Orbitally dependent kinetic exchange in cobalt(II) pairs: origin of the magnetic anisotropy

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Abstract

A comprehensive theoretical study of the magnetic exchange between Co^{2+} ions is reported. Using the microscopic background we deduce the general Hamiltonian for a corner-shared bioctahedral system involving kinetic exchange, spin–orbit coupling and low-symmetry local crystal field. This Hamiltonian acting within orbitally degenerate ground manifold $^4(T_{1g})_A \otimes \,^4(T_{1g})_B$ of the cobalt pair is expressed in terms of orbital and spin operators. We elucidate the major electronic factors controlling the exchange anisotropy in the Co(II) pairs. The degree of the magnetic anisotropy is shown to depend on the strength of the cubic crystal field and on the relative efficiency of two kinds of electron transfer pathways (e–e and t_2–t_2) contributing to the kinetic exchange. An unusual role of spin–orbit interaction is revealed. This interaction tends to reduce the anisotropy caused by the orbitally dependent exchange. Finally, we discuss conditions of the applicability of the isotropic Lines' model conventionally accepted in magnetochemistry of cobalt clusters.
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1. Introduction

The study of the factors governing the magnetic anisotropy in transition metal compounds is directly related to the problem of the rational design of new single molecular magnets. In this view the systems comprising ions with unquenched orbital angular momenta seem to be quite attractive. Among them the exchange coupled polynuclear compounds of cobalt(II) are especially interesting as the systems exhibiting strong orbital contributions to the magnetic moments and thus strong magnetic anisotropy. This orbital magnetism arises from the ground orbital triplet $^4T_1$ of each cobalt(II) ion in a cubic crystal surrounding.

The study of the magnetic properties of the magnetic materials containing cobalt(II) ions always called many difficult theoretical questions which are still open. These questions arise mainly from the intrinsic complexity that is peculiar to the problem of the magnetic exchange in the presence of the unquenched orbital angular momenta. Most of the works dealing with the magnetic properties of cobalt complexes have been performed in the framework of the Lines theory [1,2] proposed more than 30 years ago. Lines developed an approximate approach to the problem of the magnetic exchange in which the low-lying levels of individual ions (Kramers doublets) stabilized by the relatively strong spin–orbit coupling are treated quantum-mechanically meanwhile the excited states are taken into account using molecular field approximation. This theory deals with the situation when the cobalt ions occupy perfect octahedral sites and hence no magnetic anisotropy is imposed. Recently axial distortions of the octahedral surrounding of cobalt ions were taken into account [3,4]. Finally, the approach [5] based on the application of the irreducible tensor

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operator technique enabled to advance in the diagonalization of the Hamiltonian that includes spin–orbit coupling, axial and rhombic distortions, exchange and Zeeman interactions. Providing more precise results this method encounters computational difficulties arising from the high dimensionalities of the energy matrices.

Irrespective of the computational difficulties the Lines' approach and all subsequent studies face a conceptual challenge. In fact, all theoretical studies of the cobalt clusters based on the assumption that the exchange interaction between cobalt ions is described by the Heisenberg Hamiltonian $H_{ex} = -2JS_AS_B$ acting in the spin space with $S_A = S_B = 3/2$. This simple form of the exchange has been successfully used in description of some cobalt(II) cluster compounds [3–6]. Nevertheless the study of the exchange interaction between orbitally degenerate ions [7–13] clearly demonstrated that the isotropic model, in general, is not applicable. In his basic paper [1] Lines mentioned this crucial issue, but the discussion of the applicability of the Heisenberg Hamiltonian remained out of the framework of his theory.

Here we propose a more comprehensive approach to the problem of exchange interaction in cobalt(II) clusters. This approach is based on the effective Hamiltonian that involves both spin and orbital degrees of freedom and takes into account orbital degeneracy of Co(II) ions. To build this Hamiltonian we use the microscopic theory of the kinetic exchange between the orbitally degenerate ions that explicitly takes into account the relevant electron transfer pathways as well as the local interactions (cubic and low-symmetry crystal fields, intrasite Coulomb and exchange interactions, and spin–orbit coupling). As distinguished from the Heisenberg Hamiltonian, the present Hamiltonian is essentially anisotropic. An important advantage of the microscopic approach is that it allows us to comprehend the underlying mechanisms of the magnetic anisotropy or, in other words, to realize how the magnetic anisotropy of the system depends on the basic parameters. In particular, we will demonstrate that under some conditions the anisotropy vanishes and hence the Lines theory proves to be applicable.

