ISSN 2072-5981

Magnetic Resonance in Solids

Electronic Journal

Volume **16, 2014**
No. **1, 14101** – 7 *pages*

http://mrsej.ksu.ru

Established and published by Kazan University
Sponsored by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press, August 2, 1996
First Issue was appeared at July 25, 1997

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[*] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Transferred hyperfine interactions for O^{17}: $LaMnO_3$

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(Received January 16, 2014; revised March 16, 2014; accepted March 18, 2014)

Parameters of the transferred hyperfine interactions (THFI) for O^{17}: $LaMnO_3$ have been estimated at room temperature. Satisfactory agreement with experiment has been obtained.

PACS: 76.70.Dx, 76.30.Kg, 71.70.Ch

Keywords: transferred hyperfine interactions, NMR, $LaMnO_3$

1. Introduction

Transferred hyperfine interactions (THFI) on nuclei O^{17}: $LaMnO_3$ were studied in [1] using the nuclear magnetic resonance (NMR) method. The wave function $|\mathrm{Mn}\rangle$ was determined from the experimental data as a superposition of $|\theta\rangle = |3z^2 - r^2\rangle$ and $|\varepsilon\rangle = |x^2 - y^2\rangle$ states, which are the components of the doublet e_g belonging to the configuration $t_{2g}^3 e_g$ of the Mn^{3+} ion. The wave function was determined from the ratio of the hyperfine fields of oxygens O_1 and O_2. Ions of oxygen of O_1 lie between the planes of manganese ions. Ions of oxygen of O_2 lie in the plane of manganese ions. The covalency parameters were taken proportional to the overlap integrals. The direction from Mn^{3+} to the oxygen ion O_2 determining the largest (long) covalent bond was chosen as the quantization axis. The choice of this coordinate system is dictated by the fact that the nearest environment of the Mn^{3+} ion is almost orthorhombic. At the same time, it is obvious that similar estimates have most likely the qualitative character for the clarification of mechanisms leading to different values of the local magnetic fields on O_1 and O_2 nuclei. In this work, the quantitative estimates of these fields at room temperature were obtained.

2. Theory

Processes leading to the appearance of hyperfine fields on nuclei of ligands were considered in [2]. One of these processes describing the transfer of the electron from the ligand to the partly filled shell of the cation and denoted as V_1 according to [2] has the following form

$$V_1 = \sum a_{\xi}^{+} a_{\xi'} \left[\frac{1}{4} \langle \xi | q | \zeta \rangle \langle \theta | q | \xi' \rangle - \frac{1}{2} \bar{\gamma}_{\xi\zeta} \langle \theta \| \xi' \rangle - \frac{1}{2} \langle \xi \| \zeta \rangle \bar{\gamma}_{\theta\xi'} + \bar{\gamma}_{\xi\zeta} \bar{\gamma}_{\theta\xi'} \right] \langle \zeta | v | \theta \rangle, \qquad (1)$$

where v is the operator of the hyperfine interaction, ξ, η and θ, ζ are quantum numbers of cation and ligand orbitals, respectively, $\langle \xi \| \theta \rangle \equiv \langle \xi | (I+S)^{-1} | \theta \rangle$, where I is the unit operator, S is the matrix of the overlap of one-electron orbitals. $\langle \xi | q | \varsigma \rangle$ are matrix elements of the operator

$$q = \ln(I+S) = S \int_0^1 (I + \alpha S)^{-1} d\alpha \approx S \sum_{i=1}^{N} (I + \alpha_i S)^{-1} \Delta\alpha \ , \qquad (2)$$

$(I + \alpha_i S)^{-1}$ is the matrix inverse to the matrix $(I + \alpha_i S)$, $\alpha_i = i/N$, $\Delta\alpha = 1/N$, $N \approx 10^6$. The expression to the right of the sign of the approximate equality is the integral sum of the integral under consideration. It exists always, if the basis of one-particle functions is chosen to be linearly independent.

$$\bar{\gamma}_{\xi\zeta} = -\frac{\langle \xi|G|\zeta\rangle}{|\Delta_{\xi,\zeta}|}, \tag{3}$$

$\langle\xi|G|\zeta\rangle$ is the amplitude of the transition of the electron from the ligand to the cation, $|\Delta_{\xi\zeta}|$ is the energy of the transition of the system from the ground to the excited state.

