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Exchange Interaction between the Excited States of Magnetic Ions

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Abstract—Within the framework of the LDA + GTB multi-electron approach to the electron structure of Mott–Hubbard insulators a scheme is developed for constructing the effective low-energy Hamiltonian that includes not only the ground state of the magnetic cation, but also the excited terms. The mathematical apparatus of the theory are Hubbard operators built on the many-electron states of the cation in the d^n configuration. The occupation of the excited term under optical pumping can change the sign of the exchange interaction of the excited cation with the neighboring cation in the ground state. Another variant of the occupation of the excited states is connected with a spin crossover when the excited and the ground terms change over, for example, at high pressure. Examples are given for such crystals as $FeBO_3$, $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ and NiO.

Keywords: exchange interaction, spin crossover, exchange in an excited state

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INTRODUCTION

Usually, in the theory of magnetic insulators from the whole set of the multielectron terms of a magnetic cation, only the main term with a certain spin (momentum in the general case) with an interatomic exchange interaction in the form of the Heisenberg model is considered. Such a low-energy approach is justified for describing the thermodynamic properties. However, the development of optical and magneto-optical methods of studying magnetic materials, in particular femtosecond magneto-optics [1], made it necessary to take into account the exchange interactions in the excited states of magnetic cations, which this work is devoted to. High-pressure spin crossover experiments also stabilize states that were excited at low pressures, which affects the magnitude and sometimes the sign of the exchange interaction. This paper provides a brief overview of the work in this area.

CALCULATION METHODS

Since the standard methods of the density functional theory don't describe the Mott–Hubbard insulators, including the magnetic oxides of 3*d* metals, we use the hybrid approach of the generalized tight binding LDA + GTB method developed in the collaboration of the Krasnoyarsk and Yekaterinburg groups [2]. The most appropriate mathematical language in this method is the Hubbard operators, in their representation the initial multi-band *p–d* model, taking into account the electronic *d*-states of cations and the p-states of anions and all strong local Coulomb interactions within the framework of the LDA + GTB approach are projected onto an effective low-energy model with selected multi-electron terms, and the effective Heisenberg type spin Hamiltonian is obtained. This procedure is described in detail in [3]. Similar methods were also developed in [4].

SUPEREXCHANGE INTERACTION OF THE MAGNETIC IONS WITH ARBITRARY TERMS

Within the framework of the LDA + GTB approach, we can write the Hamiltonian of the multiband *p–d* model in the form of a generalized Hubbard model

$$H = H_0 + H_1, H_0 = \sum_{i,\mathrm{p}} E_p X_i^{\mathrm{pp}}$$
$$H_1 = \sum_{ij,mn} t_{ij}^{mn} X_i^{m+} X_j^n, \quad (1)$$

where the first term describes the set of multi-electron Ψ_p terms with the energy E_p and the number of electrons n_p. The second term in Hamiltonian (1) contains interatomic hopes from site *i* to site *j* with amplitude t^{pq}. X-operators are defined as usual, $X^{\mathrm{pq}} = |\mathrm{p}\rangle\langle\mathrm{q}|$. In the case of the Hubbard model with the number of electrons $n_\mathrm{e} = 1$ there are two Hubbard subbands corresponding to the filled valence and empty conduction bands. Excluding the interband hopes using the unitary transformation we can obtain the effective Hamiltonian of the Heisenberg model with the exchange integral $J = 2t^2/U$ [5, 6]. A generalization of this ideology to the multi-band case [3, 4] allows to obtain the effective Hamiltonian containing not only the main,

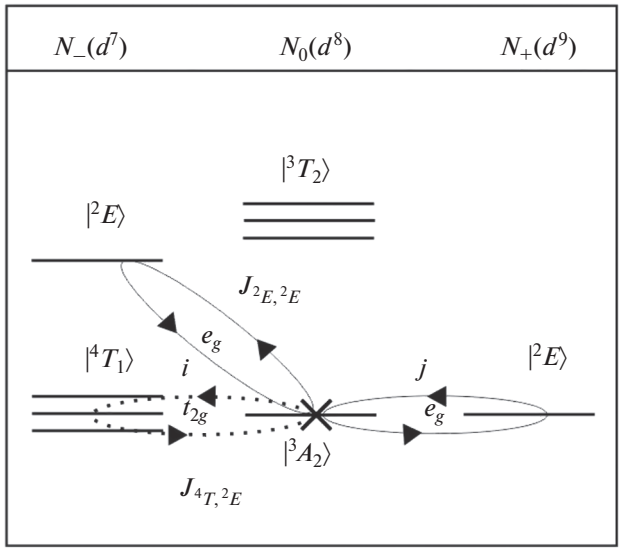

Fig. 1. The graphical scheme of the superexchange interaction in NiO at atmospheric pressure. The solid line shows the contribution $J_{^2E,^2E}$ from the virtual electron hopping with predominant AFM interaction. The dotted line shows the hopping with the possible FM contribution $J_{^4T,^2E}$ and zero e_g–t_{2g} overlap.

