ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 3, pp. 219–224. © Pleiades Publishing, Ltd., 2021.
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Research of the Properties of Gadolinium Stearate by EPR Spectroscopy

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Received March 24, 2020; revised July 28, 2020; accepted September 30, 2020

Abstract—Gadolinium stearate is synthesized in the form of a micropowder. Its composition is determined by elemental and energy dispersive X-ray analyses: $[Gd(C_{17}H_{35}COO)_3]\cdot(H_2O)_{2.42}$. The splitting parameters in the zero field (D and E) are determined for the EPR spectrum of the gadolinium stearate powder synthesized at 77 K. The magnetic susceptibility is calculated from the integral intensities of the EPR spectra of the gadolinium stearate powder recorded in a range of 77–293 K. The Curie temperature ($\theta = 0.16$ K) and Weiss constant ($C = 7.53$ cm^3 K mol^{-1}) are determined. The effective magnetic moment is calculated ($\mu_{\text{eff}} = 7.8 \pm 0.14\ \mu_B$), which is constant in the whole temperature range studied for the synthesized gadolinium stearate powder.

Keywords: gadolinium stearate, EPR spectra, zero field splitting parameters, paramagnetic susceptibility

DOI: 10.1134/S1070328421030027

INTRODUCTION

It is of interest to study gadolinium(III) compounds owing to specific features of the magnetic properties of Gd(III), which is a high-spin paramagnetic ion with seven unpaired electrons in the 4*f* shell forming the ground multiplet with the common spin $S = 7/2$ [1]. To describe splittings of the energy levels obtained from the experimental data of the EPR spectra, the spin-Hamiltonian ($\hat{H}$) is used in which the spin S is defined in such a way that the number $2S + 1$ is equal to the number of the observed levels. It is known [2, 3] that the determination of the parameters of zero-field splitting (ZFS) for the coordination sites with unpaired spins is the main area of investigations for the compounds with the spin $S > 1/2$. The Gd(III) ion is characterized by a very weak contribution of the orbital moment because of the 4*f* shell filled by 50% and, hence, the total moment is approximately equal to the spin moment ($J \approx S$). The ZFS can be described by two parameters (D and E). In addition, the magnetic properties of gadolinium stearate are of high practical interest, which is confirmed by their study using various methods in the multilayer Langmuir–Blodgett films [4–10] and also by the use of the gadolinium complexes as components of contrast reagents for magnetic resonance tomography [11, 12].

Earlier [13] we studied the synthesized polycrystalline powder of gadolinium stearate by scanning electron microscopy, IR spectroscopy, and X-ray powder diffraction analysis. The dependences of the magnetic permeability and dielectric permittivity of this powder were also studied using a vector network analyzer in a range of 0.03–7.0 GHz.

The results of the studies of the gadolinium stearate powder by the EPR method are presented in this work. The temperature dependence of the magnetic susceptibility (χ) was determined from these results. The ZFS parameters were calculated from the EPR spectrum recorded at 77 K.

Note that the EPR method of spin probes was applied [6] for recording the EPR spectra and measuring the magnetic properties of gadolinium stearate in the Langmuir–Blodgett films. However, no EPR signal of Gd^{3+} ions was observed in the synthesized films. The authors [6] used the paramagnetic radical probe of α,γ-bis(diphenylene)-β-phenyl allyl (BDPA), which was deposited on the surface of the Langmuir–Blodgett film of gadolinium stearate as a thin microcrystalline layer. This radical is a spin probe reflecting the arrangement of magnetic fields in the studied films of gadolinium stearate at different orientations of the sample in the external magnetic field in the resonator of an EPR spectrometer. The following values were obtained: $m_{\|,\text{Gd}} \approx 1.47 \times 10^{-10}$ T m for the surface magnetization of the film and $\mu \approx 1.2\ \mu_B$ for the magnetic moment (in the projection onto the perpendicular to the surface film) of the Gd^{3+} ion in the film, which is poorly consistent with the theoretical value.

EXPERIMENTAL

The problem of synthesis of stearate salts of rare-earth elements is far from the unambiguous solution. The results of syntheses of powders of rare-earth element stearates using different methods [14–23] are presented in Table 1.

