnetic contribution to the super-exchange is given by the exchange loop $J_{2T_2, 4T_1}^{FM}$. The value of this contribution is equal to

$$J_{2T_2, 4T_1}^{FM} = \frac{1}{(2S_h + 1)} \frac{1}{(2S_{n_0} + 1)} \frac{2t^2}{(2T_2, 4T_1)}, \quad (2)$$

where S_h, S_{n_0} — the spins of the neutral and hole terms, t — the hopping integral, and $\Delta = E(d^5) + E(d^7) - 2E(d^6)$ — the energy denominator, similar to the parameter U in the Hubbard model. The energies of the hole, electroneutral and electron terms participating in this exchange loop are equal

$$E(d^5) = -20Dq - 4J_H + 10U, \quad (3)$$

$$E(d^6) = -14Dq - 7J_H + 15U, \quad (4)$$

$$E(d^7) = -8Dq - 11J_H + 21U, \quad (5)$$

where J_H and Dq are the parameters of the Hund interaction and the crystal field, respectively. Hence $\Delta = U - J_H$. Thus, the contribution from the ferromagnetic loop to the super exchange is equal to

$$J_{2T_2, 4T_1}^{FM} = \frac{1}{2} \frac{1}{3} \frac{2t^2}{U - J_H}. \quad (6)$$

Similarly for the antiferromagnetic exchange loop $J_{2T_2, 2T_1}^{AFM}$, shown in Fig. 2, b, the energy of the terms forming it and the energy denominator are equal

$$E(d^5) = -20Dq - 4J_H + 10U, \quad (7)$$

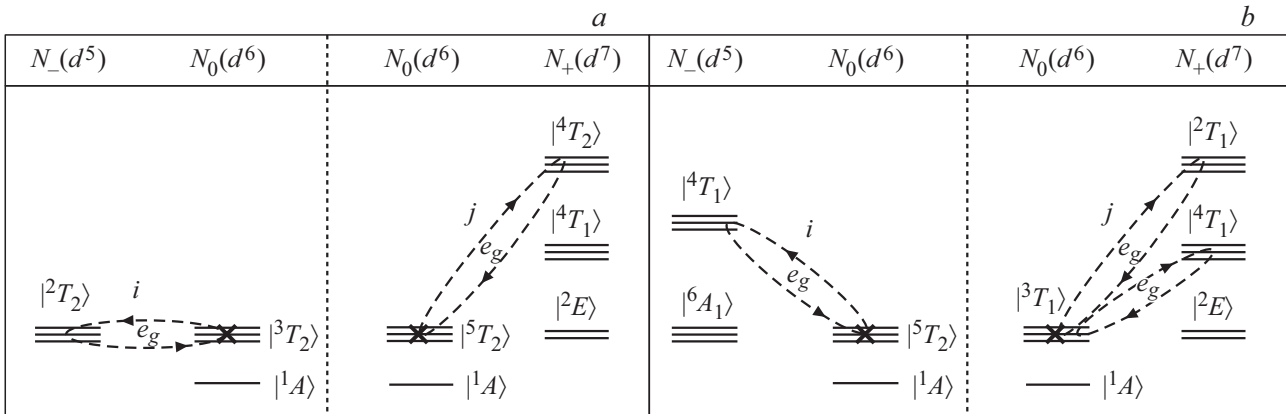


Figure 2. Exchange loops that make up the main contribution to the exchange between Co³⁺ ions in HS- and IS-states: loop $J_{2T_2,4T_2}^{AFM}$, which gives a contribution to the exchange in the case when the HS-state is j -th ion (a), and two loops $J_{4T_1,4T_1}^{FM}$, $J_{4T_1,2T_1}^{FM}$, giving the main contribution to the exchange when the HS-state is i -th ion (b).

$$E(d^6) = -14Dq - 7J_H + 15U, \quad (8)$$

$$E(d^7) = -8Dq - 9J_H + 21U, \quad (9)$$

$$\Delta = U + J_H, \quad (10)$$

where does the value of the AFM contribution to the super exchange come from

$$J_{2T_2,2T_1}^{AFM} = -\frac{1}{2} \frac{1}{3} \frac{2t^2}{U + J_H}. \quad (11)$$

