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Article

Isotropic and Antisymmetric Double-Exchange, Zero-Field, Zeeman, and Hyperfine Splittings in Trinuclear Valence-Delocalized [Cu_3^{7+}] Clusters

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Valence delocalization in the [Cu_3^{7+}] trimer is considered in the model of the double-exchange coupling, in which full delocalization corresponds to the migration of the single $\bar{d}_{x^2-y^2}$ hole and relatively strong isotropic double-exchange coupling. Strong double exchange results in the pairing of the individual spins in the delocalized trimer even at room temperature. The model explains the delocalized singlet $^1A_1$ ground state in the planar $Cu_3(\mu_3\text{-}O)$ core by strong double exchange with positive double-exchange parameter t_0, whereas the delocalized triplet ground state of the [Cu_3^{7+}] trimer, which was observed in the $Cu_3(\mu_3\text{-}S)_2$ cluster, may be explained by the double exchange with relatively weak positive t_0: $0 < t_0 < 2J$ (degenerate ^3E ground state) or negative t_0 (triplet $^3A_2$ ground state). An analysis of the splitting of the delocalized degenerate ^3E term requires inclusion of the antisymmetric double-exchange interaction, which takes into account the spin–orbit coupling in the double-exchange model. The cluster parameter K_Z of the antisymmetric double-exchange coupling is proportional to t_0 and anisotropy of the g factor $\Delta g_{\|}$[Cu(II)], $K_Z \ll t_0$. Antisymmetric double exchange is relatively large in the [Cu_3^{7+}] cluster with the $d_{x^2-y^2}$ magnetic orbitals lying in the Cu_3 plane [$Cu_3(\mu_3\text{-}O)$ core], whereas for the $d_{x^2-y^2}$ magnetic orbitals lying in the plane perpendicular to Cu_3, antisymmetric double-exchange coupling is weak [$Cu_3(\mu_3\text{-}S)_2$ cluster]. The antisymmetric double-exchange coupling results in the linear zero-field splitting $\Delta_K = 2\sqrt{3}K_Z$ ($\sim t_0$) of the delocalized degenerate ^3E term that leads to strong anisotropy of the Zeeman splittings in the external magnetic field and a complex electron paramagnetic resonance (EPR) spectrum. The delocalized model of hyperfine interaction explains the hyperfine structure [10 hyperfine lines with the relative intensities 1:3:6:10:12:12:10:6:3:1 and the interval $a/3$] of the EPR transitions in the triplet states that was observed in the EPR spectra of the $Cu_3(\mu_3\text{-}S)_2$ cluster.

1. Introduction

Polynuclear clusters of Cu ions have attracted significant interest as active centers in several copper proteins, their synthetic models,[1,2] and models of molecular magnetism.[3] The mixed-valence (MV) [Cu_2(II)Cu(III)] clusters[4−8] represent the trigonal Cu_3 systems with a diamagnetic Cu(III) ion. The localized [Cu_2(II)Cu(III)] cluster in the [Cu_2(II)Cu(III)(μ-O)$_2$]$^{3+}$ core[4,5,8a] possesses the triplet ground state $S_{gr} = 1$, $J = 7$ cm^{-1}, and $H_0 = -2J\mathbf{s}_1\mathbf{s}_2$.[5] The synthesis and magnetic properties of the valence-delocalized [Cu_3^{7+}] clusters were recently described.[6,7] The hyperfine structure (10 hyperfine patterns) of the electron paramagnetic resonance (EPR) spectra at room temperature and at 10 K demonstrates the

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(1) (a) Solomon, E. I.; Sandaram, U. H.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563. (b) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521.

(2) (a) Lee, S. K.; George, S. D.: Antholine, W. E.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 6180. (b) Quinatar, L.; Yoon, J.; Aznar, C. P.; Palmer, A. E.; Andersson, K. K., Britt, R. D.; Solomon, E. I. *J. Am. Chem. Soc.* **2005**, *127*, 13832. (c) Oganesyan, V. S.; Rasmussen, T.; Fairhurst, S.; Thomson, A. J. *Dalton Trans.* **2004**, 996. (d) Chen, P.; George, S. D.; Carbito, I.; Antholine, W. E.; Moura, J. J. G.; Moura, I.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 744. (e) Gorelsky, S. I.; Ghosh, S.; Solomon, E. I. *J. Am. Chem. Soc.* **2006**, *128*, 278.

(3) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) *Molecular Magnetism: from Molecular Assemblies to the Devices*; Coronado, E., Delhaes, P., Gatteschi, D., Miller, J. S., Eds.; NATO Advanced Study Institute Series 321; Kluwer: Dordrecht, The Netherlands, 1996. (c) *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; NATO Advanced Study Institute Series 343; Kluwer: Dordrecht, The Netherlands, 1992.

(4) Cole, A. P.; Root, D. E.; Mukherjee, P.; Solomon, E. I.; Stack, T. D. P. *Science* **1996**, *273*, 1848.

(5) Root, D. E.; Henson, M. J.; Machonkin, T.; Mukherjee, P.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 4982.

(6) Brown, E. C.; York, J. T.; Antholine, W. E.; Ruiz, E.; Alvarez, S.; Tolman, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 13752.

(7) Mezei, G.; McGrady, J. E.; Raptis, R. G. *Inorg. Chem.* **2005**, *44*, 7271.

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valence delocalization among all three Cu centers of the triangle and a fully delocalized $S = 1$ ground state for the [Cu_3^{7+}] cluster of the [$Cu_2(II)Cu(III)(\mu\text{-}S)_2$]$^{3+}$ core.[6] The orbitally degenerate ^3E term is the ground state of the valence-delocalized [Cu_3^{7+}] cluster in the trigonal-bipyramidal centers.[5,6] The valence-delocalized [Cu_3^{7+}] cluster in the planar $Cu_3(\mu_3\text{-}O)$ core[7] is characterized by the orbital singlet $^1A_1$ ground state.[7] The energy spectrum of the valence-delocalized [Cu_3^{7+}] cluster was considered (see the Supporting Information of ref 6) in the Heisenberg model with strong ferromagnetic exchange. The influence of the valence delocalization on the spectrum of the valence-delocalized [Cu_3^{7+}] clusters and the origin of the splittings of the delocalized degenerate ^3E triplet were not considered.

In the valence-delocalized MV dimers, the migration of the extra d electron results in the Anderson−Hasegawa double-exchange splitting[9]

$$E_{\pm}(S) = \pm B(S + {}^1/_2) - JS(S + 1) \qquad (1)$$

where $B = t_0/(2s_0 + 1)$ is the double-exchange parameter[10−12] and t_0 the electron-transfer (ET) parameter. The double-exchange model is widely used for consideration of the valence-delocalized [$Fe^{2.5+}Fe^{2.5+}$] dimers in synthetic[10−25] and native[26] systems. Strong double-exchange coupling ($B = 800-1400\ cm^{-1}$) was found in compounds with the MV class III[30] fully delocalized [$Fe^{2.5+}Fe^{2.5+}$] dimers.[14−20] The double-exchange parameter B and Heisenberg exchange parameter J for the valence-delocalized [$Fe^{2.5+}Fe^{2.5+}$] dimers were calculated in the broken-symmetry density functional theory model.[11,15,19c,22,23] In trimeric MV [Fe_3S_4] and tetrameric MV [Fe_4S_4] centers of ferredoxins, enzymes, and synthetic model systems,[10−12,27−29] the valence delocalization is associated with double exchange within one [$Fe^{2.5+}Fe^{2.5+}$] pair.

The double-exchange model of trimeric [$d^nd^nd^{n\pm1}$] clusters[31−39] with delocalization of the extra electron over all three ions shows that the double exchange in the MV trimers cannot be explained by the Anderson−Hasegawa equation (1). The theory of the double-exchange parameters in tetramers and more complicated clusters was developed.[34a] The double-exchange model for the valence-delocalized [Cu_3^{7+}] cluster was not considered.

The degeneracy and the origin of the zero-field splitting (ZFS) of the valence-delocalized ^3E state are of interest for the trigonal valence-delocalized [Cu_3^{7+}] clusters because this splitting determines the EPR spectra and hyperfine structure.

Magnetic properties of the monovalent [$Cu_3(II)$] clusters[13,40−55] were described in the Heisenberg exchange

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(8) (a) Daul, C.; Fernandes-Ceballos, S.; Ciofini, I.; Rauzy, C.; Schläpfer, *Chem.—Eur. J.* **2002**, *8*, 4392. (b) Berces, A. *Chem.—Eur. J.* **1998**, *4*, 1297.

(9) Anderson, P. W.; Hasegawa, H. *Phys. Rev.* **1955**, *100*, 675.

(10) Girerd, J.-J. *J. Chem. Phys.* **1983**, *79*, 4788.

(11) (a) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316. (b) Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423.

(12) Blondin, G.; Girerd, J.-J. *Chem. Rev.* **1990**, *90*, 1359.

(13) Tsukerblat, B. S.; Belinsky, M. I.; Fainzilberg, V. E. *Sov. Chem. Rev.* **1987**, *9*, 337.

(14) (a) Ding, X.-Q.; Bominaar, E. L.; Bill, E.; Winkler, H.; Trautwein, A. X.; Drücke, S.; Chaudhuri, P.; Wieghardt, K. *J. Chem. Phys.* **1992**, *92*, 178. (b) Drücke, S.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Ding, X.-Q.; Bill, E.; Sawaryn, A.; Trautwein, A. X.; Winkler, H.; Gurman, S. J. *J. Chem. Soc., Chem. Commun.* **1989**, 59. (c) Ding, X.-Q.; Bominaar, E. L.; Bill, E.; Winkler, H.; Trautwein, A. X.; Drücke, S.; Chaudhuri, P.; Wieghardt, K. *Hyperfine Interact.* **1990**, *53*, 311.

(15) (a) Gamelin, D. R.; Bominaar, E. L.; Kirk, M. L.; Wieghardt, K.; Solomon, E. I. *J. Am. Chem. Soc.* **1996**, *118*, 8085. (b) Gamelin, D. R.; Bominaar, E. L.; Mathoniere, C.; Kirk, M. L.; Wieghardt, K.; Girerd, J.-J.; Solomon, E. I. *Inorg. Chem.* **1996**, *35*, 4323.

(16) Knapp, M. J.; Krzystek, J.; Brunel, L.-C.; Hedrickson, D. N. *Inorg. Chem.* **1999**, *38*, 3321.

(17) Peng, G.; van Elp, J.; Jang, H.; Que, L., Jr.; Armstrong, W. H.; Cramer, S. P. *J. Am. Chem. Soc.* **1995**, *117*, 2515.

(18) Hagadorn, J. R.; Que, L., Jr.; Tolman, W. B.; Prisecaru, I.; Münck, E. *J. Am. Chem. Soc.* **1999**, *121*, 9760.

(19) (a) Dutta, S. J.; Ensling, J.; Werner, R.; Flörke, U.; Haase, W.; Gütlich, P.; Nag, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 152. (b) Saal, C.; Bohm, M.; Haase, W. *Inorg. Chim. Acta* **1999**, *291*, 82. (c) Ostrovsky, S. M.; Werner, R.; Nag, K.; Haase, W. *Chem. Phys. Lett.* **2000**, *320*, 295.

