Physics of the Solid State, 2022, Vol. 64, No. 12

04,05

Exchange interaction in $LaCoO_3$ between cobalt ions Co^{3+} in different spin states

© S.I. Polukeev, V.A. Gavrichkov, S.G. Ovchinnikov

Kirensky Institute of Physics, Federal Research Center KSC SB, Russian Academy of Sciences,
Krasnoyarsk, Russia

E-mail: psi@iph.krasn.ru

Received July 7, 2022
Revised July 7, 2022
Accepted July 10, 2022

The values and signs of the contributions to the superexchange interaction of Co^{3+} ions in $LaCoO_3$ 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.

DOI: 10.21883/PSS.2022.12.54381.426

1. Introduction

Unusual properties of undoped $LaCoO_3$ with Co^{3+} ions in the low-spin (LS) state $^1A_1$ and thermally induced spin states $^3T_1$ and $^5T_2$ are of great interest [1–3]. In the experiment, two blurred transitions are observed: from the diamagnetic to the paramagnetic state at $T_S \approx 120\,K$ and the dielectric-metal transition with a further increase in temperature to $T_{IM} \approx 530\,K$ [4–7]. The LS-state existing at low temperatures is characterized by zero spin on the Co^{3+} ion and the absence of magnetic moments in the bulk sample. In this state, the $LaCoO_3$ 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 $LaCoO_3$ with a stretchable substrate [25–31].

The magnetic structure of the deformed $LaCoO_3$ 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 $LaCoO_3$ 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 $LaCoO_3$ 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 Co^{3+} 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 Co^{3+} ions in IS-states has not been considered. In this paper, we generalized the results of [8] to the exchange interaction in $LaCoO_3$ between cobalt ions Co^{3+} 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.

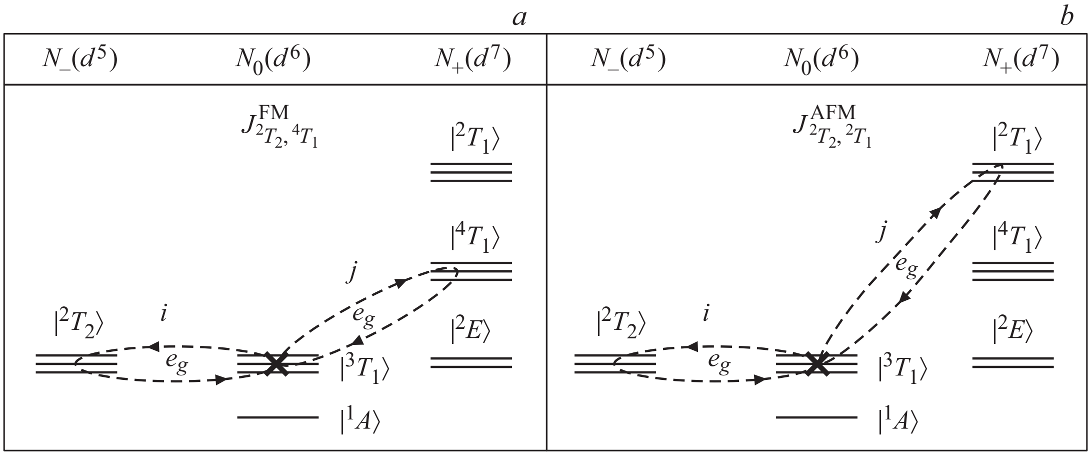

Figure 1. Scheme of neutral, hole and electron terms of Co^{3+} ions. Two exchange loops $J^{FM}_{^2T_2,^4T_1}$ (*a*) and $J^{AFM}_{^2T_2,^2T_1}$ (*b*), giving the main contribution to the super-exchange interaction for IS-states in $\mathrm{LaCoO_3}$.

