Effects of Dyaloshinskiĭ interaction in the Mössbauer spectra of three-nucleus exchange clusters

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We consider the interaction of the electron shell of an exchange trimer cluster with Mössbauer nuclei. A new type of quadrupole splitting, essentially dependent on the deformations and on the external magnetic field, is predicted. The noncollinear spin structure of the exchange cluster is found; it is shown that the effective magnetic fields at the Mössbauer nuclei are not parallel to the external field and depend on the latter. The character of all the considered effects is predetermined by the Dzyaloshinskiĭ interaction. The theory developed makes it possible to explain qualitatively the experimentally observed contradiction between identical quadrupole splittings in the zero-field spectrum of crystals of the type $[Fe_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$, on the one hand, and the difference between the effective magnetic fields at the Mössbauer nuclei in a strong external field, on the other.

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1. INTRODUCTION

As first deduced by Dzyaloshinskiĭ[1] from an analysis of the macroscopic symmetry conditions of a crystal, antisymmetrical exchange interaction leads to weak feromagnetism. Recently the researchers have been paying attention to crystals containing structural elements in the form of clusters—groups of paramagnetic ions coupled by exchange interaction. A group-theoretical classification[2] of the Heisenberg model (in particular, of "random" degeneracies) has shown that the Dzyaloshinskiĭ interaction is active in the presence of orbital degeneracy of exchange multiplets with total spin $S \neq 0$. Since the microscopic conditions for the appearance of the Dzyaloshinskiĭ interaction are connected with orbital degeneracy, this interaction predetermines the character of the resonance phenomena in the discrete energy spectrum of the cluster.[3]

A number of Mössbauer experiments were performed in the last few years on crystals containing antiferromagnetic three-nucleus clusters of trivalent iron.[4-9] The Mössbauer spectra were interpreted using the Heisenberg model of the exchange interaction.[1-5] Within the framework of this model, the role of the exchange interaction reduces to formation of a ground state with a minimum spin that governs the effective magnetic field at the iron nuclei. It is assumed here that the other crucial parameter of the Mössbauer spectra (the quadrupole splitting) is not connected in any way with the electron shell of the cluster and is determined only by the local point symmetry of the cluster nuclei.

It is shown below that a correct allowance for the interaction between the electron shell of the cluster and the nuclei of the exchange system leads to a number of new effects. In particular, we predict a new type of quadrupole splitting that depends on the external field, as well as an anisotropy and a field dependence of the effective magnetic fields at the Mössbauer nuclei. The character of the indicated effects is predetermined by the Dzyaloshinskiĭ which governs the specific spin structure of the cluster.

We discuss the experimental data[4-9] obtained on Mössbauer spectra and not adequately interpreted to date.

2. GROUND STATE OF TRIMER CLUSTER. THE DZYALOSHINSKIĬ INTERACTION

We consider a trimer exchange system made up of orbitally nondegenerate ions. The isotropic Heisenberg Hamiltonian that describes the system in the zeroth approximation is of the form

$$\mathcal{H}_0 = -2J \sum_{i,j=1}^{3} \mathbf{s}_i \mathbf{s}_j \tag{1}$$

with eigenvalues

$$E_0 = -J\left[S(S+1) - \sum_{j=1}^{3} s_j(s_j+1) \right], \tag{2}$$

where s_j are the ion spins. The energy levels, which are characterized by a total spin S, are degenerate in the values of the intermediate spin $\mathbf{S}_{12} = \mathbf{s}_1 + \mathbf{s}_2$ in the scheme of addition of three angular momenta. For antiferrmagnetic clusters ($J < 0$) of the type M_2M' and M_3 with half-integer spins of the ions, the ground state is the one with total spin $S = \frac{1}{2}$. There are always two such states, in accord with the two possible intermediate-spin values that yield $S = \frac{1}{2}$. Thus, the ground state of the trimer cluster in the Heisenberg–Dirac–van Vleck (HDvV) model, with allowance for the degeneracy in the spin projection, is fourfold degenerate. Inasmuch as a fourfold degeneracy is impossible in trigonal point groups, the conclusion that the ground state has quadrupole degeneracy is due to the approximate character of the HDvV model. It is shown in Ref. 2 that the "unphysical" degeneracy corresponds to a doublet orbital degeneracy of the ground state of a cluster with $S = \frac{1}{2}$ (orbital doublet ^2E). Active for the ^2E level is a spin-orbit interaction that leads to an effective Dzyaloshinskiĭ exchange interaction[3]

$$\mathcal{H}_D = i \sum_{i,j=1}^{3} \{\mathbf{G}_{ij}^{(1)} \otimes \{\mathbf{S}_i^{(1)} \otimes \mathbf{S}_j^{(1)}\}^{(1)}\}^{(0)}, \tag{3}$$

where $\mathbf{G}_{ij} = -\mathbf{G}_{ji}$ is an antisymmetrical real vector con-

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stant, and standard tensor notation is used.

