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Anisotropic double exchange in mixed-valence dimeric clusters of transition metal ions

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Abstract

In the mixed-valence (MV) [d^n–d^{n+1}] clusters of non-degenerate transition metal ions with the migration of the extra electron, taking the spin–orbit coupling into account in the double exchange (DE) model results in anisotropic double exchange interaction or anisotropic spin-dependent electron transfer which is described by the effective Hamiltonian $H^{\mathrm{AN}}_{\mathrm{DE}} = \sum_\alpha \sum_{n=x,y,z}[A_n t_\mu(\underset{\leftarrow\alpha^* n}{\hat{S}}\,\hat{\boldsymbol{\tau}}_{\alpha\beta}\underset{\rightarrow\beta^* n}{\hat{S}})+ B_n t_{\mathrm{v}}(\underset{\leftarrow\alpha^* n}{\hat{S}}\,\hat{\boldsymbol{\tau}}_{\alpha\beta}\underset{\rightarrow\alpha n}{\hat{S}} + \underset{\leftarrow\beta n}{\hat{S}}\,\hat{\boldsymbol{\tau}}_{\alpha\beta}\underset{\rightarrow\beta^* n}{\hat{S}})]$, $\boldsymbol{\tau}_{ab}$ is the one-electron DE operator. For the MV [d^8–d^9] cluster, the coefficients of the double exchange anisotropy $A_n t_\mu$, $B_n t_{\mathrm{v}}$ linearly depend on the DE parameters t_μ and t_{v} of the excited and ground cluster DE states. The one-center spin operators $\underset{\leftarrow\alpha^* n}{\hat{S}}$, $\underset{\rightarrow\beta^* n}{\hat{S}}$ ($\underset{\rightarrow\alpha n}{\hat{S}}$) act in the states of different localization. The anisotropic spin-transfer interaction $H^{\mathrm{AN}}_{\mathrm{DE}}$ is active between the states of different localization of the extra electron. Anisotropic double exchange coupling results in the zero-field splitting (ZFS) of the high-spin DE levels $E^0_\pm$ ($S = 3/2$). This splitting is described by the effective ZFS Hamiltonian $H^{\mathrm{t}}_{\mathrm{ZFS}} = D_{\mathrm{t}}\hat{\mathbf{T}}_{ab}[S^2_Z - S(S+1)/3] + E_{\mathrm{t}}\hat{\mathbf{T}}_{ab}(S^2_X - S^2_Y)$, where $\hat{\mathbf{T}}_{ab}$ is the double exchange operator in the S representation. The ZFS parameters D_{t} and E_{t} of the anisotropic DE origin are linearly proportional to the double exchange parameters t_μ. In the MV clusters, the ZFS operator $H^{\mathrm{t}}_{\mathrm{ZFS}}$ acts between the S states of different localization and should be added to the standard ZFS Hamiltonian $H^0_{\mathrm{ZFS}} = D_{\mathrm{S}}[S^2_Z - S(S+1)/3] + E_{\mathrm{S}}(S^2_X - S^2_Y)$, which is active in the localized states. The anisotropic double exchange contributions to the ZFS have different sign for the $E^0_+(S)$ and $E^0_-(S)$ DE states: $D[E^0_\pm(S)] = D_{\mathrm{S}} \pm D_{\mathrm{t}}$, $E[E^0_\pm(S)] = E_{\mathrm{S}} \pm E_{\mathrm{t}}$. The anisotropic DE contributions D_{t}, E_{t} to the cluster ZFS parameters ($D_{\mathrm{S}} \pm D_{\mathrm{t}}$, $E_{\mathrm{S}} \pm E_{\mathrm{t}}$) may be larger than the single-ion (D_{i},E_{i}) and anisotropic (pseudodipolar) exchange (D_{pd}, E_{pd}) contributions.

1. Introduction

The double exchange interaction was introduced to explain the magnetism of the mixed-valence manganates [1,2]. The resonance splitting of the spin levels of the MV [d^{n+1}–d^n] dimers due to the hopping of the extra electron between the d^{n+1} and d^n ions was described by the Anderson and Hasegawa [2] double exchange model

$$E_\pm(S) = \pm(S+1/2)t_0/(2s_0+1), \tag{1}$$

where t_0 is the electron transfer (ET) integral. In the MV dimeric systems, the Anderson and Hasegawa [2] double exchange (1) and Heisenberg exchange interaction $H_0 = 2J\vec{\mathbf{S}}_1\vec{\mathbf{S}}_2$ (t–J model) form the resulting exchange-resonance states $E^0_\pm(S) = JS(S+1) \pm B(S+1/2)$, where $B = t_0/(2s_0+1)$ is considered the effective DE parameter. The double

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exchange coupling or spin-dependent ET results in isotropic splittings: the Anderson–Hasegawa levels $E^0_\pm(S)$ depend only on the total spin S and are not mixed by the DE coupling.