Ignoring the two-particle corrections and in the case of the Hund term, the operator $\hat{G}$ of the electron transition can be written in the one-particle form

$$\hat{G} = \sum a_\xi^+ b_\zeta \langle\xi|G|\zeta\rangle,$$

where $|\zeta\rangle$ is the orbital of the ligand *b*, $|\xi\rangle$ is the orbital of the cation,

$$\begin{aligned}
2\langle\xi|G|\zeta\rangle = \langle\xi||\zeta\rangle\Bigg[& \varepsilon_\xi^{q_e-1} + \sum_{\dot{\eta}_e}\langle\xi\dot{\eta}_e|g(1-P)|\xi\dot{\eta}_e\rangle\big(\langle\dot{\eta}_e||\dot{\eta}_e\rangle-1\big)+\langle\xi|H_{LR}|\xi\rangle \\
& -\langle\xi|\frac{n_b}{|\mathbf{r}-\mathbf{R}_b|}|\xi\rangle + \sum_{\dot{\eta}_b\neq\varsigma}\langle\xi\dot{\eta}_b|g(1-P)|\xi\dot{\eta}_b\rangle\langle\dot{\eta}_b||\dot{\eta}_b\rangle + \varepsilon_\zeta^{q_b} \\
& +\sum_{\dot{\eta}_b}\langle\zeta\dot{\eta}_b|g(1-P)|\zeta\dot{\eta}_b\rangle\big(\langle\dot{\eta}_b||\dot{\eta}_b\rangle-1\big)+\langle\zeta|H_{LR}|\zeta\rangle-\langle\zeta|\frac{n_e}{|\mathbf{r}-\mathbf{R}_e|}|\zeta\rangle \\
& +\sum_{\dot{\eta}_e}\langle\zeta\dot{\eta}_e|g(1-P)|\zeta\dot{\eta}_e\rangle\langle\dot{\eta}_e||\dot{\eta}_e\rangle] + \big(\langle\xi||\xi\rangle+\langle\zeta||\zeta\rangle\big)\big[\langle\xi|h_k|\zeta\rangle-\langle\xi|\frac{n_e}{|\mathbf{r}-\mathbf{R}_e|}|\zeta\rangle \\
& +\sum_{\dot{\eta}_e}\langle\xi\dot{\eta}_e|g(1-P)|\zeta\dot{\eta}_e\rangle\langle\dot{\eta}_e||\dot{\eta}_e\rangle-\langle\xi|\frac{n_b}{|\mathbf{r}-\mathbf{R}_b|}|\zeta\rangle+\sum_{\dot{\eta}_b}\langle\xi\dot{\eta}_b|g(1-P)|\zeta\dot{\eta}_b\rangle\langle\dot{\eta}_b||\dot{\eta}_b\rangle\Bigg],
\end{aligned} \tag{4}$$

where all quantities referring to the cation are marked by the subscript *e*, and those to the ligand by the subscript *b*, *g* is the Coulomb interaction of electrons, *P* is the operator of permutation of quantum numbers. Summation over $\dot{\eta}_e$ in the case of the Hund term includes summation over the orbital quantum numbers of the cation in the ground configuration. Summation over $\dot{\eta}_b$ includes summation over all orbitals of the ligand in the ground configuration. The quantities $\varepsilon_\xi^{q_e-1}$ and $\varepsilon_\zeta^{q_b}$ are Hartree-Fock energies of the electron on the orbital $|\xi\rangle$ of the cation and on the orbital $|\zeta\rangle$ of the ligand, respectively, determined for free ions. h_k is the operator of the kinetic energy. $\langle\xi|H_{LR}|\xi\rangle = \langle\xi|-\sum_{n,i}{}'\frac{q_i}{|\mathbf{r}-(\mathbf{R}_n+\mathbf{r}_i)|}|\xi\rangle$ is the energy of the interaction between the electron on the orbital $|\xi\rangle$ and the infinite crystal lattice in the ion approximation. The prime at the sign of sum denotes the exclusion of the interaction between the charge q_j and the electron on the orbital $|\xi\rangle$. Summation over *n* denotes summation over the unit cells, and summation over *i* denotes summation over the ions of the unit cell. n_e, n_b are the numbers of electrons in the ground configuration on the cation and on the ligand, respectively.