Since the conditions for the appearance of the Dzyaloshinskiĭ interaction are connected with orbital degeneracy, we introduce also small distortions ($|\delta| \sim |G_{ij}| \ll |J|$) of the cluster, described by the Hamiltonian

$$V=-2\delta_0 s_1 s_2. \tag{4}$$

Diagonalizing the perturbation $\mathcal{H}_D + V$ in the basis of the ground state of the Hamiltonian $\mathcal{H}_0$, we find that the doublet ^2E is split into two Kramers doublets with energies

$$E^{\pm}=\pm\Delta, \quad \Delta=(\delta^2+D^2)^{1/2},$$
$$D\equiv D^z=\gamma(s_1 s_2 s_3 s_{12})\sum_{i,j=1}^{3} G_{ij}^z, \tag{5}$$

where D is the effective multielectron parameter of the Dzyaloshinskiĭ interaction,

$$\gamma=(-1)^{s_1+s_2+s_3+1/2}\frac{S_0+1}{3}[(2S_0+1)(2S_0+3)]^{1/2}$$
$$\times\begin{Bmatrix} (S_0+1) & s_1 & s_2 \\ s_1 & S_0 & 1 \end{Bmatrix}\begin{Bmatrix} (S_0+1) & \frac{1}{2} & s_3 \\ \frac{1}{2} & S_0 & 1 \end{Bmatrix}\langle s_1\|s_1\|s_1\rangle, \tag{6}$$

$\delta=\delta_0(S_0+1)$ is the effective deformation parameter, S_0 is the smaller of the two possible values of S_{12}, $\{\ldots\}$ is a $6j$-symbol, and $\langle\ldots\|\ldots\|\ldots\rangle$ is a reduced matrix element. In the case of a heteronuclear cluster ($s_1=s_2 \neq s_3, S_0=s_3-\frac{1}{2}$) the expression for γ becomes

$$\gamma=\frac{2s_3+1}{24}\left[\frac{(4s_1+2s_3+3)(4s_1-2s_3+1)}{6}\right]^{1/2}. \tag{7}$$

For an exactly trigonal system

$$\sum_{i,j=1}^{3} G_{ij}^x=\sum_{i,j=1}^{3} G_{ij}^y=0.$$

At low deformations (4) we have $D^X \ll D^Z$ and $D^Y \ll D^Z$, and in formula (5) as well as hereafter we assume a simplified model in which $D^X=D^Y=0$.

3. EFFECTIVE HAMILTONIAN OF ELECTRON-NUCLEAR QUADRUPOLE COUPLING

The electric field gradients at the Mössbauer nuclei contain, first, a contribution of the electron shell and, second, ion contributions due to the crystal environment. Typical of the systems mentioned in the Introduction is a high-symmetry (close to octahedral) surrounding of the iron nuclei, so that the ion contribution to the quadrupole constants is due to remote coordination spheres.

We focus our attention below on the electronic effects. The electron shell of a mononuclear fragment Fe^{3+} is spherically symmetrical, so that in the absence of exchange interaction it makes no contribution to the electric field gradient at the iron nucleus. It is clear from physical considerations that the exchange interaction deforms the electron shell, and the resultant effects are closely connected with the orbital degeneracy of the ground state of the exchange cluster.

In fact, the components of the tensor of the quadrupole moment in the group D_{3h} transform in accord with a one-dimensional and two two-dimensional representations: $A_1(Q_{zz})$,

$$E\left[\, Q_{\pm 2}^{(2)}=\frac{1}{\sqrt{6}}(Q_{xx}-Q_{yy}\pm 2iQ_{xy})\,\right],$$
$$E'\left[\, Q_{\pm 1}^{(2)}=\frac{1}{\sqrt{2}}(Q_{xz}\pm Q_{yz})\,\right].$$

Therefore in the basis of the exact eigenfunctions of the orbital doublet ^2E the mean values of the components of the tensor of the quadrupole moment of the cluster electron shell are generally speaking different from zero.

Thus, for trimer clusters with degenerate ground state the onset of an electron-nuclear quadrupole coupling is possible. The effective Hamiltonian of the electron-nuclear quadrupole interaction is constructed in the form of an invariant convolution of tensor operators that act in the space of the spin variables pertaining to the electron (exchange) subsystems, with symmetrized combinations of the nuclear quadrupole-moment operators.