(20) (a) Lee, D.; Krebs, K.; Huynh, H.; Hendrich, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 5000. (b) Lee, D.; DuBois, J. L.; Piers, B.; Hedman, B.; Hodgson, K. O.; Hendrich, M. P.; Lippard, S. J. *Inorg. Chem.* **2002**, *41*, 3172.

(21) (a) Borshch, S. A; Bominaar, E. L.; Blondin, G.; Girerd, J.-J. *J. Am. Chem. Soc.* **1993**, *115*, 5155. (b) Robert, V.; Borshch, S. A.; Bigot, B. *Chem. Phys. Lett.* **1995**, *236*, 491.

(22) (a) Barone, V.; Bencini, A.; Ciofini, I.; Daul, C. A.; Totti, F. *J. Am. Chem. Soc.* **1998**, *120*, 8357. (b) Ciofini, I.; Daul, C. A. *Coord. Chem. Rev.* **2003**, *238−239*, 187.

(23) Carissan, Y.; Heully, J.-L.; Alary, F.; Daudey, J.-P. *Inorg. Chem.* **2004**, *43*, 1411.

(24) Belinsky, M. I. *Chem. Phys.* **1999**, *240*, 303.

(25) Coropceanu, V.; Bredas, J. L.; Winkler, H.; Trauwein, A. X. *J. Chem. Phys.* **2002**, *116*, 8152.

(26) (a) Crouse, B. R.; Meyer, J.; Johnson, M. K. *J. Am. Chem. Soc.* **1995**, *117*, 9612. (b) Achim, C.; Golinelli, M.-P.; Bominaar, E. L.; Meyer, J.; Münck, E. *J. Am. Chem. Soc.* **1996**, *118*, 8168. (c) Achim, C.; Bominaar, E. L.; Meyer, J.; Peterson, J.; Münck, E. *J. Am. Chem. Soc.* **1999**, *121*, 3704.

(27) (a) Beinert, H.; Holm, R. H.; Münck, E. *Science* **1997**, *277*, 653. (b) Beinert, H. *J. Biol. Inorg. Chem.* **2000**, *5*, 2. (c) Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1.

(28) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

(29) (a) Papaefthymiou, V.; Girerd, J.-J.; Moura, L.; Moura, J.-J. G.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 4703. (b) Girerd, J.-J.; Papaefthymiou, V.; Surerus, K. K.; Münck, E. *Pure Appl. Chem.* **1989**, *61*, 805. (c) Bertini, I.; Ciurli, S.; Luchinat, C. *Struct. Bonding* **1995**, *83*, 1.

(30) Robin, M. B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.

(31) Belinsky, M. I. *Fiz. Tverd. Tela* **1985**, *27*, 1761; *Sov. Phys. Solid State* **1985**, *27*, 1057.

(32) Belinsky, M. I. *Mol. Phys.* **1987**, *60*, 793.

(33) (a) Pourrot, G.; Coronado, E.; Drillon, M.; Geores, R. *Chem. Phys.* **1986**, *104*, 73. (b) Gomes-Garsia, G. J.; Coronado, E.; Pourrot, G. *J. Appl. Phys.* **1990**, *67*, 5992. (c) Gomes-Garsia, G. J.; Coronado, E.; Pourrot, G.; Georges, R. *Phys. B: Condens. Matter* **1992**, *182*, 18.

(34) (a) Borras-Almenar, J. J.; Clemente, J. M.; Coronado, E.; Palii, A. V.; Tsukerblat, B. S.; Georges, R. *J. Chem. Phys.* **1996**, *105*, 6892. (b) Borras-Almenar, J. J.; Coronado, E.; Georges, R.; Palii, A. V.; Tsukerblat, B. S. *Chem. Phys. Lett.* **1996**, *249*, 7. (c) Borras-Almenar, J. J.; Coronado, E.; Tsukerblat, B. S. *Chem. Phys.* **1993**, *177*, 1.

(35) (a) Borras-Almenar, J. J.; Coronado, E.; Georges, R.; Palii, A. V.; Tsukerblat, B. S. *Phys. Lett. A* **1996**, *220*, 342. (b) Boldyrev, S. I.; Gamurar, V. Ya.; Tsukerblat, B. S.; Palii, A. V. *Mol. Phys.* **1994**, *81*, 621. (c) Palii, A. V.; Belinsky, M. I.; Tsukerblat, B. S. *Theor. Exp. Chem.* **1989**, *25*, 329.

(36) Gatteschi, D.; Tsukerblat, B. S. *Chem. Phys.* **1996**, *202*, 23.

(37) (a) Robert, V.; Borshch, S. A.; Bigot, B. *J. Phys. Chem.* **1996**, *100*, 580. (b) Borshch, S. A.; Chibotaru, L. F. *Chem. Phys.* **1989**, *135*, 375.

(38) (a) Belinsky, M. I. *Chem. Phys.* **1997**, *215*, 7. (b) Belinsky, M. I. *Chem. Phys.* **2001**, *263*, 279.

(39) Beissel, T.; Birkelbach, F.; Bill, E.; Glaser, T.; Kesting, F.; Krebs, C.; Weyhermiller, T.; Weinghardt, K.; Butzlaff, C.; Trantwein, A. X. *J. Am. Chem. Soc.* **1996**, *118*, 12376.

(40) (a) Beckett, R.; Colton, R.; Hoskins, B. F.; Martin, R. L.; Vince, D. G. *Aust. J. Chem.* **1969**, *22*, 2527. (b) Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537.

(41) (a) Griffith, J. S. *Struct. Bonding (Berlin)* **1972**, *10*, 87. (b) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313.

model, taking into account the Dzialoshinsky−Moriya[56,57] (D−M) antisymmetric exchange interaction $H_{DM} = \sum G_{ij}{}^{Z}[\mathbf{s}_i \times \mathbf{s}_j]_Z$, which splits linearly the ground spin-frustrated ^{2}E state of trigonal monovalent [Cu$_3$(II)] clusters.[13,42−47,53−55] Strong D−M antisymmetric exchange was found recently in the monovalent [Cu$_3$(II)] clusters,[53−55] $G_Z = 28{-}47$ cm^{-1}. Is the D−M antisymmetric exchange interaction H_{DM} also active in the splitting of the delocalized degenerate ^{3}E term of the valence-delocalized [Cu$_3{}^{7+}$] cluster?

The aim of the paper is to consider the isotropic double-exchange model and energy spectrum of the trigonal valence-delocalized [Cu$_3{}^{7+}$] clusters, the origin of the ZFS of the delocalized degenerate ^{3}E term, in particular, the role of the antisymmetric double exchange in ZFS, and the splittings in magnetic field and hyperfine structure of the EPR spectra.

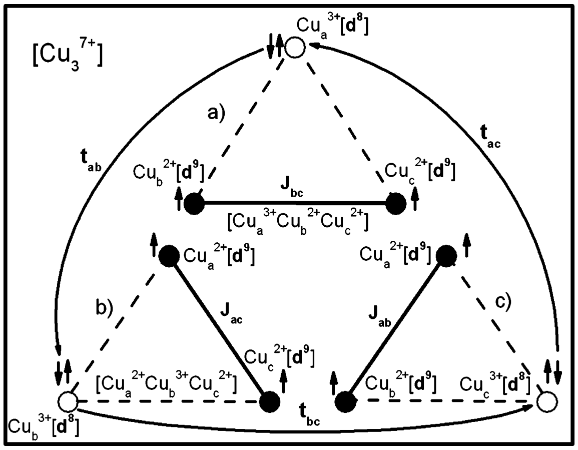

Figure 1. Three schemes of the localizations of the low-spin diamagnetic Cu(III) ion in the [Cu$_2$(II)Cu(III)] cluster and the d hole transfer (see the text).

2. Model of Isotropic Double Exchange for the Valence-Delocalized [Cu$_3{}^{7+}$] Cluster

The [Cu$_3{}^{7+}$] clusters[6,7] are the first examples of the trigonal trimers with full delocalization over all Cu sites (MV class III[30]). The three equivalent states $|i^*\rangle$ of the localization of the Cu(III) ion in the i apex of the Cu$_3$ triangle are shown schematically in Figure 1 for the trigonal cluster, i = a, b, c. The localized MV cluster includes two paramagnetic Cu(II) d^9 ions (solid circles) coupled by ferromagnetic[5] Heisenberg exchange, $J_{ij} = 7$ cm^{-1} [5] (Figure 1, solid lines). The Cu(III) site is diamagnetic[5−7] (low spin) because of the square-planar coordination[5−7] and strong ligand field.[58−60] The absence of the Heisenberg exchange interaction between the two paramagnetic Cu(II) ions and the diamagnetic low-spin Cu(III) ion (empty circles) is shown schematically by the dashed lines in Figure 1. The ground state of the low-spin Cu(III) d^8 ion is described by the spin singlet function[61] [b$_{2g}{}^2$e^{4}a$_{1g}{}^2$] = [(d$_{xy}$)^2(d$_{xz,yz}$)^2(d$_{z^2}$)^2].

In the d-hole approach[58] for the [Cu$_a$(III)Cu$_2$(II)] localized cluster, the two paramagnetic Cu(II) ions are described by the $d_{x^2-y^2}$ holes, $d_{x^2-y^2}$, $m_i = {}^1/_2 = \upsilon_i$, $d_{x^2-y^2}$, $m_i = -{}^1/_2 = \bar{\upsilon}_i$ ($d_{x^2-y^2} = \upsilon$[58,59]). The singlet wave function of the Cu$_a$(III) ion may be represented by the two paired $d_{x^2-y^2}$ holes $\chi_j^0 = |\upsilon_j\bar{\upsilon}_j|$, $\chi_j^0 = \chi_j(s_j = 0, m_j = 0)$, [$(\uparrow\downarrow)_j$ in Figure 1]. The localized [Cu$_2$(II)Cu(III)] system is represented schematically (Figure 1) as the three $d_{x^2-y^2}$ ($m = {}^1/_2$) holes (↑) in the apexes of the triangle with localization of the fourth $\bar{d}_{x^2-y^2}$ hole ($m = -{}^1/_2$, ↓) at the unique Cu,[5] giving a low-spin Cu(III) site, s_0[Cu(III)] = 0. The localized cluster triplet and singlet spin-wave functions $\Phi_{a^*}(S,M)$ may be represented in the form of

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(42) Tsukerblat, B. S.; Belinsky, M. I. *Magnetochemistry and Radiospectroscopy of Exchange Clusters*; Shtiintsa: Kishinev, USSR, 1983.

(43) (a) Belinsky, M. I.; Tsukerblat, B. S.; Ablov, A. V. *Dokl. Phys. Chem.* **1972**, *207*, 911. (b) Belinsky, M. I.; Tsukerblat, B. S.; Ablov, A. V. *Fiz. Tverd. Tela* **1974**, *16*, 989; *Sov. Phys. Solid State* **1974**, *16*, 639. (c) Belinsky, M. I.; Tsukerblat, B. S.; Ablov, A. V. *Phys. Status Solidi B* **1972**, *51*, K71. (d) Belinsky, M. I.; Tsukerblat, B. S.; Ablov, A. V. *Mol. Phys.* **1974**, *28*, 283.

