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Problem of the magnetic anisotropy in orbitally degenerate exchange and mixed-valence clusters

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Abstract

This contribution summarizes the results obtained in the problem of orbital degeneracy of the metal ions in exchange coupled and mixed-valence (MV) clusters. The theory of the double exchange is generalized and the orbitally degenerate systems are considered. The orbitally dependent double exchange parameter is deduced for the singlet–triplet and triplet–triplet transition metal pairs in three high-symmetric topologies. A new effective Hamiltonian of the magnetic exchange between the ions with unquenched orbital angular momenta is discussed. The technique of the irreducible tensor operators is applied to the problem of the kinetic exchange in these kind of metal clusters. Strong magnetic anisotropy is shown to appear in the exchange and MV clusters consisting of orbitally degenerate ions. The influence of the vibronic pseudo Jahn–Teller interaction on the degree of the magnetic anisotropy is discussed.

Keywords: Exchange interaction; Double exchange; Magnetic anisotropy; Mixed-valence compounds

1. Introduction

Molecular clusters of exchange coupled ions are currently important for the design of nanometer size magnets possessing unusual magnetic properties, in particular, paramagnetic-like behavior and quantum tunneling of magnetization [1,2]. They are also in focus of many areas of research such as solid state chemistry, magnetism and biochemistry.

The interplay between the electron delocalization (double exchange) and magnetic interactions crucially influences the properties of many mixed-valence (MV) compounds of current interest in solid state materials science. In the materials with the localized electrons the exchange interaction is responsible for the magnetic properties of these systems. Most of the existed models of the magnetic interactions took into consideration only orbitally non-degenerate terms of the interacting ions. Anderson and Hasegawa [3] proposed the theory of the double exchange and the usually accepted model for the magnetic exchange in the low-dimensional and extended materials was based on the Heisenberg–Dirac–Van Vleck (HDVV) model [4]. Recently we developed the theories of the magnetic exchange [5] and the double exchange [6,7] (see review article [8]) in materials containing orbitally degenerate ions in high-symmetric crystal fields. These orbitally degenerate ions carry an unquenched orbital angular momenta that give rise to a strong anisotropy of the exchange interaction in localized clusters and the anisotropy of the double exchange in delocalized (MV) clusters. In these view these systems seem to be of promising interest for the design of new nanosize magnetic materials. Hereunder we discuss the main approaches and the role of the orbital degeneracy in the problem of the exchange in localized and delocalized clusters paying attention on the main physical manifestations.

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2. Mixed-valence systems

2.1. Double exchange in degenerate systems

The theory of the double exchange proposed by Anderson and Hasegawa [3] is essentially based on the assumption that the ‘extra’ electron moves over non-degenerate magnetic orbitals and the interacting metal ions (in both oxidation degrees) are orbitally non-degenerate (spin systems). The main conclusion of the theory is that the delocalization of the extra electron over two spin cores produces a linear spin dependence of the double exchange splitting resulting thus in the ferromagnetic ground state of the dimer. The spin-dependent double exchange parameter is found as [3]:

$$t(S)=\frac{t\left(S+\frac{1}{2}\right)}{2S_0+1} \tag{1}$$

where t is the one-electron transfer parameter, S_0 is spin of the core.

As one can see the double exchange parameter depends on the full spin of the system and independent of the spin projection quantum numbers. In fact, this means that in spin systems the double exchange is magnetically isotropic. In a variety of compounds the metal ions possess orbitally degenerate ground states in a high-symmetric crystal surrounding. In this case the conventional theory of the double exchange proves to be inapplicable.

