ELECTRON SPIN RESONANCE OF Mn$^{2+}$ IONS IN MATRICES OF POLYCRYSTALLINE
SAMPLES OF Zn$_4$O[(CH$_3$)$_2$CHCOO]$_6$ AND Zn$_4$O[(CH$_3$)$_3$CCOO]$_6$

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The ESR spectra of polycrystalline samples of Zn$_4$O[(CH$_3$)$_2$CHCOO]$_6$ and Zn$_4$O[(CH$_3$)$_3$CCOO]$_6$, activated by Mn$^{2+}$ ions at various concentrations, were investigated. An analytical theory was developed for the contour of the hyperfine components of the permitted and various types of "forbidden" transitions. On the basis of the obtained magnetic-resonance parameters conclusions were reached about the local symmetry and coordination of the Mn$^{2+}$ ion in the investigated compounds.

The polynuclear carboxylates of transition metals are distinguished by a large variety of compositions and structures [1-4]. In the present work we investigated polycrystalline samples of Zn$_4$O[(CH$_3$)$_2$CHCOO]$_6$ (I) and Zn$_4$O[(CH$_3$)$_3$CCOO]$_6$ (II), activated by Mn$^{2+}$ ions, by ESR. The results from investigation of the ESR spectra can be summarized in the following conclusions.

1) For Mn$^{2+}$ ion concentrations in the order of 1% a strong line with $g = 2$ and with a half-width of $\sim 30$ mT containing a poorly resolved sextet of hfs lines, is observed in the spectra of (I) and (II).

2) For Mn$^{2+}$ concentrations of less than 1% a sextet of well resolved hfs lines is observed in the spectra (Fig. 1). In the spectra of powders in the X region poorly resolved additional lines, which can be assigned to the "forbidden" hyperfine transitions, are observed between these lines (Fig. 1a).

3) In the ESR spectra of slightly concentrated frozen solutions of (I) and (II) in chloroform good resolution of the "forbidden" hyperfine doublets is obtained (Fig. 1b).

4) The permitted and "forbidden" hfs lines are superimposed on a broad line of weak intensity (Figs. 1 and 2). In the spectra of (II) weak asymmetric lines are observed on both sides of the strong hfs sextets (Fig. 2).

5) The permitted and "forbidden" lines are nonequidistant. The distances between the centers of the respective lines and their width increases in the transition from the downfield to the upfield hfs components (Fig. 1).

6) In the spectra of (II) weak absorption is observed in the region with $g = 3-4$ (Fig. 2).

7) The form of the lines remains substantially unchanged with decrease in temperature from room temperature to 77$^\circ$K. In the spectra of frozen solutions of (I) and (II) in chloroform broadening of the lines is observed with approach to the melting point.

In order to interpret the results we undertook a theoretical analysis of the ESR spectra.

The Form of the Lines in the Polycrystal. The Hamiltonian of the Mn$^{2+}$ ion ($S = 5/2$, $I = 5/2$) in standard notation [5, 6] in the system of coordinates related to the external magnetic field ($\mathbf{H} \parallel Z$) has the following form:
Fig. 1. The ESR spectra: a) Polycrystalline sample of Zn_4O[(CH_3)_2CHCOO]_4, activated by Mn^{2+} ions (0.01%); ν = 9078.71 MHz, T = 140°K; b) frozen slightly concentrated solution of Zn_4O[(CH_3)_2CHCOO]_4, activated with Mn^{2+} ions (0.01%) in chloroform; ν = 9056.68 MHz, T = 143°K.

Fig. 2. The ESR spectrum of the frozen slightly concentrated solution of Zn_4O[(CH_3)_3CCOO]_4, activated with Mn^{2+} ions (0.01%) in chloroform; ν = 9057.03 MHz, T = 143°K.

Fig. 3. The theoretical line contours of the absorption of the Mn^{2+} 3d^5 ion (g = 2.003, A = 0.0087 cm^{-1}; D = 0.01 cm^{-1}; ν = 9055 MHz); a) Transitions |1/2, m>---|−1/2, m> (m = ±1); b) transitions |±3/2, m>---|±3/2, m> (solid lines) and |±3/2, m>---|±1/2, m> (dashed lines).

\[ \hat{H} = g_\beta \mu_B \vec{H} \hat{S}_z + \frac{1}{2} D \left( \hat{S}_z^2 - \frac{1}{3} S(S+1) \right)(3\cos^2\varphi - 1) + ASI - g_\beta \mu_B \vec{H} \vec{I} - D(\hat{S}_x \hat{S}_z + \hat{S}_y \hat{S}_y)\cos\varphi\sin\varphi + \frac{1}{2} D(\hat{S}_x^2 + \hat{S}_y^2)\sin^2\varphi, \]  

(1)

where \( \varphi \) is the angle between the direction of the magnetic field and the symmetry axis of the system. The eigenvalues \( E_{\lambda m} \) of the Hamiltonian (1) (\( \lambda \) and \( m \) are the electronic and nuclear magnetic quantum numbers) were calculated by means of perturbation theory with an accuracy up to the \( A^2/\hbar\nu, D^2/R\nu \) and \( AD^2/(\hbar\nu)^2 \) terms inclusive (\( \hbar\nu \) is the energy of the ratio frequency quantum). In addition to the permitted transitions with \( \Delta\lambda = 1 \) and \( \Delta m = 0 \), in the first order with respect to the parameters \( A \) and \( D \) there are the following "forbidden" transitions: hyperfine, \( \Delta\lambda = 1, \Delta m = 1 \); fine, \( \Delta\lambda = 1, \Delta m = 0 \); "doubly forbidden," and \( \Delta\lambda = 2 \) and \( \Delta m = 1 \) [5, 7-10].

Examples of numerical computer calculations of the line contours were given in [9]. In order to identify the spectra it is of interest to undertake analytical calculations and investigate the special points of the spectrum, which directly determine the values of the magnetic-resonance parameters. It is possible to obtain analytic expressions in the model of nonbroadened individual absorption lines for the line forms of the polycrystals. These