Acoustic study of tunneling states in Kramers-ion-doped glasses: Wave propagation and phonon echoes

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We report on an acoustic study of insulating glasses doped with dysprosium, gadolinium, and europium ions, which have Kramers degeneracy. The magnetic-ion content is varied between 1 and 10 at. %. The measurements are performed down to 10 mK, using acoustic frequencies up to 900 MHz and in magnetic fields up to 50 kG. There is an effect of the magnetic-ion concentration and the magnetic field on the sound velocity at low temperature. This effect is explained by assuming the existence of two kinds of low-energy excitations: the usual elastic tunneling states and some magnetic tunneling states, which are magnetic moments whose local anisotropy axis is almost perpendicular to the local magnetic field. These magnetic tunneling states have relaxation times shorter than the elastic ones by several orders of magnitude at low temperature. They couple strongly to the latter whose dynamics is then drastically changed. This one is directly observed in saturation-recovery and phonon-echo experiments. The relaxation time T_1 of the elastic tunneling states is strongly shortened by the magnetic ions, whereas their dephasing time T_2 remains almost unchanged. This effect implies a relaxation process much more efficient than the usual one-phonon process at low temperature.

I. INTRODUCTION

The acoustic properties of glasses at low temperature have been extensively studied.[1,2] They have been explained very successfully in the framework of the theory of the elastic tunneling states (TS).[3,4] More recently, another theory, also phenomenological, has been introduced to explain simultaneously the properties of glasses at low temperature and those at higher temperature.[5] This is a soft potential model which explains the plateau in the thermal conductivity as well as the TS at lower temperature.[6] Obviously, these phenomenological theories do not allow to precise the microscopic nature of the TS, which is still unknown. The interaction of TS with electrons has been considered for a long time,[7] but it is only recently that the effect of magnetic ions upon the TS has attracted attention. This field has been approached in two kinds of materials: spin glasses[8] and glasses containing dilute magnetic ions.[9] In the two cases, there was no evidence of existence of some magnetic TS. Such two-level systems have been considered theoretically in amorphous materials with random anisotropy axis.[10] It has been shown that due to the large spin of the rare-earth Kramers ions, the splitting of the ground doublet (initially degenerate in zero magnetic field) is small for the spins whose the local anisotropy axis is almost perpendicular to the local magnetic field. These have a splitting distribution constant down to very low energy. A large contribution to the specific heat at low temperature in an amorphous Dy-Cu alloy has been explained by involving these excitations.[11] More recently, the problem of tunneling of large spins has been reconsidered in terms of the semiclassical WKB theory.[12]

In this paper we report on a set of experiments performed in insulating glasses doped with dysprosium, gadolinium, and europium ions. These three rare-earth ions have Kramers degeneracy. The results differ from those obtained in glasses doped with non-Kramers ions.[9] In this case, due to the Jahn-Teller effect, there is no degeneracy of the ground state. Moreover, the ions can couple directly with phonons by means of the electrostatic perturbation associated with the elastic field. In contrast, the degeneracy of the ground doublet of the Kramers ions can only be lifted by a magnetic field, and consequently, they cannot couple directly with phonons. The coupling can arise only from a change of the local dipolar field or of the anisotropy-axis direction induced by the elastic field. Our acoustic study includes sound velocity measurements, saturation recovery and phonon echoes. We show that the Kramers-ion-doped glasses behave in an original way. So, there are low-energy magnetic excitations which can be described as magnetic tunneling states and which couple very strongly with the usual elastic TS. Hence, a relaxation process of the TS, much more efficient than the one-phonon process, is found.

Acoustic measurements and phonon echoes are done in the frequency range 10–1000 MHz, down to 10 mK, in magnetic fields up to 50 kG, and for different ion concentrations between 1.5 and 10 at. %. The plan of the paper is as follows: Sec. II contains a brief description of the TS model and of the random anisotropy model, Sec. III gives information on the sample composition, and Sec. IV on the experimental procedure. Measurements of sound velocity and their interpretation are reported in Sec. V. Measurements of the relaxation time T_1 from saturation recovery and stimulated phonon echoes are reported in Sec. VI. Lastly, measurements of the phase memory time from spontaneous phonon echoes and free precession are reported in Sec. VII.

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II. THEORETICAL BACKGROUND

The TS model is now well known.[3,4] We recall here the main behaviors which will be useful to account for our experimental results. This presentation will be followed by a brief theoretical description of magnetic rare-earth ions in glasses.