Since the basis operators of the exchange type $\{S_l^{(1)} \otimes \mathbf{S}_j^{(1)}\}_\nu^\varkappa$ act in a space of states with $S=\frac{1}{2}$, only convolutions with $\varkappa=0$ and $\varkappa=1$ need be taken into account. The final expression for the effective Hamiltonian of the electron-nuclear quadrupole coupling takes the form

$$\mathcal{H}_Q=\sum_{l,j,\alpha=1}^{3}\{[q_1\mathbf{s}_l\mathbf{s}_j-iq_2\{\mathbf{S}_l^{(1)}\otimes\mathbf{S}_j^{(1)}\}_0^{(1)}]I_{0\alpha}^{(2)}$$
$$+[q_3\mathbf{s}_l\mathbf{s}_j-iq_4\{\mathbf{S}_l^{(1)}\otimes\mathbf{S}_j^{(1)}\}_0^{(1)}](I_{2\alpha}^{(2)}+I_{-2\alpha}^{(2)})\}$$
$$+[q_5 I_{01}^{(2)}+q_6(I_{21}^{(2)}+I_{-21}^{(2)})]$$
$$\times(2\mathbf{s}_2\mathbf{s}_3-\mathbf{s}_1\mathbf{s}_2-\mathbf{s}_1\mathbf{s}_3)$$
$$+[q_5 I_{02}^{(2)}+q_6(I_{22}^{(2)}+I_{-22}^{(2)})]$$
$$\times(2\mathbf{s}_1\mathbf{s}_3-\mathbf{s}_1\mathbf{s}_2-\mathbf{s}_2\mathbf{s}_3)+[q_5 I_{03}^{(2)}$$
$$+q_6(I_{23}^{(2)}+I_{-23}^{(2)})](2\mathbf{s}_1\mathbf{s}_2-\mathbf{s}_1\mathbf{s}_3-\mathbf{s}_2\mathbf{s}_3), \tag{8}$$

where the indices l, j, and α number respectively the exchange-coupled ions and nuclei; $\chi_{\nu\alpha}^{(\varkappa)}$ is the ν-th cyclic component of the irreducible tensor χ of rank $\varkappa$ pertaining to the α-th nucleus[10]; q_j are the semi-empirical constants of the method of invariants. The nuclear operators are written in local coordinate systems with the x_α directed towards the center of the triangle, the z_α are perpendicular to the plane, and the y_α form with z_α and x_α a right-hand Cartesian triad (Fig. 1). The operators of the electron subsystem are expressed in the common coordinate frame (XYZ) of the cluster (Fig. 1). Since the deformations are small, the Hamiltonian (8) is written in the form of an invariant on the D_{3h} group.

In exchange clusters of transition metals, all the exchange parameters, generally speaking, greatly exceed the quadrupole interaction constants ($\Delta \gg q_j$). Therefore in first-order perturbation theory we can neglect those matrix elements of the Hamiltonian (8) which couple states belonging to different Kramers doublets. As a result of this approximation we arrive at three single-nucleus quadrupole operators of the form

$$\mathcal{H}_{Q\alpha}=Q_\alpha^{\pm}[3I_z^2-I(I+1)+\eta_\alpha^{\pm}(I_+^2+I_-^2)], \tag{9}$$

where the + and − signs pertain respectively to the upper and lower Kramers doublets $I_\pm=\mp(1/\sqrt{2})(I_x \pm iI_y)$.

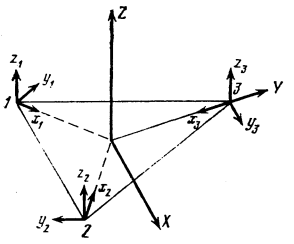

FIG. 1. Local and common coordinate frames used in the Hamiltonian (8).

The principal axes of the gradient tensor are directed, in the assumed approximation, along the axes z_α of the local coordinate systems (i.e., along the common axis Z), while the axes x and y of the gradient tensor coincide with the axes x_α and y_α of the underformed cluster.

It should be noted that averaging over the electronic states was made possible by the presence of Kramers degeneracy and by the large gap width 2Δ relative to the quadrupole parameters. In this approximation the system is described by multiplicative rather than hybrid electron-nuclear wave functions.[11] The physical meaning of this result is that the electron subsystem is fast relative to the nuclear one, and the latter is situated in the effective field produced by the electron shell of the cluster.