According to the data in Table 1, powders of rare-earth element stearates were earlier synthesized by the dissolution methods using stearic acid or sodium stearate and lanthanide salts (nitrates or chlorides) predominantly in water at the temperatures from room to 100°C. The obtained precipitates of lanthanide stearates were washed with water and sometimes additionally by ethanol and acetone to remove unreacted reagents. Powders of lanthanide stearates were recrystallized only in [14, 15]. Powders of lanthanide stearates were dried using diverse methods: either in air, or in vacuum at various temperatures from room to 110°C. In the most part of cases, the content of water of crystallization in the obtained products of lanthanide stearates was not determined. We modified the method of the synthesis described previously [23] and used it in the work.

The contents of chemical elements in the synthesized powder of gadolinium stearate were determined by the elemental analysis results.

For $[Gd(C_{17}H_{35}COO)_3]\cdot(H_2O)_{2.42}$

Anal. calcd., %	C, 61.51	H, 10.51
Found, %	C, 61.52	H, 10.50

The composition of the synthesized gadolinium stearate powder $[Gd(C_{17}H_{35}COO)_3]\cdot(H_2O)_{2.42}$ was confirmed by C,H,N analysis using a Vario MICRO Cube elemental analyzer and by energy dispersive analysis to gadolinium, carbon, and oxygen atoms on a JEOL JSM-7500F scanning electron microscope equipped with an INCA X-sight accessory.

The EPR spectra of the gadolinium stearate powder and a TEMPO powder ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl, “for ESR spectroscopy” grade, Sigma-Aldrich) used as a spin standard were recorded on a JEOL JES FA-300 EPR spectrometer at a frequency of 9.14 GHz with a modulation frequency of 100 kHz. The EPR spectra were recorded on a range of 103–293 K with an increment of 20 K using pumping liquid nitrogen vapors through the resonator, and the temperature was monitored using an ES-DVT 4 temperature controller. The EPR spectrum was recorded at 77 K using a Dewar microflask with liquid nitrogen in which the quartz tube filled with the studied sample was placed. The resonance field (H_r), absorption linewidth (ΔH), intensity of the first derivative of the absorption signal (I), and integral intensity of the EPR spectra were determined from the EPR spectra. The D and E parameters were determined for the EPR spectrum recorded at 77 K. The EPR standard MgO:Mn^{2+} (JEOL) was used as a standard for the g factor.

RESULTS AND DISCUSSION

The EPR spectra were described similarly to [24–26], where the properties of the gadolinium salts and contrast reagents for magnetic resonance tomography based on the gadolinium complexes were studied [27].

When studying the EPR spectra of the gadolinium stearate powder, we started from the fact that the main contribution to the spin-Hamiltonian was made by the Zeeman electron interaction parameters ($\hat{H}_{ezi}$) (Eq. 1) and ZFS parameters ($\hat{H}_{zfs}$) (Eq. 2). Then the general equation of ($\hat{H}$) can be written in the form of Eq. (3) [2, 3]

$$\hat{H}_{\mathrm{ezi}} = \mu_B(gB_0\hat{S}), \tag{1}$$

where μ_B is Bohr’s magneton, B_0 is the static magnetic field strength, g is the Lande factor of spectroscopic splitting (presumably isotropic), and $\hat{S}$ is total spin operator.

$$\hat{H}_{\mathrm{zfs}} = D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + E\left(S_x^2 - S_y^2\right), \tag{2}$$

where S_x, S_y, and S_z are the projections of the total spin operator on the axes x, y, and z, respectively; $S = 3.5$ is the total spin; and D and E are the splitting parameters in the zero field.

As known [28], Eq. (2) is applied in two cases: (a) $g\mu_B B << D$, E for a strong crystalline field and (b) $g\mu_B B >> D$, E for a strong Zeeman interaction and a weak crystalline field. In this case, the EPR spectrum consists of only one very broad line with $g \approx 2$, which is observed in our case.

$$\hat{H} = \hat{H}_{\mathrm{ezi}} + \hat{H}_{\mathrm{zfs}}. \tag{3}$$

Figure 1, *1* shows the EPR spectrum recorded at 77 K, and the theoretical EPR spectrum is shown in Fig. 1, *2*. The theoretical spectrum for the studied gadolinium stearate was simulated in the MATLAB program based on the Easyspin module [29–31]. The spin system in EasySpin was specified by the following parameters: spin $S = 7/2$, isotropic factor $g = 2.0$, and selected ZFS parameters D = 1260 MHz and E = 420 MHz. As can be seen from Fig. 1, the theoretical calculation of the EPR spectrum is consistent with the experimental measurements for the gadolinium stearate powder.

