Reply to "Comment on 'Unusual magnetic transitions and nature of magnetic resonance spectra in oxide glasses containing gadolinium' "

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In this Reply we show that, contrary to the suggestion of Dubroca, Hack, and Hummel (DHH), the feature observed at ca. 55 K in the magnetic susceptibility of gadolinium-containing oxide glasses [as in our earlier paper, Kliava *et al.* Phys. Rev. B **71**, 104406 (2005)] cannot be due to a magnetic transition in oxygen contaminant. In support of this statement, we supply transformed data at low Gd content as well as magnetization curves for a series of glasses containing dysprosium oxide measured with the same superconducting quantum interference device as in our earlier paper. In all these cases the feature in question is absent. Thus, our previous assignment of the 55 K feature to a paramagnetic-to-ferromagnetic transition in Gd clusters in the glass remains the only one consistent with the experimental results.

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Recently we reported a complex magnetic behavior of glasses doped with gadolinium oxide.[1] In particular, we described two features in the temperature dependence of magnetic susceptibility occurring at 55 and 12 K and ascribed, respectively, to ferromagnetic and antiferromagnetic transitions in gadolinium-containing clusters.

In preceding Comment,[2] Dubroca, Hack, and Hummel (DHH) suggest that the 55 K peak might be due to oxygen contamination of our glass samples and/or the apparatus in the course of measurements using a superconducting quantum interference device (SQUID) magnetometer. Magnetism of oxygen is well known and much attention has been paid to magnetic transitions in oxygen adsorbed in nanochannels in such materials as carbon nanotubes,[3] nanohorns,[4] and microporous polymers.[5] In particular, solidification of adsorbed oxygen is accompanied by a paramagnetic-to-antiferromagnetic transition giving rise to a feature in the temperature dependence of magnetic susceptibility at 50 K.[3] The results presented by DHH,[2] doubtlessly, are due to the same phenomenon. Interestingly, this feature bears some similarity with the 55 K peak reported by us;[1] therefore, it can readily lend itself to a misinterpretation. Below we show that such a misinterpretation has occurred in the case of the DHH suggestion. Indeed, a thorough and unprejudiced examination of the results presented in Refs. 1 and 2 shows this similarity to be accidental. In order to avoid further misinterpretations, we have supplemented our data presented in Ref. 1 and included some additional results obtained for glasses doped with dysprosium oxide.

The sample preparation and characteristics as well as experimental details have been described previously.[1] Four gadolinium-containing glass samples of the final mass composition (in mass %) $\{x\mathrm{Gd_2O_3}\text{-}(51.35-x)\mathrm{La_2O_3}\text{-}17.4\mathrm{Al_2O_3}\text{-}12.4\mathrm{B_2O_3}\text{-}18.85(\mathrm{SiO_2}+\mathrm{GeO_2})\}$ were synthesized: Gd1, Gd2, Gd3, and Gd4 with, respectively, $x=0.1$, 1.0, 5.0, and 10 mass % $\mathrm{Gd_2O_3}$ substituting for equivalent amounts of $\mathrm{La_2O_3}$. The dysprosium-containing glasses were the following: Dy1 and Dy2 of composition $\mathrm{Dy_2O_3}\text{-}\mathrm{LiB_3O_5}$ with 8.56 and 15 mass % of $\mathrm{Dy_2O_3}$, respectively, and Dy3 of basic composition similar to that of the Gd-containing glasses with 56.1 mass % of $\mathrm{Dy_2O_3}$ (the content of $\mathrm{Dy_2O_3}$ is given with respect to the total mass composition). All samples were bulk, about $4\times4\times4$ mm^3 in size.

First, we address the results obtained for the glasses doped with $\mathrm{Gd_2O_3}$. In our earlier papers[6,7] we plotted the temperature dependence of inverse magnetization, $M^{-1}(T)$. The $M^{-1}(T)$ function was nearly linear (no weak features could be seen with this presentation). The intersection point of its graph with the temperature axis at $T\neq0$ for Gd2-Gd4 and some features in the corresponding electron paramagnetic resonance spectra were indicative of Gd ion clustering in these glasses via the indirect exchange mechanism.