2. Kinetic exchange Hamiltonian for Co(II)-dimer

Hereunder we will derive the kinetic exchange Hamiltonian for the pair of equivalent Co(II) ions occupying the octahedral sites. In this case the ground state of each Co(II) ion is the orbitally degenerate state $^4T_{1g}$, so the Heisenberg spin Hamiltonian of the form $H_{ex} = -2JS_AS_B$ is not adequate to describe the exchange interaction and a more complicated Hamiltonian involving both spin and orbital operators is required.

Kinetic exchange appears as a second order contribution with respect to the intercenter hopping operator that acts as a perturbation. The effective second-order exchange Hamiltonian operating within the ground manifold $[^4T_{1g}(d^7)]_A \otimes [^4T_{1g}(d^7)]_B$ of the pair can be represented as follows:

$$H_{ex} = -\frac{1}{U} \sum_{\Gamma_A\Gamma_B\Gamma'_A\Gamma'_B} \sum_{\gamma_A\gamma_B\gamma'_A\gamma'_B} t(\Gamma_A\gamma_A, \ \Gamma_B\gamma_B)t(\Gamma'_A\gamma'_A, \ \Gamma'_B\gamma'_B)$$

$$\times \sum_{\sigma\sigma'} (c^+_{\Gamma_A\gamma_A\sigma} c_{\Gamma'_A\gamma'_A\sigma'} c_{\Gamma_B\gamma_B\sigma} c^+_{\Gamma'_B\gamma'_B\sigma'}$$

$$+ c^+_{\Gamma_B\gamma_B\sigma} c_{\Gamma'_B\gamma'_A\sigma'} c_{\Gamma_A\gamma_A\sigma} c^+_{\Gamma'_A\gamma'_A\sigma'}) \tag{1}$$

Here the operator $C^+_{\Gamma_i\gamma_i\sigma}(C_{\Gamma_i\gamma_i\sigma})$ creates (annihilates) electron with spin projection σ on the magnetic orbital $\varphi_{\Gamma_i\gamma_i}$ of the ion i, $\Gamma_i = t_2$ or e, γ_i label one-electron basis, and t is the hopping integral. We will use the real one-electron cubic basis related to the Cartesian local coordinate frames, so γ_i runs over $\xi_i \propto y_iz_i$, $\eta_i \propto x_iz_i$, $\zeta_i \propto x_iy_i$ (t_2–basis) and $u_i \propto 3z_i^2 - r_i^2$, $v_i \propto \sqrt{3}(x_i^2 - y_i^2)$ (e-basis). Finally, U is the excitation energy for the electron transfer from one magnetic center to the other resulting in charge-transfer (CT) electronic configurations $(d^8)_A - (d^6)_B$ and $(d^6)_A - (d^8)_B$. It is to be noted that different CT states have, in general, different energies which can be expressed in terms of the cubic crystal field (Dq) and Racah (A, B, C) parameters for the oxidized and reduced Co ions. A more comprehensive theory of the kinetic exchange that takes into account complex multiplet structure of the excited CT states implied by the Tanabe–Sugano diagrams has been developed recently in Refs. [9–13] and applied to the analysis of the magnetic properties of $[Ti_2Cl_9]^{3-}$ anion. The energy pattern of Co(II) is much more complicated so that consideration of Co systems requires some simplifications. For the sake of simplicity we neglect the differences between the excitation energies assuming that $A \gg B$, C, Dq.

Using tensorial properties of the creation and annihilation operators one can express the Hamiltonian in terms of many-electron orbital and spin operators. The details of this procedure can be found in Refs.[9–13]. Here we give only the final expression for the kinetic exchange Hamiltonian:

$$H_{ex} = \frac{1}{U} \sum_{\Gamma_A\Gamma_B\Gamma'_A\Gamma'_B} \sum_{\gamma_A\gamma_B\gamma'_A\gamma'_B} t(\Gamma_A\gamma_A, \ \Gamma_B\gamma_B)t(\Gamma'_A\gamma'_A, \ \Gamma'_B\gamma'_B)$$

$$\times \sum_{\Gamma\Gamma'} \sum_{\gamma\gamma'} \langle \Gamma_A\gamma_A\Gamma'_A\gamma'_A|\Gamma\gamma\rangle$$

$$\times \langle \Gamma_B\gamma_B\Gamma'_B\gamma'_B|\Gamma'\gamma'\rangle O^A_{\Gamma\gamma}O^B_{\Gamma'\gamma'} [F^{(0)}_{\Gamma\Gamma'}(\Gamma_A\Gamma'_A\Gamma_B\Gamma'_B)$$

$$+ F^{(1)}_{\Gamma\Gamma'}(\Gamma_A\Gamma'_A\Gamma_B\Gamma'_B)S_AS_B] \tag{2}$$

In Eq. (2) $O^i_{\Gamma\gamma}$ are the matrices of the cubic irreducible tensor operators acting within the orbital T_{1g}-manifold of the center i and S_i are the spin operators. The orbital operators are defined in such a way that

$\langle T_{1g}\|\boldsymbol{O}_{\Gamma}^i\|T_{1g}\rangle = \sqrt{3}$, so the matrix elements of these operators coincide with the Clebsch–Gordan coefficients appearing in the Wigner–Eckart theorem [14]. The explicit forms of orbital matrices $\boldsymbol{O}_{\Gamma\gamma}^i$ are given in Refs. [9,12]. Finally, $t(\Gamma_A\gamma_A, \Gamma_B\gamma_B)$ is the transfer integral that links orbitals $\Gamma_A\gamma_A$ and $\Gamma_B\gamma_B$.

