Hybrid electron-nuclear states in exchange clusters

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It is shown that a specific interaction between quadrupole nuclear moments and cluster electron shell may occur in the symmetrical exchange clusters, which produces hybrid electron-nuclear states. The nuclear quadrupole resonance (NQR) spectrum is analyzed.

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1. To calculate the energy levels and line intensities of the nuclear quadrupole resonance (NQR) in exchange clusters, we use the effective Hamiltonian of the quadrupole interaction, which operates in the space of nuclear variables[1]:

$$H_Q = Q[3I_Z^2 - I(I+1) + \eta(I_+^2 + I_-^2)], \tag{1}$$

where Q is the quadrupole interaction constant and η is the asymmetry parameter (for

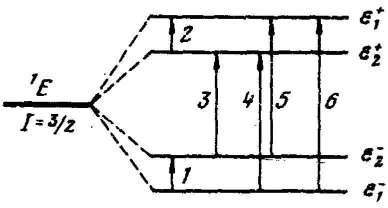

FIG. 1. Hybrid electron-nuclear states of a tetrahedral cluster; arrows indicate allowed transitions.

systems with the C_n axes at $n > 2$ $\eta = 0$). In this paper we show that in addition to the crystal-field (CF) effects in the symmetrical exchange clusters a specific interaction occurs between the quadrupole nuclear movements and the electron shell of the cluster, which is not described by the traditional Hamiltonian [Eq. (1)].

2. We examine a four-dimensional tetrahedral system (point symmetry T_d) consisting of orbitally nondegenerate exchange-coupled ions (for example, $Cu_4OCl_6[(C_6H_5)_3PO]_4$ crystals; ferroproteins containing fragments $\{Fe_4S_4[S_2C_2(CF_3)_2]_4\}^{2-}$, and others). In the zeroth approximation the cluster is described by the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian

$$H = -2J \sum_{i,j} \mathbf{s}_i \mathbf{s}_j \tag{2}$$

with the eigenvalues

$$E = -J[S(S+1) - 4s(s+1)], \tag{3}$$

where S is the total spin and s are spins of the interacting ions. In the anti ferromagnetic exchange the ground state with total spin $S = 0$ is doubly diagnostic in accordance with the two possible sets of values of intermediate spins S_{12} and S_{34}. The theoretical group investigation[2] showed that doubly degenerate ground state of the HDVV model corresponds to the orbital doublet ^1E of the bound-ion system. The aforementioned degeneration is accurate and remains valid for a refined HDVV model, in particular when the anti symmetrical Dzyaloshinskiĭ coupling is taken into account.[1)] In the presence of degeneration the quadrupole Hamiltonian operates in the space of electron and nuclear variables; the method of invariant yields:

$$H' = (1/3\sqrt{3}) \sum_a \{[(pI^{(2)}_{2a} - qI^{(2)}_{-1a})[\mathbf{s}_1\mathbf{s}_2 + \mathbf{s}_3\mathbf{s}_4 + w_1^*(\mathbf{s}_1\mathbf{s}_3 + \mathbf{s}_2\mathbf{s}_4) + w(\mathbf{s}_1\mathbf{s}_4 + \mathbf{s}_2\mathbf{s}_3)] + \text{H. C.}\} + 2\sqrt{2}\, kI^{(2)}_{oa} \sum_{i,j} \mathbf{s}_i\mathbf{s}_j\}, \tag{4}$$

where i, j, a denote exchange-bound ions and nuclei, respectively, k, p, q are quadrupole constants that are not associated by the symmetry relations, and $I^{(2)}_{\varkappa}$ are tensor operators,[4] consisting of nuclear spin operators, $w = \exp(2\pi i/3)$. In the case under consideration, the effect of electron shell on the nuclei is not reduced to the effective Hamiltonian of the type of Eq. (1) (for a T_d cluster a local C_{3v} group and $\eta = 0$), since we have a typical resonance situation similar to that occurring in Jahn-Teller systems[5,6] and in the resonance of electron and phonon states.[7] Using the terminology in Ref. 7, we shall refer to the states described by the Hamiltonian in Eq. (4) as hybrid states. The hybrid electron-nuclear states contain nuclear and electron states of equal weights with different sets of intermediate spins. The transitions between these states allow us to observe absorption of the electromagnetic field even in those cases when the local CF are characterized by cubic symmetry, and the interaction with the distant coordination spheres is negligibly small; for this approximation $Q=0$, and the quadrupole splitting in a single-nucleus fragment is not evident. Since the indicated states are genetically associated with the quadrupole nuclear moments, the aforementioned absorption may be called nuclear quadrupole resonance in the hybrid states.