The EPR spectra of the studied gadolinium stearate powder are shown in Fig. 2a. The first integral of the EPR spectra (absorption curves) obtained at the temperatures from 103 to 293 K are shown in Fig. 2b. At 283 K, the EPR spectrum of the gadolinium stearate powder has three visible local maxima ($H \approx$ 54, 194, and 279 mT) and three local minima ($H \approx$ 105, 240, and 418 mT). The resonance is observed at $H_r \approx$

Table 1. Synthesis conditions for powders of rare-earth element stearates

Method	Medium/temperature/time	Washing of stearate precipitate/recrystallization in medium	Drying	Composition	References
Precipitative metathesis	Water–ethanol (1 : 1)/20°C/1 h	3 times: water → ethanol → acetone/*n*-pentanol–ethanol (5 : 1)	10^{-3} mbar, 50°C, 24 h	$Nd(C_{17}H_{35}COO)_3$	14
Dissolution metathesis	Ethanol/room/1 h	3 times: water → ethanol → acetone/*n*-pentanol–ethanol (5 : 1)	Vacuum, 40°C, 24 h	$Pr(C_{17}H_{35}COO)_3$	15
Hydrothermal	Water/120°C/2–3 h		Sputtering		16
Dissolution	Water/heating		Air	$La(C_{17}H_{35}COO)_3$	17
Solid-phase StH + Ln_2O_3		Solution of NaOH, then solution of HCl	Air		18
Precipitative dissolution	Water/20°C		Vacuum, 110°C, 10 h	$La(C_{17}H_{35}COO)_3$	19
Precipitative dissolution	Water/76°C/1 h (pH ≈ 7)	Deionized H_2O, then ethanol	Air, 75°C, 24 h	Yttrium–magnesium stearate	20
Precipitative dissolution	Water/100°C/2 h	Distilled H_2O	Lyophilic 24 h		21
Precipitative dissolution with double decomposition	Water/90°C/0.5 h	Distilled H_2O	Air, 110°C, to constant weight	$La(C_{17}H_{35}COO)_3$	22
Dissolution	Water/76°C/1 h (pH ≈ 7)	Centrifugation, 3 times: deionized water–ethanol (1 : 1)	Air, 75°C, 24 h	$Y(C_{17}H_{35}COO)_3$	23
Dissolution	Water/76°C/1 h (pH ≈ 7)	Centrifugation, 3 times: bidistilled water–ethanol (1 : 1)	Vacuum, 75°C, 24 h	$Gd(C_{17}H_{35}COO)_3 \cdot 2.4H_2O$	This work

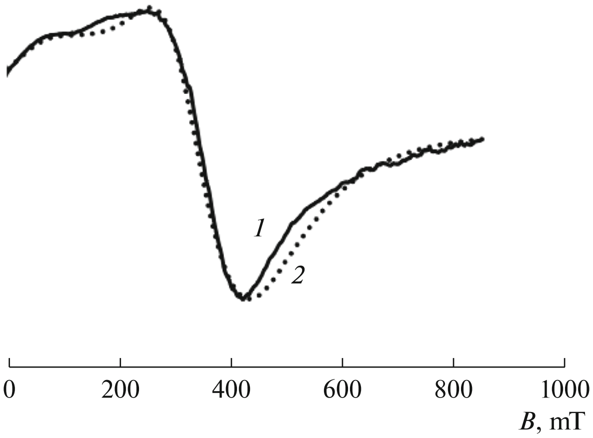

Fig. 1. (*1*) Experimental EPR spectrum of powdered gadolinium stearate recorded at 77 K and (*2*) the simulated spectrum.

326 mT. The microwave absorption intensity of the studied sample increases appreciably with the temperature decrease, and the *g* factor is ~2.0 in the whole temperature range.

