Paramagnetic resonance of mixed chromium and iron triads

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(Submitted May 25, 1973)
Zh. Eksp. Teor. Fiz. **65**, 1979–1983 (November 1973)

Paramagnetic resonance of mixed triads of the type $[Me_3O(RCOO)_6)H_2O)_3]^+$, where $Me_3 = CrFe_2$ and Cr_2Fe, was investigated at a frequency $\nu \approx 9470$ MHz and in the temperature interval 300–4.2°K. It is shown that the Heisenberg exchange model is equivalent to the Hamiltonian (2) for the description of the obtained experimental data. It is shown that it is feasible to explain the genealogy of the lower energy states of the triad, and the relative values of the antiferromagnetic exchange interactions between different ions of the triads are determined: $J_{\text{Fe-Fe}} > J_{\text{Fe-Cr}} > J_{\text{Cr-Cr}}$. The modified expression for the magnetic susceptibility of mixed triads is used to estimate the value $J_{\text{Fe-Cr}} \approx 35.5k$ ($\approx 25\ \text{cm}^{-1}$).

A study of exchange clusters of transition-metal ions, which make it possible to simulate the ferro and antiferromagnetism phenomena, is a timely problem in the physics of magnetic phenomena. In a brief communication[1] we called attention to the fact that from among the different systems of this kind, particular interest attaches to mixed triads of magnetic ions, for in such cases it is possible to obtain by simple means valuable information on the lower energy states, and to determine uniquely the relative values and the character of the exchange interactions between the ions making up the cluster. In this communication, we develop the ideas of [1] in greater detail.

We have investigated the EPR spectra of the mixed triads Cr (III) and Fe (III), which are produced in the course of joint synthesis of the corresponding carboxylates of chromium and iron, which can be described by the formula

$$[Me_3O(RCOO)_6(H_2O)_3]NO_3\cdot X,$$

where

$$Me_3=Cr_2Fe\ (A),\qquad Me_3=CrFe_2\ (B);$$

$$R=CH_3(\text{I и II}),\ ClCH_2(\text{III}),\ CH_3CH_2(\text{IV и V});$$

the symbols I–V and the compositions of the crystallization groups X are clear from the table. That the acetates of Cr(III) and Fe(III) are isostructural has been demonstrated by x-ray diffraction[2]. We note that EPR was previously observed in two other mixed chromium and iron compounds[3,4], but the obtained values of the molecular g-factors and their connection with the Heisenberg exchange model remained unexplained.

We have investigated small crystalline samples in the temperature interval 300–4.2°K, using a modified RE 13-01 spectrometer ($\nu \approx 9470$ MHz). At 300 and 77°K we observed in all the samples a complicated extended EPR spectrum, which was transformed at 4.2°K into a single slightly asymmetrical line (Figure 1). The values of g_{eff} and δH of the investigated compounds, measured at 4.2°K, are listed in the table. We see that in all cases the value of g_{eff} differs noticeably from the values of the g-factors that are typical of compounds with a single Cr^{3+} or Fe^{3+} ion[5].

Data on the EPR spectra of the investigated compounds (T = 4.2°K, $\nu \approx 9470$ MHz)

	Compounds	$g_{\text{eff}} \pm$ ± 0.01	$\delta H \pm$ ± 5Oe*	S_{12}	g_{Fe}	g_{Cr}
IA	$[Cr_2FeO(CH_3COO)_6(H_2O)_3]NO_3\cdot CH_3COOH$	1.93	125	3	2.003	1.97_5
IB	$[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3\cdot CH_3COOH$	1.95	179	1	2.003	1.97
IIA	$[Cr_2FeO(CH_3COO)_6]NO_3\cdot CH_3COOH$	1.94	140	3	2.003	1.98
IIB	$[Fe_2CrO(CH_3COO)_6]NO_3\cdot CH_3COOH$	1.96	132	1	2.003	1.98
IIIA	$[Cr_2FeO(CH_2ClCOO)_6(H_2O)_3]NO_3\cdot 3H_2O$	1.94	88	3	2.003	1.98
IIIB	$[Fe_2CrO(CH_2ClCOO)_6(H_2O)_3]NO_3\cdot 3H_2O$	1.93	187	1	2.003	1.96
IVA	$[Cr_2FeO(CH_3CH_2COO)_6(H_2O)_3]NO_3$	1.94	167	3	2.003	1.98
IVB	$[Fe_2CrO(CH_3CH_2COO)_6(H_2O)_3]NO_3$	1.93	468	1	2.003	1.96
VA	$[Cr_2FeO(CH_3CH_2COO)_6(H_2O)_3]NO_3$ $\cdot CH_3CH_2COOH$	1.92	180	3	2.003	1.97
VB	$[Fe_2CrO(CH_3CH_2COO)_6(H_2O)_3]NO_3$ $\cdot CH_3CH_2COOH$	1.94	660	1	2.003	1.96_5

*The line width was measured between the points of maximum slope.

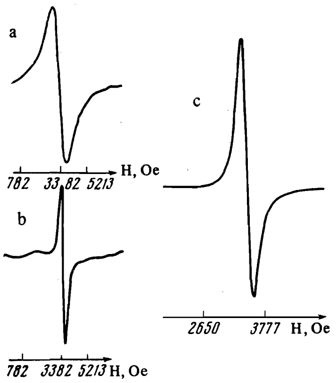

FIG. 1. EPR spectrum of $[Fe_2CrO(CH_3COO)_6\cdot(H_2O)_3]NO_3\cdot CH_3COOH$ at 9470 MHz at different temperatures: a—300°K, b—77°K, c—4.2°K.

To describe the magnetic properties of the system of three ions (we are interested here in ions having half-integer spins) located at the vertices of an equilateral triangle and containing two types of ions, we use the approximation of the isotropic exchange Hamiltonian

$$\hat{H}_{ex} = J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) + J'(\hat{S}_1\hat{S}_2) \tag{2}$$

and assume with the exchange integrals in the triads $Me_2^{(I)}Me^{(II)}$ or $Me^{(I)}Me_2^{(II)}$ are different: $J_{Me'-Me'} \neq J_{Me'-Me''} \neq J_{Me''-Me''}$. The appearance of a single EPR line at 4.2°K can be naturally explained only in the case of antiferromagnetic exchange ($J > 0$). Then the lowest state of the cluster turns out to be one of the two possible Kramers doublets with a total cluster spin $S = 1/2$; the doublet splitting is proportional to J', with $J' \gg g\beta H$.

We represent the Zeeman energy of the triad in the form

$$\hat{H}_z = (g_1\hat{S}_1 + g_2\hat{S}_2 + g_3\hat{S}_3)\beta H = g\beta H\hat{S}. \tag{3}$$

Here g_i are the values of the g-factors of the individual ions, g is the molecular g-factor (the g-factor of the cluster), and β is the Bohr magneton. Using the standard methods of the operator technique of atomic spectroscopy[6,7], we can show that for both doublets we have

$$g = \left[g_1\frac{(\hat{S}_1\hat{S}_{12})}{\hat{S}_{12}^2} + g_2\frac{(\hat{S}_2\hat{S}_{12})}{\hat{S}_{12}^2}\right]\frac{(\hat{S}_{12}\hat{S})}{\hat{S}^2} + g_3\frac{(\hat{S}_3\hat{S})}{\hat{S}^2}, \tag{4}$$

where S_{12} is the summary spin of some two cluster ions. Assuming that the first and second ions are the same and that $g_1 = g_2$, it is easy to transform (4) into

$$g=g_3+(g_3-g_1)\frac{S_3(S_3+1)-S_{12}(S_{12}+1)-S(S+1)}{2S(S+1)}. \tag{5}$$

Formulas (4) and (5) are a natural generalization of the well known expression for the g-factor of an exchange-coupled pair of unlike ions[8].

We consider now the conclusions that enable us to analyze the EPR data with the aid of (5). In the case of triad A, the doublet spin states for the assumed sequence of the addition of the angular momenta have a spin S_{12} equal to 3 and 2. The state with $S_{12} = 2$ cannot be the lowest one, since in accordance with (5) we obtain for it $g > 2$. To the contrary, for the doublet with $S_{12} = 3$ the experimental value g_{eff}, say $g_{\text{eff}} = 1.93$ for the triad IA, is obtained immediately by choosing $g_{\text{Fe}} = 2.003$ and $g_{\text{Cr}} = 1.97_5$. For the triad IIA, analogously, we get $g_{\text{eff}} = 1.94$ by choosing $g_{\text{Fe}} = 2.003$ and $g_{\text{Cr}} = 1.98$, etc. (see the table). The nonequivalence of the exchange interactions and the triad is taken into account by the term $J'(\hat{S}_1\hat{S}_2)=(J_{\text{Cr-Cr}}-J_{\text{Cr-Fe}})(\hat{S_1}\hat{S_2})$. In order for the state with $S_{12} = 3$ to be the ground state, it is necessary to have an energy

$$E={}^1/_2J'[S_{12}(S_{12}+1)-2S_1(S_1+1)]<0.$$

It follows therefore that in the Cr–Cr–Fe triad the exchange integral $J_{\text{Cr-Fe}}>J_{\text{Cr-Cr}}$, in agreement with the result of Takano[9].

Similar reasoning shows that for the triads Cr–Fe–Fe (S_{12} equal to 1 and 2) we have $J_{\text{Fe-Fe}}>J_{\text{Cr-Fe}}$. It is remarkable that in these cases values of g_{eff} equal to those observed in experiment are obtained from formula (5) at the same values of the individual g-factors of the chromium and iron ions (see the table, which indicates also the genealogy of the lower spin state of the investigated clusters), or when the values are very close.

Thus, for the entire class of the investigated compounds we have

$$J_{\text{Fe-Fe}}>J_{\text{Fe-Cr}}>J_{\text{Cr-Cr}}. \tag{6}$$

For a quantitative estimate of the exchange integral $J_{\text{Fe-Cr}}$, we use the experimental data on the magnetic susceptibility of the cluster $[Cr_2Fe(CH_3COO)_6(H_2O)_3]Cl\cdot 5H_2O$ [10]. Taking (5) into account, the formula for the magnetic susceptibility (T) of a mixed triad[11] is

$$\chi(T)=\Big(\sum_{S,S_{12}}(2S+1)\mathscr{E}_{S,S_{12}}\Big)^{-1}\sum_{S,S_{12}}(2S+1)\chi_{S,S_{12}}\mathscr{E}_{S,S_{12}}, \tag{7}$$

where

$$\chi_{S,S_{12}}=\frac{N\beta^2}{3kT}S(S+1)[g_3(1+\alpha)-\alpha g_1]^2,$$

$$\alpha=\frac{S_3(S_3+1)-S_{12}(S_{12}+1)-S(S+1)}{2S(S+1)},$$

$$\mathscr{E}_{S,S_{12}}=\exp\Big\{-\frac{1}{2kT}[JS(S+1)+J'S_{12}(S_{12}+1)]\Big\}.$$

Formula (7) has been reduced to the form used to describe $\chi(T)$ of exchange pairs of unlike ions[12].

If we assume, in accordance with the data of [13], the value $J_{\text{Cr-Cr}} = 30k$ (k is Boltzmann's constant), then the best agreement between formula (7) and experiment is obtained at $J_{\text{Fe-Cr}}=35.5k$ (Fig. 2). It is not obvious beforehand that $J_{\text{Me-Me}}$ has the same values in the mixed triad and in a triad made up of ions of the same kind. However, bearing in mind the inequalities (6), we see that an estimate of $J_{\text{Fe-Cr}}$ agrees with the values $J_{\text{Fe-Fe}} = (50–80)k$ obtained in [14-16].

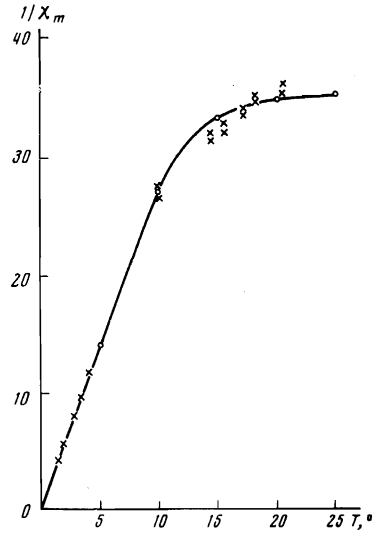

FIG. 2. Temperature dependence of the magnetic susceptibility of the trimer $[Cr_2FeO(CH_3COO)_6\cdot(H_2O)_3]Cl\cdot 5H_2O$. ×—experimental data of Gijsman et al. [10]; the theoretical curve is a plot of Eq. (7).

Let us examine also certain peculiarities of the properties of the investigated substances. From the table we see that in mixed triads the molecular g-factor (so far we have dealt, in fact, with the mean value <g>) does not change very strongly, thus evidencing even small changes of g_{ind}. It is clear here that the observed values of <g> are connected with nuances in the symmetry of the crystal field about each ion of the metal, and not with changes in the field strength. It is also clear that the Cr^{3+} and Fe^{3+} ions are in all cases in a field of predominantly octahedral symmetry; whereas in triads made up of like ions we have observed subtle influences on the energy spectrum by variations of crystallographic-lattice regions that are remote from the metal ion[4], no noticeable distortions in the crystal electric fields were produced in this case even when the water molecules were removed from the first coordination sphere of the complex (compound II).

Analogous conclusions result from an examination of the shape and width of the observed EPR lines, which make it possible to assess the anisotropy Δg of the molecular g-factor. The value $\Delta g \leq 0.03$ indicates that Δg_{ind} also lies within the usual limit[5].

These results are important because they yield information on the situation of an individual metal ion in the cluster, and such information is not available from other sources. This information will undoubtedly permit a deeper understanding of the properties of symmetrical triads of like ions[4,17].

Thus, a study of paramagnetic resonance of mixed three-nucleus clusters makes it possible to establish the genealogy of the lower energy states, to determine uniquely the relative magnitudes and characters of the exchange interactions between the ions of the cluster, and obtain other information necessary for the investigation of exchange triads. Moreover, since the considered compounds are isostructural, so that it is possible to exclude from consideration, with good approximation, the dependence of the exchange $Me^{(I)}$ - $Me^{(II)}$ interactions in the different triads on the angles and distances, the study of the dependence of the exchange between localized spins on the number of the electrons in the unfilled 3α shells becomes simplest and most effective.

The authors thank B. M. Kozyrev and M. M. Zaripov for interest in the work.

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Translated by J. G. Adashko
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