Nonlinear Magnetic Susceptibility in a Kramers-Ion Doped Glass

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The imaginary part of the magnetic susceptibility of an insulating glass doped with dysprosium ions (Kramers ions), measured at high frequency (680 MHz) and low temperature (14 mK), is strongly dependent on the amplitude of the electromagnetic field. This nonlinear effect, which is not observed in a similar glass doped with holmium ions (non-Kramers ions), is attributed to magnetic tunneling states.

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Tunneling of large spins has been treated theoretically for a long time. The possibility of tunneling between one local minimum and another has been considered in spin glasses [1,2]. In magnetic materials containing rare-earth ions, it has been shown that tunneling of large spins with strong anisotropy energy can take place along the anisotropy axis [3]. The quantum dynamics of such spins has been described in term of the semiclassical WKB formalism [4]. More recently, macroscopic tunneling of magnetization on a mesoscopic scale has been reported [5,6]. In every case, there are tunneling states (TS) which must give rise, in principle, to nonlinear effects such as saturation or TS echoes (the analog of spin echoes). These effects have been observed indeed in the acoustic properties of glasses [7,8] and they have been assigned to the elastic TS which arise from tunneling of atoms or groups of atoms in glasses [1,9]. To our knowledge, such effects have not been observed in the magnetic properties of magnetic glasses. In this Letter, we report on the observation of a large decrease of the imaginary part of the magnetic susceptibility of a Kramers-ion doped glass with increasing amplitude of the oscillating magnetic field at high frequency and low temperature. This is evidence of the existence of magnetic TS. Some properties suggesting the existence of such excitations have been published: an excess of specific heat at low temperature in an amorphous Dy-Cu alloy [10] and a magnetic field effect on the acoustic properties at low temperatures of a dilute Kramers-ion glass [11]. However, no magnetic nonlinear effect has been reported in magnetic glasses which have been described rather as relaxational glasses with Arrhenius behavior [12]. More recently, quantum fluctuations have been introduced to explain short relaxation times in these glasses [13].

We have studied the magnetic susceptibility of two aluminosilicate glasses doped with Dy^{3+} and Ho^{3+} magnetic ions, respectively. The magnetic-ion content was 1.5 at.%. The main difference between these two ions concerns Kramers degeneracy which exists for the ground level of Dy^{3+} ($J=\frac{15}{2}$), and not for the one of Ho^{3+} ($J=8$). The most significant factor determining the magnetic properties of these glasses is the single-ion anisotropy energy which is strong for these two rare-earth ions (DJ^2 is about 100 K [14]). Hence, at low temperature each ion is along its anisotropy axis which is random from one ion to another. Although simplified, the random axial anisotropy model [15] explains qualitatively the magnetic properties of amorphous alloys containing rare-earth ions [14]. The exact chemical compositions of our two samples were

$$(Dy_2O_3)_{0.029}(La_2O_3)_{0.165}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$$

and

$$(Ho_2O_3)_{0.029}(La_2O_3)_{0.165}(SiO_2)_{0.579}(Al_2O_3)_{0.227}.$$

We have also studied a lanthanum glass without magnetic ion. Its chemical composition was $(La_2O_3)_{0.194}$-$(SiO_2)_{0.579}(Al_2O_3)_{0.227}$. Hence, our three samples had the same rare-earth ion content (10.1%).

To measure the magnetic susceptibility at high frequency, we have used a split-ring resonator [16], also called a loop-gap resonator [17]. Because to a first approximation the electric field exists in the gap and not in the loop, this resonator is particularly attractive for magnetic susceptibility measurements. The sample was put in the loop and the irradiating field was perpendicular to the steady magnetic field. This one was obtained from a superconducting magnet. The resonator was fabricated from oxygen-free high-conductivity (OFHC) copper and was pressed against the wall of the mixing chamber of a ^{3}He-^{4}He dilution refrigerator. Thus, it could be cooled down to 10 mK. At 4 K, the resonance frequency of the resonator without sample was around 680 MHz and its quality factor was 3100; they do not change down to 10 mK. To measure the magnetic susceptibility χ, the resonance line of the resonator with the sample was determined using electromagnetic pulses of very low repetition rate (to avoid heating of the sample). The line shape was Lorentzian (Fig. 1). The line broadening was proportional to the imaginary part of the susceptibility (χ'') and the resonance frequency shift was proportional to the real part of this one (χ').