The systems $M_2M'(s_1=s_2\neq s_3)$ and the deformed systems $M_3(s_1=s_2=s_3)$ have quadrupole constants of two types:

$$Q_i^{\pm}=Q_2^{\pm}=6^{-1/2}(Q_0^{\pm}+\tilde{Q}^{\pm});\ Q_3^{\pm}=6^{-1/2}(Q_0^{\pm}-2\tilde{Q}^{\pm}), \tag{10}$$

where

$$Q_0^{\pm}=\frac{q_1}{2}\left[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\right]\pm 3\cdot 3^{1/2}\gamma q_2\frac{D}{\Delta},$$

$$\tilde{Q}^{\pm}=\pm\frac{3q_3}{8}(2s_3+1)\frac{\delta}{\Delta}-q_3[s_3(s_3+1)-s_1(s_1+1)]. \tag{11}$$

For the asymmetry parameters we obtain

$$\eta_1^{\pm}=\eta_2^{\pm}=\frac{1}{Q_1^{\pm}}\left\{\frac{q_3}{2}\left[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\right]\right.$$

$$\left.\pm 3\cdot 3^{1/2}\gamma q_4\frac{D}{\Delta}\pm\frac{3q_6}{8}(2s_3+1)\frac{\delta}{\Delta}-q_6[s_3(s_3+1)-s_1(s_1+1)]\right\}, \tag{12}$$

$$\eta_3^{\pm}=\frac{1}{Q_3^{\pm}}\left\{\frac{q_3}{2}\left[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\right]\right.$$

$$\left.\pm 3\cdot 3^{1/2}\gamma q_4\frac{D}{\Delta}\mp\frac{3q_6}{4}(2s_3+1)\frac{\delta}{\Delta}+2q_6[s_3(s_3+1)-s_1(s_1+1)]\right\}. \tag{13}$$

Thus, in accordance with the general considerations advanced above, the electron shell of the cluster produces at the metal nuclei an electric field gradient that depends both on the deformations and on the Dzyaloshinskiĭ interaction parameter. The qualitative character of this dependence is easiest to illustrate with a homonuclear system as an example. In the case of a strong Dzyaloshinskiĭ interaction ($D/\Delta\to 1$, $\delta/\Delta\to 0$) it follows from (10)–(13) that the parameters of the quadrupole splitting in a homonuclear system turn out to be equal ($Q_1^*=Q_2^*=Q_3^*$), and the asymmetry parameters likewise turn out to be equal. Thus, the geometrical non-equivalence of the ions does not always manifest itself in the quadrupole splittings of the nuclear levels. The physical parameters that determine the structural non-equivalence of the nuclei, from the point of view of the quadrupole splittings, are the ratios $(q_5\delta/\Delta)/(q_2D/\Delta)$ and $(q_5\delta/\Delta)/q_1$. If the parameters q_j are of the same order, then the quadrupole splittings at all nuclei are the same even in the case of appreciable geometrical distortions of the cluster, provided that the Dzyaloshinskiĭ interaction is large. Thus, the Dzyaloshinskiĭ interaction equalizes the difference produced in the quadrupole splittings by the structural nonequivalence of the ions; in other words, the Dzyaloshinskiĭ interaction restores the cluster trigonal symmetry disturbed by the statistical distortions. It can be stated that the parameters δ/J is connected with the geometrical symmetry of the system, whereas the parameter $\delta/(D^2+\delta^2)^{1/2}$ characterizes the physical symmetry. Comparing this conclusion with the results of an analysis of the magnetic susceptibility,[12] we see that the effect of suppression of the static distortion by the Dzyaloshinskiĭ interaction is quite general.

4. THE ZEEMAN EFFECT

Since the electronic Zeeman splittings of each of the doublets greatly exceed the nuclear ones, we confine ourselves, to illustrate the effects and simplify the formulas, to the simplest isotropic Zeeman Hamiltonian in the form

$$W=\mu_e\mathbf{SH}, \tag{14}$$

where $\mu_e=g_e\beta_e$, and g_e and β_e are respectively the electronic g-factor and the Bohr magneton. For the energy levels we obtain the expression

$$E_{1(2)}^{\pm}(H)=\pm\{\Delta^2+(\mu_eH/2)^2\overset{+}{(-)}\mu_eH[\Delta^2-D^2\sin^2\vartheta]^{1/2}\}^{1/2}, \tag{15}$$

where ϑ is the angle between the direction of the external magnetic field and the Z axis. The Dzyaloshinskiĭ interaction leads to anisotropy of the Zeeman splitting of the electron levels even in the simple isotropic model of the Zeeman interaction.

Since the electronic splittings in a magnetic field exceed considerably the quadrupole effects and the nuclear Zeeman splittings, the problem can be solved by perturbation theory, by averaging the Hamiltonian (8) over the wave functions pertaining to the energy levels (15). The diagonal matrix elements obtained in this manner constitute the effective Hamiltonians of the effective interaction, act only on the nuclear variables, and operate on each Zeeman sublevel (15). Thus, we again arrive and a standard quadrupole Hamiltonian of type (9). We shall consider hereafter two canonical field directions—parallel ($\vartheta=0$) and perpendicular ($\vartheta=\pi/2$).