A. The tunneling-state model

The TS model assumes that each tunneling state (TS) is described by a double-well potential whose parameters are the asymmetry ε of the double well and the overlap energy Δ. The two states of lowest energy of each TS are separated by the energy splitting

$$E=\sqrt{\Delta^2+\varepsilon^2}\ . \tag{1}$$

Since we are dealing with amorphous materials, the parameters Δ and ε are distributed according to[4]

$$f(\Delta,\varepsilon)=\frac{P}{\Delta}, \tag{2}$$

where P is a constant. Practically, Δ and ε are not very convenient parameters and one prefers to use E and the TS-phonon relaxation time T_1. Then, the distribution becomes[13]

$$g(E,T_1)=\frac{P}{2T_1\sqrt{1-T_{1,\min}(E)/T_1}}\ , \tag{3}$$

where $T_{1,\min}(E)$ is the shortest relaxation time of the TS whose splitting is E. Its value is given farther on in the text.

Each TS of energy E is coupled to an external strain e through the deformation potential $\gamma=\partial\varepsilon/\partial e$ and the Hamiltonian of the coupled system in the basis of the two states of lowest energy of the TS can be written:[13]

$$H=H_0+H_1\ , \tag{4}$$

where

$$\begin{cases} H_0=\dfrac{E}{2}\sigma_z\ , \\ H_1=M\sigma_x+D\sigma_z\ , \\ M=\gamma\Delta/E\ , \\ D=\gamma\varepsilon/E\ , \end{cases} \tag{5}$$

and σ_i $(i=x,y,z)$ are the usual Pauli matrices.

Formally, TS are analogous to spin-$\frac{1}{2}$ in a magnetic field. Hence, their dynamics can be described using the Bloch equations in the rotating frame:

$$\begin{cases} \dfrac{du}{dt}=\left[\omega-\dfrac{De(t)+E}{\hbar}\right]v-\dfrac{u}{T_2}\ , \\ \dfrac{dv}{dt}=-\left[\omega-\dfrac{De(t)+E}{\hbar}\right]u+\dfrac{Me_0}{\hbar}-\dfrac{v}{T_2}\ , \\ \dfrac{dw}{dt}=-\dfrac{Me_0}{\hbar}v-\dfrac{w-w_0}{T_1}\ , \end{cases} \tag{6}$$

where u,v,w are the average values $\langle\Psi|\sigma_x|\Psi\rangle$, $\langle\Psi|\sigma_y|\Psi\rangle$, and $\langle\Psi|\sigma_z|\Psi\rangle$ of the TS wave function Ψ, ω is the angular frequency of the harmonic perturbation $e=e_0\cos(\omega t)$, and w_0 is the thermal equilibrium value of w:

$$w_0=\frac{1}{2}\tanh\left[\frac{E+De}{2k_BT}\right]\ . \tag{7}$$

T_1 and T_2 are the relaxation times which characterize the TS-lattice interaction and the TS-TS interaction, respectively. Using the Bloch equations and the distribution law (3), it is possible to explain the phonon echoes and the saturation recovery that have been observed in glasses.[14,15] At low temperature (below 1 K), T_1 results from one-phonon processes and is given by[13]

$$T_1^{-1}(E)=\sum_\alpha\frac{\gamma_\alpha^2}{v_\alpha^5}\frac{E\Delta^2}{2\pi\rho\hbar^4}\coth(E/2k_BT)\ , \tag{8}$$

where v_α is the sound velocity for polarization α. Due to the distribution of Δ, there is also a distribution of relaxation times T_1 which exhibits a lower limit $T_{1,\min}(E)$, corresponding to the case of the symmetric double-well potential ($\varepsilon=0$ and $\Delta=E$). $T_{1,\min}(E)$ characterizes the distribution $g(E,T_1)$ and can be estimated from the experimental results. The relaxation time T_2 is a dephasing time of the TS and can be obtained from experiments such as phonon echoes, free precession or hole burning. In glasses, the dephasing process is ascribed to spectral diffusion.[16]