Figure 1 shows the resonance lines of the resonator with the dysprosium glass, for different electromagnetic powers. The filling factor was 0.1. All the peak heights have been taken to be arbitrarily the same. At 4 K, the linewidth is independent of power and its value is the same as for the lanthanum glass (nonmagnetic). It ap-

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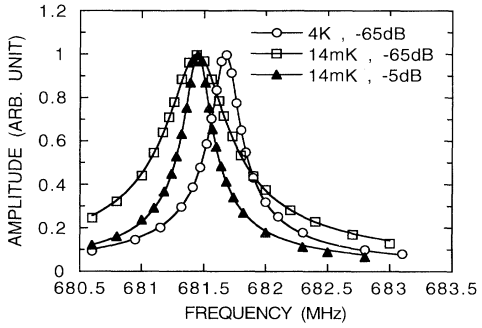

FIG. 1. Resonance lines of the resonator with the dysprosium glass for different electromagnetic powers. All the peak heights have been taken arbitrary equal to one. The solid lines are Lorentzian curves.

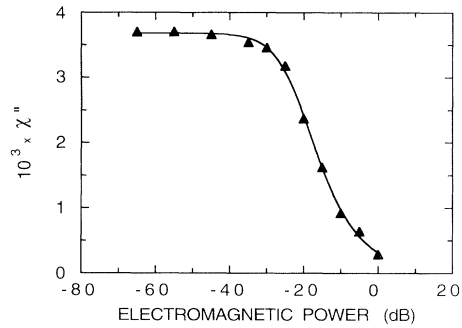

FIG. 2. Imaginary part of the magnetic susceptibility versus electromagnetic power at 14 mK for the dysprosium glass. 0 dB corresponds to an amplitude of the alternating magnetic field of about 2×10^{-4} T. The solid line is the theoretical curve obtained from Eq. (2).

pears in Fig. 1 that there is a strong decrease of the linewidth with increasing power, at low temperature. At high power (0 dB corresponds to an amplitude of the alternating field of about 2×10^{-4} T in the sample) and low temperature (14 mK), the linewidth has recovered its high-temperature value (at 4 K). We have verified that this nonlinear effect existed neither in the lanthanum glass (this is a proof there is no nonlinear effect arising from the dielectric susceptibility, since the electric field, although small, is not strictly zero in the sample) nor in the holmium glass. Hence, the existence of magnetic TS of very low energy splittings seems to be connected with Kramers degeneracy. Figure 2 shows the variation of χ'' as a function of the electromagnetic power, in zero magnetic field. We have also performed a two-pulse saturation-recovery experiment. The first, with large amplitude, saturated the TS; the second, much weaker and after a short delay, probed their recovery to the thermal equilibrium. We observed no effect on the second pulse by the first one. Taking into account the sensitivity of the resonator, that means the relaxation times of the TS were shorter than 1 μs at 14 mK. Figure 3 shows the variation of χ'' as a function of magnetic field, at low electromagnetic power (-60 dB). Last, we have measured χ'' as a function of temperature. It decreases down to zero at 4 K without exhibiting any peak.

The observed effects strongly support the existence of magnetic TS. Without specifying in this section the exact nature of these excitations, we can use the two-level-system model [1,9]. This phenomenological model assumes the existence of two-level systems with a constant density of states as a function of the splitting. They are described as one-half spins in a magnetic field. In our samples, these two-level systems are indeed magnetic moments, which is not the case in glasses. An alternating magnetic field induces transitions between the two levels of the TS having the suitable splitting ($\Delta=\hbar\omega$, where Δ is the splitting and ω is the angular frequency of the alternating field). With increasing power, the population difference between the two levels decreases. The dynamical behavior of these TS is described by the Bloch equations [18]. The imaginary part of the alternating susceptibility for a given splitting is

$$\chi''=\frac{\mu_0\gamma T_2}{1+[T_2(\omega-\omega_0)]^2+\gamma^2B_1^2T_1T_2}M_0, \qquad (1)$$

where γ is the gyromagnetic ratio of the TS, M_0 is the equilibrium value of the magnetization, T_1 and T_2 are the longitudinal and transverse relaxation times well known in spin systems, B_1 and ω are the amplitude and the angular frequency of the alternating magnetic field, $\hbar\omega_0=\Delta$ is the splitting of the TS. Then, we have to integrate over $\hbar\omega_0$. Because of the dipolar interactions between ions, there is a distribution of internal fields. Assuming a mean field $B_{\rm int}$ in the sample, this one can be evaluated and is found to be about 0.25 T [11]. Integrating Eq. (1) from zero to $\hbar\gamma B_{\rm int}$ with a constant density of states of the form of Eq. (4), we obtain