The electron transfer (double exchange) Hamiltonian in the binuclear systems composed from the orbitally degenerate metal ions can be presented in the following form:

$$\boldsymbol{V}=\sum_{\gamma\gamma'} t_{\gamma\gamma'}\sum_{\sigma}(a^{+}_{\gamma\sigma}b_{\gamma'\sigma}+b^{+}_{\gamma\sigma}a_{\gamma'\sigma})\equiv \boldsymbol{V}_{\mathrm{AB}}+\boldsymbol{V}_{\mathrm{BA}} \tag{2}$$

where the operator $a^{+}_{\gamma\sigma}$ creates electron on the orbital γ of site A with spin projection σ(↑ or ↓) and $b_{\gamma'\sigma}$ annihilates electron on the orbital γ′ of site B; $t_{\gamma\gamma'}\equiv t_{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}'}\equiv t_{\gamma_{\mathrm{B}}'\gamma_{\mathrm{A}}}$ are the one-electron transfer integrals. In Eq. (2) all relevant transfer pathways are included. We will consider transfer processes with participation of t_2 orbitals, so $\gamma,\ \gamma'=\xi,\ \eta,\ \zeta(\xi\propto yz,\ \eta\propto xz,\ \zeta\propto xy)$ denote cubic t_2 basis related to C_4 axes of the sites. In Refs. [6,7] the pairs ${}^3T_1(t_2^2)-{}^2T_2(t_2^1)$ and ${}^3T_1(t_2^2)-{}^4A_2(t_2^3)$ are considered in three high-symmetric topologies: edge-shared D_{2h}, corner-shared D_{4h}, and face shared D_{3h} bioctahedral units. Fig. 1 shows the effective overlap of the d-orbitals giving rise to the most efficient transfer pathways. T–P isomorphism [9] allows us to assign $T_{1(2)}$ bases to the P-states ($L=1$).

Calculation of the matrix of the double exchange operator in the general case of d^n-d^{n+1} pair gives the following result (for the details see our article [6]):

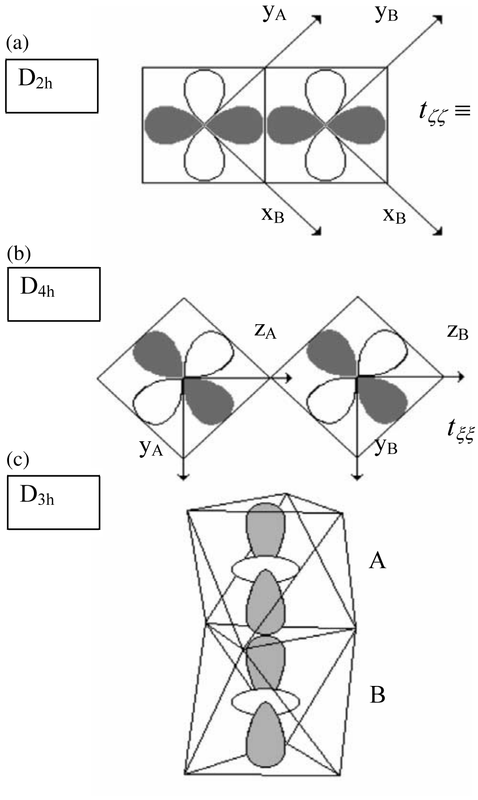

Fig. 1. The overlap patterns related to the most efficient transfer pathways: (a) $D_{2\mathrm{h}}$; (b) $D_{4\mathrm{h}}$; (c) $D_{3\mathrm{h}}$.

$$\langle\tilde S_{\mathrm{A}}\tilde L_{\mathrm{A}},\ \bar S_{\mathrm{B}}\bar L_{\mathrm{B}},\ SLM_{\mathrm{S}}M_{\mathrm{L}}|\boldsymbol{V}_{\mathrm{AB}}|\bar S_{\mathrm{A}}\bar L_{\mathrm{A}},\ \tilde S_{\mathrm{B}}\tilde L_{\mathrm{B}},\ S'L'M'_{\mathrm{S}}M'_{L}\rangle$$

$$=(-1)^{n+1+\bar S+\tilde S-S+\tilde L-\bar L}\delta_{\mathrm{SS'}}\delta_{M_{\mathrm{S}}M'_{\mathrm{S}}}\langle\tilde S\tilde L\|\boldsymbol{T}_{1\frac{1}{2}}\|\bar S\bar L\rangle^2$$