B. Characteristics of the magnetic rare-earth ions

We have studied the effects of magnetic rare-earth ions on the TS in glasses. For these tripositive ions the magnetic properties are due to the $4f$ inner shell. Hence, the magnetic behaviors of these ions in solid are very similar to those of the free ions. The energy levels are characterized by the quantum numbers (L,S,J). The main interaction between one ion and its surrounding is the electrostatic one. In the case of amorphous materials, it has been shown that this interaction can be described by the following Hamiltonian:[17]

$$H=-DJ_z^2\ , \tag{9}$$

where the z axis has been chosen as the J direction for which the energy is minimum. Of course, because we consider here amorphous materials, the z axis is different for each ion. In the case of dysprosium, the anisotropy energy is about 100 K. So, in the temperature range 0.01–1 K where we have worked, the magnetic moment J can be only oriented along the anisotropy axis. For Kramers ions (ions with a half-integer spin), the degeneracy $J_z=\pm J$ can be lifted only by a magnetic field B, which induces the following splitting:[10]

$$E=\sqrt{\Delta^2+(2g_j\mu_BJB\cos\theta)^2}\ , \tag{10}$$

where μ_B is the Bohr magneton, g_J is the Landé factor, and Δ is the coupling energy between the two states and

is given by

$$\Delta = D\left[\frac{g_J\mu_B B\sin\theta}{2D}\right]^{2J}\frac{4J}{(2J-1)!}\ , \tag{11}$$

where θ is the angle between the anisotropy axis z and the local magnetic field. Because the anisotropy energy is much larger than the magnetic one ($g_J\mu_B JB \ll DJ^2$), and J is very large, Δ is exponentially small. Hence, the main contribution to the splitting E is

$$\varepsilon = 2g_J\mu_B JB\cos\theta\ . \tag{12}$$

However, the contribution Δ remains important: It means that, even at the lowest temperature, the magnetic moments are not frozen. Their reversals on their anisotropy axis, which are impossible from the classical point of view due to the height of the barrier to overcome, become possible through the tunneling effect. So, these ions constitute indeed magnetic tunneling states. As the relative orientation between the magnetic field and the anisotropy axis [$g(\theta,\varphi)=\sin\theta$] is expected to be random. Eq. (12) leads to the following density of states for these magnetic tunneling states:

$$g(E) = \frac{C}{g_J\mu_B JB} \quad \text{for } E \le 2g_J\mu_B JB\ , \tag{13}$$

where C is the magnetic-ion concentration. We have supposed that the magnetic field is constant. In the case of a fluctuating magnetic field (due to internal fields), the distribution of Eq. (13) remains valid, but B has to be replaced by an average field $B_{\rm av}$.

III. COMPOSITION OF THE GLASSES

We have studied aluminosilicate glasses doped with dysprosium, gadolinium or europium, which are magnetic ions. The common property of these ions is they have all Kramers degeneracy (half-integer values of J). The concentration of magnetic ions was varied between 1.5 and 10.1 at. %. The concentration of rare-earth ions was kept constant (10.1 at. %) by replacing magnetic ions with nonmagnetic lanthanum ions.[9] The exact chemical compositions of our glasses were

$(Dy_2O_3)_{0.029}(La_2O_3)_{0.165}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (1.5 at. % Dy) ,

$(Dy_2O_3)_{0.065}(La_2O_3)_{0.129}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (3.38 at. % Dy) ,

$(Dy_2O_3)_{0.129}(La_2O_3)_{0.065}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (6.7 at. % Dy) ,

$(Dy_2O_3)_{0.194}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (10.1 at. % Dy) ,

$(Gd_2O_3)_{0.194}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (10.1 at. % Gd) ,

$(Eu_2O_3)_{0.029}(La_2O_3)_{0.165}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (1.5 at. % Eu) .

Moreover, to determine the intrinsic acoustic properties of our glasses, we have studied a glass without magnetic ion, only doped with lanthanum. Its chemical composition was

$(La_2O_3)_{0.194}(SiO_2)_{0.579}(Al_2O_3)_{0.227}$ (10.1 at. % La) .

The samples were cut in shape of rectangular parallelepipeds of typical size $10\times5\times4$ mm^3 and the acoustic waves were traveling lengthways.

IV. EXPERIMENTAL SETUP

A. Cryogenics

The samples were cooled down to 10 mK with a He^3-He^4 dilution refrigerator. A magnetic field up to 50 kG could be applied with a superconducting coil immerged in the liquid-He^4 bath. The homogeneity of the field was better than 10^{-5} in the whole sample. The temperature was determined by measuring the resistivity of a Matsushita carbon resistance.[18] This kind of resistance has a very low magnetoresistance and can be used even at high field.

