Unusual Magnetic Phase Transitions in Gd³⁺ Clusters in Multicomponent Oxide Glasses

Janis Kliava,[1] **Alexander Malakhovskii,**[2] **Irina Edelman,**[2] **Anatoly Potseluyko,**[2]
Eleonora Petrakovskaja,[2] **Ishai Bruckental,**[3] **Yosef Yeshurun,**[3] **and Tat'jana Zarubina**[4]

Magnetic susceptibility, EPR and optical properties have been studied in a glass system $\{20La_2O_3 - 22Al_2O_3 - 23 B_2O_3 - 35(SiO_2 + GeO_2)\}$ with a part of La_2O_3 substituted by Gd_2O_3 in different concentrations. Positive Weiss constants have been found in more heavily doped glasses; two magnetic transitions at 55 and 12 K have been detected and ascribed, respectively, to ferromagnetic and antiferromagnetic clusters of Gd^{3+} ions. The EPR spectra confirm the clustering at higher Gd contents. At low temperatures the cluster-related resonance indicates an onset of magnetic anisotropy. The clustering, depending on the Gd concentration, correlates with a shift to lower energies of the strong optical absorption band edge.

KEY WORDS: oxide glasses; gadolinium; magnetic clusters; superparamagnetism.

1. INTRODUCTION

Gadolinium-containing glasses attract much attention owing to their magnetic and optical properties promising for technical applications and related to magnetic interactions between the paramagnetic ions and, in particular, to magnetic ordering. Gadolinium most frequently occurs in the Gd^{3+} state with the ground state $^{8}S_{7/2}$; owing to the absence of orbital moment this ion is particularly well adapted to magnetic resonance experiments.

Magnetic properties of Gd compounds depend on the structure of the environment of the Gd^{3+} ions, and they are strongly influenced by clustering. Usually, *antiferromagnetic* order is observed in the Gd^{3+} clusters in glasses. Recently we have observed for the first time [1] the formation of *ferromagnetic* Gd^{3+} clusters in the glass system $\{xGd_2O_3 - (1 - x)(La_2O_3 - Al_2O_3 - B_2O_3 - SiO_2 - GeO_2)\}$ at low temperatures. As this phenomenon is very unusual, we have carried out a more extensive study with the aim to elucidate the nature of the magnetic state of the Gd^{3+} clusters in these glasses.

The glasses were prepared from Gd_2O_3, La_2O_3, H_3BO_3, SiO_2 and GeO_2 with Gd_2O_3 content: 0.1 (Gd1), 1.0 (Gd2), 5.0 (Gd3) and 10.0 (Gd4) mass %. Magnetization as a function of temperature (5-300 K) was measured with a SQUID magnetometer up to 5 T. EPR spectra at various temperatures (4.2–300 K) were measured in the X- (9.5 GHz) and Q-band (35 GHz). Optical

[1]CPMOH, UMR 5798 CNRS-Université Bordeaux-I, 33405 Talence cedex, France. (Mailing address : CPMOH, Université Bordeaux-I, 351 Cours de la Libération, 33405 Talence cedex, France. E-mail: j.kliava@cpmoh.u-bordeaux1.fr.)

[2]L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk 660036, Russia.

[3]Bar-Ilan University, Department of Physics, Ramat-Gan 52900, Israel.

[4]S.V. Vavilov State Optical Institute, St.-Petersburg 199034, Russia.

absorption was measured in the wavelength range of 180–600 nm.

2. RESULTS AND DISCUSSION

2.1. Magnetization

The magnetization curves of all four glasses are similar; meanwhile, Gd4 shows weak features in the high-field range. The temperature dependence of the magnetic susceptibility χ in the paramagnetic region can be written as $\chi = a + C_i/T + C_c/(T - \Theta)$ where the three terms account, respectively, for the diamagnetic susceptibility, isolated paramagnetic ions and clusters; $C_i = n_i m_i^2/3k$ and $C_c = n_c m_c^2/3k$ are Curie constants for isolated and clustered Gd ions, n_i and n_c are numbers of isolated and clustered ions; m_i and m_c are the corresponding high-temperature $(T \gg |\Theta|)$ values of the magnetic moment, and Θ is the Weiss constant.