(44) (a) Tsukerblat, B. S.; Novotortsev, V. M.; Kuyavskaya, B. Ya.; Belinsky, M. I.; Ablov, A. V.; Bazhan, A. N.; Kalinnikov, V. T. *Sov. Phys. JEPT Lett.* **1974**, *19*, 277. (b) Tsukerblat, B. S.; Kuyavskaya, B. Ya.; Belinsky, M. I.; Ablov, A. V.; Novotortsev, V. M.; Kalinnikov, V. T. *Theor. Chim. Acta* **1975**, *38*, 131.

(45) (a) Belinsky, M. I. *Inorg. Chem.* **2004**, *43*, 739. (b) Shames, A. I.; Belinsky, M. I. *Phys. Status Solidi B* **1997**, *203*, 235.

(46) (a) Banci, L.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 2681. (b) Banci, L.; Bencini, A.; Dei, A. Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 4018. (c) Padilla, J.; Gatteschi, D.; Chaudhuri, P. *Inorg. Chim. Acta* **1997**, *260*, 217.

(47) Bencini, A.; Gatteschi, D. *EPR of Exchanged-Coupled Systems*; Springer: Berlin, 1990.

(48) (a) Chandhuri, P.; Karpenshtein, I.; Winter, M.; Bultzlaff, G.; Bill, E.; Trautwein, A. X.; Flörke, U.; Haupt, H.-J. *J. Chem. Soc., Chem. Commun.* **1992**, 321. (b) Colacio, E.; Dominguez-Vera, J. M.; Escuer, A.; Klinga, M.; Kiverkaes, R.; Romerosa, A. *J. Chem. Soc., Dalton Trans.* **1995**, 343. (c) Hulsbergen, F. B.; Hoedt, R. W. H.; Verschooz, G. C.; Reedijk, J.; Spek, L. A. *J. Chem. Soc., Dalton Trans.* **1983**, 539.

(49) (a) Costes, J.-P.; Dahan, F.; Lanrent, J.-P. *Inorg. Chem.* **1986**, *25*, 413. (b) Kwiatkowski, M.; Kwiatkowski, E.; Olechnowicz, A.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1988**, *150*, 65. (c) Azuma, M.; Odaka, T.; Takano, M.; Vander Griend, D. A. Poeppelmeier, K. R.; Narumi, Y.; Kindo, K.; Mizuno, Y.; Maekawa, S. *Phys. Rev. B* **2000**, *62*, R3588. (d) Angaridis, P. A.; Baran, P.; Boča, Cervantes-Lee, F.; Haase, W.; Mezei, G.; Raptis, R. G.; Werner, R. *Inorg. Chem.* **2002**, *41*, 2219.

(50) (a) Kodera, M.; Tachi, Y.; Kita, T.; Kobushi, H.; Sumi, Y.; Kano, K.; Shiro, M.; Koikawa, M.; Tokii, T.; Ohba, M.; Okawa, H. *Inorg. Chem.* **2000**, *39*, 226. (b) Lopes-Sandoval, H.; Contreras, R.; Escuer, A.; Vicente, R.; Bernes, S.; Nöth, H.; Leigh, G. J.; Barba-Berhens, N. *J. Chem. Soc., Dalton Trans.* **2002**, 2648. (c) Spiccia, L.; Graham, B.; Hearn, M. T. W.; Lasarev, G.; Moubaraki, B.; Murray, K. S.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1997**, 4089. (d) Nguyen, H.-H.; Shiemke, A. K.; Jacobs, S. J.; Hales, B. J.; Lingstrom, M. E.; Chan, S. I. *J. Biol. Chem.* **1994**, *269*, 14995.

(51) (a) Cage, B.; Cotton, F. A.; Dalal, N. S.; Hillard, E. A.; Rakvin, B.; Ramsey, C. M. *J. Am. Chem. Soc.* **2003**, *125*, 5270. (b) Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Hillard, E. A.; Petrukhina, M. A.; Smuckler, B. W. *C. R. Acad. Sci., Ser. IIc: Chim.* **2001**, *4*, 315.

(52) Cole, J. L.; Clark, P. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 9534.

(53) (a) Ferrer, S.; Lloret, F.; Bertomeu, I.; Alzuel, G.; Borras, J.; Garsia-Granda, S.; Liu-Gonsalez, M.; Haasnoot, G. *Inorg. Chem.* **2002**, *41*, 5821. (b) Ferrer, S.; Haasnoot, G.; Reedijk, J.; Muller, E.; Cindi, M. B.; Lanfranchi, M.; Lanfredi, A. M. M.; Ribas, J. *Inorg. Chem.* **2000**, *39*, 1859.

(54) Liu, X.; Miranda, M. H.; McInnes, T. J. L.; Kilner, C. A.; Harlow, M. A. *Dalton. Trans.* **2004**, 59.

(55) (a) Yoon, J.; Mirica, L. M.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **2004**, *126*, 12586. (b) Mirica, L. M.; Stack, T. D. P. *Inorg. Chem.* **2005**, *44*, 2131. (c) Yoon, J.; Solomon, E. I. *Inorg. Chem.* **2005**, *44*, 8076.

(56) Dzyaloshinsky, I. *J. Phys. Chem. Solids* **1958**, *4*, 241.

(57) Moriya, T. *Phys. Rev. Lett.* **1960**, *4*, 228; *Phys. Rev.* **1960**, *120*, 91.

(58) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1964.

(59) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition-Metal Ions in Crystals*; Academic Press: New York and London, 1970.

(60) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, U.K., 1970.

(61) DeKock, R. L.; Gray, H. B. *Chemical Structure and Bonding*; The Benjamin/Cummings Publishing Company: San Francisco, CA, 1980.

the Slater determinants

$$\Phi_{a*}(S{=}1,M{=}1) = |v_a\bar{v}_a v_b v_c|$$

$$\Phi_{a*}(0,0) = 1/\sqrt{2}(|v_a\bar{v}_a v_b\bar{v}_c| - |v_a\bar{v}_a\bar{v}_b v_c|) \tag{2}$$

$\Phi_{b*}(S,M)$ and $\Phi_{c*}(S,M)$ are obtained by the cyclic permutation of the a, b, and c indexes. The Heisenberg energies are the same in the three localizations because $J_{ij} = J$, $H_0 = -2J\sum_{ij=\mathrm{ab,bc,ac}}\mathbf{s}_i\mathbf{s}_j$, $E_0(0) = 0$, and $E_0(1) = -2J$.

In the double-exchange model for the MV trimers,[32] the valence delocalization (or migration of the Cu(III) site over all three centers) is described by the spin-dependent transfer of one $\bar{d}_{x^2-y^2}$ hole (Figure 1) or resonance interaction between the three equivalent localized states. The spin-dependent ET interaction between the $|\alpha*\rangle$ and $|\beta*\rangle$ states of localization is described by eq 3, $\alpha\beta$ = ab, bc, ca,

$$\langle\Phi_{\alpha*}(S{=}1)\,|V_{\alpha\beta}|\Phi_{\beta*}(S{=}1)\rangle = t_v$$

$$\langle\Phi_{\alpha*}(0)\,|V_{\alpha\beta}|\Phi_{\beta}*(0)\rangle = -t_v \tag{3}$$

where

$$t_v = \langle v_\alpha||v_\beta\rangle = \langle \mathrm{d}_{x^2-y^2}{}^{\alpha}||\mathrm{d}_{x^2-y^2}{}^{\beta}\rangle$$

is the ET σ-type integral, $V_{\alpha\beta}$, is the intercenter electron−electron interaction [of the direct Coulomb or indirect (trough ligands) type]. The double-exchange parameter[12] $B = t_0/(2s_0 + 1)$ is $B = t_0$ for the formally MV [Cu(II)Cu(III)] pair with s_0[Cu(III)] = 0. The spin-dependent $\bar{d}_{x^2-y^2}$ hole transfer between the cluster states of different localizations is shown schematically in Figure 1. The double-exchange coupling, which leads to full delocalization of the extra $\bar{d}_{x^2-y^2}$ hole over all three Cu centers, is stronger than the interactions that result in localization of the $\bar{d}_{x^2-y^2}$ hole at the center Cu(III).

For the delocalized [Cu$_3^{7+}$] cluster, the effective Hamiltonian of the isotropic double-exchange interaction has the form ($\alpha\beta$ = ab, bc, ac)

$$H^0_{\mathrm{DE}} = \sum_{\alpha\beta}\mathbf{T}_{\alpha\beta}t_v \tag{4}$$

$$\langle\Phi_{\alpha*}(1)\,|\mathbf{T}_{\alpha\beta}|\Phi_{\beta*}(1)\rangle = 1$$

$$\langle\Phi_{\alpha*}(0)\,|\mathbf{T}_{\alpha\beta}|\Phi_{\beta*}(0)\rangle = -1$$

where $\mathbf{T}_{\alpha\beta}$ is the double-exchange operator for the $\alpha\beta$ pair of the trimer, which describes the hole transfer (eq 3).

In the valence-delocalized [Cu$_3^{7+}$] system, the double exchange and Heisenberg exchange ($H_{tJ} = H^0_{\mathrm{DE}} + H_0$) form the energy spectrum

$$E(^1\mathrm{A}_1) = -2t, \quad E(^1\mathrm{E}) = t$$

$$E(^3\mathrm{A}_2) = 2t - 2J, \quad E(^3\mathrm{E}) = -t - 2J \tag{5}$$

where $t = t_{\mathrm{ab}} = t_{\mathrm{bc}} = t_{\mathrm{ac}} = t_v$ for the trigonal system. The double-exchange interaction (migration of the d hole) forms the delocalized trigonal states ^{3}A$_2$, ^{3}E, ^{1}A$_1$, and ^{1}E of the trigonal group of symmetry of the valence-delocalized [Cu$_3^{7+}$] cluster from the localized S = 1 and 0 states. The spectrum (5) differs in the sign of t from the spectrum of the delocalized MV [Cu$_2$(II)Cu(I)] cluster[32,64] (the $\bar{d}_{x^2-y^2}$ hole transfer with $t = t_v$ corresponds to the $\mathrm{d}_{x^2-y^2}$ ET with $t = -t_v$).

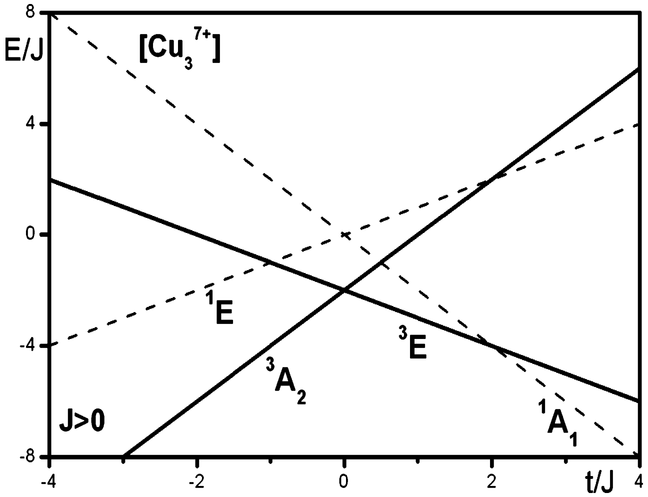

Figure 2. Dependence of the energy (E/J) of the delocalized levels of the valence-delocalized [Cu$_3^{7+}$] cluster on the double exchange (t/J parameter, where $J > 0$).