The process of the transition of the electron from the oxygen to the valence shell of Mn^{3+} was considered as the main mechanism of the creation of the hyperfine field on nuclei O^{2-}. The orbitals $|\xi\rangle$ are orbitals of the 3d-shell of the Mn^{3+} ion, and the orbitals $|\zeta\rangle$ are orbitals of the O^{2-} ion.

3. Matrix elements of operators

Further let us present the numerical values of the matrix elements of operators in (1) for the calculation of the hyperfine fields on nuclei O^{17} in $LaMnO_3$. Let us take the coordinate system for the unit cell according to [3]. Taking into account the nearest environment of two nonequivalent oxygen ions leads to the selection of a complex of five ions. For the temperature $T = 298$ K we have: $O_1(0.07452, 0.48743, 0.25)$, $O_2(0.22559, 0.19342, -0.0384)$, $Mn_1(0.5, 0, 0)$, $Mn_2(0, 0.5, 0)$, $Mn_3(0, 0.5, 0.5)$. Values are given in units of crystal lattice constants. The wave functions of 2s, 2p orbitals of oxygen ions were taken from [4]. The wave functions of 3d orbitals of Mn^{3+} were taken from [5]. Thus, the matrix of the overlap of one-electron orbitals S is the matrix of the 23th order. The isotropy of the shift of the NMR line on nuclei of oxygen ions indicates that the main contribution to the THFI constants is given by the contact part of the hyperfine interaction. The calculations show that the $|2s\rangle$ orbitals of oxygen ions have a rather large overlap with the $|z^2\rangle \equiv |2z^2 - x^2 - y^2\rangle$ and $|xy\rangle$ orbitals of manganese ions (all orbitals were determined in the coordinate system of [3]). The amplitudes of the transition to other orbitals are ignored in this work. The matrix elements $\langle \xi \| \xi \rangle \approx \langle \theta \| \theta \rangle \approx 1.005 \approx 1$. The matrix elements of matrices q, $\langle \xi \| \theta \rangle$, one-particle operators $h_i = |\mathbf{r} - \mathbf{R}_i|^{-1}$, $i = e, b$ and h_k are given in Table 1. The values of the necessary two-center integrals of the Coulomb interaction of electrons are given in Table 2.

Table 1. Matrix elements of matrices q, $\langle \xi \| \theta \rangle$ and one-particle operators (in a.u.).

	$Mn_2 - O_1$		$Mn_2 - O_2$		Mn_1 - O_2	
a, b	$z^2, 2s$	$xy, 2s$	$z^2, 2s$	$xy, 2s$	$z^2, 2s$	$xy, 2s$
$< a \| b >$	−0.0546	0.0007	0.0184	0.0309	0.0306	0.0531
$< a \| q \| b >$	0.0543	−0.0007	−0.0182	−0.0308	−0.0304	−0.0527
a, b, i	$z^2, 2s, k$	$z^2, 2s, e$	$xy, 2s, k$	$xy, 2s, e$	$z^2, 2s, k$	$z^2, 2s, e$
$< a \| h_i \| b >$	0.0034	0.0244	0.0021	−0.0132	−0.0032	−0.014
a, b, i	$z^2, 2s, b$		$xy, 2s, b$		$z^2, 2s, b$	$xy, 2s, k$
$< a \| h_i \| b >$	0.0370		−0.0189		−0.0214	−0.0057
a, b, i					$xy, 2s, e$	$xy, 2s, b$
$< a \| h_i \| b >$					−0.0242	−0.0371

The energy $\varepsilon_\xi^{q_e - 1} = \varepsilon_\xi^{\mathrm{Mn}^{2+}}$ was calculated on the wave functions of the trivalent Mn^{3+} ion. This energy can be presented as $\varepsilon_\xi^{\mathrm{Mn}^{2+}} = \varepsilon_\xi^{\mathrm{Mn}^{3+}} + \langle \xi, \xi | g | \xi, \xi \rangle$ in the zero approximation according to the definition of Hartree-Fock energies [2]. According to [5], $\varepsilon_{3d}^{\mathrm{Mn}^{3+}} = -1.9559$. According to the calculations, $\langle z^2, z^2 | g | z^2, z^2 \rangle = 0.9584$. According to [4], $\varepsilon_{2s}^{\mathrm{O}^{2-}} = -0.6286$.