In the case of a parallel field the quadrupole constants do not depend on the external field and coincide with the corresponding expressions (10)–(13) of the zero-field spectrum.

At $\vartheta=\pi/2$ the quadrupole splitting constants depend on the external field. The corresponding calculations for the heteronuclear cluster yield:

$$Q_1^{\pm}(H_\perp)=Q_2^{\pm}(H_\perp)=6^{-1/2}\Big\{\frac{q_1}{2}\Big[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\Big]+\frac{3\cdot 3^{1/2}\gamma q_2 D}{E^{\pm}_{1(2)}(H_\perp)}$$
$$+\frac{3q_5}{8}(2s_3+1)\frac{2\delta^{+}_{(-)}\mu_e H_\perp}{2E^{\pm}_{1(2)}(H_\perp)}-q_5[s_3(s_3+1)-s_1(s_1+1)]\Big\}, \quad (16)$$

$$Q_3^{\pm}(H_\perp)=6^{-1/2}\Big\{\frac{q_1}{2}\Big[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)+\frac{3\cdot 3^{1/2}\gamma q_2 D}{E^{\pm}_{1(2)}(H_\perp)}$$
$$-\frac{3q_5}{4}(2s_3+1)\frac{2\delta^{+}_{(-)}\mu_e H_\perp}{2E^{\pm}_{1(2)}(H_\perp)}+2q_5[s_3(s_3+1)-s_1(s_1+1)]\Big\}, \quad (17)$$

$$\eta_1^{\pm}(H_\perp)=\eta_2^{\pm}(H_\perp)=\frac{1}{Q_1^{\pm}}\Big\{\frac{q_3}{2}\Big[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\Big]+\frac{3\cdot 3^{1/2}\gamma q_4 D}{E^{\pm}_{1(2)}(H_\perp)}$$
$$+\frac{3q_6}{8}(2s_3+1)\frac{2\delta^{+}_{(-)}\mu_e H_\perp}{2E^{\pm}_{1(2)}(H_\perp)}-q_6[s_3(s_3+1)-s_1(s_1+1)]\Big\}, \quad (18)$$

$$\eta_3^{\pm}(H_\perp)=\frac{1}{Q_3^{\pm}}\Big\{\frac{q_3}{2}\Big[\frac{3}{4}-\sum_{j=1}^{3}s_j(s_j+1)\Big]+\frac{3\cdot 3^{1/2}\gamma q_4 D}{E^{\pm}_{1(2)}(H_\perp)}$$
$$-\frac{3q_6}{4}(2s_3+1)\frac{2\delta^{+}_{(-)}\mu_e H_\perp}{2E^{\pm}_{1(2)}(H_\perp)}+2q_6[s_3(s_3+1)-s_1(s_1+1)]\Big\}. \quad (19)$$

Equations (16)–(19) combine the equations for the constants Q_α^* and η_α^* pertaining to the four magnetic sublevels (15) at $\vartheta=\pi/2$. Accordingly, the signs + and – pertain as before to the two Kramers doublets, and the indices and the corresponding signs + and (–) number the magnetic sublevels of one Kramers doublet.

We see that a perpendicular field decreases the quadrupole splitting by reducing the terms with the constants q_2 and q_4 in the Hamiltonian (8). A similar effect is produced by the large deformations.

In the case of strong magnetic fields ($\mu_e H \gg \Delta$), expressions (16)–(19) go over into formulas (10)–(13) if we put $D=0$ in the latter. The physical meaning of this result is that the Dzyaloshinskiĭ interaction is suppressed by the perpendicular field. Suppression of the Dzyaloshinskiĭ interaction means in fact that at any ratio of the parameters δ and D (even at $\delta \ll D$) the case of strong deformations is realized in strong fields. This case corresponds to the Heisenberg model, when the constants $Q_\alpha^{\pm}$ and $\eta_\alpha^{\pm}$ do not depend at all on the parameter δ (in the presence of two types of distortions with parameters δ_1 and δ_2 the quadrupole constants $Q_\alpha^{\pm}$ and $\eta_\alpha^{\pm}$ are different for all nuclei and depend on the ratio δ_1/δ_2 even in the strong-field limit). The noted suppression effects and their dependence on the magnitude and orientation of the external magnetic field reveal the local symmetry of the exchange-cluster nuclei. In weak fields, the Dzyaloshinskiĭ interaction leads to equalization of the electric field gradients of the geometrically distorted exchange system, and, just as in strong fields that suppress the Dzyaloshinskiĭ interaction, a local symmetry of the nuclei appears in the quadrupole splittings. Thus, the physical symmetry of the nuclei in the Mössbauer experiments is determined by the relations between the Dzyaloshinskiĭ interaction parameter, on the one hand, and the magnetic field and the deformation, on the other.

5. EFFECTIVE MAGNETIC FIELDS AT THE MÖSSBAUER NUCLEI

At relatively large electronic Zeeman splittings, greatly exceeding the electron-nuclear hyperfine splitting,

$$\mathcal{H}_{hf}=a\sum_{\alpha=1}^{3}\mathbf{s}_\alpha\mathbf{I}_\alpha \quad (20)$$

the latter appear in the form of hyperfine magnetic fields at the nuclei of the paramagnetic ions of the exchange cluster, and are additive with respect to the external field. The indicated hyperfine field induced at the α-th nucleus by the polarization of the electron spin of the cluster in the k-th Zeeman state is given by

$$\mathbf{H}_\alpha(E_k)=\frac{a}{\mu_n}\langle k|\mathbf{s}_\alpha|k\rangle, \qquad (\mu_n=g_n\beta_n). \quad (21)$$

The effective field is represented by the sum $\mathbf{H}_\alpha^k=\mathbf{H}+\mathbf{H}_\alpha(E_k)$. In a parallel field we obtain the following expressions for the hyperfine fields at the nuclei of a heteronuclear cluster:

$$H_1[E^{\pm}_{1(2)}(H_\parallel)]=H_2[E^{\pm}_{1(2)}(H_\parallel)]=\overset{+}{(-)}\frac{a}{6\mu_n}\Big[1\mp\frac{2s_3+1}{2}\frac{\delta}{\Delta}\Big]. \quad (22)$$

$$H_3[E^{\pm}_{1(2)}(H_\parallel)]=\overset{+}{(-)}\frac{a}{6\mu_n}\Big[1\pm(2s_3+1)\frac{\delta}{\Delta}\Big]; \quad (23)$$

the numbering of the levels in a parallel field is determined by the relation

$$E^{\pm}_{1(2)}(H_\parallel)=\pm\Delta^{+}_{(-)}\mu_e H_\parallel/2. \quad (a)$$

Formulas (22) and (23) retain their meaning also for a homonuclear system. The hyperfine field components lying in the plane of the cluster vanish so that the effective field is directed along the external field. At $D=0$ we obtain the Heisenberg-model results cited by Takano.[4] It follows from Eqs. (22) and (23), which generalize the results of the Heisenberg model, that the Dzyaloshinskiĭ interaction plays a substantial role. It is seen that at $\delta \ll D$ the effective fields at all the nuclei are the same, despite the presence of deformations. This limiting case is realized even for a weak Dzyaloshinskiĭ interaction in a symmetric (D_{3h}) system or a distorted system if the Dzyaloshinskiĭ interaction is strong enough. Thus, the Dzyaloshinskiĭ exchange interaction leads to magnetic equivalence of the nuclei even in those systems where they are geometrically non-equivalent.

When the external field is perpendicular, the picture of the effective fields is much more complicated. The hyperfine field at nucleus 3 is collinear with the external field arbitrarily oriented in the cluster plane, and is described by the expression

$$\mathbf{H}_3[E^{\pm}_{1(2)}(H_\perp)]=\overset{+}{(-)}\frac{a}{6\mu_n}\Big[(2s_3+1)+\frac{2\delta^{+}_{(-)}\mu_e H_\perp}{2E^{\pm}_{1(2)}(H_\perp)}\Big]\frac{\mathbf{H}}{H}. \quad (24)$$

Thus, for the electronic states $E_1^{\pm}$ the effective field is parallel to the external one, and for the states $E_2^{\pm}$ it is antiparallel. The absolute magnitude of the hyperfine fields at the first and second nuclei is the same and is given by

$$H_1[E^{\pm}_{1(2)}(H_\perp)]=H_2[E^{\pm}_{1(2)}(H_-)]$$
$$=\frac{a}{6\mu_n}\frac{\{[2\delta^{+}_{(-)}\mu_e H_\perp-(2s_3+1)E^{\pm}_{1(2)}(H_-)]^2-4B^2D^2\}^{1/2}}{2|E^{\pm}_{1(2)}(H_-)|}, \quad (25)$$

where

$$B=\{(2s_1+s_2+{}^3/_2)(2s_1-s_2+{}^1/_2)\}^{1/2}.$$

An important consequence of the Dzyaloshinskiĭ interaction is the polarization of the spins along a direction

that does not coincide with that of the external magnetic field. The hyperfine magnetic fields in the electronic states $E^{\pm}_{1(2)}(H_\perp)$ at the nuclei 1 and 2 make with the external magnetic field angles determined by the relations

$$\varphi_1(E_1^{\pm}) = -\varphi_2(E_1^{\pm}) = \varphi_1(E^{\pm}_{(3)}) + \pi = -\varphi_2(E^{\pm}_{(3)}) + \pi = \operatorname{arctg}\frac{2BD}{2\delta^{\pm}_{(-)}\mu_e H_\perp - (2s_3+1)E^{\pm}_{1(3)}}. \quad (26)$$

The characteristic spin structure of the cluster, governed by the angles (26), is shown in Fig. 2. Of course, for an axial Dzyaloshinskiĭ interaction the system, as expected, is isotropic in the plane, so that the average total magnetic moment $\langle s_1 + s_2 + s_3\rangle$ of the cluster is directed along the external field for all the electronic Zeeman sublevels.