The spin functions that diagonalize the double-exchange coupling in the considered [Cu$_3^{7+}$] system have the form

$$\begin{aligned}
\Phi(^3\mathrm{A}_2) &= 1/\sqrt{3}[\Phi_{a*}(1) + \Phi_{b*}(1) + \Phi_{c*}(1)],\\
\Phi(^1\mathrm{A}_1) &= 1/\sqrt{3}[\Phi_{a*}(S{=}0) + \Phi_{b*}(0) + \Phi_{c*}(0)],\\
\Phi(^{2S+1}\mathrm{E}_x) &= 1/\sqrt{6}[2\Phi_{a*}(S) - \Phi_{b*}(S) - \Phi_{c*}(S)],\\
\Phi(^{2S+1}\mathrm{E}_y) &= 1/\sqrt{2}[\Phi_{b*}(S) - \Phi_{c*}(S)],\\
\Phi_{\pm}[^{2S+1}\mathrm{E}(M)] &= 1/\sqrt{2}\{\Phi[^{2S+1}\mathrm{E}_x(M)] \pm i\Phi[^{2S+1}\mathrm{E}_y(M)]\}
\end{aligned} \tag{6}$$

The spectrum and ground state of the valence-delocalized [Cu$_3^{7+}$] clusters depend on the sign and magnitude of the double-exchange (ET) parameter t and Heisenberg exchange parameter J (Figure 2). In the case of a strong double-exchange coupling $t \gg J$, where $t > 0$, the cluster ground state is the delocalized spin singlet ^{1}A$_1$ (Figure 2). The delocalized singlet ^{1}A$_1$ ground state of the double-exchange model (5) confirms the conclusion[7] that the ground state of the valence-delocalized [Cu$_3^{7+}$] cluster in the planar Cu$_3$(μ_3-O) core[7] is antiferromagnetic delocalized singlet ^{1}A$_1$. In the molecular orbital calculations,[7] D_{3h} symmetry of the planar Cu$_3$(μ_3-O) core generates linear combinations (of the a_1' and e′ symmetries) of Cu $\mathrm{d}_{x^2-y^2}$ orbitals, which lie in the Cu$_3$ plane.[7] The splitting in the Cu $\mathrm{d}_{x^2-y^2}$ manifold with the ^{1}A$_1$ ground state is 1.85 eV for this system.[7] The total double-exchange splitting between the ^{1}E and ^{1}A$_1$ terms is $\Delta[^1\mathrm{E},^1\mathrm{A}_1] = 3t$ in the model (5). One can roughly estimate the value of the double-exchange parameter $t \approx 5000$ cm^{-1}. The

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(62) Kanamori, J. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; Vol. 1, p 127.
(63) Belinsky, M. I. *Chem. Phys.* **2003**, *288*, 137.
(64) Belinsky, M. I. *Chem. Phys.* **2003**, *291*, 1.

double-exchange parameter in the valence-delocalized [$Fe^{2.5+}$-$Fe^{2.5+}$] clusters[14,15] is $B = 1350$ cm^{-1} and $t_u = 6750$ cm^{-1}.

The model of the valence-delocalized [Cu_3^{7+}] cluster with the singlet $^1A_1$ ground state[7] cannot explain the triplet ($S_{gr} = 1$) ground state, which was observed experimentally for the valence-delocalized [Cu_3^{7+}] cluster of the trigonal-bipyramidal $Cu_3(\mu_3\text{-}S)_2$ core.[6] The double-exchange model (5) results in a triplet spin ground state in the two cases (Figure 2).

(I) In the case of the relatively weak positive double-exchange coupling $0 < t < 2J$, the ground state of the system is an orbitally degenerate delocalized ^3E term (Figure 2). The delocalized triplet $^3A_2$ excited state is separated by the double-exchange interval $\Delta[^3A_2,{}^3E] = 3t$ (eq 5). The molecular orbital calculations of Solomon and co-workers[5] for the [Cu_3^{7+}] cluster in the trigonal-bipyramidal $Cu_3(\mu_3\text{-}O)_2$ core result in an orbitally degenerate triplet ^3E ground state. The splitting within the Cu $d_{x^2-y^2}$ manifold is relatively small[5] (~0.5 eV). Jahn–Teller distortion[5,8a] leads to localization of the valence electron in the $Cu_3(\mu_3\text{-}O)_2$ cluster with an $S = 1$ ground state because the vibronic stabilization energy in this cluster is larger than the electronic delocalization energy.[5] For the $Cu_3(\mu_3\text{-}S)_2$ cluster, the ground state is a fully delocalized $(e'')^2$ triplet state[6] and the Heisenberg singlet–triplet interval was estimated[6] as $E_{HS} - E_{LS} = -J$, where $J = 523$ cm^{-1}.

The authors[6] suggested that the two valence electrons are unpaired and fully delocalized at room temperature in the $Cu_3(\mu_3\text{-}S)_2$ cluster. In the double-exchange model (5) (Figure 2), valence delocalization in the [Cu_3^{7+}] cluster corresponds to full delocalization of one $\bar{d}_{x^2-y^2}$ hole. If the extra $\bar{d}_{x^2-y^2}$ hole (Figure 1) is fully delocalized over the three Cu centers at room temperature, relatively strong double-exchange coupling occurs in the system. In the valence-delocalized [Cu_3^{7+}] clusters, the electronic delocalization energy (double-exchange coupling) is larger than the vibronic stabilization energy, $t_0 > V_{vibr}$. In the valence-delocalized trimer, strong double-exchange coupling results in the pairing of the individual spins at room temperature ($S = 1$ and $S = 0$; eq 5 and Figure 2) even in the case of weak (or zero) Heisenberg exchange $J \ll t$.

In the case $0 < t < 2J$ (Figure 2), the interval $\Delta[^3A_2,{}^3E] = 3t$ may be on the order of 300–400 cm^{-1} and the delocalized $^3A_2$ excited-state level (magnetic moment $\mu = 2.8\ \mu_B$) may be thermally populated at room temperature. The EPR spectrum of the delocalized $^3A_2$ term with the 10-line hyperfine structure (see section 6) may be observed at room temperature. In this model, the EPR spectrum of the valence-delocalized ^3E ground-state term may be observed at low temperature.

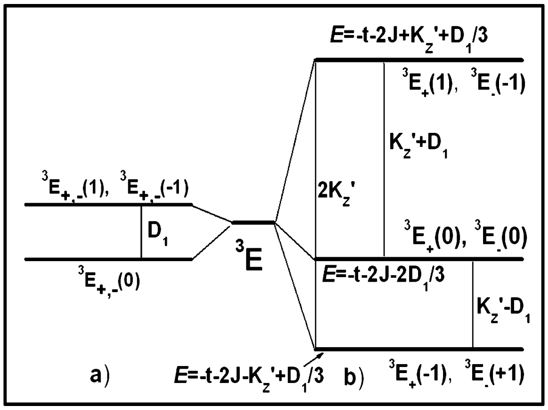

Figure 3. (a) Standard trigonal ZFS (H^0_{ZFS}; eq 7) of the degenerate ^3E term. (b) Linear ZFS of the delocalized degenerate ^3E term of the valence-delocalized [Cu_3^{7+}] cluster induced by the antisymmetric double-exchange coupling (eq 12).

(II) Double-exchange coupling with the negative ET parameter $t < 0$ leads to the valence-delocalized $^3A_2$ ground state (Figure 2). This valence-delocalized $^3A_2$ state is an orbitally nondegenerate triplet without a Jahn–Teller instability. In the case $-J < t < 0$, the first excited state is the valence-delocalized ^3E term (Figure 2). In the case of the strong double exchange $|t| \gg J$, only the lowest delocalized $^3A_2$ state is thermally populated at room temperature. The negative double-exchange parameter t can be realized in the MV trimers because the value and sign of t depend on the angle of overlap of the d orbitals in the trimers.[33a]

The isotropic double-exchange splittings for the slightly distorted [Cu_3^{7+}] trimer with nonequivalent ET parameters $t_{ab} = t_{ac} \neq t_{bc}$ are represented in eq 1A of Appendix A.

3. Antisymmetric Double-Exchange Splitting and ZFS of the Delocalized Degenerate ^3E Term

The delocalized degenerate ^3E term is the triplet ground state in the valence-delocalized [Cu_3^{7+}] centers of the bipyramidal clusters.[5,6] In the clusters with the delocalized $^1A_1$ (and $^3A_2$) ground state, the degenerate ^3E term is the first EPR-detectable excited state (Figure 2). The splitting of this ^3E term determines the EPR spectra. In a symmetrical ($t_{ij} = t$) delocalized [Cu_3^{7+}] cluster, the degeneracy of the delocalized ^3E term cannot be lifted by the electron–electron coupling. In the trigonal cluster, the ZFS of the triplet levels is described by the standard trigonal ZFS Hamiltonian[60]

$$H^0_{ZFS} = D_1[S_z^{\ 2} - S(S + 1)/3] \tag{7}$$

The axial ZFS parameter $D_{S=1}$ is formed by the anisotropic exchange[62] between the Cu(II) ions.[55a,c] The ZFS operator H^0_{ZFS} lifts only partially the degeneracy of the ^3E term (Figure 3a).

For consideration of the splitting of the delocalized degenerate ^3E term, it is necessary to go beyond the framework of the isotropic double-exchange model H^0_{DE} and include the antisymmetric double-exchange coupling.[63–67] This interion coupling in the MV systems is the result of taking into account the spin–orbit coupling (SOC) in the Anderson–Hasegawa[9] isotropic double-exchange model in second-order perturbation theory.

The antisymmetric double exchange in trimeric clusters of high-spin ions was considered in ref 64. We will use the results[64] for the valence-delocalized trimeric [Cu_3^{7+}] cluster

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(65) (a) Belinsky, M. I. *Phys. Status Solidi A* **2004**, *201*, 3293. (b) Belinsky, M. I. *J. Magn. Magn. Mater.* **2004**, *272–276*, e775.

(66) Belinsky, M. I. *Chem. Phys.* **2006**, *325*, 313, 326.

(67) Belinsky, M. I. *Chem. Phys.* **2004**, *308*, 27.

with the low-spin Cu(III) ion. The effective Hamiltonian of the antisymmetric double-exchange coupling for the valence-delocalized trimeric [Cu_3^{7+}] cluster has the form

$$H_1 = i\sum_{\alpha\beta}\{K^Z_{\alpha\beta}[(S_{\alpha Z} - S_{\beta Z})\mathbf{T}_{\alpha\beta} + \mathbf{T}_{\alpha\beta}(S_{\beta Z} - S_{\alpha Z})]\} \quad (8)$$

where $\mathbf{T}_{\alpha\beta}$ is the isotropic double-exchange operators (eq 4) and $\alpha\beta$ = ab, bc, ca is the cyclic condition for the pair indexes. The Hamiltonian of the spin-flop hopping in the form of annihilation and creation operators was considered[57,68,69] for the D−M exchange and for hole transfer[68a] in the hole-doped La_2CuO_4.