Let us calculate the matrix elements of the operator H_{LR} using the results of [6]. The structural factor $G_j(\mathbf{g})$ for $LaMnO_3$ at room temperature has the following form:

$$G_j(\mathbf{g}) = \cos(\mathbf{g}\mathbf{r}_j) F_1(\mathbf{g}), \quad F_2(\mathbf{g}) = 0,$$

$$\begin{aligned} F_1(\mathbf{g}) = 3\left[(-1)^{n_x} + (-1)^{n_y}\right]\left[1+(-1)^{n_z}\right] \\ +12\cos\left[\pi\left(a_1 n_y + n_x/2 + n_z/2\right)\right]\cos\left[\pi\left(a_2 n_x + n_y/2\right)\right] \\ -8\cos\left[\pi\left(a_3 n_y + n_x/2 + n_z/2\right)\right]\cos\left[\pi\left(a_4 n_x - n_y/2\right)\right] \\ -16\cos\left[\pi\left(a_5 n_y + n_x/2 + n_z/2\right)\right]\cos\left[\pi\left(a_6 n_z\right)\right]\cos\left[\pi\left(a_7 n_x - n_y/2\right)\right], \end{aligned} \tag{5}$$

where $a_1 = 0.59802$, $a_2 = 0.51562$, $a_3 = 0.47486$, $a_4 = 0.35096$, $a_5 = 0.11316$, $a_6 = 0.42320$, $a_7 = 0.04882$.

Let us give further the values of the matrix elements of the operator H_{LR}. For the O_1 ion the matrix element $\langle 2s|H_{LR}|2s\rangle = -0.8262$. For the O_2 ion $\langle 2s|H_{LR}|2s\rangle = -0.8158$. For the Mn^{3+} ion the matrix elements $\langle z^2|H_{LR}|z^2\rangle = 1.3542$, $\langle xy|H_{LR}|xy\rangle = 1.3495$. For the pair $Mn_2 - O_1$ the matrix element $\langle z^2|\frac{1}{|\mathbf{r}-\mathbf{R}_b|}|z^2\rangle = 0.2621$. For the pair $Mn_1 - O_2$: $\langle xy|\frac{1}{|\mathbf{r}-\mathbf{R}_b|}|xy\rangle = 0.2615$.

Table 2. Two-center integrals of the Coulomb interaction of electrons $(\times 10)$, $\langle ab|g|cd\rangle \equiv \langle ab|cd\rangle$ (in a.u.).