$$\times\begin{Bmatrix}\frac{1}{2} & \bar S & \tilde S\\ S & \bar S & \tilde S\end{Bmatrix}$$

$$\sqrt{2L'+1}\sum_{k=0,\ 1,\ 2}\sqrt{2k+1}\begin{Bmatrix}L & \tilde L & \bar L\\ L' & \bar L & \tilde L\\ k & 1 & 1\end{Bmatrix}$$

$$\times\sum_{mm'}t_{mm'}(-1)^{m'}\boldsymbol{C}^{k\ \ m-m'}_{\leftrightarrows 1\ m\ 1-m'}\boldsymbol{C}^{L\ \ M_L}_{L'\ M'_L\ k\ m-m'} \tag{3}$$

Here $\begin{Bmatrix}\cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot\end{Bmatrix}$ are the 6j-symbols, $\begin{Bmatrix}\cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot\end{Bmatrix}$ are the 9j-symbols. $\langle\tilde S_{\mathrm{A}}\tilde L_{\mathrm{A}}\|a^{\mathrm{A}}_{1\frac{1}{2}}\|\bar S_{\mathrm{A}}\bar L_{\mathrm{A}}\rangle$ is the reduced matrix element of the creation operator, the last can be considered as an irreducible tensor of rank 1 ($m,m'=0,+1,-1$) in the orbital subspace and as that of rank 1/2 in spin space, $t_{\mathrm{mm'}}$ are the transfer parameters in the angular momentum representation. $\tilde S\tilde L$ are the quantum numbers for the ground term for d^{n+1}, and $\bar S\bar L$ are those for d^n-ions, $\bar L=1(\tilde L=1)$ for orbital triplets and $\bar L=$

$0(\tilde{L}=0)$ for orbital singlets. One can see that the matrix of the double exchange is diagonal with respect to the spin quantum numbers S and M_S. The matrix element of the double exchange proves to be proportional to $S+1/2$ (this dependence is contained in the 6j-symbol in Eq. (3)). As one can see from Eq. (3), the effective double exchange parameter in the case of orbital degeneracy can be presented as:

$$t(SM_S,\ LM_L \rightarrow SM_S,\ L'M'_L) = \sum_{\substack{mm' \\ \text{(all transfer pathways)}}} t_{mm'} f(LM_L,\ L'M'_L)\frac{(S+1/2)}{2S_0+1} \qquad (4)$$

In Eq. (4) the double exchange parameter for orbitally degenerate dimers linearly depends on S and is independent of the spin projections M_S just as in the Anderson–Hasegawa theory, Eq. (1). In the case of orbitally degenerate systems the double exchange parameter depends on the orbital quantum numbers L, L', M_L, M'_L. This dependence reflects the magnetic anisotropy of the orbital subsystem and as a consequence the anisotropy of the system as a whole. As distinguished from the anisotropic contribution that appears like a small corrections to the isotropic terms in spin-systems, the anisotropy in degenerate systems appears as main effect of the orbitally dependent double exchange. For this reason we proposed [6] to refer this kind of the double exchange to as 'anisotropic double exchange'. Character of the anisotropy is closely related to the set of the relevant transfer integrals in Eqs. (3) and (4), reflecting both the point symmetry of the dimer and the specific choice of physically significant transfer pathways. Strong magnetic anisotropy of the double exchange is to be considered as the main physical consequence of the orbital degeneracy.