Only $K^Z_{\alpha\beta}$ components of the vector coefficients (8) of the antisymmetric ($K_{\alpha\beta} = -K_{\beta\alpha}$) double-exchange interaction in the pairs of the trimer contribute to the cluster parameter

$$K_Z = \frac{1}{3}(K^Z_{\text{ab}} + K^Z_{\text{bc}} + K^Z_{\text{ca}}) \quad (9)$$

$K_X = K_Y = 0$. The pair parameters $K^Z_{\alpha\beta}$ of the MV trimer ($\alpha\beta$ = ab, bc, ca)

$$K^Z_{\alpha\beta} = \frac{\lambda}{\Delta(\text{d}_{x^2-y^2},\text{d}_{xy})}[\langle \text{d}^{\alpha}_{x^2-y^2}|V_{\alpha\beta}|\text{d}^{\beta}_{xy}\rangle - \langle \text{d}^{\alpha}_{xy}||\text{d}^{\beta}_{x^2-y^2}\rangle] = \gamma_\zeta[\langle v_\alpha||\zeta_\beta\rangle - \langle \zeta_\alpha||v_\beta\rangle] \quad (10)$$

depend on (1) the double-exchange (ET) coupling between the $\text{d}_{x^2-y^2}$ ($=v$) ground state of the Cu_α ion and the d_{xy} ($=\zeta$) excited state on the neighboring Cu_β center of the trimer and (2) the SOC admixture of the d_{xy} excited state to the $\text{d}_{x^2-y^2}$ ground state. In the SOC admixture parameter $\gamma_\zeta = \lambda/\Delta(\text{d}_{x^2-y^2},\text{d}_{xy})$, λ is the SOC constant for the Cu(II) d^9 ion and $\Delta(\text{d}_{x^2-y^2},\text{d}_{xy})$ is the interval between the $\text{d}_{x^2-y^2}$ ground and d_{xy} excited states.[58]

The antisymmetric double-exchange coupling H_1 leads to the dependence of the double exchange on the projection M of S and the mixing of the sates with different total spins:

$$\langle\Phi_{\alpha*}(1,M)|\tilde{H}_{\text{DE}}|\Phi_{\beta*}(1,M)\rangle = t_v - iK^Z_{\alpha\beta}M;$$
$$\langle\Phi_{\alpha*}(0,0)|\tilde{H}_{\text{DE}}|\Phi_{\beta*}(0,0)\rangle = -t_v;$$
$$\langle\Phi_{\alpha*}(1,0)|H_1|\Phi_{\beta*}(0,0)\rangle = iK^Z_{\alpha\beta} \quad (11)$$

$\tilde{H}_{\text{DE}} = H_{\text{DE}} + H_1$ and $M = (\pm1, 0)$. Using eqs 11, 6, and 7, one obtains the splitting of the delocalized degenerate ^{3}E term, which is induced by the antisymmetric double exchange

$$E[^3\text{E}_\pm(M)] = -t_v - 2J \pm K'_Z M + D_1[(M^2 - 2)/3],$$
$$\Delta_K = E[^3\text{E}_\pm(\pm1)] - E[^3\text{E}_{\mp-}(\pm1)] = 2K'_Z; \quad K'_Z = \sqrt{3}K_Z;$$
$$D_1 = \frac{1}{3}(D^1_{\text{ab}} + D^1_{\text{bc}} + D^1_{\text{ca}}) \quad (12)$$

The antisymmetric double exchange H_1 results in the linear $\Delta_K = 2\sqrt{3}K_Z$ splitting of the delocalized degenerate ^{3}E term represented in Figure 3b ($K_Z > D_1$, where $D_1 > 0$). The antisymmetric double-exchange coupling H_1 results in the splitting of the valence-delocalized degenerate $^{2S+1}$E states in the delocalized MV trimers.[64]

In the framework of the effective Hamiltonian[58−60] method for individual d ions, the linear SOC of the orbital momentum of the trigonal ^{3}E term and total spin S is described by the effective Hamiltonian[59]

$$H_{\text{eff}} = \Delta\mathbf{T}(\text{A}_2)\, S_Z; \quad \mathbf{T}(A_2) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (13)$$

where $\mathbf{T}(\text{A}_2)$ is the orbital operator[59] [in the (u_+u_-) bases of the orbital E doublet], which coincides with the matrix of the operator L_Z. H_{eff} (eq 13) results in the splitting of the ^{3}E term:

$$\epsilon[^3\text{E}_\pm(\pm1)] = -\epsilon[^3\text{E}_\mp(\pm1)] = \Delta; \quad \epsilon[^3\text{E}_\pm(0)] = 0 \quad (14)$$

A comparison of eqs 12 and 14 shows that the Hamiltonian H_1 of the antisymmetric double exchange is the operator of the linear SOC between the total cluster spin S and the cluster orbital momentum formed by the migrating d hole in the delocalized [Cu_3^{7+}] trimer and oriented along the trigonal (Z) cluster axis, $\Delta = \sqrt{3}K_Z$.

H_1 mixes the isotropic double-exchange states with different spins S:

$$\langle\Phi[^3\text{E}_\pm(1,0)]|H_1|\Phi[^1\text{E}_\pm(0,0)]\rangle = -iK_Z;$$
$$\langle\Phi[^3\text{A}_2(1,0)]||\Phi[^1\text{A}_1(0,0)]\rangle = 2iK_Z \quad (15)$$

The splitting of the valence-delocalized ^{3}E term in a distorted [Cu_3^{7+}] trimer with the nonequivalent ET parameters $t_{\text{ab}} = t_{\text{ac}} \neq t_{\text{bc}}$ is represented in eqs 2A and 3A of Appendix A.

4. Orbital Origin of Antisymmetric Double Exchange in the [Cu_3^{7+}] Cluster

Antisymmetric double-exchange interaction originates from the combined effect of the SOC admixture of the excited states to the ground state of the Cu(II) ion and ET between the excited and ground states of the neighboring ions.[63−66] In the localized clusters $[\text{Cu}_2(\text{II})\text{Cu}(\text{III})]_{\text{loc}}$, the local crystal field forms orbitally nondegenerate ground state $\text{d}_{x^2-y^2} = v$ of the Cu(II) ion.[6,7] SOC admixes the excited state $\text{d}_{xy} = \zeta$ to the ground state $\text{d}_{x^2-y^2}$:[58,59] $v(\pm^1/_2) = v_0(\pm^1/_2) \pm i\gamma_\zeta\zeta(\pm^1/_2)$. In the $|\alpha*\rangle$ localization, it corresponds to an admixture of the excited-state cluster $\Phi'_{\alpha*}$ to the ground state $\Phi^0_{\alpha*}$: $\Phi_{\alpha*} = \Phi^0_{\alpha*} + i\gamma_\zeta\Phi'_{\alpha*}$. For the double-exchange matrix elements $\langle\Phi_{\alpha*}||\Phi_{\beta*}\rangle = \langle\Phi^0_{\alpha*}||\Phi^0_{\beta*}\rangle + i\gamma_\zeta[\langle\Phi^0_{\alpha*}||\Phi'_{\beta*}\rangle - \langle\Phi'_{\alpha*}||\Phi^0_{\beta*}\rangle]$, the standard isotropic double exchange (eq 11) describes the migration of the extra d hole between the neighboring MV Cu ions in the $\text{d}_{x^2-y^2}$ ground state (the first term in the right part). This strong isotropic double exchange (the parameter t_0) is accompanied by the antisymmetric double exchange (the second term) due to the SOC admixture

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(68) (a) Koshibae, W.; Ohta, Y.; Maekawa, S. *Phys. Rev. B* **1993**, *47*, 3391. (b) Koshibae, W.; Ohta, Y.; Maekawa, S. *Phys. Rev. B* **1994**, *50*, 3767. (c) Bonesteel, N. E.; Rice, T. M.; Zhang, F. C. *Phys. Rev. Lett.* **1992**, *68*, 2684.

(69) (a) Shekhtman, L.; Entin-Wohlman, O.; Aharony, A. *Phys. Rev. Lett.* **1992**, *69*, 836. (b) Shekhtman, L.; Aharony, A.; Entin-Wohlman, O. *Phys. Rev. B* **1993**, *47*, 174.

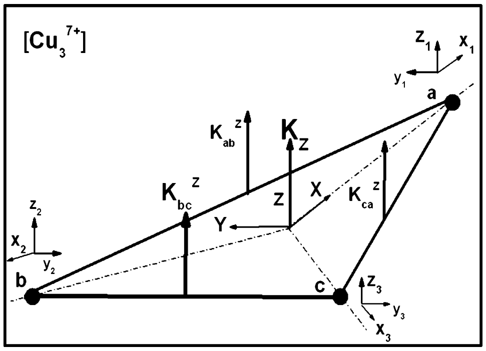

Figure 4. Cluster parameter K_Z of the antisymmetric double-exchange coupling H_1 of the valence-delocalized [Cu_3^{7+}] trimer, $K_Z = (K_{ab}^{Z} + K_{bc}^{Z} + K_{ca}^{Z})/3$ (see the text).

of the excited state (d_{xy}) and nonzero ET between the $\Phi_{\alpha*}^{0}$ ground and $\Phi'_{\beta*}$ excited states.

Microscopic calculations result in an expression (10) for the pair parameter $K_{\alpha\beta}^{Z}$ of the antisymmetric double-exchange coupling. Only a SOC admixture of the d_{xy} excited state determines the $K_{\alpha\beta}$ parameters. In the $K_{\alpha\beta}^{Z}$ coefficients, the ET integrals $\langle \upsilon_\alpha || \zeta_\beta \rangle$ and $\langle \zeta_\alpha || \upsilon_\beta \rangle$ of the coupling between the $d_{x^2-y^2}^{\alpha}$ orbital ground state of the α-Cu ion and the d_{xy}^{β} excited state of the neighboring β-Cu ion may be considered[64] with use of the approach to the local d functions, which was used in the theory of the D−M antisymmetric exchange in the monovalent dimers.[57,68] The d-orbital functions in $K_{\alpha\beta}^{Z}$ refer to the local Cartesian frame of each Cu ion in the trimer. The local coordinate frames are noncollinear in the trimer (Figure 4).