$< ab \vert cd >$	$\vert a > = \vert z^2 >$	$Mn_2 - O_1$				
bcd	$z^2, 2s, z^2$	*ε*, 2*s*, *ε*	*ε*, *ε*, 2*s*	*xz*, 2*s*, *xz*	*xz*, *xz*, 2*s*	*yz*, 2*s*, *yz*
$< ab \vert cd >$	0.2647	0.2122	−0.0119	0.2470	0.0121	0.2467
bcd	*yz*, *yz*, 2*s*	2*s*, 2*s*, 2*s*	*pz*, 2*s*, *pz*	*pz*, *pz*, 2*s*	*px*, 2*s*, *px*	*px*, *px*, 2*s*
$< ab \vert cd >$	0.0115	0.3350	0.2940	0.1299	0.2709	0.0514
bcd	*py*, 2*s*, *py*	*py*, *py*, 2*s*				
$< ab \vert cd >$	0.2679	0.0401				
$< ab \vert cd >$	$\vert a > = \vert xy >$	$Mn_2 - O_2$				
bcd	*xy*, 2*s*, *xy*	*ε*, 2*s*, *ε*	*ε*, *ε*, 2*s*	*xz*, 2*s*, *xz*	*xz*, *xz*, 2*s*	*yz*, 2*s*, *yz*
$< ab \vert cd >$	−0.1323	−0.1295	−0.0013	−0.1254	−0.0022	−0.1264
bcd	*yz*, *yz*, 2*s*	2*s*, 2*s*, 2*s*	*pz*, 2*s*, *pz*	*pz*, *pz*, 2*s*	*px*, 2*s*, *px*	*px*, *px*, 2*s*
$< ab \vert cd >$	−0.0024	−0.1730	−0.1421	−0.0195	−0.1440	−0.0217
bcd	*py*, 2*s*, *py*	*py*, *py*, 2*s*				
$< ab \vert cd >$	−0.1530	−0.0499				
$< ab \vert cd >$	$\vert a > = \vert z^2 >$	$Mn_1 - O_2$				
bcd	$z^2, 2s, z^2$	*ε*, 2*s*, *ε*	*ε*, *ε*, 2*s*	*xz*, 2*s*, *xz*	*xz*, *xz*, 2*s*	*yz*, 2*s*, *yz*
$< ab \vert cd >$	−0.1180	−0.1528	−0.0228	−0.1260	0.0083	−0.1234
bcd	*yz*, *yz*, 2*s*	2*s*, 2*s*, 2*s*	*pz*, 2*s*, *pz*	*pz*, *pz*, 2*s*	*px*, 2*s*, *px*	*px*, *px*, 2*s*
< ab|cd >	0.0076	−0.1912	−0.1530	−0.0147	−0.1640	−0.0454
bcd	*py*, 2*s*, *py*	*py*, *py*, 2*s*				
$< ab \vert cd >$	−0.1601	−0.0368				

$< ab\vert cd >$	$\vert a > = \vert xy >$	$\mathrm{Mn}_1 - \mathrm{O}_2$				
bcd	$xy, 2s, xy$	$\varepsilon, 2s, \varepsilon$	$\varepsilon, \varepsilon, 2s$	$xz, 2s, xz$	$xz, xz, 2s$	$yz, 2s, yz$
$< ab\vert cd >$	−0.2432	−0.2375	−0.0027	−0.2313	−0.0045	−0.2296
bcd	$yz, yz, 2s$	$2s, 2s, 2s$	$pz, 2s, pz$	$pz, pz, 2s$	$px, 2s, px$	$px, px, 2s$
< ab|cd >	−0.0045	−0.3321	−0.2690	−0.0404	−0.2877	−0.0863
bcd	$py, 2s, py$	$py, py, 2s$				
$< ab\vert cd >$	−0.2716	−0.0415				

4. Calculations

Let us find the contributions to the THFI parameters for the considered oxygen ions. Substituting the values of the calculated matrix elements into expression (4), we obtain the following values for the amplitudes of the transition. For the pair $\mathrm{Mn}_2 - \mathrm{O}_1$ we obtain the value $\left\langle z^2 \middle| G \middle| 2s \right\rangle = -0.09$. For the pair $\mathrm{Mn}_2 - \mathrm{O}_2$: $\left\langle z^2 \middle| G \middle| 2s \right\rangle = 0.026$, $\left\langle xy \middle| G \middle| 2s \right\rangle = 0.044$. For the pair $\mathrm{Mn}_1 - \mathrm{O}_2$: $\left\langle z^2 \middle| G \middle| 2s \right\rangle = 0.051$, $\left\langle xy \middle| G \middle| 2s \right\rangle = 0.086$.

The energy of the transition $\left|\Delta_{\xi,\zeta}\right|$ can be estimated according to [7, 8]:

$$\left|\Delta_{\xi,\zeta}\right| = -I^{\mathrm{Mn}^{2+}} + I^{\mathrm{O}^{2-}} + E_M^{\mathrm{Mn}^{3+}} - E_M^{\mathrm{O}^{2-}} - \varepsilon_{2s}^{XF} + E_{eh}, \tag{6}$$