B. Electronics

The acoustic waves were generated by X-cut quartz transducers of 100 MHz fundamental frequency. We were able to work up to 900 MHz by using the harmonic frequencies. The transmitted waves through the sample were detected either by a second quartz transducer attached on the opposite side of the sample or by the emitter quartz after a reflection on the opposite side of the sample. The diameter of the acoustic beam was about 3 mm^2. The duration of the acoustic pulses could be chosen in the range 30 ns–2 μs. The duration limitation was mainly due to the mechanical damping of the quartz transducers (around 20 ns) for the shortest times and to the overlap of the reflected echoes for the longest times.

The electronic setup was able to generate any sequence of one, two or three pulses. The pulses transmitted through the sample were amplified and detected by a phase sensitive device. Then, the signal was sent to a digital transient analyzer which allowed recording of very fast events. The nonlinear attenuation was measured by varying the input acoustic power with an attenuator and measuring the deviation from the linearity of the acoustic traveling pulses. Hence a good linearity of the whole

chain was required in this type of experiment. It was achieved correctly with our apparatus which was linear within 0.08 dB in the whole attenuation range. It must be pointed out that a calibration was always possible at 4 K where all the nonlinear effects in glasses disappeared.

V. SOUND VELOCITY VARIATION

A. Dysprosium-doped glasses

The results we have obtained for the dysprosium-doped glasses are reported in Figs. 1 and 2. Figure 1 shows the variation of the sound velocity in glasses as a function of temperature for several dysprosium concentrations. Above 40 mK, the velocity increases according to a logarithmic law, as expected from the resonant interaction between the acoustic waves and the TS.[1] The interesting effect is the dependence of the slope of the logarithmic variation on the dysprosium concentration. This slope decreases as the magnetic-ion concentration increases. Below 40 mK, the temperature variation is no longer logarithmic, but the acoustic measurements in this temperature range become very suspicious due to very large time constants which appear in the samples (many hours at the lowest temperatures). This effect is not presently explained and will not be further considered in this paper. Figure 2 shows the influence of the magnetic field on the sound velocity variation as a function of temperature for a sample containing 10.1% of dysprosium ions. The usual logarithmic increase of the sound velocity with increasing temperature is again well verified at low temperature. The particular behavior is the increase of the slope as the magnetic field is increased. This one tends towards the value of the slope in the nonmagnetic sample at high magnetic field. A preliminary report on this effect has been published.[19] Our experimental results are well fitted with the following phenomenological law:

$$Y = Y_0 - \frac{kC}{B_{\mathrm{av}}} , \tag{14}$$

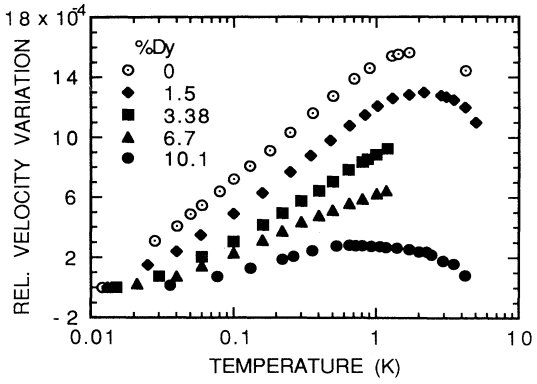

FIG. 1. Relative velocity variation of longitudinal acoustic waves as a function of temperature, in aluminosilicate glasses with different atomic concentrations of dysprosium, in zero magnetic field. The acoustic frequency is 100 MHz and the absolute sound velocity is 5.95×10^{5} cm s^{-1} at 10 mK.

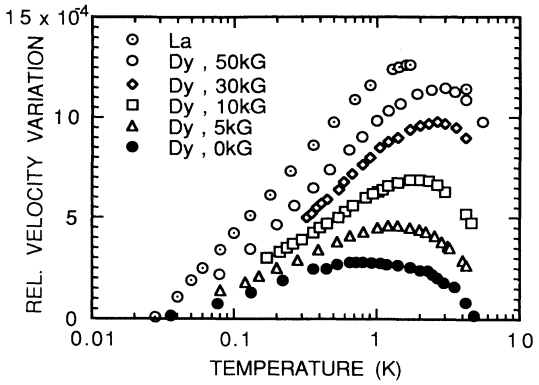

FIG. 2. Relative velocity variation of longitudinal acoustic waves as a function of temperature in the 10.1% dysprosium-doped glass, for different values of the magnetic field. The acoustic frequency is 100 MHz.

where Y is the value of the slope of the logarithmic increase, Y_0 is its value for the nonmagnetic sample, k is a constant, C is the dysprosium concentration, and B_{av} is the mean value of the amplitude of the local magnetic field, which takes into account the dipolar field $\mathbf{B}_{\mathrm{int}}$ due the other magnetic ions. The latter assumption is well justified for rare-earth ions in our concentration range. B_{av} can be written

$$B_{\mathrm{av}} = \langle \|\mathbf{B}_0 + \mathbf{B}_{\mathrm{int}}\| \rangle , \tag{15}$$

where $\mathbf{B}_0$ is the applied magnetic field. Assuming random locations of the magnetic ions in the sample and taking a Gaussian distribution for the amplitudes of the local internal fields, we find the following expression for B_{av}:

$$B_{\mathrm{av}} = B_{\mathrm{loc}} \exp\left[-\left[\frac{B_0}{\sqrt{\pi} B_{\mathrm{loc}}}\right]^2\right] + B_0 \,\mathrm{erf}\left[\frac{B_0}{\sqrt{\pi} B_{\mathrm{loc}}}\right] , \tag{16}$$

where B_{loc} is given by

$$B_{\mathrm{loc}} = \sqrt{\langle \mathbf{B}_{\mathrm{int}}^2 \rangle} . \tag{17}$$

In Fig. 3, the slope values of the logarithmic variation

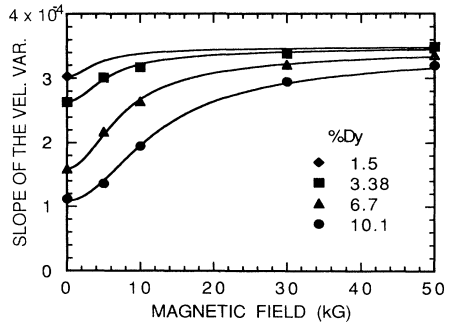

FIG. 3. Slope of the velocity variation as a function of temperature, for different values of the magnetic field and of the dysprosium concentration. The solid lines are the fits obtained with Eqs. (14) and (16).

of the sound velocity for different dysprosium concentrations and magnetic fields are reported. The solid lines are the theoretical curves obtained from Eqs. (14) and (16). We can see that the agreement is very good. The fitting of our experimental data on the theoretical curves enables us to determine $B_{\rm loc}$. Their values for the different concentrations are reported in Fig. 4. The solid line is a parabolic curve. It can be seen that for the three lower concentrations, the internal field varies as the square root of the concentration (by taking into account the fact that the curve must go to zero as the magnetic-ion content vanishes). The point for the highest concentration (10.1%) deviates from this variation.

The logarithmic increase of the sound velocity with increasing temperature is usual in glasses. It is due to the resonant interaction between the thermal phonons and the TS and is given by[20]

$$\frac{\Delta v_{\rm res}}{v} = \frac{P\gamma^2}{\rho v^2} \ln\left[\frac{T}{T_0}\right], \tag{18}$$

where v is the sound velocity and ρ is the specific mass (P and γ have been defined in Sec. II A). However, there is a second contribution to the sound velocity due to the relaxation processes. In the case of insulating glasses, for which ωT_1 is usually much greater than 1 below 1 K (ω being the pulsation of the acoustic wave), this contribution is negligible, but it must be taken into account if ωT_1 is much shorter than 1. This contribution gives also a logarithmic variation of the sound velocity versus temperature but with an opposite sign as compared with the resonant contribution[21]

$$\frac{\Delta v_{\rm rel}}{v} = -\frac{3P\gamma^2}{2\rho v^2} \ln\left[\frac{T}{T_0}\right]. \tag{19}$$