2. Exchange interaction in $\mathrm{LaCoO_3}$ 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

$$\hat{H}_S = -\sum_{i\neq j} J^{tot}_{ij}\left(\hat{S}_{in_0}\hat{S}_{jn_0} - \frac{1}{4}\hat{n}^{(h)}_{in_0}\hat{n}^{(e)}_{jn_0}\right), \tag{1}$$

where J^{tot}_{ij} — full node pair exchange, $\hat{S}_{in_0}$ — spin operator on i-m node, $\hat{n}^{(h,e)}_{in_0}$ — 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 $\mathrm{LaCoO_3}$ 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 $J^{FM}_{^2T_2,^4T_1}$. The value of this contribution is equal to

$$J^{FM}_{^2T_2,^4T_1} = \frac{1}{(2S_h+1)}\,\frac{1}{(2S_{n_0}+1)}\,\frac{2t^2}{(^2T2,\,^4T_1)}, \tag{2}$$

where S_h, S_{n0} — 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

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

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

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

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

$$J^{FM}_{^2T_2,^4T_1} = \frac{1}{2}\,\frac{1}{3}\,\frac{2t^2}{U - J_H}. \tag{6}$$

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

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

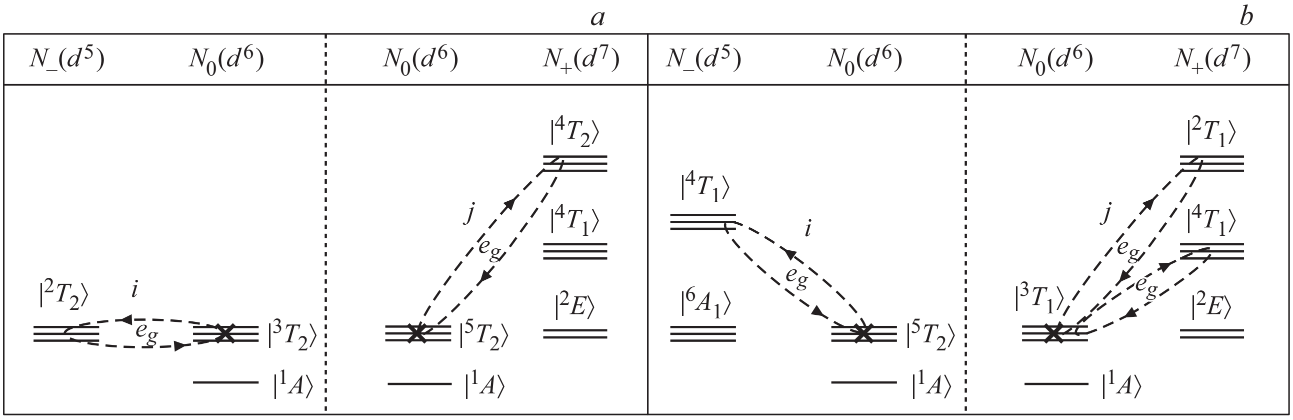

Figure 2. Exchange loops that make up the main contribution to the exchange between Co^{3+} ions in HS- and IS-states: loop $J^{AFM}_{^2T_2,^4T_2}$, which gives a contribution to the exchange in the case when the HS-state is j-th ion (a), and two loops $J^{FM}_{^4T_1,^4T_1}$, $J^{AFM}_{^4T_1,^2T_1}$, giving the main contribution to the exchange when the HS-state is i-th ion (b).

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

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

$$\Delta = U + J_H, \tag{10}$$

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

$$J^{AFM}_{^2T_2,^2T_1} = -\frac{1}{2}\,\frac{1}{3}\,\frac{2t^2}{U + J_H}. \tag{11}$$

Summing up the expressions obtained, we obtain the total contribution from the IS-states to the complete super-exchange interaction of Co^{3+} ions, which is ferromagnetic:

$$J^{FM}_{tot} = \frac{t^2}{3}\left\{\frac{2J_H}{(U^2 - J^2)}\right\} = \frac{2}{3}\,\frac{4}{100}\,\frac{1}{16-1}$$

$$= 0.002\,\text{eV} = 2\,\text{meV}. \tag{12}$$

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

3. Exchange interaction in LaCoO$_3$ between cobalt ions Co^{3+} in intermediate IS- and high spin HS-states

A pair of Co^{3+} 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 $J^{AFM}_{^2T_2,^4T_1}$, $J^{AFM}_{^4T_1,^2T_1}$ and one ferromagnetic $J^{FM}_{^4T_1,^4T_1}$ (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 $J^{AFM}_{^2T_2,^4T_2}$, 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:

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

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

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

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

$$\Delta = U + J_H, \tag{17}$$

$$J^{AFM}_{^2T_2,^4T_2} = -\frac{1}{2}\,\frac{1}{5}\,\frac{2t^2}{U + 2J_h}. \tag{18}$$

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 $J^{AFM}_{^4T_1,^2T_1}$ and $J^{FM}_{^4T_1,^4T_1}$ (Fig. 2, b). A similar calculation gives the following values for these loops:

$$J^{AFM}_{^4T_1,^2T_1} = -\frac{1}{4}\,\frac{1}{3}\,\frac{2t^2}{U + 2J_h}, \tag{19}$$

$$J^{FM}_{^4T_1,^4T_1} = \frac{1}{4}\,\frac{1}{3}\,\frac{2t^2}{U}. \tag{20}$$

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

$$J^{AFM}_{tot} = J^{AFM}_{^2T_2,^4T_2} + J^{AFM}_{^4T_1,^2T_1} + J^{FM}_{^4T_1,^4T_1}$$

$$\sim -3 \cdot 10^{-4}\,\text{eV} = -0.3\,\text{meV}. \tag{21}$$

4. Conclusion

Thus, cobalt ions Co^{3+} in the same IS-states are bound by the FM super-exchange $J^{FM}_{tot} = 2$ MeV, and ions in different IS- and HS-states — AFM interaction $J^{AFM}_{tot} = 0.5$ 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.

Funding

The work was carried out with the financial support of the Russian Foundation for Basic Research (project No. 20-42-240016).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J.B. Goodenough. Prog. Solid State Chem. **5**, 145 (1971).

[2] M.A. Senaris-Rodriguez, J.B. Goodenough. J. Solid State Chem. **116**, *2*, 224 (1995).

[3] N.B. Ivanova, S.G. Ovchinnikov, M.M. Korshunov, I.M. Eremin, N.V. Kazak. UFN **179**, *8*, 837 (2009). (in Russian).

[4] S. Yamaguchi, Y. Okimoto, H. Taniguchi, Y. Tokura. Phys. Rev. B **53**, 2926R (1996).

[5] S. Tajima, A. Masaki, S. Uchida, T. Matsuura, K. Fueki, S. Sugai. J. Phys. C **20**, 3469 (1987).

[6] S. Yamaguchi, Y. Okimoto, Y. Tokura. Phys. Rev. B **55**, 14, 8666R (1997).

[7] A. Ishikawa, J. Nohara, S. Sugai. Phys. Rev. Lett. **93**, 136401 (2004).

[8] Yu.S. Orlov, S.V. Nikolaev, V.A. Gavrichkov, S.G. Ovchinnikov. Comput. Mater. Sci. **204**, 111134 (2022).

[9] S. Zhou, L. Shi, J. Zhao, L. He, H. Yang, S. Zhang. Phys. Rev. B **76**, *17*, 172407 (2007).

[10] K. Asai, A. Yoneda, O. Yokokura, J. Tranquada, G. Shirane, K. Kohn. J. Phys. Soc. Jpn. **67**, *1*, 290 (1998).

[11] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, M. Takano. Phys. Rev. B **55**, 4257 (1997).

[12] R.F. Klie, J.C. Zheng, Y. Zhu, M. Varela, J. Wu, C. Leighton. Phys. Rev. Lett. **99**, 047203 (2007).

[13] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorenz, P. Reutler, A. Revcolevschi. Phys. Rev. B **66**, 020402 (2002).

[14] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorenz, P. Reutler, A. Revcolevschi. Phys. Rev. B **71**, 019902 (2005).

[15] P.G. Radaelli, S.-W. Cheong. Phys. Rev. B **66**, 094408 (2002).

[16] M.J.R. Hoch, S. Nellutla, J. van Tol, E.S. Choi, J. Lu, H. Zheng, J.F. Mitchell. Phys. Rev. B **79**, *21*, 214421 (2009).

[17] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, M. Motokawa. Phys. Rev. B **66**, *9*, 094404 (2002).

[18] M.W. Haverkort, Z. Hu, J.C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N.B. Brookes, H.H. Hsieh, H.-J. Lin, C.T. Chen, L.H. Tjeng. Phys. Rev. Lett. **97**, 176405 (2006).

[19] A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Conder, A. Tanaka, M.W. Haverkort, D.I. Khomskii. Phys. Rev. Lett. **97**, 247208 (2006).

[20] A. Podlesnyak, K. Conder, E. Pomjakushina, A. Mirmelstein, P. Allenspach, D. Khomskii. J. Magn. Magn. Mater. **310**, *2*, 1552 (2007).

[21] M. Rotter, Z.-S. Wang, A.T. Boothroyd, D. Prabhakaran, A. Tanaka, M. Doerr. Sci. Rep. **4**, 7003 (2014).

[22] T. Ishikawa, K. Yamada, H. Itoh, S. Iwai, T. Arima, S. Yamada, T. Sasaki. EPJ Web Conf. **41**, 03013 (2013).

[23] J. Androulakis, N. Katsarakis, J. Giapintzakis. Phys. Rev. B **64**, *17*, 174401 (2001).

[24] J.-Q. Yan, J.-S. Zhou, J.B. Goodenough. Phys. Rev. B **70**, *1*, 014402 (2004).

[25] A. Harada, T. Taniyama, Y. Takeuchi, T. Sato, T. Kyomen, M. Itoh. Phys. Rev. B **75**, *18*, 184426 (2007).

[26] D. Fuchs, C. Pinta, T. Schwarz, P. Schweiss, P. Nagel, S. Schuppler, R. Schneider, M. Merz, G. Roth, H.V. Lohneysen. Phys. Rev. B **75**, *14*, 144402 (2007).

[27] A. Herklotz, A.D. Rata, L. Schultz, K. Dorr. Phys. Rev. B **79**, *9*, 092409 (2009).

[28] V.V. Mehta, M. Liberati, F.J. Wong, R.V. Chopdekar, E. Arenholz, Y. Suzuki. J. Appl. Phys. **105**, *7*, 07E503 (2009).

[29] N. Biskup, J. Salafranca, V. Mehta, M.P. Oxley, Y. Suzuki, S.J. Pennycook, S.T. Pantelides, M. Varela. Phys. Rev. Lett. **112**, *8*, 087202 (2014).

[30] H. Liu, L. Shi, Y. Guo, S. Zhou, J. Zhao, C. Wang, L. He, Y. Li. J. Alloys Compd. **594**, 158 (2014).

[31] Q. Feng, D. Meng, H. Zhou, G. Liang, Z. Cui, H. Huang, J. Wang, J. Guo, C. Ma, X. Zhai, Q. Lu, Y. Lu. Phys. Rev. Mater. **3**, *7*, 074406 (2019).

[32] H. Seo, A. Posadas, A.A. Demkov. Phys. Rev. B **86**, 014430 (2012).

[33] A. Sotnikov, K.-H. Ahn, J. Kunes. Sci. Post. Phys. **8**, *082*, 1 (2020).

[34] V.A. Gavrichkov, S.I. Polukeev, S.G. Ovchinnikov. Phys. Rev. B **95**, *14*, 144424 (2017).

[35] V.A. Gavrichkov, S.I. Polukeev, S.G. Ovchinnikov. ZHETF (in Russian) **154**, *4*, 835 (2018).

[36] R.V. Mikhaylovskiy, T.J. Huisman, V.A. Gavrichkov, S.I. Polukeev, S.G. Ovchinnikov, D. Afanasiev, R.V. Pisarev, T. Rasing, A.V. Kimel. Phys. Rev. Lett. **125**, *15*, 157201 (2020).

[37] K.A. Chao, J. Spalek, A.M. Oles. J. Phys. C **10**, *10*, L271 (1977).

[38] V.A. Gavrichkov, S.I. Polukeev, S.G. Ovchinnikov. Phys. Rev. B **101**, *10*, 094409 (2020).