where $I^{\mathrm{Mn}^{2+}}$, $I^{\mathrm{O}^{2-}}$ are the ionization energies of manganese and oxygen ions, in this work $E_M^{\mathrm{Mn}^{3+}}$, $E_M^{\mathrm{O}^{2-}}$ have the meaning of the matrix elements of the operator H_{LR}. The energy of the electron-hole interaction for the pair $\mathrm{Mn}_2 - \mathrm{O}_1$: $E_{eh} = -0.2621$, and for the pair $\mathrm{Mn}_1 - \mathrm{O}_2$: $E_{eh} = -0.2615$. According to [9], the ionization energy $I^{\mathrm{Mn}^{2+}} = 1.234$. The O^{2-} ion does not exist in the free state, therefore let us take the $I^{\mathrm{O}^{2-}}$ value as zero. The estimates obtained above give the value $\left|\Delta_{3d,2s}\right| \approx 1.3$ a.u. We obtain the following values for the covalency parameters. For the pair $\mathrm{Mn}_2 - \mathrm{O}_1$: $\bar{\gamma}_{z^2,2s} \approx 0.069$, $\mathrm{Mn}_2 - \mathrm{O}_2$: $\bar{\gamma}_{z^2,2s} \approx -0.020$, $\bar{\gamma}_{xy,2s} \approx -0.033$. For the pair $\mathrm{Mn}_1 - \mathrm{O}_2$: $\bar{\gamma}_{z^2,2s} \approx -0.039$, $\bar{\gamma}_{xy,2s} \approx -0.067$.

Let us take the wave functions of the electron belonging to the doublet e_g of manganese ions in the form

$$\mathrm{Mn}_1\text{: } \left|1\right\rangle = c_1\left|xy\right\rangle - c_2\left|z^2\right\rangle, \qquad \mathrm{Mn}_2\text{: } \left|2\right\rangle = c_1\left|xy\right\rangle + c_2\left|z^2\right\rangle. \tag{7}$$

Wave functions are chosen from the condition of maximum length of the electron density in the direction of the long covalent bond.

Let us introduce the following notations $q_{\xi\theta} \equiv \left\langle \xi \middle| q \middle| \theta \right\rangle$, $p_{\xi\theta} \equiv \left\langle \xi \middle\| \theta \right\rangle$. According to [2], the spin densities of the considered processes have the form

$$f_{\xi,\zeta}^{(ij)} = \frac{1}{4} q_{\xi,\zeta}^2 - p_{\xi,\zeta}\bar{\gamma}_{\xi,\zeta} + \bar{\gamma}_{\xi,\zeta}^2, \qquad \xi,\xi' = \left|xy\right\rangle, \left|z^2\right\rangle, \zeta = \left|2s\right\rangle, \tag{8}$$

$$f_{\xi,\xi',\zeta}^{(ij)} = \frac{1}{4} q_{\xi,\zeta} q_{\xi',\zeta} - \frac{1}{2} p_{\xi,\zeta}\bar{\gamma}_{\xi',\zeta} - \frac{1}{2}\bar{\gamma}_{\xi,\zeta} p_{\xi',\zeta} + \bar{\gamma}_{\xi,\zeta}\bar{\gamma}_{\xi',\zeta}, \tag{9}$$

where *ij* denote the pair $\mathrm{Mn}^{3+} - \mathrm{O}^{2-}$.

Using equalities (7) – (9) we obtain for the isotropic part $A_s(1)$ of the THFI tensor of the O$_1$ ion

$$A_s(1) = 2c_2^2 f^{(12)}_{z^2,2s} a_s = 12.75\ \mathrm{MHz}, \tag{10}$$

where $a_s = 3.46 \times 10^3$ MHz is the hyperfine interaction parameter of the oxygen ion determined on the wavefunction $|2s\rangle$. The factor 2 arises owing to the contributions of Mn$_2$ and Mn$_3$ ions. The square of the coefficient $c_2^2 = 0.2$. Coefficients c_1 and c_2 are determined from rather good agreement with the experiment. The absence of the coefficient c_1 is a consequence of the smallness of the matrix element $\langle xy||2s\rangle$.