(1) For the cluster with the lobes of the ground-state $d_{x^2-y^2}^{\alpha}$ magnetic orbitals of individual ions lying in the plane of the Cu_3 triangle,[7] the local x_i axes are oriented along the C_2 axes, all z_i local axes are parallel to the cluster trigonal Z axis, and y_i axes are in the plane of triangle (Figure 4). The $d_{x^2-y^2}^{\alpha}$ orbital transforms in the $d_{x^2-y^2}^{\beta}$ orbital by the 120° rotation. The local 3d orbitals $d_{x^2-y^2}^{\alpha} = \upsilon_\alpha$ and $d_{xy}^{\alpha} = \zeta_\alpha$, where α = a, b, and c (in their local coordinate system), may be written in the cluster XYZ coordinate system (Figure 4) in the form

$$\upsilon_a = \upsilon'_A, \quad \zeta_a = \zeta'_A; \quad \upsilon_b = -\frac{1}{2}(\upsilon'_B + \sqrt{3}\zeta'_B),$$
$$\zeta_b = \frac{1}{2}(\sqrt{3}\upsilon'_B - \zeta'_B); \quad \upsilon_c = -\frac{1}{2}(\upsilon'_C - \sqrt{3}\zeta'_C),$$
$$\zeta_c = -\frac{1}{2}(\sqrt{3}\upsilon'_C - \zeta'_C) \quad (16)$$

$\varphi'_{A,B,C}$ are the d functions in the cluster XYZ coordinate system. The orbitals $d_{x^2-y^2}^{\alpha}$ and $d_{xz,yz}^{\beta}$ of the neighboring ions are orthogonal, which leads to $K_{\alpha\beta}^{X} = K_{\alpha\beta}^{Y} = 0$ and $K_X = K_Y = 0$. Using eq 16, one obtains the nonzero ET integrals $t_{\upsilon\zeta}$ between the ground $d_{x^2-y^2}^{\alpha}$ (υ_α) and excited d_{xy}^{β} (ζ_β) hole states of the neighboring ions of the trimer in the cluster XYZ system

$$\langle d_{x^2-y^2}^{\alpha} || d_{xy}^{\beta} \rangle = \langle \upsilon_\alpha || \zeta_\beta \rangle = -\langle \zeta_\alpha || \upsilon_\beta \rangle = -\frac{\sqrt{3}}{2} t'_\upsilon \quad (17)$$

where $\alpha\beta$ = ab, bc, and ca. Strong double-exchange coupling (17) between the υ_α ground and ζ_β excited states of the neighboring ions is determined by the geometry of the local d functions in the trigonal trimer (16): the orbitals $d_{x^2-y^2}^{\alpha}$ and d_{xy}^{β} of the neighboring ions are nonorthogonal in the trimer.[33a,55a,64]

The isotropic double-exchange parameter for the ground-to-ground state transfer of the $d_{x^2-y^2}$ holes has the form $t_0 = \langle \upsilon_\alpha || \upsilon_\beta \rangle = t_{\upsilon\upsilon} = (1/2)t'_\upsilon$ in the cluster coordinate system, where $t'_\upsilon = \langle \upsilon'_i || \upsilon'_j \rangle$ is the double-exchange parameter of the MV trimer in the cluster coordinate system, ij = AB, BC, CA, $t'_\upsilon = t'_\zeta = \langle \zeta'_i || \zeta'_j \rangle$ in the trigonal cluster, $\langle \zeta_\alpha || \zeta_\beta \rangle = (1/2)t'_\upsilon$. The parameters of the double exchange for ground-to-excited $t_{\upsilon\zeta}$ and ground-to-ground $t_{\upsilon\upsilon}$ states are comparable in magnitude and opposite in sign.

Using eqs 10 and 17, one obtains the components $K_{\alpha\beta}^{Z}$ of the pair vector coefficients of the antisymmetric double-exchange interaction in the MV trimer

$$K_{ab}^{Z} = K_{bc}^{Z} = K_{ca}^{Z} = -t'_\upsilon \gamma_\zeta \sqrt{3} = t'_\upsilon \Delta g_{||} \sqrt{3}/8 \qquad (18)$$

$t_{\alpha\beta} = \sqrt{(t_{\alpha\beta}^{0})^2 + (K_{\alpha\beta}^{Z})^2}$. The correlation $\Delta g_{||}(Cu^{2+}) = -8\lambda/\Delta_\zeta$[58,60] was used in eq 18 ($\gamma_\zeta \sim -0.05$; $\lambda = -700$ cm^{-1} [60]).

The $K_{\alpha\beta}^{Z}$ components of the vector pair $\mathbf{K}_{\alpha\beta}$ parameters are directed perpendicular to the $\alpha\beta$ side and parallel to the cluster Z axis (Figure 4). The cluster vector parameter has the form $\mathbf{K} = (\mathbf{K}_{ab} + \mathbf{K}_{bc} + \mathbf{K}_{ca})/3$. The K_X and K_Y components (in the Cu_3 plane) are equal to zero, which determines the axial form of the Hamiltonian H_1 (eq 8). The resulting cluster $\mathbf{K}$ parameter of the antisymmetric double exchange

$$K_Z = \frac{1}{3}(K_{ab}^{Z} + K_{bc}^{Z} + K_{ca}^{Z}) = t'_\upsilon \Delta g_{||} \sqrt{3}/8 \qquad (19)$$

$K_X = K_Y = 0$ is oriented along the trigonal Z axis (Figure 4). In the delocalized [Cu_3^{7+}] trimer, the cluster coefficient K_Z of the antisymmetric double exchange is linearly proportional to the ground-to-ground state double-exchange parameter t'_υ and the anisotropy of the g factor $\Delta g_{||}(Cu^{2+})$. Because $\Delta g_{||}\sqrt{3}/8$ can be estimated as ~0.05−0.08,[60] the value of K_Z may be relatively large, $K_Z \sim (0.05-0.08)t'_\upsilon$. The large magnitude of K_Z originates from the presence of efficient ground-to-excited state double-exchange pathways ($t_{\upsilon\zeta}$) for the cluster with the lobes of the ground $d_{x^2-y^2}^{\alpha}$ magnetic orbitals of individual ions lying in the plane of the Cu_3 triangle. At the same time, the antisymmetric double exchange is small in comparison with the isotropic double-exchange coupling, $K_Z \ll t'_\upsilon$. However, only antisymmetric double exchange splits the delocalized degenerate ^3E term and determines the magnetic anisotropy of the system.

Large positive ground-to-ground state double-exchange parameter $t_0 = (1/2)t'_\upsilon$ of the hole transfer corresponds to the singlet $^1A_1$ ground state (Figure 2). The ^3E term is the first excited state. This consideration does not take into account the role of the ligands in the hole transfer.

(2) The antisymmetric double exchange essentially depends on the orientation of the local d orbitals. In the case of the Cu_3 cluster with the lobes of the ground $d^{\alpha}_{x^2-y^2}$ magnetic orbitals of individual ions lying in the plane ($x_\alpha y_\alpha$) perpendicular to the Cu_3 triangle, $x_i || C_2$, all y_i local axes are parallel to the cluster trigonal Z axis and all z_i axes lie in the plane of the triangle.[5] In this case, the cluster parameter K_Z

$$K_Z = \frac{\sqrt{3}}{2}\gamma_\zeta \vartheta(2t'_\xi - t'_\upsilon) = \frac{\sqrt{3}}{16}\Delta g_{||}\vartheta(t'_\upsilon - 2t'_\xi) \qquad (20)$$

depends linearly on the double-exchange parameters ($t'_\upsilon - 2t'_\xi$), coefficient γ_ζ, and small angle ϑ of deformation, $K_X = K_Y = 0$. (The planes ($x_\alpha y_\alpha$) of the lobes of the $d^{\alpha}_{x^2-y^2}$ magnetic orbitals of each individual ion are slightly tilted on the angle $\vartheta(\ll 1)$ around the x_α axes.) The sign of K_Z in eq 20 depends on the relationship between the double-exchange parameters t'_υ and t'_ξ. The estimate leads to $K_Z \approx 1$ cm^{-1} for the parameters $t_{\upsilon\upsilon} = 500$ cm^{-1}, $t'_\upsilon \gg t'_\xi$, $\Delta g_{||} = 0.2$,[60] and $\vartheta = 0.1$. The linear ZFS ($\sim K_Z$) of the valence-delocalized ^{3}E term of the antisymmetric double-exchange origin is $\Delta_K \approx 3$ cm^{-1} in this case. In the considered case, the value of the ground-to-ground state isotropic double-exchange parameter t_0 [$t_{\upsilon\upsilon} = (t'_\upsilon - 6t'_u)/8$] may be relatively small and positive, which results in the ^{3}E ground state for $0 < t_0 < 2J$ (Figure 2), or negative, which results in the $^3A_2$ ground state.

In the case when the lobes of the Cu d_{xy} orbitals point at the ligands O and N in the bipyramidal [Cu_3^{7+}] cluster,[5] the K_Z parameter has the form in eq 20, $K_Z = 0$ for $\vartheta = 0$. The value of the ground-to-ground state double-exchange parameter for the hole transfer is $t'_\xi/2$; the ground state may be the delocalized ^{3}E term.

5. Comparison of the Antisymmetric Double Exchange with the D−M Exchange

The D−M antisymmetric exchange coupling H_{DM} plays the central role in the splitting of the spin-frustrated ^{2}E ground state of the [Cu_3(II)] clusters.[42−47,53−55] The action of the D−M exchange in the valence-delocalized [Cu_3^{7+}] cluster is different: The antisymmetric D−M exchange $H^0_{DM} = G^Z_{lm}[\vec{s}_l \times \vec{s}_m]_Z$ is active in the localized states (Cu_2(II) dimer; Figure 1) and results in the standard mixing of the levels with $S = 0$ and 1: $\langle \Phi_{k*}(1,0)|H_{DM}|\Phi_{k*}(0,0)\rangle = -iG^Z_{lm}/2$. For the valence-delocalized cluster, the Hamiltonian of the antisymmetric D−M exchange has the form (lm = ab, bc, ca)

$$H_{DM} = \sum_{lm} G^Z_{lm}[\vec{s}_l \times \vec{s}_m]_Z \qquad (21)$$

The antisymmetric D−M exchange H_{DM} (eq 21) does not result in the linear splitting of the valence-delocalized ^{3}E term (because the D−M exchange is not active in the triplet state).

The D−M exchange contributes to the mixing ($H_{mix} = H_1 + H_{DM}$) of the valence-delocalized states[64] with different total spins S and axial parameters $D_{eff}(^3\Gamma)$ of the ZFS splitting (7) of the triplet states:

$$\langle \Phi(^3A_2, M{=}0)|H_{mix}|\Phi(^1A_1, 0)\rangle = i\left(2K_Z - \frac{1}{2}G_Z\right)$$

$$\langle \Phi_\pm(^3E, 0)||\Phi_\pm(^1E, 0)\rangle = -i\left(K_Z + \frac{1}{2}G_Z\right) \qquad (22a)$$

$$D_{eff}(^3E) = D_1 + (K_Z + G_Z/2)^2/2(t + J)$$

$$D_{eff}(^3A_2) = D_1 + (K_Z - G_Z/4)^2/(|t| + J/2) \qquad (22b)$$

The microscopic theory of the D−M exchange was developed by Moriya,[57] and the D−M exchange parameters for the [Cu_3(II)] cluster were considered in refs 55a,c. In the case of the superexchange[57] coupling in the Cu_2^{II} pair of the [Cu_3^{7+}] cluster and for the magnetic $d_{x^2-y^2}$ orbitals lying in the Cu_3 plane (Figure 4), the cluster D−M exchange parameter has the form

$$G_Z = J_0 \Delta g_{||}\sqrt{3}/2$$

$$G_Z = \frac{1}{3}(G^Z_{ab} + G^Z_{bc} + G^Z_{ca}), \quad G_X = G_Y = 0 \qquad (23)$$

The D−M exchange coefficient G_Z is proportional to the superexchange parameter J_0,[57] whereas the coefficient of the antisymmetric double exchange K_Z (eq 19) is proportional to the double-exchange parameter t_0.

In the valence-delocalized MV trimer, the relationship between the parameters $K^Z_{\alpha\beta}$ and $G^Z_{\alpha\beta}$ (K_Z and G_Z) of the antisymmetric double-exchange coupling and the D−M exchange interaction is the following:

$$\frac{K^Z_{\alpha\beta}}{G^Z_{\alpha\beta}} = \frac{t_0}{2J_0}, \quad \frac{K_Z}{G_Z} = \frac{t_0}{2J_0} \qquad (24)$$

The antisymmetric double-exchange interaction in the valence-delocalized [Cu_3^{7+}] cluster may be stronger than the D−M antisymmetric exchange coupling, $K_Z \gg G_Z$, in the case of $t'_\upsilon \gg J_0$.