Fig. 2 shows the energy splitting for a singlet–triplet pair $^3T_1(t_2^2)-^4A_2(t_2^3)$ with different overall symmetries. Providing D_{2h}, D_{3h} symmetries (Fig. 2(a)) the energy pattern involves three pairs (signs + and −) of levels with $S = 1/2$, 3/2, 5/2; the energies are $\pm 1/3t'(S+1/2)$. All these levels correspond to $M_L = 0$. The spectrum contains also one highly degenerate level at $E = 0$. This level comprises states with all S values, each belonging to $M_L = \pm 1$. In the case of D_{4h} symmetry (Fig. 2(b)) we find the reverse situation. The state with $E = 0$ involves all S-values and corresponds to $M_L = 0$, while all the states with the energies $\pm 1/3t(S+1/2)$ possess $M_L = \pm 1$. One can see that the D_{4h} system exhibit strong magnetic anisotropy with the C_4 easy axis of magnetization meanwhile D_{2h}, D_{3h} systems are also anisotropic but possess only Van Vleck-type paramagnetism in the ground state. More complicated cases of the 'anisotropic double exchange' are considered in Ref. [6], special symmetry properties of the double exchange in the general case (when all relevant transfer pathways are taken into consideration) are revealed in Ref. [7].

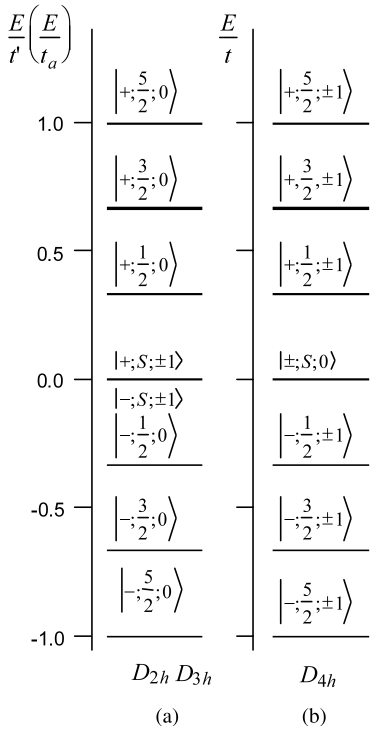

Fig. 2. Energy diagram for $^3T_1(t_2^2)-^4A_2(t_2^3)$ MV dimers: (a) D_{2h}, D_{3h}; and (b) D_{4h}. A short notation $|\pm; S, M_s L=1, M_L\rangle \equiv |S; M_L\rangle$ is used.

2.2. Vibronic model

The vibronic interaction in MV compounds is usually important and the manifestations of the mixed valency are closely related to the strength of the vibronic coupling. In order to illustrate (at least at the qualitative level) the main effects of the vibronic coupling we will use the vibronic model dealing with the local breathing modes (PKS model [10], see review paper [8]) and including also intercenter (stretching) vibrations as proposed by Piepho [11]. Such-type vibronic model was used in our paper [12] to study the adiabatic potentials and localization–delocalization effects in spin-dimers. We leave outside of our discussion the role of the local Jahn–Teller vibrations, this problem will be discussed elsewhere.

In order to inspect the role of vibronic effects in the context of the magnetic properties we will restrict ourselves by the most simple case of a singlet–triplet pair. Let us denote the coordinate of out-of-phase PKS vibration as q and that for the intercenter vibration as Q. PKS interaction mixes the states with the same quantum numbers S, M_S, M_L and opposite parity leading thus to the pseudo Jahn–Teller effect. On the other side the interaction with Q-mode is diagonal in

$|p;\ S;\ M_L\rangle$ basis. In fact, this interaction leads to the modulation of transfer integrals t and t' due to the changes of the metal–metal distances (see [8]). The S, M_L-block of the matrix of the vibronic Hamiltonian involving the interactions with the dimensionless q and Q vibrations can be presented as:

$$D_{2h}{:}\,\boldsymbol{V}_{ev}(S;\ M_L)=\frac{v}{\sqrt{2}}q\boldsymbol{\sigma}_X+\frac{\lambda}{3}(1-|M_L|)\left(S+\frac{1}{2}\right)Q\boldsymbol{\sigma}_Z,$$

$$D_{4h}{:}\,\boldsymbol{V}_{ev}(S;\ M_L)=\frac{v}{\sqrt{2}}q\boldsymbol{\sigma}_X+\frac{\lambda}{3}|M_L|\left(S+\frac{1}{2}\right)Q\boldsymbol{\sigma}_Z \qquad (5)$$