Another important consequence of the Dzyaloshinskiĭ interaction is the dependence of the absolute magnitude and orientation of the hyperfine fields at the nuclei on the absolute value of the external field. The angles (26) of deviation from the external-field directions do not depend on the orientation of the external field in the plane of the cluster and when the external field is increased they tend, as follows from (26), to zero or to π, corresponding to parallel and antiparallel orientations of the hyperfine fields relative to the external field. The physical reason is that a magnetic field parallel to the axis of the Dzyaloshinskiĭ interaction suppresses this interaction. In the limit of strong magnetic fields, Eqs. (24)–(26) go over into Eqs. (22) and (23) for parallel field orientation, with $D=0$; the latter equations correspond to an isotropic Heisenberg model in which the spins are always polarized along the directionof the external magnetic field.

Of importance from the point of view of the spin structure of the cluster are the values of the angles φ_α for a strong Dzyaloshinskiĭ interaction and relatively small distortions in the magnetic fields ($D \gg \delta, \mu_e H_\perp$). In this limiting case the expressions for φ_α are given by

$$\varphi_1(E_1^{\pm}) = -\varphi_2(E_1^{\pm}) = \varphi_1(E_2^{\pm}) + \pi = -\varphi_2(E_2^{\pm}) + \pi = \mp \operatorname{arctg}\frac{2B}{2s_3+1}. \quad (27)$$

It is instructive that in the case of a homonuclear cluster the angles of inclination for the first and second nuclei amount to

$$\varphi_1(E_1^{\pm}) = -\varphi_2(E_1^{\pm}) = \varphi_1(E_2^{\pm}) + \pi = -\varphi_2(E_2^{\pm}) + \pi = \mp\pi/3. \quad (28)$$

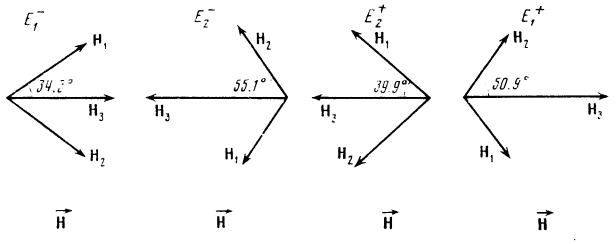

FIG. 2. Spin structure of exchange three-nucleus cluster and the hyperfine fields H_α at the nuclei in a perpendicular orientation of the external magnetic field H (indicated under the figures by arrows in the same scale as the hyperfine fields). The figures are presented in increasing order of the Zeeman-sublevel energy $E^{\pm}_{1(2)}(H_\perp)$; $\delta/D = 0.2$, $\mu_e H/D = 3$, $H = 50$ kOe, $s_1 = s_2 = s_3 = 5/2$ (Fe^{3+} ions).

6. DISCUSSION OF EXPERIMENTAL DATA

Takano[4] was the first to investigate the Mössbauer spectra of three-nucleus exchange clusters. At $T = 1.5$ K and in external fields up to 50 kOe, he investigated iron-acetate crystals

$$[Fe_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O,$$

as well as the corresponding heteronuclear analogs of the Cr_2Fe type. In the absence of a magnetic field, a single asymmetrical quadrupole doublet is observed. In a magnetic field there is observed a complicated spectrum comprising a superposition of three spectra with different effective fields. Such a spectrum indicates magnetic non-equivalence of all three ions, and Takano interprets it by assuming, within the framework of the HDvV model, the presence of two types of cluster distortions, δ_1 and δ_2.

The number of investigated crystals containing exchange triplets was subsequently greatly increased. Wilson and Rumbold[3] measured the Mössbauer spectra for a number of crystals—acetates, benzoates, chloracetates, and formiates of iron. In all the investigated compounds[5] there is observed a single doublet line of the zero-field spectrum and a considerable structural non-equivalence of the iron ions in a strong magnetic field. The quadrupole splitting is quite sensitive to replacement of the ligands both within and outside the complex cation. Takano, Rumbold, and Wilson[4,5] assume that the observed line widths do not have an internal structure connected with the superposition of noticeably different quadrupole splitting. Such a sensitivity to the nature of the ligand, together with the good resolution of the quadrupole doublet, is evidence of a high degree of equivalence of the three iron ions.