The concentration of paramagnetic centers for the studied substance was calculated by comparing the surface area under the absorption curve (Fig. 2b) with that for the commonly accepted paramagnetic standard. A powder of the stable TEMPO radical with the known concentration of electron spins was used as a paramagnetic EPR standard. The following equation is used for the calculation of the concentration of paramagnetic centers in the samples studied by the EPR method using the paramagnetic standard [32]:

$$N = \frac{N_{\mathrm{std}} A_x (\mathrm{scan}_x)^2 G_{\mathrm{std}} M_{\mathrm{std}} (g_{\mathrm{std}})^2 [S(S+1)]_{\mathrm{std}}}{A_{\mathrm{std}} (\mathrm{scan}_{\mathrm{std}})^2 G_x M_x (g_x)^2 [S(S+1)]_x}, \quad (4)$$

where N_{std} is the concentration of spins of the standard, *A* is the surface area under the absorption curve (expressed in relative units and the same for the standard (std) and studied sample (*x*)), scan is the scanning increment over the field (mT), *G* is the relative enhancement of the signal, and *M* is the modulation amplitude, *g* is the *g* factor, and *S* is the spin of the ions in the ground state. Note that the temperature dependence of the EPR spectra of the standard (TEMPO) should be taken into account, since in the temperature range studied the integral dependence of the EPR spectra of the standard on going from 293 to 77 K increases by ~2.5 times, as well as that for the studied gadolinium stearate. The concentration of paramagnetic centers of studied gadolinium stearate calculated by Eq. (4) with allowance for the temperature dependence of the integral intensity of the EPR spectra of the standard on going from 293 to 77 K takes the value $N \approx (5.6 \pm 0.2) \times 10^{18}$ in the whole range studied.

The magnetic susceptibility of the studied gadolinium stearate powder can be calculated from the EPR data using Eq. (5)

$$\chi = \frac{N g^2 \mu_{\mathrm{B}}^2 J(J+1)}{3 k_{\mathrm{B}} T}, \quad (5)$$

where *N* is the calculated concentration of paramagnetic centers (number of spins/g); *g* is the *g* factor, whose value was obtained from the EPR experiment; μ_{B} is Bohr's magneton; *J* is the total angular moment ($J = S + L$, where *S* is the spin of the ion in the ground state, which is equal to 3.5 for the gadolinium(III) ion; *L* is the orbital moment, which is equal to zero for the

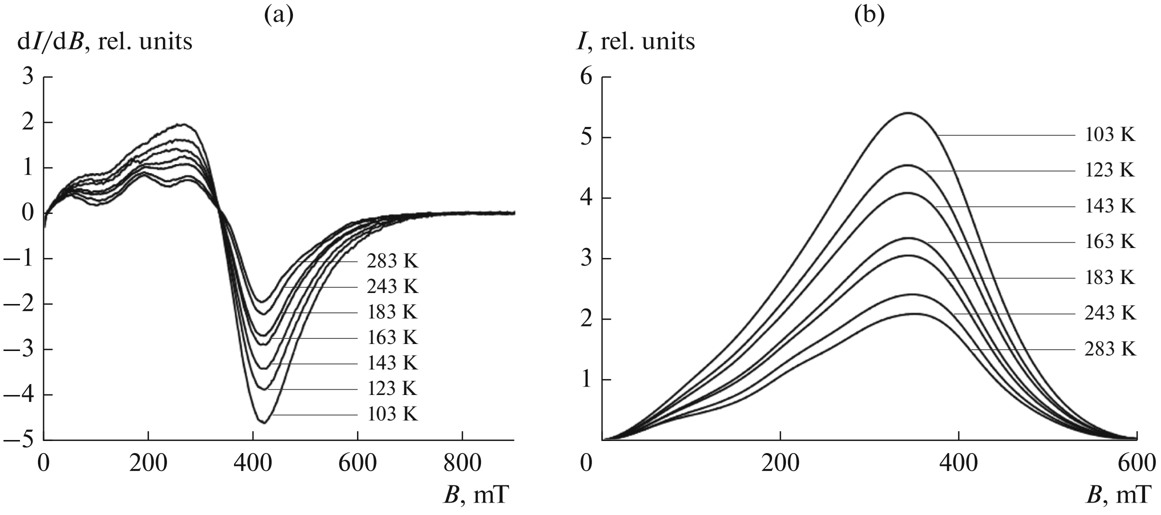

Fig. 2. (a) EPR spectra of the studied powder of gadolinium stearate and (b) the integral intensity of the EPR spectra recorded in a range of 103–293 K.