where $\boldsymbol{\sigma}_X$ and $\boldsymbol{\sigma}_Z$ are the Pauli matrices defined in the basis $|+;\ S;\ M_L\rangle, |-;\ S;\ M_L\rangle$, v and λ are the vibronic coupling parameters. The adiabatic surfaces are given by:

$$D_{2h}{:}\ U_{\pm}^{S;M_L}(q,\ Q)=\frac{1}{2}(\omega q^2+\Omega Q^2)\pm\left[\frac{1}{9}(t-\lambda Q)^2(1-|M_L|)\left(S+\frac{1}{2}\right)^2+\frac{1}{2}v^2q^2\right]^{1/2},$$

$$D_{4h}{:}\ U_{\pm}^{S;M_L}(q,\ Q)=\frac{1}{2}(\omega q^2+\Omega Q^2)\pm\left[\frac{1}{9}(t-\lambda Q)^2(|M_L|)\left(S+\frac{1}{2}\right)^2+\frac{1}{2}v^2q^2\right]^{1/2} \qquad (6)$$

where ω and Ω are the frequencies of q and Q modes, respectively. For both considered topologies the energy pattern contains highly degenerate level $\varepsilon=0$ comprising all S states with $M_L=\pm 1$ for D_{2h} and $M_L=0$ for D_{4h}. These levels give rise to the intersected paraboloids shifted along q axis to the points $\pm v/\omega\sqrt{2}$ ($Q=0$). The remaining surfaces belong to the definite S and their shapes are quite similar to those studied in details in our recent paper [12] dealing with the spin-systems. Let us summarize the main features of these adiabatic surfaces responsible for the magnetic behavior of the system.

Providing strong PKS coupling $v^2/2\omega>(\lambda^2/9\Omega)(S+1/2)^2$ and comparatively weak transfer $(t/3)(S+1/2)<(v^2/2\omega)-(\lambda^2/9\Omega)(S+1/2)^2$ we are dealing with the double-well surface so that in each minimum the excess electron is localized. In the case of strong PKS coupling and strong transfer $(t/3)(S+1/2)<(v^2/2\omega)-(\lambda^2/9\Omega)(S+1/2)^2$ the surface possesses the only minimum with shifted Q and the excess electron is fully delocalized. Finally, in the case of weak PKS coupling $v^2/2\omega<(\lambda^2/9\Omega)(S+1/2)^2$ the system is fully delocalized independently of the rate of transfer.

The vibronic interaction (pseudo Jahn–Teller effect [13–15]) in MV compounds is usually strong. In order to illustrate (at least qualitatively) the influence of the vibronic interaction we employ the PKS model dealing with the out-of-phase mode q. The main effect of the vibronic interaction is illustrated in Fig. 3 where the adiabatic potentials of a singlet–triplet pair $^3T_1(t_2^2)-{}^4A_2(t_2^3)$ are depicted. The vibronic interaction is operative within the sets of states with a given full spin S, Fig. 3 shows selected $S=5/2$ group of levels. One can see that the gap $2t$ between the levels with $S=5/2$, $M_L=0$ and $S=5/2$, $|M_L|=1$ is strongly reduced in a deep minima of the lower sheet of the adiabatic potential. In the limit of strong pseudo Jahn–Teller coupling one can see that the states with $M_L=0$ and $|M_L|=1$ become degenerate so that the electronic wavefunction in the minimum point can be identified with ^6P term of a spherically symmetric system. Thus the vibronic effect of the localization of the extra electron is accompanied by the reduction of the anisotropy induced by the double exchange in the orbitally degenerate system.

3. Magnetic exchange in the systems with unquenched orbital angular momenta

In the case of orbital degeneracy of the constituent ions, the isotropic spin-Hamiltonian of the magnetic exchange HDVV model becomes invalid even as a zeroth order approximation. In our recent papers [5]

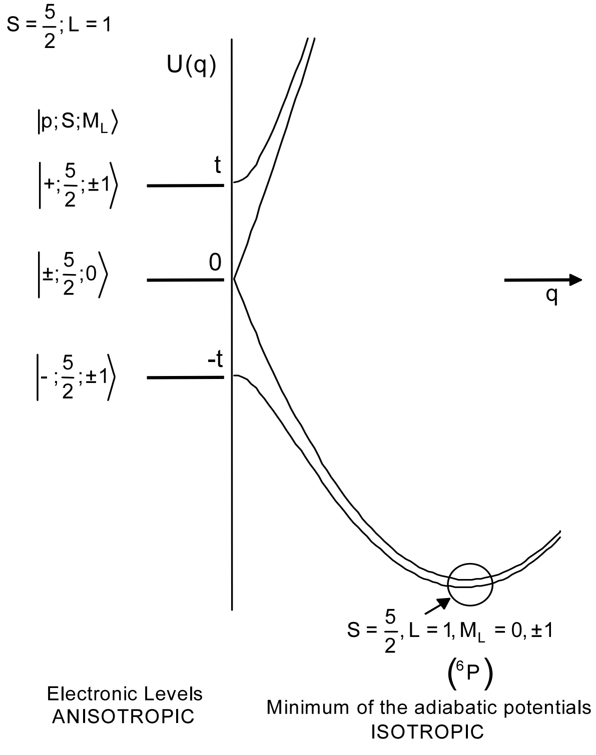

Fig. 3. Suppression of the magnetic anisotropy by PKS vibration: illustration for a singlet–triplet pair in the D_{4h} system.

we proposed a new approach to the problem of the kinetic exchange between orbitally degenerate many-electron transition metal ions. Our consideration takes into account explicitly complex energy spectrum of charge transfer crystal field states exhibited by the Tanabe–Sugano diagrams. Taking advantage from the symmetry arguments we have deduced the effective exchange Hamiltonian in its general form for an arbitrary overall symmetry of the dimer taking into account all relevant electron transfer pathways. The effective Hamiltonian was constructed in terms of spin-operators and standard orbital operators (cubic irreducible tensors). All parameters of the Hamiltonian incorporate physical characteristics of the magnetic ions in their crystal surroundings. In fact, they are expressed in terms of the relevant (in a given overall symmetry) transfer integrals and crystal field and Racah parameters for the constituent ions.

Along with the isotropic spin–spin interactions the effective Hamiltonian in the case of orbital degeneracy contains terms like $\boldsymbol{O}_{\Gamma_A\gamma_A}\boldsymbol{O}_{\Gamma_B\gamma_B}$ (orbital matrices) and mixed terms like $\boldsymbol{S}_A\boldsymbol{S}_B\boldsymbol{O}_{\Gamma_A\gamma_A}\boldsymbol{O}_{\Gamma_B\gamma_B}$ containing both types of operators. All these operators can be expressed in terms of the irreducible tensor operators acting in the orbital and spin subspaces. Then the effective Hamiltonian can be represented as linear combination of the irreducible products. The last step of the mathematical procedure involves decoupling of these products and the calculation of the eigenvectors and energy levels. Along with the orbitally dependent kinetic exchange the main factors controlling the magnetic anisotropy have been also studied in details: local low symmetry crystal fields, spin–orbit coupling, Coulomb interactions between unfilled shells.

The results can be illustrated by the application of the developed approach to the binuclear unit $[Ti_2Cl_9]^{-3}$ in $Cs_3Ti_2Cl_9$ that represents a face-shared ${}^2T_2$–${}^2T_2$ cluster with D_{3h} overall symmetry. Fig. 2c shows the most important electron transfer pathway t_a. The energy levels are obtained as the functions of the ratio t_e/t_a, where t_e is associated with the e-orbitals in the trigonal symmetry. The model takes into account also local trigonal crystal field (parameter Δ) and also spin–orbital coupling. Fig. 4 shows that the calculated magnetic susceptibility is in a good agreement with the experimental data [16]. In the agreement with the experimental data the system exhibits the magnetic anisotropy arising from the orbitally dependent exchange interaction.