but also excited terms for various configurations. For the effective exchange Hamiltonian, the filled (electroneutral) configuration d^n, and the unfilled (virtual) configurations with one additional electron d^{n+1} and one hole d^{n-1} play a role. Excitations between different terms $d^n \to d^{n+1}$ determine the processes of electron creation and, similarly, $d^n \to d^{n-1}$ determine the creation of a hole. In this case, the unitary transformation, excluding interband transitions, looks more cumbersome, but nevertheless it can be done. The effective Hamiltonian contains several terms in each sector of the Hilbert space: neutral, electron, and hole. In addition to the exchange interaction with involving both the ground and excited states, the effective Hamiltonian also contains excitons-neutral excitations between different terms of the d^n configuration, as well as the spin-exciton interactions. Two types of physically different problems can be considered in the framework of this theory: (1) spin crossovers (2) the change in the exchange interaction induced by light.

CHANGES OF THE EXCHANGE INTERACTION AT THE SPIN CROSSOVER

Spin crossovers can take place in the d^n configuration, when under normal conditions the high-spin term HS is filled at each site of the lattice, and the higher energy low-spin term LS is empty at $T = 0$. Under the influence of external perturbations, for example, pressure, the low-spin term lowers its energy and becomes ground above the critical pressure P_c. At $T = 0$ the occupation numbers of the HS/LS terms also change abruptly. At $P < P_c$ the exchange is determined mainly by the high-spin term (if we neglect the population of the LS term exponentially small at finite temperatures), and at $P > P_c$ namely LS term determines the exchange. For Fe^{+3} iont with d^5 configuration, the spin crossover occurs for different oxides: Fe_2O_3, $FeBO_3$, $RFeO_3$ (R-rare earth), $BiFeO_3$, $Y_3Fe_5O_{12}$, $GdFe_3(BO_3)_4$ [7]. At low pressures in the HS state they all are antiferromagnets in the ground state. At high pressure, we conclude that the sign of the exchange interaction changes and we predict the ferromagnetic ground state. Such a prediction was made earlier for $FeBO_3$ [8], in this paper we show that it is valid for all oxides with a d^5 cation configuration. In addition to the above iron compounds MnO also enter this group.

The spin crossover under pressure is not available for configurations d^2, d^3 or d^8. Since the unfilled virtual d^{n+1} and d^{n-1} terms also participate in the formation of superexchange interaction, the spin crossover in virtual terms also affects the exchange interaction.

For example, in the antiferromagnetic nickel oxide NiO (d^8 configuration) the ground term of a hole configuration d^7 $\left(\left|{}^4T_1\right\rangle\right)$ gives no contribution to the exchange interaction due to the zero overlap of the e_g and t_{2g} orbitals and the main contribution results from the first excited state $\left|{}^2E\right\rangle$ with a strong e_g–e_g overlap (Fig. 1). Under the high pressure the spin crossover occurs in d^7 sector and the state that makes the main contribution to the exchange interaction becomes the ground state (Fig. 2). In this case the nature of magnetic ordering will not change, however an increase in the magnitude of the exchange interaction with an increase in the Néel temperature is predicted.

CHANGES IN EXCHANGE INTERACTION UNDER OPTICAL PUMPING

Using the optical pumping, one can also occupy the excited terms and change the superexchange interaction, since the overlap of the wave functions of the cation in the excited state with the p-functions of oxygen differs from that in the ground state. As a result, the exchange interaction of the excited cation-cation in the ground state couple changes compared to two cations in the ground state. For example, in $FeBO_3$ under optical pumping of the excited $^4T_2$ term the sign of the exchange changes from antiferromagnetic to ferromagnetic and the Dzyaloshinsky–Moriya interaction increases simultaneously [3]. These results qualitatively explain the observed magnetic oscillations in $FeBO_3$ by the methods of femtosecond magnetooptics [9, 10].

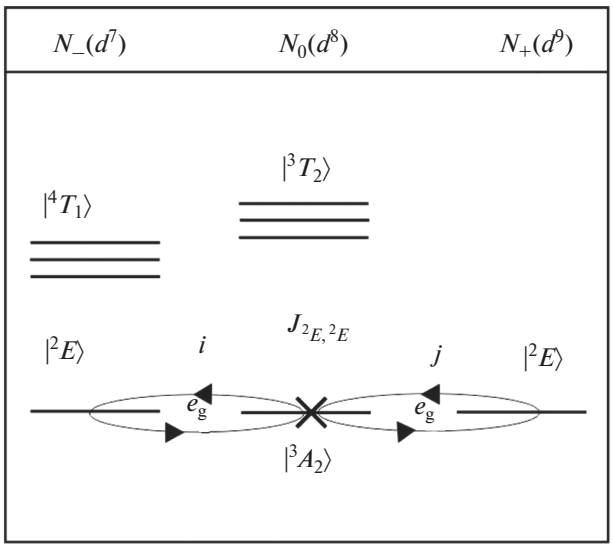

Fig. 2. The graphical scheme of the main contribution $J_{^2E,^2E}$ to AFM superexchange interaction in NiO monoxide at high pressure.