3. The electron-nuclear quadrupole interaction [Eq. (4)] at $I_a = I = 3/2$ produces four energy levels: $\epsilon_1^{\pm} = \pm \Delta$, $\epsilon_2^{\pm} = \pm k$ ($\Delta = \sqrt{k^2 + p^2 + q^2}$, (Fig. 1). In the circular polarization perpendicular to the C_3 axis of the tetrahedron, the nuclear spectrum situated on this axis has six transitions which give four NQR lines with the following intensities (transition numbers are shown in parentheses):

$$J_I(1,2) = [3q^2 + 2(\Delta + k)^2]/\Delta(\Delta + k);\quad J_{II}(3) = 3p^2/(\Delta^2 - k^2);$$
$$J_{III}(4,5) = [3q^2 + 2(\Delta - k)^2]/\Delta(\Delta - k);\quad J_{IV}(6) = 3p^2k^2/\Delta^2(\Delta^2 - k^2). \qquad (5)$$

Thus, the spectrum of the hybrid states differs substantially from the two doublets ($M = \pm 3/2,\ \pm 1/2$) of the quadrupole Hamiltonian [Eq. (1)] that leads to a single NQR line.

4. Since the conditions for the occurrence of hybrid states are strongly associated with the level degeneration with respect to values of intermediate spins and cluster symmetry, it is interesting to analyze the effect of deformation. We shall introduce a tetragonal-type deformation perturbation ($T_d \rightarrow D_{2d}$):

$$V = \delta(\mathbf{s}_1\mathbf{s}_2 + \mathbf{s}_3\mathbf{s}_4), \qquad (6)$$

which splits the orbital doublet into states with fixed sets of intermediate spins ($^1E \rightarrow {}^1A_1 + {}^1B_1$). Diagonalizing the Hamiltonian $H' + V$, we obtain

$$E^{\pm}_{1(2)} = \underset{(-)}{+}(1/\sqrt{2})\sqrt{k^2 + \Delta^2 + 2\delta^2 \pm \sqrt{(p^2 + q^2 + 2\delta^2)^2 + 4\delta^2(4k^2 - \delta^2)}} \qquad (7)$$

At sufficiently large deformations ($|\delta| \gg |\Delta|$, however, $|\delta| \ll |J|$), hybrid states disappear and become nuclear sublevels that are described by the traditional-type quadrupole Hamiltonian [Eq. (1)] in which

$$Q = (2k + \sqrt{3}p)/12;\quad \eta = \sqrt{3(2\sqrt{3}k - p)^2 + 12q^2}/(2k + \sqrt{3}p. \qquad (8)$$

This result has a clear physical meaning: for large splitting the electron subsystem becomes fast and it separates from the nuclear; moreover, the electron cloud of the exchange system appears as a source of effective average field that acts (together with CF) on the nuclei of exchange-bound ions. The Z axis of the electric field gradient is perpendicular to the symmetry plane, and the directions of the other two axes are determined by quadrupole parameters. Deformation leads to gradient asymmetry ($\eta \neq 0$) and a partial reduction of the quadrupole interaction. In conclusion, we should emphasize that the necessary condition for the occurrence of hybrid states requires the presence of a degenerate (or pseudo-degenerate) quadrupole-active orbital multiplet (group-theoretical investigation of the HDVV model, see Ref. 2). The obtained results must also be taken into account in the analysis of the Mössbauer spectra of exchange clusters.

[1)] The Dzyaloshinskiĭ interaction is active for orbitally degenerate exchange multiplets for states with total spin $S \neq 0$.[3]

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[1] A. Abragam, Yadernyi magnetizm (Nuclear Magnetism), M., IIL, 1963.
[2] M. I. Belinskiĭ, B. S. Tsukerblat, and A. V. Ablov, Dok. Akad. Nauk SSR **207**, 125 (1972), B.S. Tsukerblat, M.I. Belinskiĭ, and A. V. Ablov, Phys. Lett. **41A** 109 (1972).
[3] B. S. Tsukerblat, V. M. Novotortsev, B. Ya. Kuyavskaya, M. I. Belinskiĭ, A. V. Ablov, A. N. Bazhan, and V. T. Kalinnikov, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 525 (1974) [JETP Lett. **19**, 277 (1974)].
[4] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, Kvantovaya teoriya uglovogo momenta [Quantum Theory of Angular Momentum], L., Nauka, 1975.
[5] I. B. Bersuker and I. Ya. Ogurtsov, Fiz. Tverd. Tela **12**, 3651 (1968) [Sov. Phys. Solid State **12**, (1968)].
[6] Yu. E. Perlin and B. S. Tsukerblat, Effeckty elekronnokolebatel'nogo vzaimodeĭstviya v opticheskikh spectrakh primesnykh paramagnitnykh ionov [Electronic-Vibrational Interaction Effects in Optical Spectra of Paramagnetic Impurity Ions], Kishinev, Shtiintsa, 1974.
[7] I. B. Levinson and E. I. Rashba, Usp. Fiz. Nauk **111**, 683 (1973) Rep. Prog. in Phys. **36**, 1499 (1973).