Our experimental results can be explained with these two contributions, assuming the existence of two types of TS in our glasses: the first would have long relaxation times and would give only a resonant contribution (at the low temperatures considered here); the second would have much shorter relaxation times, and would introduce a relaxation contribution. Summing the two contributions, we get an equation for the slope such as our phenomenological law [Eq. (14)], the density of states of the second type of TS being proportional to $C/B_{\rm av}$. Now the question is, what are the two types of TS? The first are obviously the usual elastic TS of amorphous materials. They give a constant contribution Y_0 to Y. The second might be the magnetic TS described in Sec. II B. Indeed their density of states has the right form [Eq. (13) as compared with Eq. (14)]. In this way, we can explain our experimental results. However, there is another possible explanation which implies also magnetic TS but does not assume a direct coupling between these and the acoustic waves. There would be only one kind of TS (the standard elastic TS) which couple with the acoustic waves, but they would be separated into two groups: the first would contain the TS that are not coupled with the magnetic TS. They have long relaxation times and give only a resonant contribution to the sound velocity. The second would contain the TS strongly coupled with the magnetic TS. Due to this new coupling, they would have much shorter relaxation times and would give a relaxation contribution to the sound velocity. Assuming that the density of states of this second group of TS is proportional to the one of the magnetic TS, we get again a velocity variation in the form of Eq. (14). Presently, we cannot say which of these two explanations is the right one but we can say that it is necessary to consider fast magnetic TS to explain our experimental results.

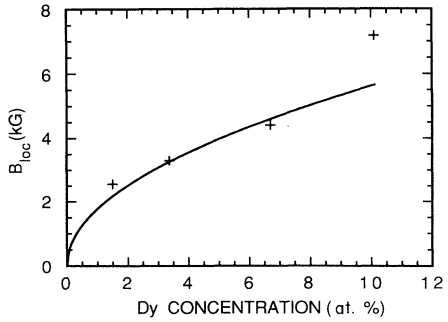

FIG. 4. Internal magnetic field as a function of the dysprosium concentration. These values are obtained from the fits using Eqs. (14) and (16). The solid line is the parabolic curve giving the best fit to the experimental points.

B. Gadolinium-doped glasses

Gd^{3+} is a Kramers ion, as Dy^{3+}. The main difference between these two ions is their anisotropy energy: For Dy^{3+}, it is around 100 K, whereas for Gd^{3+} it is about 2 K. This big difference arises from the fact that Gd^{3+} has a half-filled $4f$ shell. So it has an almost spherical symmetry and its anisotropy energy is very low. Figure 5 shows the variation of the sound velocity as a function of temperature, in a 10.1% gadolinium-doped glass, for different magnetic field. It can be seen that the velocity increases with increasing temperature up to 0.15 K,

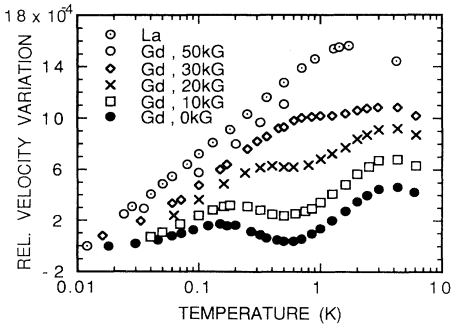

FIG. 5. Relative velocity variation of longitudinal acoustic waves as a function of temperature in the 10.1% gadolinium-doped glass, for different values of the magnetic field. The acoustic frequency is 120 MHz and the sound velocity is 5.94×10^5 cm s^{-1} at 10 mK. The velocity variation in the 10.1% lanthanum-doped glass is shown as reference to the nonmagnetic glass.

which is the signature of the TS. However, above 0.2 K there is a step which arises from activation processes. These give correlatively a peak in the acoustic attenuation.[22] Nevertheless, the effect of the magnetic field on the logarithmic variation at the lowest temperatures still exists. The slope of this variation increases with increasing magnetic field, as in dysprosium. At the highest fields, the variation is logarithmic up to higher temperatures because the magnetic field increases the barrier height of the activation processes.[22]

C. Europium-doped glasses

Europium is a special rare-earth, because it can give two types of ions: Eu^{2+} and Eu^{3+}. The latter has a total magnetic moment equal to zero at 0 K. Its first excited multiplet $J=1$ has a low energy ($\sim$450 K). The result of this is there is a magnetic moment different from zero at room temperature, but at liquid-helium temperature the occupation of the level $J=1$ is negligible and Eu^{3+} is nonmagnetic. This is not the case with Eu^{2+}, which has its $4f$ shell half-filled like Gd^{3+}. So, europium glasses are expected to behave in a similar way as gadolinium ones. Figure 6 shows the variation of the sound velocity as a function of temperature, in a 1.5% europium-doped glass, for two magnetic-field values. Below 0.5 K, the slope of the velocity variation increases again as the magnetic field is set up. This increase is small (14% between 0 and 50 kG, as deduced from Fig. 6) but it is due to the low europium content. It is of the same order of magnitude than the one for the 1.5% dysprosium-doped glass (Fig. 3). It would be useful to study glasses with higher concentration of europium. Unfortunately, it has not been possible to dissolve more than 1.5% of europium in our glasses. Figure 6 shows a change of the slope of the velocity variation above 0.5 K, in zero magnetic field. This is due to activation processes which appear at these temperatures, like in gadolinium glasses.[22]