In the case of the direct exchange in the Cu_2(II) pair, the D−M exchange coefficient $G'_{ab} = -8\gamma_\zeta J^{\zeta_b \upsilon_a}_{\upsilon_a \upsilon_b}$ is proportional to the parameter $J^{\zeta_b \upsilon_a}_{\upsilon_a \upsilon_b}$ of the direct Heisenberg exchange coupling between the ground and excited states.[55a] In the cluster coordinate system (16), the cluster parameters are

$$G'_Z = 2\gamma_\zeta\sqrt{3}(J'_{\upsilon\upsilon} - J'_{\upsilon\zeta}), \quad J = (J'_{\upsilon\upsilon} + 3J'_{\upsilon\zeta})/4,$$
$$D'_1 = -\gamma_\zeta^{\,2}(3J'_{\upsilon\upsilon} + J'_{\upsilon\zeta}), \quad K_Z > G'_Z, \quad K_Z \gg D'_1 \qquad (25)$$

Equation 23 leads to the estimate $G_Z/|J_0| = 0.35$ for the value $\gamma_\zeta = -0.05$.[60] This relationship is close to the experimental observation[55a] $G_Z/|J_0| = 0.34$. The relation $G_Z/|J_0| = 0.35$ confirms the conclusion of Solomon and coworkers[55a] that the D−M antisymmetric exchange coupling in trimeric [Cu_3(II)] clusters with the $d_{x^2-y^2}$ orbitals in the Cu_3 plane may be strong [and does not follow the estimate[57] $G_Z \sim (\Delta g/g)\vartheta J_0$], in accordance with the experimental observation [G_Z (cm^{-1}), J_0 (cm^{-1})] for these systems: $G_Z = 36$, $J_0 = -105$,[55a] $G_Z = 27.8$, $J_0 = -95.5$, $G_Z = 31$, $J_0 = -87.7$,[53a] $G_Z = 33$, $J_0 = -97$, and $G_Z = 47$, $J_0 = -105$.[54]

In the case of the $d_{x^2-y^2}$ magnetic orbitals perpendicular to the Cu_3 plane (Figure 4), the coefficient of the antisymmetric D−M exchange coupling

$$G_Z = \sqrt{3}J_0\vartheta\Delta g_{\|}(t'_v - 2t'_\xi)/(t'_v - 6t'_u) \qquad (26)$$

is proportional to the small deformation parameter ϑ ($\ll$1) and depends on the relationship between the ET parameters t'_v, t'_u, and t'_ξ. The estimate leads to $G_Z \sim 0.03J_0$ for $\Delta g_{\|} = 0.2$, $\vartheta = 0.1$, $t'_v \gg t'_u$, t'_ξ, and $G_Z \ll J_0$. This result is in agreement with the $G_Z \sim (\Delta g/g)\vartheta J_0$ estimate[57] and confirms the conclusion[55a] that the D−M antisymmetric exchange may be weak in the $[Cu_3(II)]$ cluster with the $d_{x^2-y^2}$ magnetic orbitals perpendicular to the Cu_3 plane.

6. Zeeman and Hyperfine Splittings

The ZFS of the delocalized ^{3}E term is determined by eq 12, Figure 3, whereas the ZFS of the delocalized $^3A_2$ term is described by the standard ZFS Hamiltonian (7) with the axial parameter $D'_1(^3A_2)$. In the spin-coupling model for the $|a^*\rangle$ localized cluster $[Cu_a(III)Cu_2(II)]$, the Hamiltonian of the Zeeman and hyperfine interactions in the parallel external magnetic field ($H_z||Z$) may be represented in the form[70] $H^Z_{\mathrm{pair(a^*)}} = (g_{bZ}\hat{s}_{bZ} + g_{cZ}\hat{s}_{cZ})\beta H_Z + a(\hat{s}_{bZ}\hat{I}_{bZ} + \hat{s}_{cZ}\hat{I}_{cZ})$, where g_{iZ} and a are individual g factors and hyperfine constants, respectively, of the Cu(II) ions of the bc pair, $z_i||Z$ (Figure 4). The Hamiltonians for the $|b^*\rangle$ and $|c^*\rangle$ localizations are obtained by the permutations of the indexes a*bc → b*ca → c*ab. $H^Z_{\mathrm{pair(a^*)}}$ results in the standard g factor for the localized triplet state of the $Cu_2(II)$ dimer[41,42,47,70] $g_{\mathrm{pair}(i^*)} = (g_l + g_k)/2$ and the hyperfine structure of the EPR spectrum [1:2:3:4:3:2:1] with the interval $a/2$.

For the valence-delocalized $^3A_2$ and ^{3}E states, the sum of the localized operators $H^Z_{\mathrm{pair(a^*)}}$ leads to the Zeeman splittings $g_Z\beta H_Z M$ of the $S = 1$ [$M = (\pm1, 0)$] levels, which is determined by the cluster g factor $g_Z = (1/3)(g_{aZ} + g_{bZ} + g_{cZ})$ for the $^3A_2$ and ^{3}E terms.

The Zeeman splittings of the delocalized ^{3}E term are described by eq 27,

$$E[^3E_+(M{=}\pm1)] = -t - 2J \pm \sqrt{(K'_Z + g_Z\beta H_Z)^2 + (g_\perp\beta H_X)^2};$$
$$E[^3E_-(M{=}\pm1)] = -t - 2J \mp \sqrt{(K'_Z - g_Z\beta H_Z)^2 + (g_\perp\beta H_X)^2};$$
$$E[^3E_\pm(M{=}0)] = -t - 2J \qquad (27)$$

where $g_\perp = (1/3)(g_{aX} + g_{bX} + g_{cX})$ and $D_1 = 0$. The splitting of the delocalized ^{3}E term in the parallel external magnetic field ($H_z||Z$) is shown schematically in Figure 5 for the cases $K_Z = 0$, $D_1 > 0$ (Figure 5a) and $K_Z \neq 0$, $K_Z > D_1$ (Figure 5b). In the case $K_Z = 0$, $h\nu < D_1$, two double EPR transitions $^3E_\pm(M{=}0) \leftrightarrow {}^3E_\pm(M{=}-1)$ with $\Delta M = 1$ may be observed (1 and 1′; Figure 5a). In the case $K_Z \neq 0$, $D_1 \neq 0$ (Figure 5b), the scheme of transitions, positions of the EPR lines, and their intensities are different. In the localized $[Cu_2(II)Cu(III)]$ cluster, the ZFS parameter D_1 is very small.[5] In the case of strong antisymmetric double-exchange splitting ($K_Z \gg D_1$, $g\beta H_z$), there are no $\Delta M = 1$ EPR transitions for the ^{3}E term. In the case $K_Z \sim D_1$, $g\beta H_z$, the EPR transitions 1, 1′, and 1″ may be observed (Figure 5b).

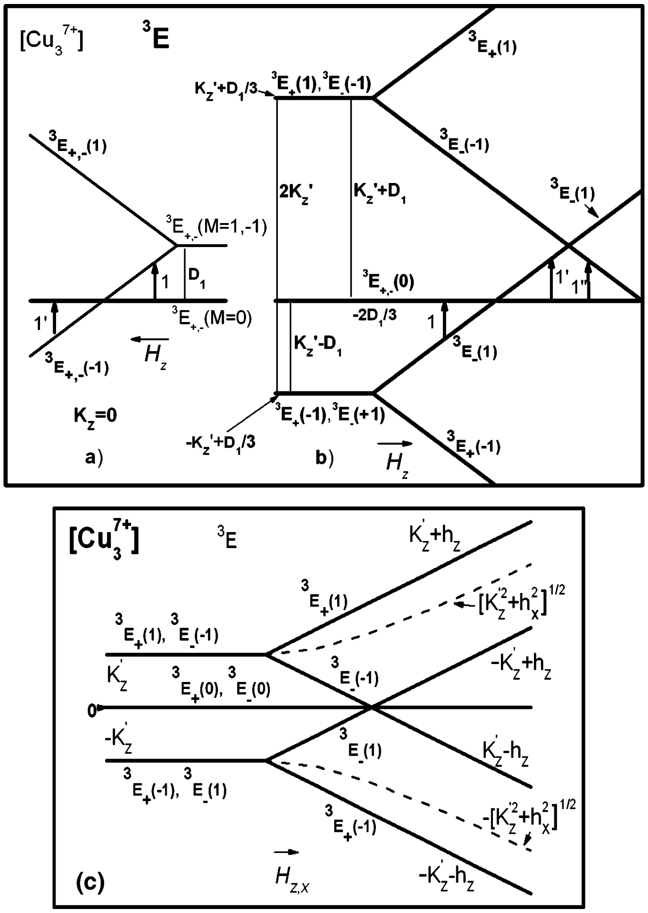

Figure 5. (a) Scheme of the Zeeman splitting ($H = H_Z$) and EPR transitions for the delocalized ^{3}E term in the case of the standard ZFS, H^0_{ZFS} (eq 7). (b) Zeeman splitting ($H = H_Z$) and EPR transitions for the delocalized ^{3}E term with the linear ZFS ($\Delta_K = 2K'_Z$) induced by the antisymmetric double exchange. (c) Anisotropy of the Zeeman splitting of the delocalized ^{3}E term in the external magnetic field: the linear splitting in magnetic field $H = H_Z$ parallel to the cluster Z axis; the nonlinear behavior in magnetic field $H = H_X$.

Because of the ZFS of the antisymmetric double-exchange origin ($\sim K_Z$), the Zeeman splitting of the valence-delocalized ^{3}E term is strongly anisotropic (Figure 5c; $h_Z = g\beta H_Z$, $h_X = g\beta H_X$, and $D_1 = 0$). In the magnetic field parallel to the trigonal cluster axis Z ($H = H_z||Z$; eq 27), the Zeeman splitting is linear: $K'_Z \pm (g\beta H_Z)$, $-K'_Z \pm (g\beta H_Z)$ (solid lines). In the case of the magnetic field lying in the plane of the Cu triangle ($H = H_X$), the magnetic behavior is nonlinear $\pm\sqrt{K'^2_Z + (g\beta H_X)^2}$ (eq 27; dashed lines in Figure 5c), which leads to strong magnetic anisotropy of the delocalized ^{3}E term [$\mu(H_Z) \neq \mu(H_X)$].

The isotropic double exchange H^0_{DM} and Heisenberg exchange H_0 form the trigonal double-exchange triplet and singlet states (Figure 2); however, the system remains isotropic. In an isotropic delocalized cluster ($t \neq 0$, $J \neq 0$, $K_Z = 0$, and $D_1 = 0$), the magnetic behavior is isotropic

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(70) Owen, J.; Harris, E. A. In *Electron Paramagnetic Resonance*; Geshwind, S., Ed.; Plenum Press: New York, 1972.

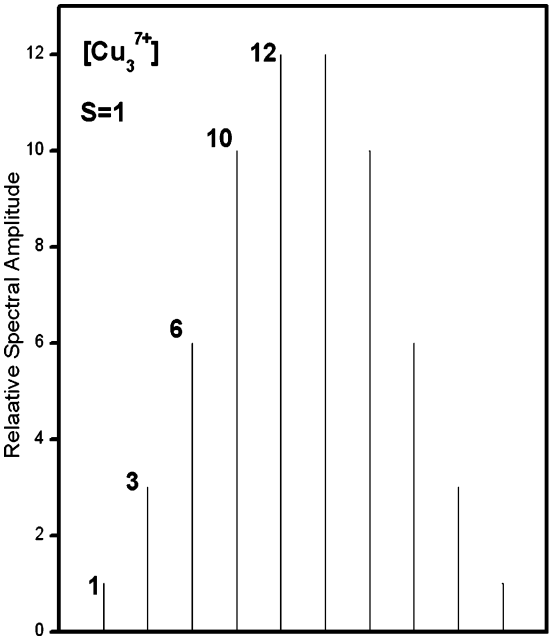

Figure 6. Hyperfine structure of the EPR lines for the delocalized degenerate ^{3}E term ($H = H_Z$; Figure 5b) and delocalized $^3A_2$ triplet state.

$\{E[^3E(H_Z)] = E[^3E(H_X)]$ in eq 27 for $K_Z = 0$ and $\mu(H_Z) = \mu(H_X)]$. In the delocalized system, the antisymmetric double exchange determines large anisotropy of the Zeeman splitting of the delocalized ^{3}E term (Figure 5c) and magnetic anisotropy.

The hyperfine splittings of the Zeeman levels of the valence-delocalized terms are considered in the spin-coupling model, using the spin-wave functions (6) in the cluster electron−nuclear spin-wave functions, for example, for the $^3A_2$ state, $\Omega(^3A_2,I) = \Phi(^3A_2)\ \psi(I_a,M_{Ia})\ \psi(I_b,M_{Ib})\ \psi(I_cM_{Ic})$, where $\psi(I_\alpha,M_{I\alpha})$ is the nuclear wave function of the α ion, in which $I_\alpha = {}^3/_2$ and $M_{I\alpha} = \pm{}^3/_2, \pm{}^1/_2$. In the delocalized cluster, the pair of hyperfine operators $[a(\hat{s}_{\alpha Z}\hat{I}_{\alpha Z} + \hat{s}_{\beta Z}\hat{I}_{\beta Z})]$ for all localizations leads to the effective Hamiltonian $H_I = aM(\hat{I}_{az} + \hat{I}_{bz} + \hat{I}_{cz})/3$ of the hyperfine coupling for the Zeeman levels M of the triplet, which results in the hyperfine splittings of the M levels $\epsilon(I,M_I) = aM(M_{Ia} + M_{Ib} + M_{Ic})/3$. In the delocalized cluster, the effective hyperfine constant for each Cu ion has the form $A_i = a\langle|s_{iZ}|\rangle/\langle S_Z\rangle$, $A_i = a/3$. For the EPR transitions with $\Delta M = 1$, $^3A_2(M{=}0) \leftrightarrow {}^3A_2(|M|{=}1)$ $(H_z||Z)$, the hyperfine structure has the form of the 10 hyperfine lines with relative intensities 1:3:6:10:12:12:10:6:3:1 (Figure 6) and the interval $a/3$.

The isotropic EPR signal with $g = 2.05$ and 10-line hyperfine pattern, which was observed at room temperature by Tolman and co-workers,[6] was interpreted as evidence of two fully delocalized unpaired electrons.[6] In the double-exchange model, the valence delocalization in the [Cu_3^{7+}] cluster is described by the delocalization of one $\bar{d}$ hole (Figure 1). Full delocalization in the system is associated with strong double-exchange coupling ($t'_v \neq 0$), which results in the pairing of the spins ($S = 1$ and 0). The double-exchange model leads to the delocalized ^{3}E ground and $^3A_2$ first excited terms in the case of $0 < t < 2J$ (Figure 2). In this scheme, the EPR spectrum at room temperature[6] with $g = 2$ and 10 line hyperfine structures may be attributed to the EPR spectrum of the delocalized $^3A_2$ excited state with the hyperfine structure (10 hyperfine lines) discussed above.

For the delocalized ^{3}E ground-state term with the ZFS of the antisymmetric double-exchange origin ($\sim K_Z$), the number and positions of the EPR transitions depend on the ZFS parameters K_Z and D_1 and magnetic field ($g\beta H$) splitting. For the delocalized ^{3}E term with ZFS (Figure 5), the hyperfine structure of the EPR transitions $^3E_\pm(M{=}0) \leftrightarrow {}^3E_\pm(|M|{=}1)$ 1, 1′, and 1″ (Figure 5b), $H_z||Z$, has also the form of the 10 hyperfine lines (Figure 6). The EPR signals with $g \sim 2$ and $g = 4$ (with hyperfine pattern), which were observed[6] at 10 K, may be attributed to the EPR transitions in the delocalized ^{3}E ground-state term. In the case of the $t < 0$ parameter (Figure 2), the order of the levels is opposite: $^3A_2$ is the ground state and ^{3}E the excited state.

In the case of the external magnetic field in the plane of the triangle and/or nonzero rhombic ZFS in eq 7, the EPR transition with $\Delta M = 2$[71] may be observed for the $^3A_2$ and ^{3}E terms.

7. Conclusion

In the delocalized [Cu_3^{7+}] cluster, the valence delocalization (migration of the extra d hole over all three Cu centers) is described by the model of the isotropic double-exchange interaction H^0_{DE}. The isotropic double exchange H^0_{DE} results in the pairing of individual spins at room temperature and forms the delocalized trigonal states $^3A_2$, ^{3}E, $^1A_1$, and ^{1}E of the delocalized [Cu_3^{7+}] cluster. The model explains the delocalized singlet $^1A_1$ ground state in the planar $Cu_3(\mu_3\text{-}O)$ core[7] by the strong double-exchange coupling with positive double-exchange parameter $2J < t_0$, whereas the delocalized triplet ground state of the [Cu_3^{7+}] trimer, which was observed in the $Cu_3(\mu_3\text{-}S)_2$ core,[6] may be explained by the double exchange with relatively weak positive t_0: $0 < t_0 < 2J$ (the degenerate ^{3}E ground state) or negative t_0 (the triplet $^3A_2$ ground state).

The antisymmetric double-exchange coupling H_1 results in the linear ZFS of the delocalized degenerate ^{3}E term of the valence-delocalized [Cu_3^{7+}] cluster, $\Delta_K = 2K_Z\sqrt{3}$. The operator of the antisymmetric double exchange H_1 describes the SOC between the total cluster spin S and the cluster orbital momentum formed by the migrating d hole in the delocalized [Cu_3^{7+}] cluster. The parameter of the antisymmetric double exchange K_Z is proportional to the isotropic double-exchange parameter t_0 and anisotropy of the g factor $\Delta g_{||}$[Cu(II)], $K_Z \ll t_0$. The antisymmetric double-exchange coupling is relatively large in the [Cu_3^{7+}] cluster, with the $d_{x^2-y^2}$ magnetic orbitals lying in the Cu_3 plane [$Cu_3(\mu_3\text{-}O)$ core[7]]. For the cluster with the $d_{x^2-y^2}$ magnetic orbitals lying in the plane perpendicular to the Cu_3 triangle [$Cu_3(\mu_3\text{-}S)_2$

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(71) (a) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Chapman & Hall: London, 1978. (b) Weil, J.; Bolton, J.; Wertz, J. *Electron Paramagnetic Resonance*; Wiley-Interscience: New York, 1994. (c) Mabbs, F. E.; Collison, D. *Electron Paramagnetic Resonance of d-transition Metal Compounds*; Elsevier: New York, 1992.

cluster[6]], antisymmetric double-exchange coupling is weak and K_Z is proportional to the cluster deformation parameter ϑ.

In the delocalized [Cu_3^{7+}] cluster, the D−M antisymmetric exchange coupling H_{DM} is not active in the linear splitting of the delocalized degenerate ^3E term and only participates in the mixing of the delocalized levels with different total spins. In the valence-delocalized [Cu_3^{7+}] cluster, the antisymmetric double-exchange interaction H_1 plays the same role in the splitting of the degenerate ^{3}E state as the D−M exchange coupling H_{DM} plays in the splitting of the spin-frustrated $2(S = {}^1/_2)$ state of the monovalent exchange [Cu_3(II)] cluster.

The ZFS Δ_K of the ^{3}E term induced by the antisymmetric double exchange leads to strong anisotropy of the Zeeman splittings in the external magnetic field and complex EPR spectrum. The theory predicts the linear Zeeman splitting of the delocalized ^{3}E term in the magnetic field $H = H_Z$ directed along the trigonal Z axis, whereas the magnetic behavior is nonlinear in the case of the magnetic field lying in the plane of the Cu triangle ($H = H_X$). The model explains the hyperfine structure [10 hyperfine lines with relative intensities 1:3:6:10:12:12:10:6:3:1 and the interline interval $a/3$] of the EPR transitions, which was observed for the triplet states of the delocalized [Cu_3^{7+}] cluster in the$Cu_3(\mu_3\text{-}S)_2$ core.[6]

Acknowledgment. I thank the reviewers for helpful comments.

Appendix A

In the case of the different double-exchange (ET) parameters in the pairs of the MV trimer, $t_{ab} = t_{ac} = t$, $t_{bc} = t_1$, and $t \neq t_1$, the double-exchange coupling H^0_{DE} results in the isotropic double-exchange splitting in the form

$$E_1(^3A_2) = \frac{2}{3}(2t + t_1) - 2J, \quad E_2(^3E_x) = \frac{1}{3}(t_1 - 4t) - 2J,$$
$$E_3(^3E_y) = -t_1 - 2J; \quad E_3(^1A_1) = -\frac{2}{3}(2t_1 + t),$$
$$E_1(^1E_x) = \frac{1}{3}(4t - t_1), \quad E_2(^1E_y) = t_1 \quad (1A)$$

The isotropic "deformation" splitting of the ^{3}E term is Δ_0-(^{3}E) = 2τ, where $\tau = (2/3)(t_1 - t)$ and $\Delta_0(^1E) = -\Delta_0(^3E)$. In this case of the slightly distorted trimer ($t \neq t_1$; $\tau \neq 0$), the antisymmetric double-exchange coupling results in the following splitting of the ^{3}E term:

$$E_\pm(S{=}1,M{=}1) = -2J - \tilde{t} \pm [3K_Z^{\,2} + \tau^2]^{1/2},$$
$$E_\pm(1,-1) = -2J - \tilde{t}[3K_Z^{\,2} + \tau^2]^{1/2},$$
$$E_x(1,0) = -2J - \tilde{t} + \tau, \quad E_y(1,0) = -2J - \tilde{t} - \tau \quad (2A)$$

where $\tilde{t} = (1/3)(2t + t_1)$ and the splitting

$$2\Delta = 2[3K_Z^{\,2} + \tau^2]^{1/2} \qquad (3A)$$

The spin-wave functions of the ^{3}E term, which diagonalize the isotropic and antisymmetric double-exchange coupling in the cluster with the τ deformation, have the form

$$\Phi_\pm(1,M) = \sqrt{\frac{1}{2}(1 \pm \tau/\Delta)}\,\Phi_x(1,M) \pm$$
$$iM\sqrt{\frac{1}{2}(1 \mp \tau/\Delta)}\,\Phi_y(1,M), \quad M = \pm 1 \quad (4A)$$

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