For isolated Gd ions $C_c = 0$, so, the product χT is a linear function of T. The temperature dependence of χT for Gd1 is perfectly linear, so this glass contains only isolated Gd ions. From this dependence we find the value of a and, subtracting the diamagnetic contribution from the experimental susceptibilities of Gd2–Gd4, we further consider the function $(\chi - a)T$. For a perfect paramagnet (isolated ions, as for Gd1) this function is a constant. In the case of coexistence of isolated and clustered ions,
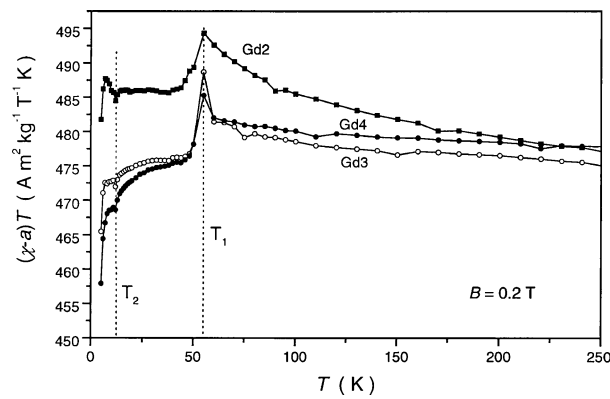
$$(\chi - a)T = C_i + C_c T/(T - \Theta). \quad (1)$$

Fig. 1. Temperature dependence of $(\chi - a)T$ for the Gd2–Gd4 glasses in the magnetic field $B = 0.2T$.

Table I. Gd_2O_3 contents, Weiss constants (Θ), estimates of the clustering degree (K) in the glasses from the susceptibility (χ) and EPR data, and intrinsic resonance linewidths (Δ_B) for isolated Gd^{3+} ions

Sample	Gd1	Gd2	Gd3	Gd4
Gd_2O_3(mass %)	0.1	1	5	10
Θ(K)	0	50	11	8
$K(\%, \chi)$	0	3	8	11
$K(\%, EPR)$	–	–	25	40
Δ_B(mT)	< 0.1	< 0.3	6.5	10

The temperature dependence of $(\chi - a)T$ in Gd2, Gd3 and Gd4 glasses shown in Fig. 1 exhibits well-defined features indicating the existence of magnetically ordered clusters. The shape of the feature at $T_1 = 55$ K is typical of a ferromagnetic phase transition. At $T_2 = 12$ K one more peak is observed, related to magnetic (presumably antiferromagnetic) or structural phase transition in the same clusters or in clusters of another structure. Indeed, the gadolinium oxide can exist in two forms: cubic and monoclinic [2].

When $T \to 0$, even a small amount of isolated ions can make a substantial contribution to the magnetic susceptibility. The second term in (1) is no more valid for $T < |\Theta|$, however, the low-temperature susceptibility of disordered antiferromagnets and ferromagnets changes slowly, approaching some finite value when $T \to 0$ [3]. Therefore, $(\chi - a)T \to C_i$, cf. [4].

At high temperatures $(\chi - a)T \approx C_i + C_c(1 + \Theta/T)$ approaches $C_i + C_c$. Neglecting a difference in the magnetic moments of isolated and clustered Gd^{3+} ions, the ratio $K = C/(C_l + C) \approx n_c/(n_i + n_c)$ characterises the degree of clustering. Next, we can substitute into Eq. (1) the experimental values of $(X - a)T$ from Fig. 1 and determine the Weiss constants of clusters. The estimated values of K and Θ are quoted in Table I.