Summing up the expressions obtained, we obtain the total contribution from the IS-states to the complete super-exchange interaction of Co³⁺ ions, which is ferromagnetic:

$$\begin{aligned} J_{tot}^{FM} &= \frac{t^2}{3} \left\{ \frac{2J_H}{(U^2 - J^2)} \right\} = \frac{2}{3} \frac{4}{100} \frac{1}{16 - 1} \\ &= 0.002 \text{ eV} = 2 \text{ meV}. \end{aligned} \quad (12)$$

The following parameter values characteristic of transition metal oxides were used for numerical evaluation: $J_H = 1 \text{ eV}$, $U = 4 \text{ eV}$, $t = 0.2 \text{ eV}$. It is important that the total ferromagnetic contribution is obtained for any parameter values, since $U > J_H$.

3. Exchange interaction in LaCoO₃ between cobalt ions Co³⁺ in intermediate IS- and high spin HS-states

A pair of Co³⁺ ions, one of which is in the high-spin HS-, and the other — in the intermediate IS-states, are connected by a super-exchange consisting of three exchange loops: two antiferromagnetic $J_{2T_2,4T_1}^{AFM}$, $J_{4T_1,2T_1}^{AFM}$ and one ferromagnetic $J_{4T_1,4T_1}^{FM}$ (Fig. 2).

The situation in this case depends on which of the nodes goes into a state with an additional electron, and which — into a state with an additional hole. There is one exchange

loop $J_{2T_2,4T_2}^{AFM}$, corresponding to the birth of a virtual electron on a high-spin ion and a hole on an ion with an intermediate spin (see Fig. 2, a). To calculate the exchange value, it is necessary to take into account the energies of the HS- and IS-states:

$$E(d^5) = -20Dq - 4J_H + 10U, \quad (13)$$

$$E_{IS}(d^6) = -14Dq - 7J_H + 15U, \quad (14)$$

$$E_{HS}(d^6) = -4Dq - 10J_H + 15U, \quad (15)$$

$$E(d^7) = 2Dq - 11J_H + 21U, \quad (16)$$

$$\Delta = U + J_H, \quad (17)$$

$$J_{2T_2,4T_2}^{AFM} = -\frac{1}{2} \frac{1}{5} \frac{2t^2}{U + 2J_h}. \quad (18)$$

The birth of an electron on the IS-ion and holes on the HS-ion are answered by two exchange loops of the opposite sign $J_{4T_1,2T_1}^{AFM}$ and $J_{4T_1,4T_1}^{FM}$ (Fig. 2, b). A similar calculation gives the following values for these loops:

$$J_{4T_1,2T_1}^{AFM} = -\frac{1}{4} \frac{1}{3} \frac{2t^2}{U + 2J_h}, \quad (19)$$

$$J_{4T_1,4T_1}^{FM} = \frac{1}{4} \frac{1}{3} \frac{2t^2}{U}. \quad (20)$$

The total value of the exchange interaction is equal to the sum of the contributions from the three exchange loops and has an antiferromagnetic sign

$$\begin{aligned} J_{tot}^{AFM} &= J_{2T_2,4T_2}^{AFM} + J_{4T_1,2T_1}^{AFM} + J_{4T_1,4T_1}^{FM} \\ &\sim -3 \cdot 10^{-4} \text{ eV} = -0.3 \text{ meV}. \end{aligned} \quad (21)$$

4. Conclusion

Thus, cobalt ions Co³⁺ in the same IS-states are bound by the FM super-exchange $J_{tot}^{FM} = 2 \text{ MeV}$, and ions in different IS- and HS-states — AFM interaction $J_{tot}^{AFM} = 0.5 \text{ MeV}$,

however, the latter is inferior to the first in magnitude, and the ratio between them does not depend on the magnitude of the crystal field $10Dq$. Taking into account the results of the work [8] on the AFM interaction between Co^{2+} ions in the same HS-states, we identify the observed FM interaction in some cobaltites as signs of the presence of cobalt ions Co^{3+} in the intermediate spin state of IS.

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Conflict of interest

The authors declare that they have no conflict of interest.

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