4. Supplementary material

The material is available from the authors on request.

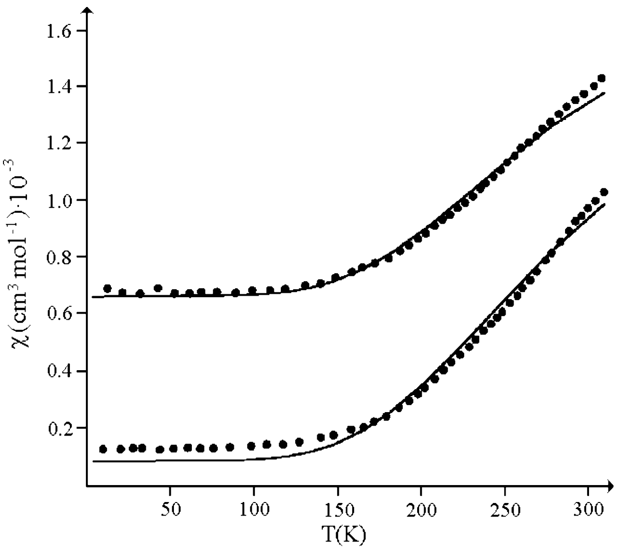

Fig. 4. Magnetic behavior of the $[Ti_2Cl_2]^{-3}$ unit: comparison with the theoretical curve (solid line) calculated at $t_e/t_a = -0.154$, $t_a = 52028$ cm^{-1}, $\Delta = -320$ cm^{-1}, $\lambda = 155$ cm^{-1} and orbital reduction $k = 0.71$.

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References

[1] D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, Science 265 (1994) 104.
[2] R. Sessoli, D. Gatteschi, A. Caneschi, M. Novaik, Nature 365 (1993) 141.
[3] P.W. Anderson, H. Hasegawa, Phys. Rev. 100 (1955) 675.
[4] O. Kahn, Molecular Magnetism, VCH, 1993.
[5] (a) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, J. Phys. Chem. 102 (1998) 200;
(b) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, J. Chem. Phys. 114 (2001) 1148;
(c) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, Chem. Phys. 274 (2001) 131;
(d) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, Chem. Phys. 274 (2001) 145;
(e) J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, J. Solid State Chem. 159 (2001) 280.
[6] J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, Chem. Phys. 254 (2000) 275.
[7] A.V. Palii, Phys. Lett. A 295 (2002) 147.

[8] J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Palii, B.S. Tsukerblat, Magnetic properties of mixed-valence systems: theoretical approaches and applications, in: J. Miller, M. Drillon (Eds.), Magnetoscience—From Molecules to Materials, Willey-VCH, 2001, pp. 155–210.

[9] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.

[10] K.Y. Wong, P.N. Schatz, Prog. Inorg. Chem. 28 (1981) 369.

[11] (a) S.B. Piepho, J. Am. Chem. Soc. 110 (1988) 6319;
(b) S.B. Piepho, J. Am. Chem. Soc. 112 (1990) 4197.

[12] J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado, S.M. Ostrovsky, A.V. Palii, B.S. Tsukerblat, Chem. Phys. 240 (1999) 14.

[13] R. Englman, The Jahn–Teller Effect in Molecules and Crystals, Wiley, London, 1972.

[14] I.B. Bersuker, V.Z. Polinger, Vibronic Interactions in Molecules and Crystals, Springer, Berlin 1989, Chem. Rev. 101(2001) 1067.

[15] B.S. Tsukerblat, Group Theory in Chemistry and Spectroscopy, Academic Press, London, 1994.

[16] B. Briat, O. Kahn, I. Morgenstern-Badarau, J.C. Rivoal, Inorg. Chem. 20 (1981) 4193.