The Weiss constant of clusters in Gd2 is larger than that in Gd3 and Gd4. This supports the above assumption of two types of clusters with different type of magnetic ordering. In Gd2 the clusters with ferromagnetic ordering at 55 K prevail. The degree of clustering in Gd3 and Gd4 is larger but the Weiss constants are smaller than in Gd2. This can be explained by an increase of the part of clusters with antiferromagnetic low temperature ordering in Gd3 and Gd4.
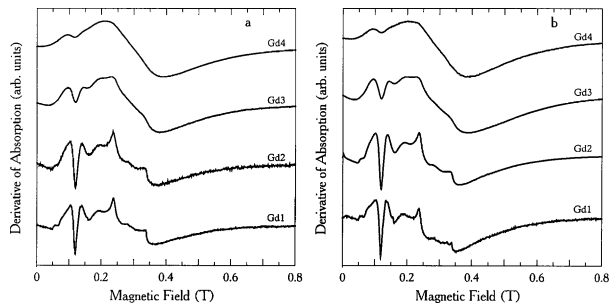
Fig. 2. Experimental X-band (9.45 GHz) EPR spectra at 300 (a) and 4.5 K (b).

2.2. EPR

Preliminary data on room temperature EPR spectra have been reported previously [1]. In cooling down to the liquid nitrogen temperature the spectra remain nearly the same; more pronounced changes are observed below 60 K. Figure 2 compares the X-band EPR spectra at room and liquid helium temperatures. In the Q-band spectra only a relatively narrow line with $g_{eff} = 2.0$ is present.

In the EPR spectra of Gd2 in comparison with the Gd1 glass, only a slight line broadening is observed. On the other, hand, in the Gd3 and Gd4 glasses all spectral features are broadened. In order to account for this transformation, we put forward an approach based on a numerical analysis of *experimental* EPR spectra. As a working hypothesis, we assume that the spin Hamiltonian parameters governing the EPR spectra at higher gadolinium contents are the same as in the Gd1 glass, however, the *intrinsic* EPR lines are broadened by dipole-dipole interactions between the Gd^{3+} ions. In this case the spectra of Gd2–Gd4 glasses can be "simulated" by appropriately transforming the experimental EPR spectrum of the Gd1 glass measured at the same temperature.

The theoretical background for this transformation is a general expression of the EPR spectrum of an isolated paramagnetic ion in a disordered host matrix (the glass) [5,6] :

$$\mathcal{P}(B) = \int P(X)W(X)F[B - B_r(X), \Delta_B]\mathrm{d}V(X). \quad (2)$$

Here the various spin Hamiltonian parameters and orientation angles are considered as components of a random vector X. A multivariate distribution density $P(X)$ pondered by a transition intensity $W(X)$
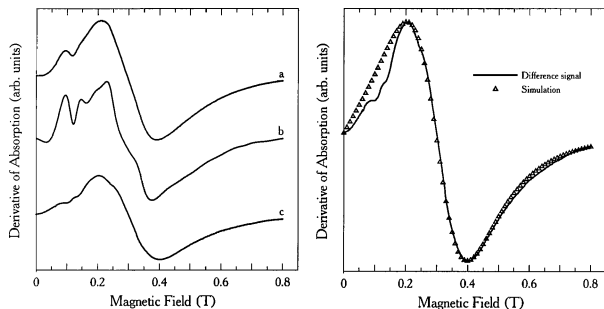

Fig. 3. Left : representation of the EPR spectrum of Gd4 at 300 K (a) as a linear combination of the room-temperature spectrum of Gd1 convoluted with a $\Delta_B = 0.010$ T (b) and an underlying resonance : (c) = (a) -0.32 (b). Right: fitting to the curve (c) with the modified Bloch lineshape for $B_r = 0.30$ T and $\Delta_B = 0.010$ T.

is convoluted with an *intrinsic* lineshape function $F[B - B_r(X), \Delta_B]$ including all broadening mechanisms other than structural disorder (e.g., dipole-dipole interaction or spin-lattice relaxation). For diluted paramagnetic ions in the glass the intrinsic lineshape is the "*modified* Bloch" one and becomes Lorentzian if the linewidth is small in comparison with the resonance field [5]. The linewidth is adjusted to reproduce the features of the EPR spectra in more heavily doped glasses. The results of this fitting for the Gd4 glass are shown in the left parts of Figs. 3 and 4. One can see that the curves calculated according to the procedure outlined above (b) do not satisfactorily reproduce the experimental spectra; therefore, the spectra transformations with the Gd concentration cannot be ascribed exclusively to the dipole-dipole broadening. This confirms our earlier conclusion reached using computer-generated
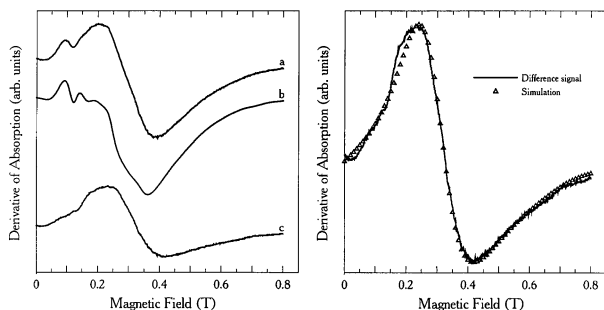

Fig. 4. Left: representation of the EPR spectrum of Gd4 at 4.5 K (a) as a linear combination of the liquid helium-temperature spectrum of Gd1 convoluted with a $\Delta_B = 0.010$ T line (b) and an underlying resonance : (c)=(a) -0.55 (b). Right: fitting to the curve (c) with a superparamagnetic resonance signal (see the main text for the simulation parameters).

theoretical spectra [1]. On the other hand, the overall shape of the EPR spectra in Gd3 and Gd4 can be suitably reproduced by linear combination of the (b) curve, presumably representing the contribution of isolated ions and a broad featureless underlying resonance (c, see figure legends for the simulation parameters). The latter signal can be ascribed to Gd^{3+} clusters. The linewidths of the diluted Gd^{3+} ions spectra are given in Table I.

The shape of the underlying resonance in the high (between room and liquid nitrogen) and low (from ca. 50 K down to the liquid helium) temperatures is manifestly different, cf. the right parts of Figs. 3 and 4. In the first case this resonance can be well fitted by a single "modified Bloch" line with $B_r = 0.30$ T and linewidth $\Delta_B = 0.10$ T. The situation is more complex at low temperatures when the underlying resonance becomes clearly asymmetric, similar to the *superparamagnetic resonance* spectrum observed for ferromagnetic $\alpha - Fe_2O_3$ nanoparticles in heat-treated sol-gel silica glass [5,7]. So, we have attempted to computer simulate this signal following the procedure outlined in this work. As in the actual case magnetic parameters of the nanoparticles are not known, we have rather arbitrarily assumed the saturation magnetization $M_s = 5 \times 10^5$ A m^{-1}. With this assumption, the following parameters could be deduced from the fitting to the low-temperature underlying resonance in Gd4: the magnetic anisotropy constant $K = -10$ kJm^{-3} (including contribution of both the magnetocrystalline anisotropy and particle shape anisotropy); the average diameter of 1 nm and the distribution width (for the log-normal diameter distribution) $\sigma = 0.2$; an isotropic intrinsic lineshape with the linewidth parameter $\Delta_B = 0.065$ T. The parameter values estimated for Gd3 are close to those quoted for Gd4. From the above analysis the fraction of clustered Gd^{3+} ions in the glasses can be evaluated as the relative intensity of the underlying resonance with respect to that of the total EPR spectrum. This fraction, obtained by double integration of the corresponding derivative-of-absorption spectra, is also shown in Table I. Note the disagreement between the estimations of the clustering degree from susceptibility and EPR measurements. The nature of clusters giving predominate contributions to the static susceptibility and to the EPR spectra can be different. Besides, in the case of coexistence of different types of clusters in the glass, characterized by both positive and negative Weiss constants, the static magnetization measurements may underestimate the total clustering degree.

Note a persisting discrepancy between the experimental resonance due to clusters and the corresponding theoretical spectra in the low magnetic field range, Figs. 3 and 4 right parts. This discrepancy is indicative of certain modifications in the spin Hamiltonian parameters, related to different ordering degree in the glass matrix at different doping levels.

2.3. Optical absorption

The optical absorption spectra shown in Fig. 5 are markedly different for the Gd1 and all other glasses. In the first case, the absorption is due to basic glass components and La; the gadolinium contribution is negligible because of its low content. In the second case, the change of the absorption spectra, *viz.*, a shift of the absorption edge to lower energies, an appearance of a shoulder in the region of $\sim(35-45)10^3$ cm^{-1}, and of weak narrow line sets are attributed to electron transitions associated with the Gd^{3+} ions. The narrow lines centred at ca. 32, 36, and $40 \cdot 10^3$ cm^{-1} are identified, respectively, as $^8S_{7/2} \rightarrow {}^6P_J$, $^8S_{7/2} \rightarrow {}^6I_J$ and $^8S_{7/2} \rightarrow {}^6D_J$. A part of the f-f spectrum in the region of $^8S_{7/2} \rightarrow {}^6I_J$ transitions has been considered previously, and no distinct correlation was found between the manifold component characteristics and the Gd content [1].

Because of a low transparency of the glasses the high-energy parts of the absorption curves could be obtained only in a narrow spectral range, nevertheless, they clearly show the onset of the fundamental
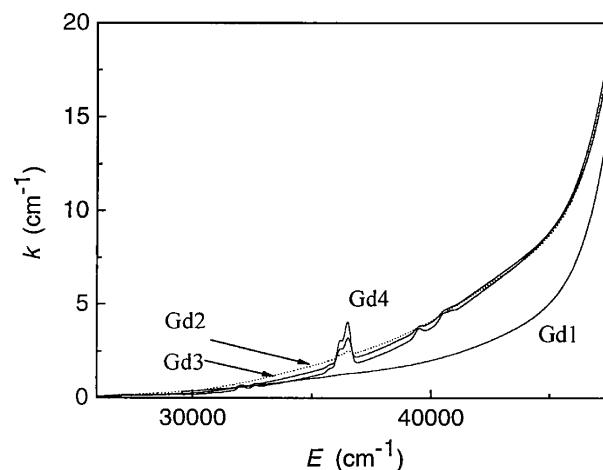
Fig. 5. Absorption spectra for Gd1–Gd4 at room temperature.

absorption band. In this range the absorption coefficient is approximately a linear function of the photon energy, and its extrapolation to the intersection with the energy axis gives a rough estimate of the absorption band edge E_g as ca. $44 \cdot 10^3$ and $\sim42 \cdot 10^3 \, \mathrm{cm}^{-1}$ for Gd1 and Gd2–Gd4, respectively. This shift can be accounted for by charge transfer transitions Gd–Gd in the clusters.

3. SUMMARY

We have observed for the first time a complex magnetic behaviour in the glasses $\{x\mathrm{Gd_2O_3} - (51.35 - x) \, [\mathrm{La_2O_3} - 17.4\mathrm{Al_2O_3} - 12.4\mathrm{B_2O_3} - 18.8 \, (\mathrm{SiO_2} + \mathrm{GeO_2})]\}$. The magnetic susceptibility χ follows the Curie-Weiss low with *positive* Weiss constant Θ, besides, the latter decreases with an increase of x. To elucidate this uncommon situation we have analysed the $(\chi - a)T$ function. Two features are found: at 55 and at 13 K and ascribed to ferromagnetic and antiferromagnetic phase transitions in the Gd clusters. A computer-assisted EPR study reveals gadolinium clustering in heavily doped glasses and magnetic ordering at low temperatures; on the other hand, it indicates certain modifications in the ordering degree in the glass matrix at different doping levels. Optical absorption spectra show the strong absorption band edge shift as a function of Gd concentration, corroborating the formation of clusters at higher gadolinium contents.

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