Thus, all the Mössbauer experiments[4-9] reveal a contradiction between the non-equivalence of the iron ions in a strong magnetic field and the identity of the quadrupole splittings in the zero-field spectra.

The experimental data can be qualitatively interpreted within the framework of the theory developed here. In fact, the closest coordination sphere of the metal ion is sufficiently symmetrical, so that the observable quadrupole splittings might be attributed to effects of the crystal fields of the following coordination spheres, as well to the interaction of the nuclei with the electron shell of the cluster. If we assume that the latter makes the predominant contribution to the quadrupole splitting and confine ourselves in the qualitiative treatment to a simplified model with one type of distortion, then the quadrupole constants are given by Eqs. (10)–(13). In the case of a strong Dzyaloshinskiĭ interaction the parameters connected with the system distortion vanish, and the quadrupole-splitting energy $E_Q = Q[3(3+\eta^2)]^{1/2} \times (I_\alpha = \frac{3}{2})$ turns out to be the same for all three nuclei of the distorted system.

We turn now to experiments in a strong magnetic field. For the mixed Cr_2Fe cluster the zeroth splitting is $\Delta(Cr_2Fe) \sim 3$ cm^{-1} (Ref. 4). For the symmetrical system F_3, this splitting should apparently be much smaller. The value of $\Delta(Fe_3)$ is determined by the upper limit of the Dzyaloshinskii interaction parameter in the consid-

ered systems. Therefore the fields used in the experiment $H=50$ kOe ($\mu_e H \sim 5$ cm^{-1}) suppress the Dzyaloshinskiĭ interaction. This physical situation corresponds to the limiting strong field, when the effective fields (14) and (25) for perpendicular orientation (the experiment was performed on a polycrystalline sample) goes over into the formulas of the Heisenberg model for the distorted system. In the ground state, which is populated under the conditions of the Takano experiment ($T=1.5$ K), we have

$$H_1=H_2=-4a/6\mu_n, \quad H_3=5a/6\mu_n. \tag{29}$$

Thus, the suppression of the Dzyaloshinskiĭ interaction by a magnetic field manifests itself in the experiment as a restoration of the geometric symmetry of the cluster. The presented arguments interpret qualitatively the experimentally observed contradiction between the identical quadrupole splittings and the non-equivalence of the effective fields at the nuclei in a strong magnetic field.

Indirect evidence favoring the presented interpretation is provided by the following facts:

1) The experimentally observed noticeable broadening of the Mössbauer spectra in a magnetic field (see Fig. 4 of Ref. 4). This broadening can be interpreted as the result of the scatter of the effective fields that depend on the orientation of the external field. This dependence is absent in the Heisenberg model and manifests itself only in the presence of the Dzyaloshinskiĭ interaction.

2) for mixed Cr_2Fe clusters, in which the static distortions are certainly not small, the Dzyaloshinskiĭ interaction is suppressed by statistical distortions. In fact, the experiments with Cr_2Fe are splendidly explained within the framework of the Heisenberg model.[4] The widths of the Cr_2Fe spectral lines are much smaller than for the homonuclear system.

3) The important role played by the Dzyaloshinskiĭ interaction is proved by the lowered Curie-Weiss constant.[4] Actually, it follows from the qualitative behavior of the magnetic sublevels, which follows in turn from Eq. (15), the magnetic susceptibility is low in the region of relatively weak fields that do not suppress the Dzyaloshinskiĭ interaction.

Quantitative estimates show that $D \sim \delta$. Since the values of the semiempirical parameters q_j are presently unknown, no qualitative conclusions can be drawn concerning the agreement between theory and experiment. Nonetheless, the presented relation enable us to recommend further experiments: 1) It is necessary to study the field dependence of the quadrupole-Hamiltonian parameters and of the effective fields at the nuclei. Unfortunately, the measurements made in Ref. 4 for two fields (30 and 50 kOe) pertained to the least interesting case of a mixed cluster. 2) It is necessary to measure the Mössbauer spectra for single crystals and to investigate the angular dependences of the parameters of the quadrupole Hamiltonian. An investigation of single crystals would make it possible to observe the spin-orientation field dependence brought about by the Dzyaloshinskiĭ interaction. The character of the spin structure of the cluster, which is directly connected with the considered effects, can be investigated also by other methods, that yield direct information. In fact, the exchange-cluster nuclei are a polarized target of sorts, with the spins oriented in accord with Eqs. (26). This uncovers possibilities of investigating the spin structure by the methods of scattering slow polarized neutrons.[13]

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