$$\chi''=\frac{K}{B_{\rm int}}\frac{1}{\sqrt{1+\gamma^2B_1^2T_1T_2}}, \qquad (2)$$

where K is a constant we shall consider in the next para-

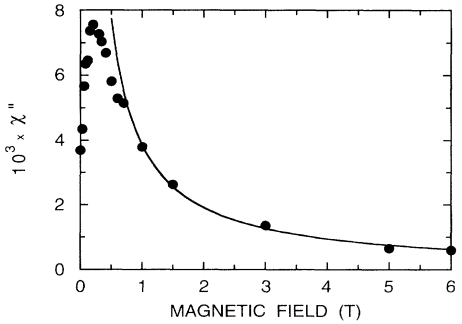

FIG. 3. Imaginary part of the magnetic susceptibility versus magnetic field at 14 mK and low electromagnetic power (-65 dB) for the dysprosium glass. The solid line is a hyperbolic curve as a function of magnetic field.

graph. This expression is similar to the one obtained for the acoustic saturation in glasses [7,8]. The solid line in Fig. 2 is the theoretical curve obtained from the above equation and giving the best fit with the experimental points. From this fit, we find a critical power (for which $\gamma^2 B_1^2 T_1 T_2 = 1$) equal to -21 dB and corresponding to $B_1 = 1.8 \times 10^{-5}$ T. Hence, $\gamma^2 T_1 T_2 = 3 \times 10^9$. The value of γ is unknown, but taking the value for the free electron we get $T_1 T_2 = 10^{-13}$ s^2, which is quite a small value at low temperature (in fused silica at 18 mK and 692 MHz, the relaxation times of the elastic TS are $T_1 = 2 \times 10^{-5}$ s and $T_2 = 10^{-4}$ s [19]). To fit the variation of χ'' versus magnetic field at low electromagnetic power (Fig. 3), Eq. (1) must be integrated over the splitting. Neglecting the saturation term $\gamma^2 B_1^2 T_1 T_2$ which is much smaller than 1, taking a density of states according to Eq. (4), and assuming a relaxation time proportional to the magnetic field, one can obtain a theoretical curve with a maximum around the value of the internal field and a hyperbolic variation in high field, in agreement with the experimental results. However, from the fit we obtain a value of T_2 in zero field equal to 10^{-12} s which is indeed too short and is not consistent with the product $T_1 T_2$ found above.

The nonobservation of the effect here reported in the holmium glass requires some precisions. Often, the ground state of the Ho^{3+} is taken as a doublet [13]. It is in fact a quasidoublet since the Jahn-Teller effect can lift the degeneracy of a non-Kramers ion. Since the nonlinear susceptibility results from a resonant absorption of the electromagnetic field by the magnetic TS, as soon as the splitting of the two lowest states is larger than $\hbar\omega$ the effect disappears. In our experimental conditions this lower value is quite small ($\hbar\omega = 0.03$ K).

We can attempt to describe the magnetic TS we have observed as ground doublets of the rare-earth ions whose local axis of anisotropy is almost perpendicular to the local magnetic field [3]. In a quantum-mechanical treatment a splitting Δ of the doublets appears due to the local magnetic field perpendicular to the anisotropy axis [2,3]. For arbitrary mutual orientation of these two directions there is, in addition, a Zeeman splitting. Hence, the total splitting of the ground doublet is [3]

$$\Delta = \sqrt{\varepsilon^2 + (2 g_J \mu_B J B \cos\theta)^2}, \tag{3}$$

where g_J is the Landé factor, μ_B is the Bohr magneton, and θ is the angle between the anisotropy axis and the local magnetic field. Because the anisotropy energy is much larger than the magnetic one ($g\mu_B JB \ll DJ^2$) and J is very large, ε is very small [3]. Hence, the main contribution to the splitting is the Zeeman term in Eq. (3). However, the contribution ε remains important: it means that, even at the lowest temperature, the magnetic moments are not frozen. Since the relative orientation between the magnetic field and the anisotropy axis is random, Eq. (3) leads to a density of states of the form [3,10]