The isotropic double exchange and Heisenberg exchange in dimeric MV clusters has been the subject of theoretical and experimental investigations [3–39]. Strong DE interaction ($B = 1350$ cm^{-1}, $t_0 = 6750$ cm^{-1}), which destroys the Heisenberg antiferromagnetic ordering ($J_{AF} = 70$ cm^{-1}, $J \ll B$) and results in the delocalized ground state $S_{gr} = S_{max} = 9/2$, was found first in the synthetic MV compound $[Fe_2(OH)_3(tmtacn)_2]^{2+}$ [14,15,20–22]. Strong DE interaction ($t_0 = 2250$–6750 cm^{-1} ($B = 450$–1350 cm^{-1}), $J = 5$–100 cm^{-1}, $J \ll B$) was found also for the MV [Fe(II)-Fe(III)] centers with delocalized $S_{gr} = 9/2$ in the synthetic compounds [26–28,30,31,39] and $[Fe_2S_2]^+$ centers of the *Clostridium pasterianum* mutant 2Fe ferredoxins [23,24,29]. Strong DE results in the $S_{gr} = 3/2$ ground state of the MV [Ni(II)Ni(I)] cluster [7]. Valence delocalized $[Fe_2S_2]^+$ pairs with strong DE were found in a variety of the trimeric $[Fe_3S_4]$ and tetrameric $[Fe_4S_4]$ iron–sulfur clusters in ferredoxins, enzymes and synthetic models [40,41]. The localized ferromagnetic [Fe(II)Fe(III)] dimers with $S_{gr} = 9/2$ were investigated in the model synthetic compounds [12,25,28,33] and native $[Fe_2S_2]^+$ R2 center of *Escherichia coli* ribonucleotide reductase [32].

Zero-field splittings (ZFS) of the delocalized cluster ground state with $S_{gr} = S_{max}$ is described by the standard effective ZFS Hamiltonian [42–49]:

$$H^0_{ZFS} = D_S\left[S_Z^2 - S(S+1)/3\right] + E_S\left(S_X^2 - S_Y^2\right) \tag{2}$$

with the axial D_S and rhombic E_S cluster ZFS parameters. The delocalized $S_{gr} = 9/2$ ground state of the MV [Fe(II)-Fe(III)] clusters of the model compounds {*Clostridium pasterianum* 2Fe ferredoxins} are characterized by large positive {negative} axial ZFS parameters: $D_{9/2} = +1.7$ to $+4$ cm^{-1}, $E_{9/2} = 0$–0.13 [15,31,39] {$D_{9/2} = -1.1$; -1.5 cm^{-1}, $E_{9/2} = 0.16$; 0.11 [23,24,29]}. The ground state $S_{gr} = 3/2$ of the MV [Ni(II)Ni(I)] cluster [7] {valence-delocalized [Fe(III)Fe(IV)] dimer of the low-spin ions [50–52]} is characterized by large positive axial ZFS parameter $D_{3/2} \geqslant 30$ cm^{-1} {$D_{3/2} = +38$ cm^{-1}}.

The ZFS contributions of individual ions (D_1, E_1; D_2, E_2) to the cluster ZFS were considered the origin of the ZFS of the $S_{gr} = 9/2$ state of the delocalized [15] and localized [32,33] [Fe(II)Fe(III)] MV clusters. The correlations $D_{9/2} = 1/6D_1 + 5/18D_2$ and $E_{9/2} = 1/6E_1 + 5/18E_2$ were used for the ZFS parameters of the $S_{gr} = 9/2$ ground state with the average of the local ZFS contributions due to delocalization [15], where D_1, E_1 (D_2, E_2) are the ZFS parameters of the ferrous (ferric) ion in the MV dimer.

The origin of magnetic anisotropy in the monovalent [d^n–d^n] clusters, role of the spin–orbit coupling (SOC), anisotropic (pseudodipolar (pd)) exchange inter-ion interaction

$$H_{pd} = a_x J_x S_{1x} S_{2x} + a_y J_y S_{1y} S_{2y} + a_z J_z S_{1z} S_{2z} \tag{3}$$

and anisotropic exchange contributions to ZFS were considered by Kanamori [48] (see also [49,57]). The ZFS of the levels S ($S \geqslant 1$) of the [d^n–d^n] clusters is described by the ZFS Hamiltonian (2) [49]. The origin of the axial D_S and rhombic E_S ZFS parameters for the exchange [d^n–d^n] dimers was considered in [48,49]. The dipole–dipole interaction [49] and single-ion ZFS [49,53,54] contribute to ZFS parameters D_S, E_S of dimers. The single-ion anisotropy and ZFS were discussed in [42–49,55,56].

The antisymmetric Dzyaloshinsky–Moriya exchange and symmetric anisotropic exchange in the exchange [d^n–d^n] dimers was introduced in [58,59] and discussed in [60,61].

For the MV systems, the account of the spin–orbit coupling for the transfer of hole between the neighboring sites in doped La_2CuO_4 [61] results in the spin–orbit hopping term and symmetric anisotropic exchange. Anisotropic double exchange for the MV dimers of orbitally degenerate ions was considered in [38].

For the MV [d^n–d^{n+1}] dimers of orbitally non-degenerate ions, taking SOC into account in the DE model (in the second order perturbation theory) results in an antisymmetric double exchange [62,63] interaction. The antisymmetric double exchange mixes the DE levels of the Anderson–Hasegawa model (1) that leads to the antisymmetric DE contributions to ZFS [62]. The anisotropic DE contribution to the axial ZFS parameters of the levels $E_\pm(S)$ was considered in the simplified model in [62].

The investigation of anisotropic effects and ZFS connected with anisotropic DE are of interest for the molecular magnetism, since the zero-field splittings of the high-spin ground states of the clusters are important for the molecular magnets, polynuclear metal centers in biological systems and their synthetic models. The anisotropic effects and ZFS contributions connected with the strong double exchange coupling were not considered in the double exchange model of the MV clusters.

The aim of this paper is to consider new anisotropic double exchange interaction, which is specific for the MV [d^n–d^{n+1}] clusters of orbitally non-degenerate ions with the double exchange coupling, and also the zero-field splittings of the high-spin DE levels, which are connected with the anisotropic DE. As will be shown on an example of the MV [d^8–d^9] cluster, the combined effect of spin–orbit interaction V_{SO} on the centers a and b and the isotropic double exchange