We obtain for the isotropic part $A_s(2)$ of the THFI tensor for the O$_2$ ion

$$A_s(2) = A_s(2,\mathrm{Mn}_1) + A_s(2,\mathrm{Mn}_2) = 22.90\ \mathrm{MHz}, \tag{11}$$

$$A_s(2,\mathrm{Mn}_1) = (c_1^2 f^{(21)}_{xy,2s} - 2c_1c_2 f^{(21)}_{z^2,xy,2s} + c_2^2 f^{(21)}_{z^2,2s})a_s = 12.57\ \mathrm{MHz},$$

$$A_s(2,\mathrm{Mn}_2) = (c_1^2 f^{(22)}_{xy,2s} + 2c_1c_2 f^{(22)}_{z^2,xy,2s} + c_2^2 f^{(22)}_{z^2,2s})a_s = 10.33\ \mathrm{MHz},$$

where $A_s(2,\mathrm{Mn}_1)$ is the contribution from the Mn$_1$ion, $A_s(2,\mathrm{Mn}_2)$ is the contribution from the Mn$_2$ ion.

The experimental values can be estimated using the temperature perturbation theory and the experimental temperature dependence of the spectrum. The H_N is the Hamiltonian of interaction of the nucleus with magnetic field for the noninteracting spins.

$$H_N = -\boldsymbol{\mu}_\mathbf{I}\mathbf{H} - \mathrm{Z}^{-1} \sum_{M,M'} \frac{\langle SM|H_z|SM'\rangle\langle SM'|H_L|SM\rangle}{kT}, \tag{12}$$

where **H** is magnetic field, H_z is the electron Zeeman interaction, $H_L = A(\mathbf{SI})$ is the ligand hyperfine interaction. Magnetic shift $A_s(T)$ of NMR line is defined experimentally in [1]. The $A_s(T)$ follows a Curie-Weiss law, but with different temperatures θ for the O$_1$ and O$_2$. Then for the interacting spins

$$A_s(T) = \frac{g\beta HAS(S+1)}{3k(T-\theta)},$$

where H is magnetic field value. The experimental values are $\theta(\mathrm{O}_1) = -15$ K, $\theta(\mathrm{O}_2) = 23$ K.

We obtain for the magnetic field of 11.7 T, $S = 2$ at room temperature

$$A_s(\mathrm{O}_1,T) \approx 1.25\ \mathrm{MHz}, \qquad A_s^{\exp}(\mathrm{O}_1,T) = 1\ \mathrm{MHz}, \tag{13}$$

$$A_s(\mathrm{O}_2,T) \approx 2.56\ \mathrm{MHz}, \qquad A_s^{\exp}(\mathrm{O}_2,T) = 2.4\ \mathrm{MHz}. \tag{14}$$

It is seen from equalities (13) and (14) that the theory and experiment are in rather good agreement.

The wavefunction $|\mathrm{Mn}_1\rangle = \overline{c}_1|\theta\rangle + \overline{c}_2|\varepsilon\rangle$, where $\overline{c}_1 = 0.995$, $\overline{c}_2 = -0.10$ [1]. It is determined in the local coordinate system specified above. The wavefunction $|\mathrm{Mn}_1\rangle$ and the wavefunction Mn$_1$: $|1\rangle = c_1|xy\rangle - c_2|z^2\rangle$ can be compared if the function Mn$_1$: $|1\rangle = c_1|xy\rangle - c_2|z^2\rangle$ is written in the coordinate system obtained from the coordinate system of [3] as follows. The origin of the coordinate system should be placed at the Mn$_1$ ion, and the *z* axis rotated by 90 degrees in the plane passing through the z axis and the O_2 ion forming the largest (long) covalent bond. Then in the new coordinate system the wavefunction Mn_1: $|1\rangle = c_1'|\theta\rangle + c_2'|\varepsilon\rangle$, where $c_1' = 0.998$, $c_2' = 0.06$. The coefficients $\overline{c}_1$ and c_1' almost coincide. The coefficient c_2' is determined as the difference of rather large quantities of the same order of magnitude. Its uncertainty is of the order of magnitude within the approximations made under ignoring the overlap of orbitals $|xz\rangle$, $|yz\rangle$, $|x^2 - y^2\rangle$ with the orbitals of the O^{2-} ion. Thus, it is obvious that the approximations made in this work should be taken into account in the forthcoming publications.

In Ref. [2] the secondary-quantization representation with a basic of partially nonorthogonal orbitals was applied to impurity center. In accordance with the present paper this method can be applied to concentrated systems.

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