$$n(\Delta) = \frac{c}{2 g_J \mu_B J B}, \tag{4}$$

where c is the magnetic-ion concentration. A density of states according to Eq. (4) allows us to determine the constant K in Eq. (2) which is found to be $\pi\mu_0 c M_0 / 2J$, where μ_0 is the permeability of vacuum. Then, from the fit in Fig. 2 we obtain $M_0 = 0.3\mu_B$. This single-ion anisotropy model can explain, partly, the behavior of the dysprosium glass. However, processes which give so short relaxation times for single ions are unusual in insulating glasses, and this is an important objection against the application of this model in the present case. Other models which imply more collective excitations must be considered. Actually, our samples have some behaviors of insulating spin glasses: The susceptibility as a function of temperature at low frequency (around 10 Hz) for our dysprosium glass exhibits a peak around 200 mK [20]. Moreover, very large time constants (several hours) appear in the samples at low temperature. Like the activated motions of small clusters considered in magnetic insulating glasses [12,21], tunneling motions of similar clusters could exist in our glasses, as shown theoretically for spins with frustrated dipolar interactions [22].

In summary, the observation of the saturation of the magnetic susceptibility as a function of electromagnetic power is a direct evidence of the existence of magnetic TS. In our glasses, Kramers degeneracy of the magnetic ions is necessary to observe these states. An acoustic study of similar glasses doped with different Kramers ions (gadolinium and europium) shows such magnetic TS exist also in these glasses [23]. The relaxation times of these magnetic TS are very short and the problem is to know what exactly is tunneling: single ions or clusters. It must be pointed out that the same problem arises in magnetic glasses as in nonmagnetic ones: their properties at low temperature are well explained within a phenomenological model, but there is not, unambiguously, a microscopic description of these ones. However, to clarify this point in dilute magnetic glasses there are physical parameters which can be changed. A study for different concentrations and also for different lattice structures (crystalline instead of amorphous) could give further information about these magnetic tunneling states.

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[1] P. W. Anders, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[2] P. W. Anderson, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, New York, 1973).

[3] I. Ya. Korenblit and E. F. Shender, Zh. Eksp. Teor. Phys. **75**, 1862 (1978) [Sov. Phys. JETP **48**, 937 (1978)].

[4] J. L. van Hemmen and A. Sütö, Europhys. Lett. **1**, 481 (1986).
[5] D. D. Awschalom, J. F. Smyth, G. Grinstein, D. P. DiVincenzo, and D. Loss, Phys. Rev. Lett. **68**, 3092 (1992).
[6] P. C. E. Stamp, E. M. Chudnovsky, and B. Barbara, Int. J. Mod. Phys. **6**, 1355 (1992).
[7] S. Hunklinger, W. Arnold, S. Stein, R. Nava, and K. Dransfeld, Phys. Lett. **42A**, 311 (1972).
[8] B. Golding, J. E. Graebner, B. I. Halperin, and R. J. Schultz, Phys. Rev. Lett. **30**, 223 (1973).
[9] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[10] J. M. D. Coey and S. von Molnar, J. Phys. (Paris), Lett. **39**, L-327 (1978).
[11] N. Vernier and G. Bellessa, Europhys. Lett. **14**, 349 (1991).
[12] D. H. Reich, T. F. Rosenbaum, and G. Aeppli, Phys. Rev. Lett. **59**, 1969 (1987).
[13] Wenhao Wu, B. Ellman, T. F. Rosenbaum, G. Aeppli, and D. H. Reich, Phys. Rev. Lett. **67**, 2076 (1991).
[14] K. Moorjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, New York, 1984).
[15] R. Harris, M. Plischke, and M. J. Zuckermann, Phys. Rev. Lett. **31**, 160 (1973).
[16] W. N. Hardy and L. A. Whitehead, Rev. Sci. Instrum. **52**, 213 (1981).
[17] W. Froncisz and J. S. Hyde, J. Magn. Reson. **47**, 515 (1982).
[18] A. Abragam, *The Principle of Nuclear Magnetism* (Oxford Univ. Press, Oxford, 1961).
[19] J. E. Graebner and B. Golding, Phys. Rev. B **19**, 964 (1979).
[20] J. L. Tholence (private communication).
[21] G. Eiselt, J. Kötzler, H. Maletta, D. Staufer, and B. Kinder, Phys. Rev. B **19**, 2664 (1979).
[22] S. N. Coppersmith, Phys. Rev. Lett. **17**, 2315 (1991).
[23] N. Vernier and G. Bellessa, Phys. Rev. B **48**, 12842 (1993).