VI. MEASUREMENTS OF THE RELAXATION TIME T_1

There are two kinds of experiments that allow a direct determination of the relaxation time T_1: saturation recovery and stimulated phonon echoes. A saturation recovery experiment consists in saturating the medium with a first strong acoustic pulse and afterwards measuring the variation of the attenuation of a probing pulse as a function of the delay time between the two pulses.[15] A phonon-echo experiment consists in sending three pulses in the sample: the first two are separated by a short time interval t_{12} and the third with a much longer delay t_{13} with respect to the first. The first two pulses (of suitable intensity and duration) create in the sample a spontaneous echo at the time $2t_{12}$. Its amplitude variation as a function of $2t_{12}$ gives access to the phase memory time T_2. At the time t_{12} after the third pulse, a stimulated echo is created in the sample. Its amplitude variation as a function of t_{13} gives access to the TS-lattice relaxation time.[14]

A. Saturation recovery in dysprosium-doped glasses

Figures 7 and 9 show the results of two saturation recovery experiments in two dysprosium-doped glasses of concentration 1.5 and 6.7 %, respectively, for two magnetic fields. Firstly, we can see that the decay is nonexponential. This behavior is usual and arises from the distribution of the relaxation time T_1 of the TS (see Sec. II A). However, in nonmagnetic glasses such as silica[15] or our 10.1% lanthanum-doped sample (Fig. 8), there is an exponential decay for the shortest delays ($t_{12}<50$ μs). Hence, a value for $T_{1,\min}$ can be deduced and is found to be around 200 μs in the 10.1% lanthanum-doped glass at 697 MHz and 13 mK. For the two dysprosium-doped glasses, Figs. 7 and 9 do not show any exponential variation in any delay range (for technical reasons, we cannot use a delay t_{12} shorter than 1 μs). This implies a very short $T_{1,\min}$, which confirms our assumption of very short relaxation times to explain the sound velocity effect (Sec. V A). Moreover, it appears that the relaxation times become faster as the dysprosium concentration is increased: The initial variation of the saturation is faster for the 6.7% Dy sampled (Fig. 9) than for the 1.5% Dy sample (Fig. 7). For the 10.1% Dy sample the effect is still stronger: The relaxation is so fast that after only 1

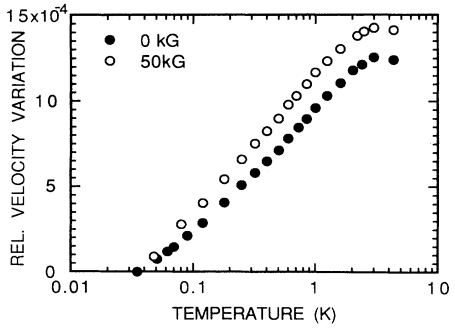

FIG. 6. Relative velocity variation of longitudinal acoustic waves as a function of temperature in the 1.5% europium-doped glass, for two values of the magnetic field. The acoustic frequency is 600 MHz and the sound velocity is 5.86×10^5 cm s^{-1} at 10 mK.

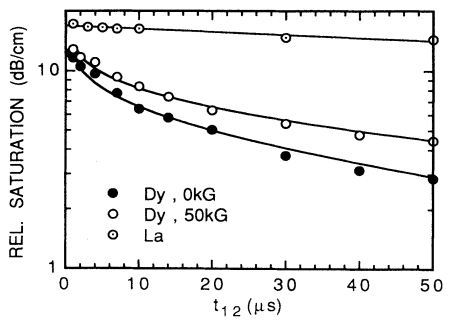

FIG. 7. Attenuation variation of a probing acoustic pulse as a function of its delay with respect to a first saturating acoustic pulse, for two values of the magnetic field, in a 1.5% dysprosium-doped glass. The acoustic frequency is 655 MHz and the temperature 13 mK. The solid lines are the theoretical curves obtained from Eq. (23).