Next, in order to throw into relief the fine magnetic features observed in Gd2-Gd4, in Ref. 1 (Fig. 3) we have chosen to show the temperature dependence of the function $(\chi-a)T$, where χ is the total magnetic susceptibility of the glass and a is its diamagnetic part, so that $\chi-a$ represents the contribution of Gd ions only, both isolated and included in

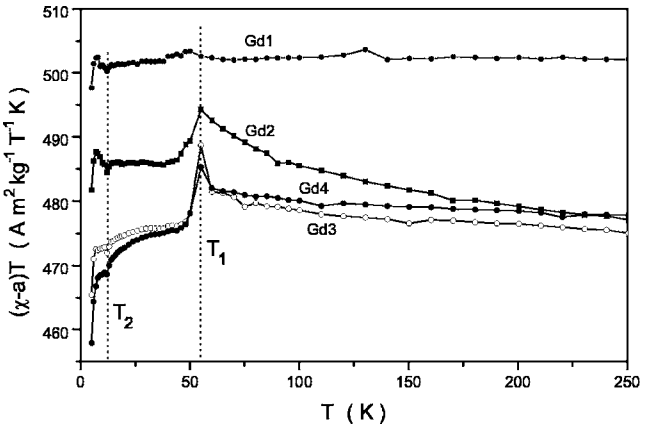

FIG. 1. Temperature dependence of $(\chi-a)T$ for Gd1-Gd4 samples in the magnetic field $B=0.2$ T.

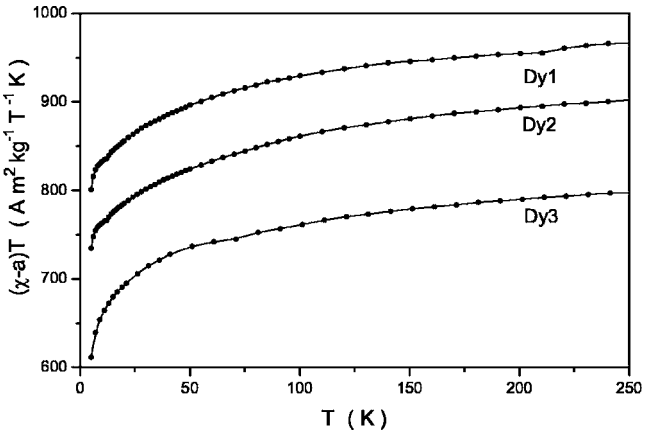

FIG. 2. Temperature dependence of $(\chi-a)T$ for Dy1-Dy3 samples in the magnetic field $B=0.2$ T.

clusters. The general trend of the temperature dependence of $(\chi-a)T$ is close to a constant, therefore, weak deviations from this trend of curve become obvious.

In contrast, in Gd1 no distinct feature at 55 K was observed. Therefore, we illustrated the temperature trend of the total susceptibility by showing in Fig. 2 of Ref. 1 the χT product for this sample. In Ref. 1 this procedure was clearly explicated and the vertical axes of the corresponding Figs. 2 and 3, were labeled accordingly. DHH have overlooked this distinction; indeed, they state "In the Kliava *et al.* paper the control sample, where no 55 K peak is observed, has a much larger strength (1000 A m^2 kg^{-1} T^{-1} K) than the rest of the samples (30 A m^2 kg^{-1} T^{-1} K), where the 55 K is observed." In fact, the total magnetization of Gd1 (the "control" sample) was much weaker that that of Gd2-Gd4.

In order to avoid further misinterpretations, in Fig. 1 of the present work we show the $(\chi-a)T$ function for Gd1, as well as for Gd2-Gd4. One can see that the sharp peak near 55 K is observed for Gd2-Gd4 and is absent for Gd1. On the scale used by DHH the amplitudes of this peak are 1.0×10^{-4} emu for Gd2 and 1.1×10^{-3} emu for Gd4. These values are orders of magnitude larger than those observed by DHH—proportional to 10^{-6} and 10^{-5} emu. Traces of adsorbed oxygen, if any, could give rise to the very weak feature observed for Gd1 as well as to the shoulder in the curve for Gd2 (both slightly below 50 K; see Fig. 1) but in no case to the much more intense sharp peak at 55 K.

Another piece of evidence is supplied by the $(\chi-a)T$ function for Dy1-Dy3 glasses (measured with the same SQUID instrument); see Fig. 2. The inverse magnetization for Dy3 had been previously reported by several of the present authors[8] (Dy3 corresponds to Dy8 in Ref. 8) but the $(\chi-a)T$ curves for the dysprosium-containing glasses were not shown there. Clearly, there is no observable feature at 55 K in these glasses, contrary to the Gd2-Gd4 glasses.

Thus, the sharp peak at the temperature 55 K appears only in the glasses containing Gd_2O_3 in concentrations above 1.0 mass %. The peak position in Gd2-Gd4 glasses is the same but its amplitude and width depend on the Gd_2O_3 concentration. It would be unlikely if such a behavior were observed for a feature arising from oxygen adsorbed on the surface of the glasses. Indeed, we do not see why the amount of adsorbed oxygen would be dependent both on the content and on the nature of the rare-earth oxide component present in the glass matrix. (We recall that our samples were in bulk form.) Besides, the intensity of the feature observed in Gd2-Gd4 glasses was several orders of magnitude stronger than that expected to arise from a possible oxygen contaminant, as reported by DHH.

In conclusion, the results presented here confirm our previous viewpoint relating the 55 K susceptibility feature to a magnetic transition in gadolinium-containing clusters in the glass matrix.

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