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Magnetic ordering processes in manganese(II) di(hydrogen malonate) monohydrate complex studied by ESR spectroscopy

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A new manganese complex of malonic acid $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ was synthesized. Temperature dependence of the electron spin resonance (ESR) spectrum of Mn(II) was investigated in the 4.2– 295 K temperature range. The obtained ESR spectra were successfully fitted by using a Lorentzian-shape function. The fitting revealed existence of about 2% of a spurious phase of the manganese(II) complex. Strong magnetic interactions have been observed in the investigated temperature range with expected magnetic phase transition at $T_N \approx 2.5$ K. The integrated intensity, linewidth and resonance field of the ESR spectrum have shown that the spin dynamical fluctuations essentially influence the magnetic system. An anomalous behaviour of the ESR resonance field parameter has been observed below 100 K and with decreasing temperature the resonance field shifted to higher magnetic fields.

Key words: *manganese complex; ESR*

1. Introduction

Coordination compounds containing malonic acid as a ligand have been recently intensively studied due to their potential application as materials in molecular electronics, catalysts, biologically active compounds, molecular-based magnetic materials, etc. [1, 2]. Malonic acid, HOOC–CH_2–COOH, acts as a ligand with various dentate abilities. As the coordination modes depend on the nature of the metal and on synthesis conditions, the crystal structures of malonate complexes are very diverse – from ionic

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to three-dimensional polymers [3]. The malonate ligand occupies one or two coordination positions and neutralizes two positive charges of the metallic ion, allowing the inclusion of other ligands in the coordination sphere of the metal. An important feature of the malonic bridge is the fact that the magnitude of the exchange interaction depends on the possible bridging modes that it can adopt. Thus the ferro- or antiferromagnetic interactions may appear in malonate complexes, governed by the dimensionality of the structure.

Organic complexes of manganese(II) are interesting due to a variety of physical properties. In particular, their magnetic interactions have been studied in view of possible applications [4, 5]. Organic complexes of metal ions could form self-assemblies of molecular rods and tubes where long distance phenomena, such as the electron-energy transfer or magnetic coupling in transition ions, are complicated and can be changed by structural modifications [6, 7]. The manganese(II) ions in the organometallic compounds can be easily ordered into short or long order magnetic states [4, 5].

The aim of this report is to describe the results of investigations of temperature dependence of the electron spin resonance (ESR) spectra of the $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ complex. Especially the magnetic interactions with possible magnetic ordering processes will be presented and discussed.

2. Experimental

The $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ manganese complex of malonic acid was obtained in the form of pink powder by a slow evaporation of an aqueous solution prepared by dissolving stoichiometric amounts of malonic acid and manganese carbonate in water [7, 8].

ESR measurements were carried out with a conventional X-band ($\nu = 9.43$ GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. The samples containing around 20 mg of the material were placed into 4 mm diameter quartz tubes. The measurements were performed in the temperature range from room down to liquid helium temperature with $\Delta T = \pm 1.0$ K stability using an Oxford cryogenic system.

3. Results and discussion

Figure 1 presents the temperature dependence of the ESR spectra of the $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ complex. A very intense, broad and almost symmetrical line is observed in the investigated temperature range. The intensity, linewidth and resonance field of the line strongly depends on temperature. The obtained ESR spectra has been fitted successfully by using the Lorentzian function. The fitting revealed also the existence of about 2% of spurious phase of manganese(II) complex (Fig. 2). This was calculated from the area below the absorption ESR spectra which is proportional to the number of paramagnetic species participating in the resonance.

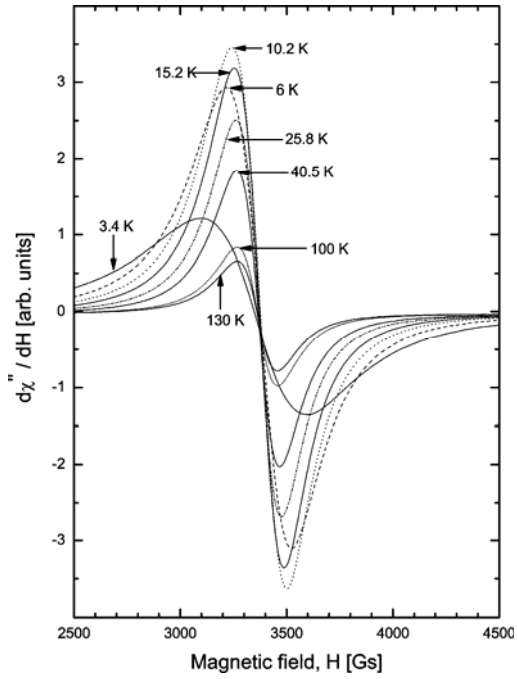

Fig. 1. Temperature dependence of the ESR spectra of the $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ complex

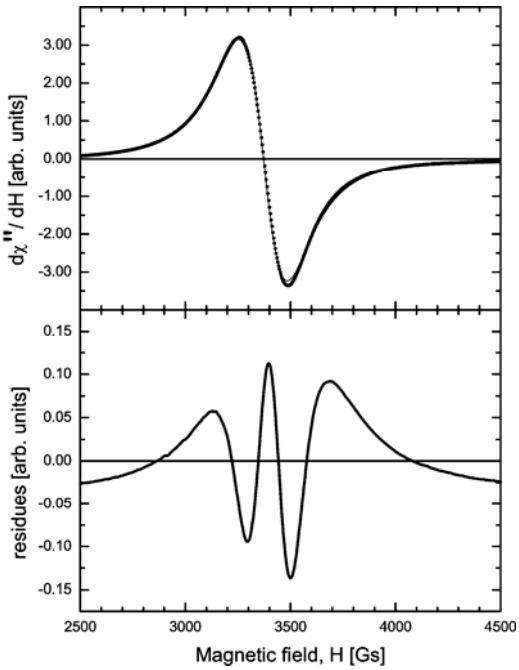

Fig. 2. The experimental (circles) and fitted (solid line) ESR spectra at room temperature. The lower panel presents the difference between the experimental and fitted spectra

At room temperature the ESR line is centered at $g_{\mathrm{eff}} = 2.0135(5)$, with the linewidth $\Delta H = 325(4)$ Gs. The value of about 2 for the g-factor is commonly expected for an S state ion like manganese(II) or iron(III) ($S = 5/2$). The ESR spectra arising from divalent manganese usually show splitting into 6 hyperfine components separated by about 70 to 100 Gs. If the intrinsic linewidth is larger than the splitting, the six hyperfine components overlap giving a single broad (over 600 Gs) ESR line. In the present case, at high temperatures, the linewidth is twice smaller than that value. This could indicate that the observed signal does not originate from isolated paramagnetic manganese(II) ions. It is thus possible that the ions are strongly coupled by the exchange interaction (ferromagnetic or antiferromagnetic). Large exchange narrowing effects could suppress the hyperfine splitting. Figure 3 gives the temperature dependence of the linewidth (ΔH), resonance field (H_r) and integrated intensity (I_{integ}). The integrated intensity, calculated as the area below the absorption line or the product of line amplitude and the square of the linewidth, is proportional to the number of spins participating in the resonance. The temperature dependence of the integrated intensity at higher temperatures could be described well by the Curie–Weiss law, $I_{\mathrm{integ}} = C/(T - \Theta)$, with the Curie–Weiss temperature $\Theta = -6.2(5)$ K. The product $I_{\mathrm{integ}}T$, which is proportional to the effective magnetic moment, is almost constant in the temperature range

from room down to 30 K. Below that temperature a slow decrease of the effective magnetic moment with decreasing temperature is observed.

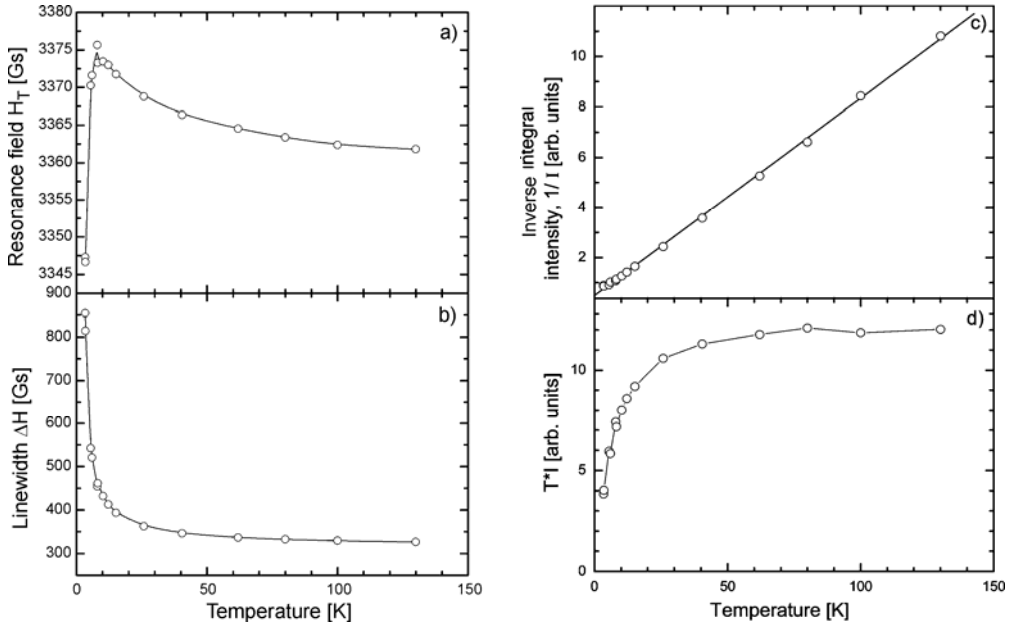

Fig. 3. Temperature dependence of the ESR resonance field (a), linewidth (b), inverse integral intensity (c) and the product of the integral intensity and temperature (d)

This indicates the existence of antiferromagnetic ordering processes involving manganese(II) ions inside the lattice (Fig. 3d). The ESR linewidth exhibits an increase as temperature decreases, most pronounced below 10 K and a rapid increase at lower temperatures where the antiferromagnetic phase transition is expected to occur (Fig. 3b). Broadening of the ESR line is usually observed in anisotropic antiferromagnets due to the slowing down of spin fluctuations as the critical temperature is approached from above [9–11]. This results in a divergence of the spin-correlation length, which, in turn, affects the spin-spin relaxation time of the exchange narrowed ESR lines resulting in the critical broadening of the ESR linewidth in the vicinity of T_N (T_N being the Neel temperature). The temperature dependence of the linewidth in this case can be described by the following relation [11]:

$$\Delta H = \Delta H_{00} + A\left(\frac{T - T_N}{T_N}\right)^{-\gamma} \tag{1}$$

where the first term describes the high temperature exchange narrowed linewidth, which is temperature independent, while the second term reflects the critical behaviour and γ is the critical exponent. Using the best fit procedure to the experimental

results, the following values were obtained: $\Delta H_{00} = 308(3)$ Gs, $A = 266(11)$ Gs, $\gamma = 0.70(3)$ and $T_N = 2.5(1)$ K.

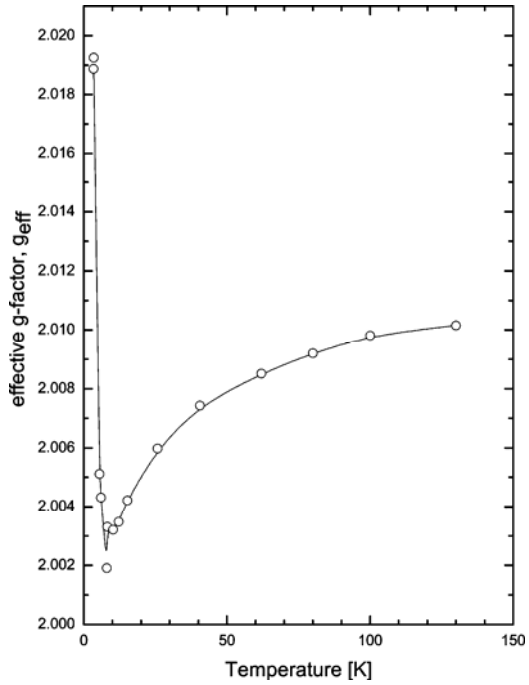

Fig. 4. Temperature dependence of the g_{eff} parameter

The magnetic resonance field increases with decreasing temperature but below 8 K a strongly opposite behaviour is observed (Fig. 3a). From room temperature down to 8 K the increase of the magnetic resonance field is about $\Delta H_r \approx 15$ Gs but from 8 K to 4.2 K the decrease is twice larger. The resonance condition for the spins is:

$$h\nu = g\mu_B(H_0 \pm H_{\text{int}}) \tag{2}$$

where μ_B is the Bohr magneton, H_0 is the applied external magnetic field, and H_{int} is the internal magnetic field. The antiferromagnetic ordering process is responsible for the observed temperature shift of the magnetic resonance field H_r. The shift is positive (toward higher magnetic fields) for temperatures higher than 8 K and is negative for temperatures lower than 8 K. Figure 4 presents the temperature dependence of the g_{eff} parameter. At temperature $T = 8$ K, the minimum value of that parameter is reached with $g_{\text{eff}} = 2.0019(4)$ which is very close to the g-value of a free electron ($g_e = 2.0023$).

4. Conclusions

The manganese(II) complex of malonic acid $CH_2(COOH)_2 \cdot MnCO_3 \cdot H_2O$ shows a strong antiferromagnetic interaction between the manganese(II) ions. At higher temperatures ($T > 50$ K), exchange coupling processes dominate, while at lower tempera-

tures (T < 10 K) the magnetic ordering processes have been observed. The magnetic resonance field increases with the decreasing temperature in the high-temperature range, while below 8 K a sharply opposite behaviour is observed leading to the g-value very close to that of a free electron. Temperature analysis of the linewidth has shown that the temperature of antiferromagnetic phase transition is T_N = 2.5 K.

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