3. Parameters of the kinetic exchange Hamiltonian for a corner-shared Co(II)-dimer of D_{4h} symmetry

For the evaluation of the parameters $F_{\Gamma\Gamma'}^{(0)}$ and $F_{\Gamma\Gamma'}^{(1)}$ in the Hamiltonian Eq. (2) one has to know the explicit form of the wave-function of the ground state of octahedrally coordinated Co(II) ion and the overall symmetry of the pair. The wave-function of the ground state is a mixture of two $^4T_{1g}$ terms[14] arising from strong crystal field electronic configurations $t_{2g}^5 e_g^2$ and $t_{2g}^4 e_g^3$:

$$\Phi_g(^4T_{1g}) = C_1\Phi[t_{2g}^5(^2T_{2g})e_g^2(^3A_{2g}), \ ^4T_{1g}]$$
$$+ C_2\Phi[t_{2g}^4(^3T_{1g})e_g^3(^2E_g), \ ^4T_{1g}] \quad (3)$$

where the coefficients are of the following form:

$$C_1 = \frac{1}{\sqrt{2}}\left\{1 + \frac{9B + 10Dq}{[(9B + 10Dq)^2 + 144B^2]^{1/2}}\right\}^{1/2},$$

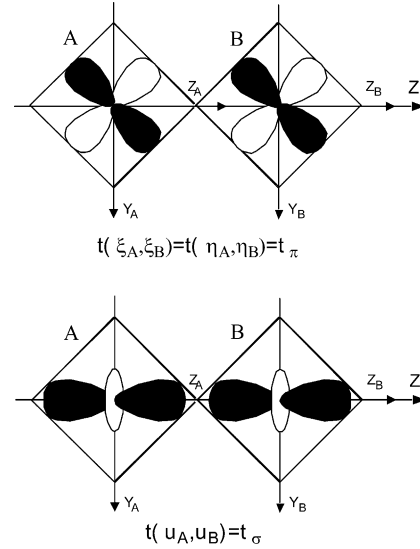$$C_2 = \frac{1}{\sqrt{2}}\left\{1 - \frac{9B + 10Dq}{[(9B + 10Dq)^2 + 144B^2]^{1/2}}\right\}^{1/2} \quad (4)$$

Fig. 1. The overlaps related to the relevant transfer pathways in a dimer of D_{4h} symmetry.

$\xi\leftrightarrow\xi$, $\eta\leftrightarrow\eta$ (π-transfer) and $u\leftrightarrow u$ (σ-transfer). The corresponding transfer integrals will be denoted as $t(\xi_A, \xi_B) = t(\eta_A, \eta_B)\equiv t_\pi$ and $t(u_A, u_B)\equiv t_\sigma$. Retaining only these dominant contributions one can express kinetic exchange Hamiltonian as:

$$\boldsymbol{H}_{\text{ex}} = \boldsymbol{R}_0 + \boldsymbol{R}_1\boldsymbol{S}_A\boldsymbol{S}_B \quad (5)$$

where $\boldsymbol{R}_0$ and $\boldsymbol{R}_1$ contain the orbital operators and have the following form:

$$\boldsymbol{R}_k = \frac{1}{U}\left\{\left[\frac{2}{3}t_\pi^2 F_{A_1A_1}^{(k)}(t_2t_2t_2) + \frac{1}{2}t_\sigma^2 F_{A_1A_1}^{(k)}(eeee)\right]\boldsymbol{O}_{A_1}^A\boldsymbol{O}_{A_1}^B + \left[\frac{1}{3}t_\pi^2 F_{EE}^{(k)}(t_2t_2t_2) + \frac{1}{2}t_\sigma^2 F_{EE}^{(k)}(eeee)\right]\boldsymbol{O}_{Eu}^A\boldsymbol{O}_{Eu}^B\right.$$

$$+ t_\pi^2 F_{EE}^{(k)}(t_2t_2t_2)\boldsymbol{O}_{Ev}^A\boldsymbol{O}_{Ev}^B + t_\pi^2 F_{T_1T_1}^{(k)}(t_2t_2t_2)\boldsymbol{O}_{T_1\gamma}^A\boldsymbol{O}_{T_1\gamma}^B + \frac{3}{2}t_\pi t_\sigma F_{T_1T_1}^{(k)}(t_2et_2e)(\boldsymbol{O}_{T_1\alpha}^A\boldsymbol{O}_{T_1\alpha}^B + \boldsymbol{O}_{T_1\beta}^A\boldsymbol{O}_{T_1\beta}^B)$$

$$+ t_\pi^2 F_{T_2T_2}^{(k)}(t_2t_2t_2)\boldsymbol{O}_{T_2\zeta}^A\boldsymbol{O}_{T_2\zeta}^B + \frac{1}{2}t_\pi t_\sigma F_{T_2T_2}^{(k)}(t_2et_2e)(\boldsymbol{O}_{T_2\xi}^A\boldsymbol{O}_{T_2\xi}^B + \boldsymbol{O}_{T_2\eta}^A\boldsymbol{O}_{T_2\eta}^B)$$

$$\left. - \left[\frac{\sqrt{2}}{3}t_\pi^2 F_{A_1E}^{(k)}(t_2t_2t_2) + \frac{1}{2}t_\sigma^2 F_{A_1E}^{(k)}(eeee)\right](\boldsymbol{O}_{A_1}^A\boldsymbol{O}_{Eu}^B + \boldsymbol{O}_{Eu}^A\boldsymbol{O}_{A_1}^B)\right\} \quad (6)$$

Providing $Dq/B \gg 1$ (weak crystal field limit) one finds $C_1 \approx 2/\sqrt{5}$, $C_2 \approx 1/\sqrt{5}$ (^4F-state of a free Co(II)-ion). In the opposite case of strong crystal field limit $Dq/B \gg 1$ one obtains $C_1 = 1$, $C_2 = 0$.

Let us specify now the overall geometry of the Co(II)-dimer and consider a corner-shared bioctahedral system belonging to the point group D_{4h}. As one can see from Fig. 1 the main contributions to the superexchange in this case arise from the most efficient transfer pathways

The parameters in Eq. (6) are calculated using the method described above, the results are given by Eq. (7). Eq. (7) combined with Eq. (4) provides the dependencies of the parameters of the Hamiltonian on the strength of the cubic crystal field (parameter B/Dq). An efficient procedure for treating orbitally dependent exchange Hamiltonian was suggested in our recent paper [12]. Following this procedure one can express the cubic irreducible tensors $\boldsymbol{O}_{\Gamma\gamma}^i$ defined in T_{1g} space through the

$$F^{(0)}_{A_1A_1}(t_2t_2t_2t_2) = -\frac{1}{3}(5C_1^2 + 4C_2^2)(C_1^2 + 2C_2^2) \qquad F^{(1)}_{A_1A_1}(t_2t_2t_2t_2) = \frac{4}{27}(C_1^2 + 2C_2^2)^2$$

$$F^{(0)}_{A_1A_1}(eeee) = -\frac{1}{2}(2C_1^2 + 3C_2^2)(2C_1^2 + C_2^2) \qquad F^{(1)}_{A_1A_1}(eeee) = \frac{2}{9}(2C_1^2 + C_2^2)^2$$

$$F^{(0)}_{EE}(t_2t_2t_2t_2) = \frac{2}{3}(C_1^2 - C_2^2)^2 \qquad F^{(1)}_{EE}(t_2t_2t_2t_2) = \frac{8}{27}(C_1^2 - C_2^2)^2$$

$$F^{(0)}_{EE}(eeee) = \frac{1}{2}C_2^4, \qquad F^{(1)}_{EE}(eeee) = \frac{2}{9}C_2^4$$

$$F^{(0)}_{T_1T_1}(t_2t_2t_2t_2) = -\frac{1}{4}(2C_1^2 - C_2^2)^2, \qquad F^{(1)}_{T_1T_1}(t_2t_2t_2t_2) = -\frac{1}{9}(2C_1^2 - C_2^2)^2$$

$$F^{(0)}_{T_2T_2}(t_2t_2t_2t_2) = \frac{1}{4}(2C_1^2 + C_2^2)^2, \qquad F^{(1)}_{T_2T_2}(t_2t_2t_2t_2) = \frac{1}{9}(2C_1^2 + C_2^2)^2$$

$$F^{(0)}_{T_1T_1}(et_2et_2) = F^{(0)}_{T_1T_1}(t_2et_2e) = -\frac{1}{2}C_1^2C_2^2, \qquad F^{(1)}_{T_1T_1}(et_2et_2) = F^{(1)}_{T_1T_1}(t_2et_2e) = -\frac{2}{9}C_1^2C_2^2$$

$$F^{(0)}_{T_2T_2}(et_2et_2) = F^{(0)}_{T_2T_2}(t_2et_2e) = \frac{3}{2}C_1^2C_2^2, \qquad F^{(1)}_{T_2T_2}(et_2et_2) = F^{(1)}_{T_2T_2}(t_2et_2e) = \frac{2}{3}C_1^2C_2^2$$

$$F^{(0)}_{A_1E}(t_2t_2t_2t_2) = F^{(0)}_{EA_1}(t_2t_2t_2t_2) = -\frac{\sqrt{2}}{3}(C_1^2 - C_2^2)(2C_1^2 + C_2^2), \qquad F^{(1)}_{A_1E}(t_2t_2t_2t_2) = F^{(1)}_{EA_1}(t_2t_2t_2t_2) = \frac{4\sqrt{2}}{27}(C_1^2 - C_2^2)(C_1^2 + 2C_2^2)$$

$$F^{(0)}_{A_1E}(eeee) = F^{(0)}_{EA_1}(eeee) = \frac{1}{2}C_2^4, \qquad F^{(1)}_{A_1E}(eeee) = F^{(1)}_{EA_1}(eeee) = -\frac{2}{9}C_2^2(2C_1^2 + C_2^2)$$

$$(7)$$

irreducible tensor operators of R_3-group (for the details see Ref. [12]).

4. Full Hamiltonian

There are several more interactions that are relevant to the system under consideration and should be taken into account in the model aimed to provide adequate description of the magnetic properties of the system of exchange-coupled Co(II)-ions. These interactions are the following:

(i) Spin–orbit coupling that splits the ground $^4T_{1g}$ term of Co(II) ion into Γ_6 (ground Kramers doublet), Γ_7 and two quadruplets Γ_8. The operator of spin–orbit interaction acting within the ground manifold with fictious orbital angular momenta $L_A = L_B = 1$ is given by:

$$H_{SO} = \kappa a\lambda(L_A S_A + L_B S_B) \qquad (8)$$

where λ is the spin–orbit parameter for a free ion ($\lambda \approx -180\ \mathrm{cm}^{-1}$) for Co(II)), κ is the orbital reduction factor that takes into account covalence effect. Depending on

the ligands this factor for Co(II) can vary from 0.6 to 0.9. The factor a is introduced to distinguish between the matrix elements of the orbital angular momentum operator calculated with the wave-functions of the ground $^4T_{ig}$ term with those calculated within P-basis. One can easily find that:

$$a = \frac{3}{2}C_2^2 - (C_1 + C_2)^2 \qquad (9)$$

Eq. (9) describes the dependence of a-factor on the strength of the cubic crystal field. In the weak field limit one obtains that $a = -3/2$ (the value used in most of the studies dealing with the magnetism of Co(II)-compounds including Lines theory [1,2]) and in strong crystal field limit one gets $a = -1$.

(ii) Low-symmetry crystal field operator. Very often the symmetry of the ligand environments of Co(II) ions is lower than O_h, so the additional components of the crystal field split the orbital triplet $^4T_{1g}$. The operator responsible for axial and rhombic distortions can be expressed in a conventional form:

$$H_{cr} = \sum_{i=A,B} \left\{ D\left[L_{iZ}^2 - \frac{1}{3}L_i(L_i+1) \right] + E(L_{iX}^2 - L_{iY}^2) \right\}$$

(10)

where D and E are the parameters of axial and rhombic distortions, respectively. While writing Eq. (10) we took into account that in the present study both metal sites are assumed to occupy structurally equivalent sites and hence $D_A = D_B \equiv D$ and $E_A = E_B \equiv E$.

(iii) Zeeman interaction operator can be represented as follows:

$$H_Z = \beta(a\kappa L + g_e S)H$$

(11)

where $L = L_A + L_B$ and $S = S_A + S_B$ are the operators of total orbital angular momentum and spin of dimer, respectively.

Our aim is to find the eigenvalues and the eigen-states of the full Hamiltonian involving all interactions introduced above:

$$H = H_{SO} + H_{cr} + H_{ex} + H_Z$$

(12)

To solve this problem one has to choose an appropriate basis for the dimer. The most convenient choice of this basis corresponds to the Russell–Saunders scheme in which two fictitious local orbital angular momenta $L_A = L_B = 1$ are coupled to give the total orbital angular momentum $L = 0, 1, 2$ and the local spins $S_A = S_B = 3/2$ are coupled to give the total spin $S = 0, 1, 2$. So, the matrix of the Hamiltonian (Eq. (12)) will be built using the wave-functions $|LSM_L L_S\rangle$ as a basis. Using the irreducible tensor operator technique for R_3 group [15] one can calculate the matrix elements of all operators involved in Eq. (12). We will not present here rather complicated expressions for the matrix elements and proceed to the discussion of the factors controlling the exchange anisotropy.

5. Discussion of the exchange anisotropy

As was already mentioned, in all approaches so far proposed for the description of the magnetic properties of Co(II) system, the exchange interaction between cobalt ions was assumed to have a simple Heisenberg form. At the same time the validity of the isotropic exchange model in the case of orbital degeneracy is not clear a *priori*. In this view it seems to be important to elucidate the main factors resulting in the origin of the exchange anisotropy in cobalt systems.

In order to realize with the utmost clarity the particular role of the main factors affecting the exchange anisotropy we will exclude the low-symmetry crystal fields from the consideration assuming thus that Co(II) ions are in the perfect octahedral ligand fields. At the first stage of the discussion we will exclude also the
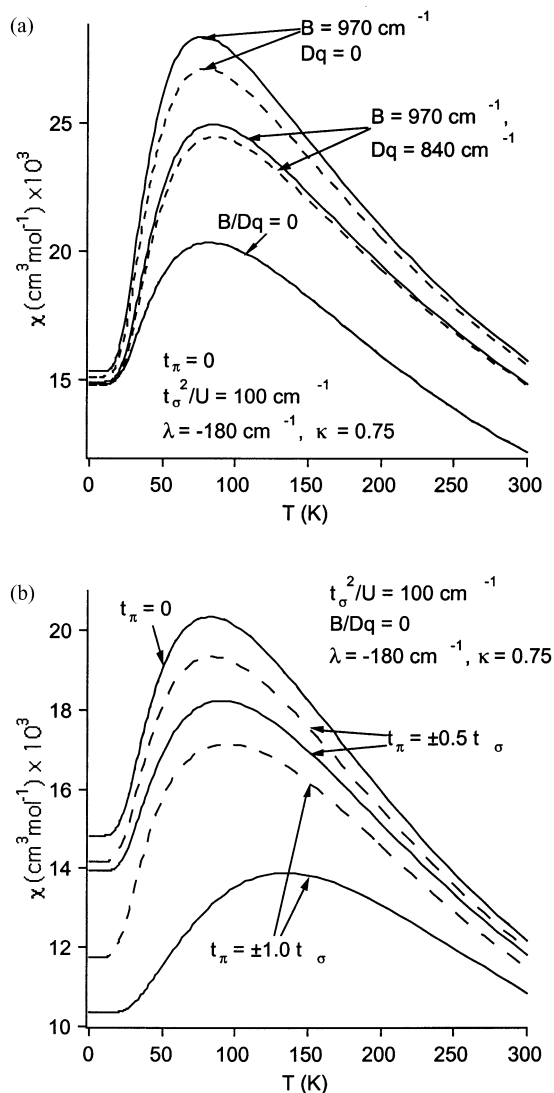

Fig. 2. Illustration for two factors resulting in the exchange anisotropy: (a) χ vs. T curves for different values B/Dq (only σ-transfer is involved); (b) χ vs. T curves for different values t_π/t_σ and $B/Dq = 0$. Here and in Fig. 3 the curves for $\chi_\parallel$ are shown by solid lines and for $\chi_\perp$ by dashed lines.

spin–orbit coupling and focus on the exchange interaction. Let us discuss separately different factors controlling the anisotropy.

5.1. Role of the cubic crystal field and e−e transfer

Let us start with the limit case when the transfer integral t_π is negligible comparatively to t_σ. Fig. 2(a) shows the temperature dependence of the magnetic susceptibility of the pair calculated for different values of cubic crystal field providing $t_\pi = 0$. One can see that in a strong crystal field limit $B/Dq = 0$ the system does

not posses magnetic anisotropy. In general case ($B/Dq \neq 0$) the curves χ vs. T exhibit a negative magnetic anisotropy ($\Delta\chi = \chi_{\perp} - \chi_{\|} < 0$) in the full temperature range. The magnetic anisotropy $|\Delta\chi|$ increases when we pass from the strong crystal field limit (isotropic case) to the weak crystal field limit when the mixing of two strong field $^4T_1$ terms is most efficient (maximal anisotropy). The isotropic result in the former case can be easily extracted from Eqs. (6) and (7). In fact by setting $t_\pi = 0$, $C_1 = 0$, $C_2 = 0$, ($B/Dq = 0$) one immediately arrives at the Heisenberg Hamiltonian:

$$H_{ex} = \frac{t_\sigma^2}{U}\left(-1 + \frac{4}{9}S_A S_B\right) \tag{13}$$

To realize the physical origin of the magnetic behavior depicted in Fig. 2(a) one can inspect the electronic subshells participating in the transfer processes. In fact, in the case under consideration the ground state of each Co(II) ion is $\Phi[t_{2g}^5(^2T_{2g})e_g^2(^3A_{2g}),\,^4T_{1g}]$, so t_σ transfer connects (via excited states) the orbitally non-degenerate subshells $e_g^2(^3A_{2g})$, resulting thus in the Heisenberg-type interaction. In general ($B/Dq \neq 0$) the ground state involves also a contribution of $\Phi[t_{2g}^4(^3T_{1g})e_g^3(^2E_g),\,^4T_{1g}]$ containing orbitally degenerate subshell $e_g^3(^2E_g)$. This results in the anisotropic contributions to the Hamiltonian. In fact, when $B/Dq \neq 0$ one finds that $C_2 \neq 0$ and hence the terms containing $O_{Eu}^A O_{Eu}^B$ and $O_{A_1}^A O_{Eu}^B + O_{Eu}^A O_{A_1}^B$ will appear along with the isotropic term. Applying the relation $O_{Eu}^i = 1 - 3/2 L_{iZ}^2$ one can see that these terms are expressed through L_{AZ}^2, L_{BZ}^2 and the product $L_{AZ}^2 L_{BZ}^2$. These terms produce a splitting of the eigenvalues of the isotropic Hamiltonian, Eq. (13), resulting thus in the axial exchange anisotropy.

5.2. Role of the t_2-t_2-transfer

The electron transfer between t_2 orbitals links orbitally degenerate $t_{2g}^5(^2T_{2g})$ subshells and for this reason this kind of transfer is expected to be an another origin of the exchange anisotropy. The role of t_2-t_2-transfer pathways in the limit of strong crystal field is illustrated in Fig. 2(b). In this case the exchange anisotropy associated with the electron hoppings between e-orbitals is excluded (only orbitally non-degenerate $e_g^2(^3A_{2g})$ subshells participate in t_σ transfer), so providing $t_\pi = 0$ the system exhibits isotropic magnetic behavior. When $t_\pi \neq 0$ the anisotropy appears due to the contribution of the orbitally degenerate $t_{2g}^5(^2T_{2g})$ subshells. As distinguished from the previous case, now the magnetic anisotropy is positive.

It should be noted that the values of B/Dq in Co(II) complexes are usually far from those in the strong crystal field limit. For example, the experimental values for the complexes with H_2O ligands [14] are $Dq = 840$ cm^{-1}, $B = 970$ cm^{-1}. Also, in reality, the transfer
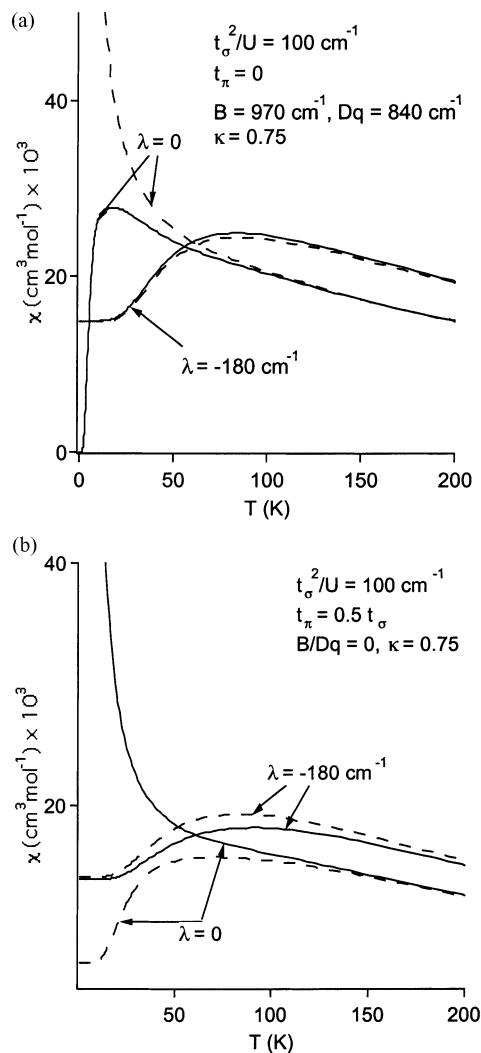

Fig. 3. Effect of reduction of the exchange anisotropy by spin–orbit interaction: (a) χ vs. T curves for $B/Dq \neq 0$, $t_\pi = 0$; (b) χ vs. T curves for $B/Dq = 0$, $t_\pi \neq 0$.

between t_2-orbitals can not often be neglected. Therefore the anisotropy of the magnetic exchange is, in general, a result of the interplay of both named contributions.

To complete this discussion we will compare a realistic situation when the spin–orbit parameter is taken to be $\lambda = -180$ cm^{-1} with the idealized situation when only the exchange interaction is operative but spin–orbit interaction is excluded. Fig. 3(a) shows χ vs. T curves for these two cases providing $t_\pi = 0$ when only the exchange anisotropy induced by cubic crystal field ($B/Dq \neq 0$) is retained. One can see that at $\lambda = 0$ the anisotropy is very high and positive. When the spin-orbit coupling is included the magnetic anisotropy changes the sign being at the same time strongly reduced comparatively to the case $\lambda = 0$.

The same two cases for the strong field limit ($B/Dq = 0$) and $t_\pi = 0.5t_\sigma$ are shown in Fig. 3b. In this case $\chi_{\|}$

diverges at low temperatures when $\lambda = 0$. This divergence appears due to first order orbital magnetic contribution to $\chi_\parallel$ while only a second order magnetic effect contributes to $\chi_\perp$. When $\lambda \neq 0$ the situation is similar to that previously considered, namely, the spin–orbit coupling strongly reduces the exchange anisotropy and changes its sign.

6. Concluding remarks

In this paper a comprehensive microscopic approach to the problem of the exchange interaction between cobalt(II) ions is developed. We have deduced the kinetic exchange Hamiltonian for corner-shared biocta-hedral Co(II) pair of D_{4h} symmetry, taking into account the relevant hopping integrals of σ- and π-types. An important effect of mixing of two ^4T_i terms arising from the electronic configurations $t_2^5 e^2$ and $t_2^4 e^3$ is taken into account. The main difference between our theory and the theory of Lines and subsequent studies is to be emphasized. In the Lines' approach [1,2] the un-quenched orbital angular momenta of cobalt ions is taken into account through the inclusion of the spin–orbit coupling and orbital part of Zeeman interaction. At the same time the exchange interaction is assumed to be of the isotropic form. Therefore, in this theory the unquenched orbital angular momenta by no means manifests itself in the exchange interaction. On the contrary, in the present paper the exchange Hamiltonian includes both spin and orbital operators and is essentially anisotropic. Along with the interactions directly involved in the exchange our approach includes also the spin–orbit coupling that is inherent to the magneto-chemistry of cobalt(II) ion and non-cubic crystal fields. All these interactions are expressed through the spherical irreducible tensor operators that provides an efficient way to treat the Hamiltonian. To summarize, the following results are to be emphasized:

(1) When only the transfer between e-orbitals is operative and $B/Dq \neq 0$, the exchange anisotropy is negative ($\chi_\parallel > \chi_\perp$). This anisotropy appears due to the mixing of two strong field ^4T_i terms. The absolute value of the anisotropy increases with the decrease of cubic crystal field (increase of B/Dq). In the strong crystal field limit ($B/Dq = 0$) the system becomes magnetically isotropic.

(2) When $B/Dq = 0$ and both kinds of transfer processes (e–e and t_2–t_2) are active, the anisotropy is of the opposite sign.

(3) If $B/Dq \neq 0$ and both transfer processes are involved, the sign of the anisotropy is determined by the competition of the contributions described in items (1) and (2).

In addition to these results it should be underlined that spin–orbit coupling can significantly reduce the exchange anisotropy. This is due to the fact that spin–orbit coupling operator does not commute with the exchange Hamiltonian. In other words spin–orbit coupling tends to keep spherical symmetry linking spin and orbital angular momenta on each site and reducing thus axial anisotropy caused by the orbitally dependent exchange. To make this assertion more clear the analogy with the situation in the Jahn–Teller systems seems to be relevant. In fact, spin–orbit coupling reduces Jahn–Teller distortions restoring thus spherical symmetry. Note that the ability of the spin–orbit coupling to suppress the magnetic anisotropy is in contradiction with the conventional belief that the spin–orbit interaction always favors the anisotropy. In general, this is true only for the individual Co^{2+} ions in which the spin–orbit coupling acts together with the local non-cubic crystal fields. In clusters along with this anisotropy the exchange anisotropy appears and this anisotropy is subjected to reduction by spin–orbit coupling.

The results outlined clearly show that the isotropic Lines model proves to be a good approximation if the cubic crystal field is strong and the parameters of t_2–t_2 transfer are negligible as compared to those for e–e transfer. Besides, the item (3) demonstrates that the Lines approach can be applicable also for some specific relationships between the t_2–t_2 transfer parameters and the value of B/Dq. In this situation the exchange anisotropy can become small as a result of interplay of two competing contributions. Finally the discussion of the role of spin–orbit coupling shows that the last makes less rigorous the restrictions of this theory implied by the anisotropy of exchange interaction. These arguments could probably explain why the Lines' theory proved to be successful in many cases despite the fact of completely ignoring the anisotropic orbital contributions to the exchange.

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