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EPR and magnetic properties of Gd^{3+} in oxide glasses

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Abstract

Magnetic susceptibility and EPR have been studied in a glass system $x Gd_2O_3 \cdot (20-x) \cdot La_2O_3 \cdot 22Al_2O_3 \cdot 23B_2O_3 \cdot 35(SiO_2 + GeO_2)$ with $x = 0.03$, 0.35, 1.75 and 3.5 mol%. Positive Weiss constants have been found in more heavily-doped glasses and ascribed to clustering of Gd^{3+} ions. In less-doped glasses the EPR spectra have a typical "U"-type shape; at higher doping levels the spectral features are broadened. Computer simulations show that in the latter case the spectra are superposition of signals arising from isolated ions and ferromagnetic clusters.

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Keywords: Oxide glasses; Gadolinium; Electron paramagnetic resonance; Magnetic susceptibility

The magnetic and optical properties of gadolinium-containing glasses, promising for technical applications, are determined by the environment of Gd^{3+} ions, gadolinium concentration and its distribution in the glass matrix. Whereas the local structure of the Gd^{3+} sites seems to be similar in different types of glasses, the correlation between the doping level and clustering depends on the glass type and composition [1–3]. In this work, a glass system of the composition $x Gd_2O_3 \cdot (20-x)\ La_2O_3 \cdot 22Al_2O_3 \cdot 23B_2O_3 \cdot 35(SiO_2 + GeO_2)$ has been studied. The glasses were prepared from Gd_2O_3, La_2O_3, Al_2O_3, H_3BO_3, SiO_2 and GeO_2 as starting materials, melted in platinum crucibles at 1400–1500°C in an electric furnace. Four synthesised samples, Gd1 Gd2, Gd3 and Gd4, correspond, respectively, to $x = 0.03$, 0.35, 1.75 and 3.5.

The magnetisation measurements as a function of temperature (5–300 K) were made in the field range 0–5 T using a commercial SQUID magnetometer (Quantum Design MPMS-55). The EPR spectra were measured at 78 and 293 K in the X (9.5 GHz) and Q (35 GHz) bands.

The temperature dependence of the paramagnetic part of the magnetisation, see Fig. 1, in all glasses is well described by the Curie-Weiss law. The Weiss constant Θ is very close to zero for Gd1 and Gd2; for Gd3 and Gd4, respectively, $\Theta = 5.0$ and 3.0 K. Such behaviour indicates the presence of magnetically ordered (presumably, ferromagnetic) clusters. Note that actual Weiss constants can differ from those obtained by fitting the temperature dependence of the magnetisation, because isolated Gd^{3+} ions can coexist with the clusters [4]. Usually, Gd-containing glasses have negative Weiss constants [5,6] while some gadolinium compounds have positive Weiss constants [7], attributed to exchange-coupled Gd ions. In any case, the non-zero Weiss constants found for the Gd3 and Gd4 glasses, indicate the presence of Gd clusters.

High-temperature effective magnetic moments μ_{eff} of Gd^{3+}, determined from the temperature dependence of magnetisation, are 7.15, 7.48, 7.60 and 7.74 μ_B for Gd1,

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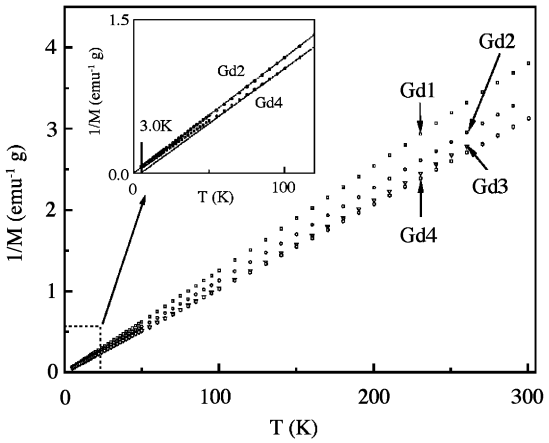

Fig. 1. Temperature dependence of the inverse of the paramagnetic part of the reciprocal magnetisation measured in the magnetic field of 0.2 T. The inset shows low-temperature data for the Gd2 and Gd4 glasses.

Gd2, Gd3 and Gd4, respectively. These values are close to the magnetic moment of the free Gd^{3+} ion, $\mu_{eff} = 7.94\,\mu_B$, indicating a weak effect of the crystal field on the magnetic moments, as expected for Gd^{3+} having $L = 0$ in the ground state. This effect is clearly more pronounced at lower Gd concentrations. This can be related to distortions in the glass network caused by the difference in the radii of the host and the substituting ions (for La^{3+} $r = 1.172$ Å, while for Gd^{3+} $r = 1.078$ Å [8]).

Fig. 2 shows the X-band EPR spectra for all glasses at 78 K. Between 78 and 300 K, the EPR spectra intensities vary in proportion to the magnetic susceptibility, while their shapes remain nearly the same. In the Gd1 and Gd2 glasses, the spectra show well-resolved features at the effective g-values $g_{eff} = 5.9$, 2.8 and 2.0, characteristic of the so-called U-spectrum [1–3]. In the Q-band spectra only a single line with $g_{eff} = 2.0$ is observed. The absence of any evidence of Gd clustering in the EPR spectra of Gd1 and Gd2 is consistent with the temperature dependence of the magnetisation.

In the Gd3 and Gd4 glasses, all spectral features are severely broadened.

The spectra have been computer simulated by means of an ab initio code [9], directly relating the atomic positions in the environment of the paramagnetic ions to the spin Hamiltonian parameters using the superposition model with parameters determined in Ref. [10]. In order to account for the short-range disorder in the glasses, a *randomly* distorted octahedral environment of Gd^{3+} has been assumed. A satisfactory fit to the experimental EPR spectra of the Gd1 and Gd2 glasses has been obtained for the mean distribution width and the rms deviation of the ligand coordinates of 0.045 and 0.012 Å, respectively.

Next, the computer simulations have shown that the transformation in the low-field part of the Gd3 and Gd4

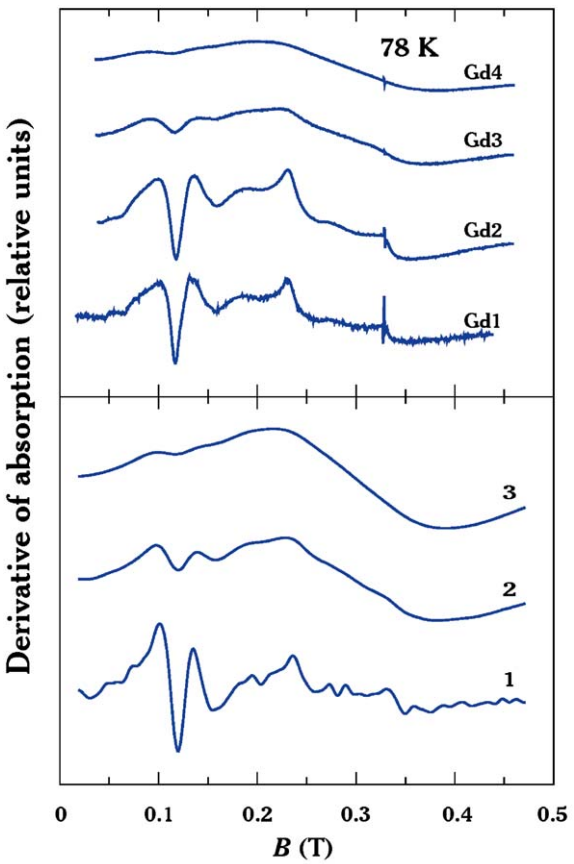

Fig. 2. Top: experimental EPR spectra. Bottom: computer-generated spectra assuming 100% of isolated ions (1), 70% isolated and 30% clustered ions (2) and 30% isolated and 70% clustered ions (3). The intrinsic lineshape for the isolated ions is Gaussian, with the linewidth $\Delta_B = 5$, 10 and 15 mT for the (1), (2) and (3) curves, respectively. The clusters are described by a Gaussian lineshape with $g_{eff} = 2.25$ and $\Delta_B = 95$ mT.

glass spectra can be explained by dipole–dipole broadening. Meanwhile, a good fit to the high-field part of these spectra could be reached only by superposing a signal due to isolated Gd^{3+} ions and a broad resonance with $g_{eff} = 2.25$, see Fig. 2, bottom. This latter signal can be ascribed to clusters of Gd^{3+} ions, linked with each other through the oxygen bridges, consistently with the Weiss constant values for the Gd3 and Gd4 glasses.

A systematic study of the correlation between the glass composition, structure of Gd^{3+} sites and its distribution in the glass at different concentrations is in progress.

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