Table 2. Specific ($\chi \times 10^{-5}$, cm^3/g) and molar ($\chi_M \times 10^{-2}$, cm^3/mol) magnetic susceptibilities for powdered gadolinium stearate at various temperatures

Absolute temperature T, K	$\chi \times 10^{-5}$, cm^3/g	$\chi_M \times 10^{-2}$, cm^3/mol
77	9.90	10.44
103	7.29	7.69
123	5.66	5.97
143	4.79	5.05
163	4.26	4.49
183	3.84	4.05
203	3.58	3.78
223	3.15	3.33
243	2.99	3.16
263	2.60	2.75
283	2.51	2.65
293	2.50	2.64

gadolinium ion ($L = 0$)); k_B is the Boltzmann constant; and T is the absolute temperature (K).

The theoretical magnetic moment (μ_{eff}) for the gadolinium(III) ion calculated by the equation $\mu_{eff} = g[S(S + 1)]^{1/2}$ (where g is the spin value of the g factor for a free electron, and S is the spin of the gadolinium(III) ion in the ground state) is 7.94 μ_B. The experimental μ_{eff} of the gadolinium stearate powder can be calculated by Eq. (6)

$$\mu_{eff} = \sqrt{\chi_M T}, \qquad (6)$$

where χ_M is the molar magnetic susceptibility. Thus calculated μ_{eff} for the gadolinium stearate powder is 7.8 ± 0.14 μ_B in the whole temperature range studied.

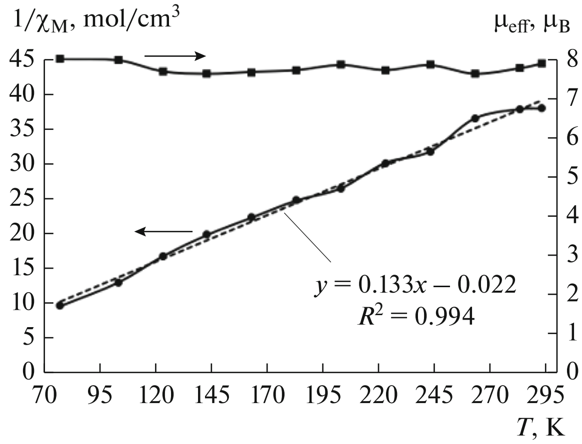

Fig. 3. Dependences of $1/\chi_M$ and experimentally calculated μ_{eff} on the absolute temperature for powdered gadolinium stearate. Dashed line shows the approximation of the experimental data by the Curie–Weiss equation for $1/\chi_M$ in a range of 77–293 K.

The procedure for the calculation of the magnetic susceptibility from the integral intensities of the EPR spectra used by us was earlier described in detail [33–36]. The results of our calculations are presented in Table 2. When calculating the molar magnetic susceptibility (χ_M), one should take into account the molar weight of the sample, which is 1054 g/mol for the studied sample of gadolinium stearate.

The dependences of the inverse molar magnetic susceptibility ($1/\chi_M$) and μ_{eff} on the absolute temperature are presented in Fig. 3 and show that the gadolinium stearate powder is characterized by a monotonic decrease in $1/\chi_M$ with the temperature decrease. The plots in Fig. 3 demonstrate the following. If a straight line described by the Curie–Weiss law is superimposed on the curve of the inverse paramagnetic susceptibility in the studied temperature range, its intersection with the x axis gives the Curie temperature (θ) for the studied sample. In our case, the straight line is described well by the equation $y = 0.133x - 0.022$ (the quadratic correlation coefficient is $R^2 = 0.994$), the solution of which gives $\theta = 0.16$ K. The obtained value of the Curie temperature ($\theta \approx 0$) indicates the absence of magnetic ordering between the atom-carriers of the magnetic moment of gadolinium stearate, which is characteristic of the paramagnetic state of the substance. Then the Curie constant was calculated by the Curie law ($\chi_M = C/T$): $C \approx 7.53$ cm^3 K mol^{-1}.

Thus, the gadolinium stearate powder was studied by EPR spectroscopy in a wide temperature range, and its molar magnetic susceptibility was calculated from the integral intensities of the EPR spectra. The change in the inverse molar magnetic susceptibility with the temperature decrease in the studied gadolinium stearate powder was found to be described well by the Curie law. According to the data obtained, no magnetic ordering is observed between the gadolinium atoms in the gadolinium stearate powder.

ACKNOWLEDGMENTS

The studies were carried out on the equipment of the Scientific Educational Center "Diagnostics of Structure and Properties of Nanomaterials" at the Center for Collective Use of the Kuban State University.

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of state assignment no. FZEN-2020-0022.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya