

Study of the zero-field magnetic ordering, charge fluctuation and trapping in the oxo-bridged heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$; ($R = \text{C}_5\text{H}_7$)

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The Mössbauer, magnetic susceptibility and EXAFS data for the oxo-bridged heterometallic acetylacetonate $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$) are analyzed in terms of a *bound-to-free* model describing the transition from the state of “delocalized valence”, denoted $\text{Fe}_{\text{deloc}}^{(3-\delta)+}$, in the magnetically disordered “paramagnetic” complex at 300 K to the states of “localized valence”, denoted $\text{Fe}_{\text{loc}}^{2+}$ and $\text{Fe}_{\text{loc}}^{3+}$, in the magnetically ordered complex at 4.2 and 77 K. © 2003 Kluwer Academic Publishers

1. Introduction

Transition metal β -diketonates, alkoxides, catecholates, oxalates, carboxylates, etc., can serve as molecular precursors of multicomponent oxides and therefore acquisition of knowledge of the effects of “cooperativity” between neighboring repeating units of a precursor is desired [1]. In fact, such properties of molecular and cluster precursors as electron fluctuations, ion and photon transfer, cooperative magnetic behavior, alignment of the local dipole moment, etc., can mimic the most important properties of target oxide structures. Extended magnetic interactions between transition metal ions have been observed for a number of chain polymers and inorganic compounds [2, 3]. There is a lack of data, however, about the coexistence of magnetic ordering and charge fluctuations in heterometallic complexes and ligand clusters [4].

The present work deals with the Mössbauer study of zero-field magnetic ordering and electron trapping at 4.2 and 77 K, paramagnetism and electron delocalization at 300 K in the oxo-bridged acetylacetonate $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$) obtained by

anodic electrochemical dissolution of an Fe-Y alloy in acetylacetonone.

2. Experimental

The heterometallic complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$) was obtained by anodic electrochemical dissolution [5] of an Fe-Y alloy in acetylacetonone. The alloy was a solid solution of YFe_2 in metallic yttrium (both of spectroscopic purity) with the ratio $\text{YFe}_2/\text{Y}_{\text{metal}} = 1$. The product of the electrochemical dissolution was carefully purified from $\text{Fe}(\text{acac})_3$ and $\text{Y}(\text{acac})_3$ by multiple recrystallization from benzene/acetone solutions. A brown polycrystalline powder with the granulometric size of 5–10 μ was obtained after allowing the solvent to evaporate in air at room temperature. A more detailed description for the synthesis procedure can be found elsewhere [6]. The synthesis and the corresponding analyses were conducted repeatedly at least twice. Elemental analysis of the complex (Perkin-Elmer AS-400 spectrometer) revealed the following mass composition: Y, 22.2;

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Fe, 3.8; O, 24.5; C, 43.5; H, 6.0%. This composition corresponds to the empirical formula $\text{FeY}_4\text{C}_{60}\text{H}_{100}\text{O}_{25}$. On the base of previous studies [6], this complex appeared to be $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$), probably hydrated. In fact, the calculated composition for $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ is found to be: Y, 22.2; Fe, 3.5; O, 24.0; C, 45.0; H, 5.3%. X-ray diffraction analysis (Philips PW 1700 device, Fe K_α radiation) testified to a monoclinic structure resembling monoclinic $\text{Y}(\text{acac})_3$ and differing completely from rhombohedral $\text{Fe}(\text{acac})_3$. Where data from X-ray diffraction on monocrystals were not available, the information on the local coordination of the Fe atoms was obtained from complementary EXAFS measurements. Room temperature EXAFS spectra were recorded with the use of the VEPP-3 electron storage rings of the Institute of Nuclear Physics (Novosibirsk) and analysed as in [7]. Electronic and magnetic properties of the complex were studied by Mössbauer spectroscopy at 300 K, 77 K and 4.2 K and by magnetic susceptibility measurements at $300 \text{ K} > T > 77 \text{ K}$. The Mössbauer spectra were recorded on a conventional gamma-resonance spectrometer operating in constant-acceleration mode with $^{57}\text{Co}(\text{Cr})$ ($T = 300\text{--}77 \text{ K}$) and $^{57}\text{Co}(\text{Rh})$ ($T = 4.2 \text{ K}$) as sources. The spectra were computer-analyzed using the common fit procedure for a series of Lorentzians. The resulting isomer shifts (IS) are reported relative to $\alpha\text{-Fe}$ at room temperature (RT). The static magnetic susceptibility was measured by a Faraday balance device at $B = 0.125 \text{ T}$ [8].

3. Results and discussion

The Mössbauer spectra of the heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ at 300 K, 77 K and 4.2 K are shown in Fig. 1, and the fitting results are listed in Table I together with the data for

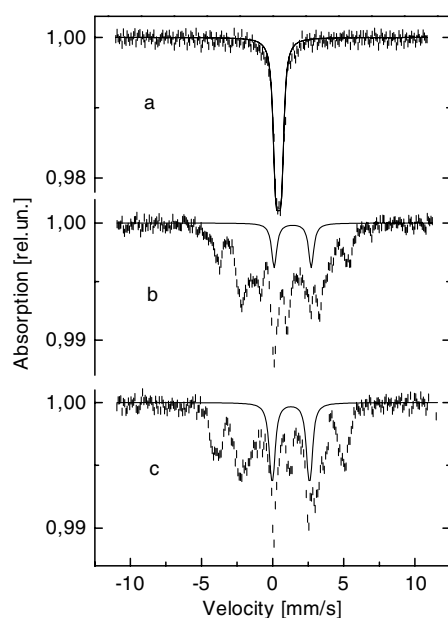


Figure 1 Mössbauer spectra of the heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$): a, 300 K; b, 77 K; c, 4.2 K. The solid lines in the spectra b and c are drawn as a visual guide for the presence of Fe^{2+} sites.

TABLE I Hyperfine parameters and effective magnetic moments for iron sites in the acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ and other relevant compounds

Parameter Compound	Non-equivalent sites					Ref.
	T (K)	(1)	(2)	(3)	(4)	
<i>IS</i> (mm/s)						
Complex	300	0.49				
- " -	77	0.66	0.58	0.52		
- " -	4.2	0.45	0.55	0.42		
YFe_2	300	-0.01				[8]
Y_2Fe_{17}	85	0.25	0.04	-0.03	0.03	0.04
$\text{Fe}(\text{acac})_3$	300	0.30				
	4.2	0.53				
<i>B_{in}</i> (T)						
Complex	300	0				
- " -	77	26.5	25.0	15.9		
- " -	4.2	29.0	26.5	18.3		
YFe_2	300	18.9				
- " -	80 ^a	22.1	22.1			[8]
- " -	4.2 ^a	22.0	21.0			
Y_2Fe_{17}	85	35.0	32.6	28.4	27.9	[9]
$\text{Fe}(\text{acac})_3$	4.2 ^b	0				
<i>μ_{eff}</i> (μ_B)						
Complex	85	~5.1				
Y_2Fe_{17}	85	2.53	1.92	2.25	2.00	[8]
$\text{Fe}(\text{acac})_3$	85	5.8				[7]

^aMeasured at the easy direction of magnetization [111].

^bHigh-spin site Fe^{3+} exhibits slow relaxation with more than one Kramers doublet populated [3].

the Laves phase YFe_2 [9] (i.e., a precursor for the heterometallic complex), the related intermetallic compound Y_2Fe_{17} [10] and the acetylacetonate $\text{Fe}(\text{acac})_3$. The RT spectrum (Fig. 1a) shows a doublet with the following parameters: isomer shift $IS = 0.49 \text{ mm/s}$, quadrupole splitting $QS = 0.37 \text{ mm/s}$ and line width $\Gamma = 0.36 \text{ mm/s}$. The parameters differ completely from those of the Laves phase YFe_2 , the intermetallic compound Y_2Fe_{17} and the complex $\text{Fe}(\text{acac})_3$. They are also different from the parameters of high-spin Fe^{3+} and Fe^{2+} states in the binary oxides but resemble the parameters of mixed-valence $\text{Fe}^{(3-\delta)+}$ states in non-stoichiometric ferric molybdate exhibiting "ferrous" character ($IS \sim 0.45 \text{ mm/s}$, $QS \sim 0.22 \text{ mm/s}$) [11, 12]. The spectrum recorded at 77 K (Fig. 1b) shows the presence of magnetic hyperfine structure (HFS) lines arising from three non-equivalent Fe sites involved in spontaneous magnetic ordering and a doublet from "paramagnetic" high-spin Fe^{2+} sites. The relative intensity ratio for magnetically ordered sites is found to be $\text{Fe}(1):\text{Fe}(2):\text{Fe}(3) \sim 1.5:1:6.5$. The spectrum obtained at 4.2 K (Fig. 1c), compared to that obtained at 77 K, is characterized by larger values of B_{in} of the three non-equivalent magnetic sites and by larger contribution of Fe^{2+} sites to the overall resonance absorption. The relative intensity ratio of magnetically ordered Fe sites at 4.2 K is $\text{Fe}(1):\text{Fe}(2):\text{Fe}(3) \sim 0.8:1:1.8$.

The type of magnetic order in the heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ is determined from the temperature dependence of magnetic susceptibility which can be described by a Curie-Weiss law (Fig. 2). An extrapolated paramagnetic Curie temperature $\theta = (17 \pm 1) \text{ K}$ is found together

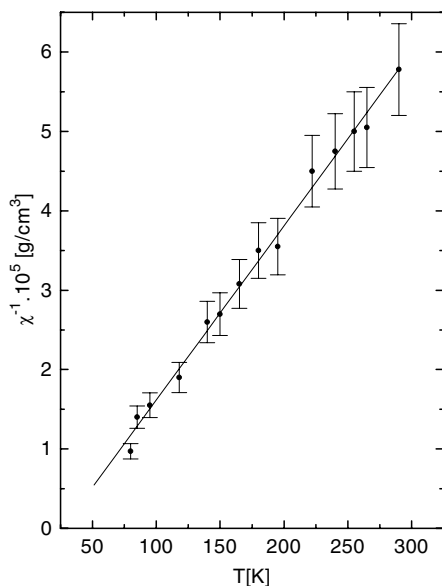
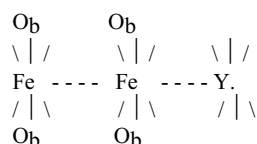


Figure 2 Inverse susceptibility of the heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ ($R = \text{C}_5\text{H}_7$) against temperature.

with the effective magnetic moment per iron atom $\mu_{\text{eff}} \sim 5.1 \mu_{\text{B}}$. The latter value is greater than for the high-spin state $3d^6\text{Fe}^{2+}$ ($\mu_{\text{eff}} \sim 4.9 \mu_{\text{B}}$), but smaller than for the high-spin state $3d^5\text{Fe}^{3+}$ ($\mu_{\text{eff}} \sim 5.9 \mu_{\text{B}}$).

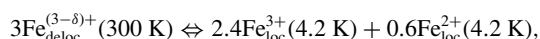
The local coordination of the Fe atoms in $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ was determined from the radial distribution functions (RDF) curves of the room temperature Fe K-edge EXAFS spectra. The maxim of the RDF curves at $R = 209, 240$ and 256 pm were tentatively assigned to the Fe–O, Fe–Fe and Fe–Y bonds of the oxo-bridged metals of the heterometallic complex. These bonds are most likely the two $\text{FeO}_6(\text{YO}_6)$ polyhedrons conjunct via double-bridged oxygen (O_b) forming an array as stretched in the Scheme 1



Scheme 1

In fact, in binuclear Mo(V) complexes with a double oxygen bridge, the Mo–Mo distance is found to be $R \sim 255$ pm [13] which is about the same as in the Me–Me distances ($R \sim 248$ pm in the oxo-bridged heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$).

The Mössbauer, magnetic susceptibility and EXAFS data allow to suggest the following Scheme 2 for the charge disproportionation process



Scheme 2

where $\text{Fe}_{\text{deloc}}^{(3-\delta)+}(300 \text{ K})$ is the “paramagnetic” delocalized state of the Fe^{3+} site at $T = 300$ K, $\text{Fe}_{\text{loc}}^{3+}(4.2 \text{ K})$ is the magnetically ordered localized state of the Fe^{3+}

site at $T = 4.2$ K and $\text{Fe}_{\text{loc}}^{2+}(4.2 \text{ K})$ is the “paramagnetic” localized state of the Fe^{2+} site at $T = 4.2$ K.

Thus, the charge disproportionation process depends on temperature and coincides, at some critical temperature T_{cr} , with the onset of magnetic ordering. As the temperature is decreased, the sites of “delocalized valency” $\text{Fe}_{\text{deloc}}^{(3-\delta)+}$ disproportionate to $\text{Fe}_{\text{loc}}^{3+}$ contributing to the spectrum of magnetically ordered iron atoms and $\text{Fe}_{\text{loc}}^{2+}$ contributing to the “paramagnetic” spectrum of atoms with “localized valence”. The reverse process can be understood as an increased delocalization of the itinerant electron in the conduction band of the $\text{Fe}_{\text{deloc}}^{(3-\delta)+}$ sites of the complex. Such a *bound-to-free* transition [14] seems to be reasonable in view of the presence of an array of equivalent iron sites which are only ~ 240 pm apart (Scheme 1), thus making band formation possible. According to [13], the existence of infinite chains, bands, or sheets of edge-shared octahedral with Fe–Fe distances below ~ 320 pm is a significant criterion for the observation of electron delocalization on the Mössbauer time scale.

Most strikingly, there is no essential line broadening in the spectrum describing the state of “delocalized valency” (Fig. 1a). This suggests that the molecular structure changes with temperature until the sites become structurally identical. The mechanism seems to include the thermally activated transition from the structure undergoing at low temperatures a small crystallographic shift, which makes possible for iron atoms to occupy different crystallographic sites (the case of localized mixed-valence states observed at 77 and 4.2 K) to the structure in which itinerant electrons are delocalized between atoms in identical crystallographic sites (the case of “delocalized valence” observed at 300 K). This suggests a transformation of certain ligands from a statistically disordered state at low temperature to a dynamically disordered state at high temperature. Thus, the onset of dynamic disorder tends to symmetrize the complex. No essential line broadening is observed because the vibrational motion operative in this process occurs at frequencies larger than 10^8 Hz. Further studies should be performed to determine the critical transition temperature and to ascertain the suggested mechanism.

4. Conclusion

The onset of magnetic ordering in the heterometallic acetylacetonate complex $\text{Fe}_3\text{YO}_6\text{R}_3[\text{Y}_{11}(\text{C}_5\text{O}_2\text{H}_7)_{33}]$ imposes a critical threshold on the electron delocalization process, resulting in frozen oxidation states below the critical transition temperature.

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