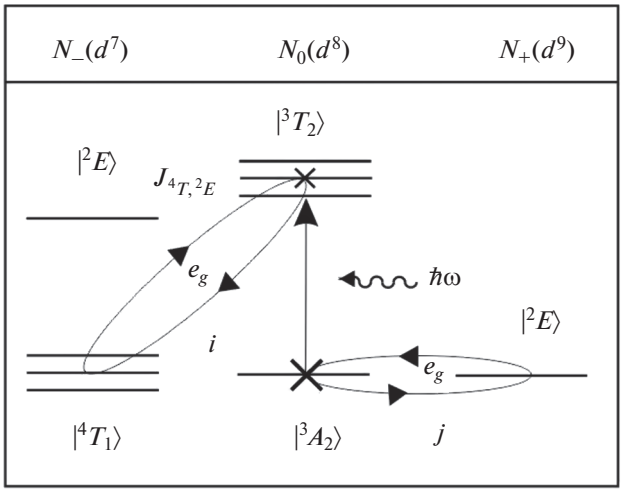

Fig. 3. The graphic scheme of the FM exchange interaction $J_{^4T,^2E}$ of the optical excited Ni^{2+} ion (i) with the neighboring ion (j) in the ground state of NiO.

In the case of NiO the optical occupation of the first excited state on the nickel ion leads to a change in the sign of the exchange interaction of this ion with the neighboring ion in the ground state from AFM to FM, since now the ground state of the d^{n-1} sector makes the main contribution to the exchange (Fig. 3).

CHANGES IN EXHANGE INTERACTION UNDER OPTICAL PUMPING IN RARE-EARTH FERROBORATES

It is known that the structural sublattices of the Fe^{3+} and Nd^{3+} ions in rare-earth ferroborates possess both intrinsic and mutual AFM ordering. Optical studies of the rare-earth AFM ferroborates $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ [9, 10] with $T_N = 32K$ demonstrate that some of the optically excited states of Nd^{3+} ions change the nature of the exchange interaction to the FM type. For example, the orientation of the magnetic moment of the Nd^{3+} ion in optically f–f excited states at the frequency of the bands $D1\left({}^4G_{5/2}, M_J = \pm 1/2\right)$ and $D2\left({}^4G_{5/2}, M_J = \pm 5/2\right)$ is different with respect to the magnetic moment of the ground ion state [10]. For states in the $D2$ absorption band, the magnetic moment is opposite to the original in the ground state. Thus the d–f exchange interaction between iron and rare earth ions depends on the nature of the state of the Nd^{3+} ion. We have generalized our approach to calculating optically induced changes in the f–d interaction. For this we used the approach developed earlier in [3] and its graphical representation. It turnes out that in rare-earth borates, even in the ground unexcited state, there are two $J_{^5E,^5I_4}$ (AFM) and $J_{^3H_4,^5T_2}$ (FM) contributions. Virtual electronic hopes corresponding to them are shown in Fig. 4. It can be seen that the AFM and FM contributions differ not only in the spin involved in the superexchange of multielectron states, but also in the type of overlap e_g–$4f$ and t_{2g}–$4f$ respectively, through the same boron–oxygen group.

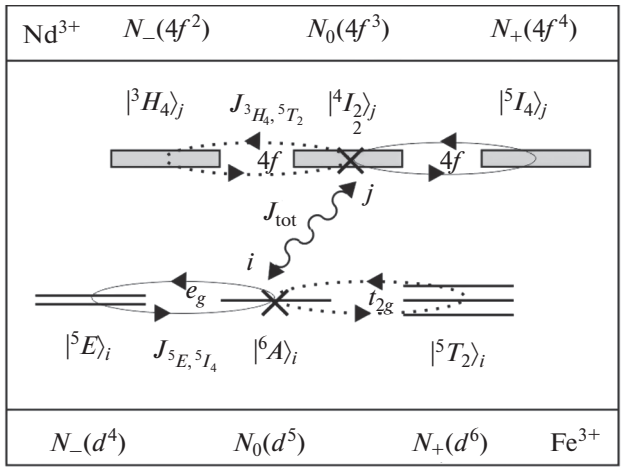

Fig. 4. The graphic scheme of the f–d exchange interaction $J_{\rm tot}$ in rare earth borates, where the $J_{^5E,^5I_4}$ contribution from AFM virtual hopping (solid line) is proportional to e_g–$4f$ overlapping, and FM $J_{^3H_4,^5T_2}$ contribution from the virtual hopping (dotted line) is proportional to t_{2g}–$4f$ types of overlap respectively.

Analyzing the superexchange interaction in rare-earth ferroborates we took into account that the ground $\left|{}^4I_{\frac{9}{2}}\right\rangle_j$ state of the Nd^{3+}ion is practically "pure", and it can be described within the *LS*—Russell–Saunders scheme [11]. Comparing with experimentally observed AFM ordering we conclude that the $J_{^5E,^5I_4}$ contribution proportional to the e_g-4f overlap to d–f exchange interaction J_{tot} prevails.

However, the AFM interaction competes with FM contribution in the rare-earth ferroborates. The relationship between them really depends on the nature of the 4f state of the Nd^{3+} ion.

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