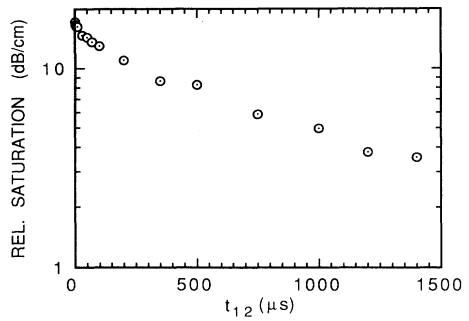

FIG. 8. Attenuation variation of a probing acoustic pulse as a function of its delay with respect to a first saturating acoustic pulse, for two values of the magnetic field, in a 10.1% lanthanum-doped glass. The acoustic frequency is 697 MHz and the temperature 13 mK.

μsec the sample is completely desaturated. So far, we have considered the initial decay of the saturation, but it is also interesting to look at the desaturation after long delays. Figure 7 shows that after 50 μsec the La sample with an amplitude variation of the probing pulse of 14 dB/cm is almost completely saturated, whereas the 1.5% Dy sample with an amplitude variation of the probe of 3 dB/cm is appreciably desaturated. Figure 9 shows that after 50 μsec the 6.7% Dy sample is totally desaturated. That means that the Dy ions reduce strongly the relaxation times of the TS. Lastly, it can be seen in Figs. 7 and 9 that the magnetic field has little effect: It slows down the relaxation and for the same delay the saturation is greater in high magnetic field than in zero field.

It is possible to fit our experimental results to the theoretical prediction by taking into account the shortness of $T_{1,\min}$ and assuming

$$T_{1,\min} \ll t_{12} \ . \tag{20}$$

Then, the expression for the density of states [Eq. (3)] can be reduced to

$$g(E,T_1)=\frac{P}{2T_1} \ . \tag{21}$$

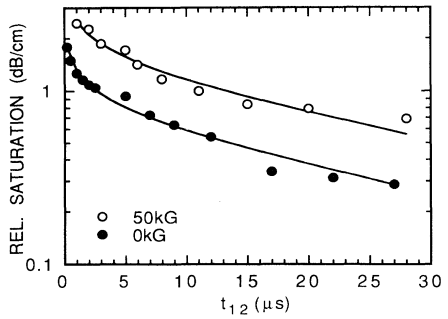

FIG. 9. Attenuation variation of a probing acoustic pulse as a function of its delay with respect to a first saturating acoustic pulse, for two values of the magnetic field, in a 6.7% dysprosium-doped glass. The acoustic frequency is 350 MHz and the temperature 13 mK. The solid lines are the theoretical curves obtained from Eq. (23).

The attenuation due to the resonant interaction between the acoustic wave and the TS is proportional to

$$\Delta n=\Delta n_0\left[1-\int_{T_{1,\min}}^{T_{1,\max}} g(E,T_1)\cdot e^{-t_{12}/T_1}dT_1\right] , \tag{22}$$

where Δn is the population difference between the two levels of the TS excited by the acoustic pulse. Using the two preceding equations, Δn can be reduced to the following expression:

$$\Delta n=K_1\Delta n_0 \ln(t_{12})+K_2 \ , \tag{23}$$

where K_1 and K_2 are two constants. The solid lines in Figs. 7 and 9 are the curves obtained from Eq. (23). We can see that the agreement with the experimental results is satisfactory. This is another way to confirm the existence of TS with $T_{1,\min}$ much shorter than 1 μs [according to Eq. (20)]. So, the elastic TS have relaxation times much shorter in dysprosium-doped glasses than in the nonmagnetic ones, which means there is a strong interaction between them and the magnetic ions.

B. Saturation recovery in a gadolinium-doped glass

We have performed a saturation recovery experiment in a 10.1% gadolinium-doped glass, for different magnetic fields, at 25 mK. The attenuation variation of the probing pulse as a function of the delay t_{12} is reported in Fig. 10. The dashed line holds for zero magnetic field. In this case the desaturation is so fast that after only 1 μsec the medium has returned to thermal equilibrium. At 10 kG, the initial variation of the saturation is still fast but measurable. From the slope of the initial decay, we obtain a relaxation time $T_{1,\min}$ shorter than 1 μsec. At 50 kG, the desaturation is slowed down. The initial decay of the saturation is exponential up to 20 μsec and gives $T_{1,\min}=45$ μsec. This value must be compared to the one obtained for the lanthanum glass: In this sample (see Sec. VI A) we have found $T_{1,\min}=200$ μsec at 13 mK and T_1 is known to vary as $\tanh(E/2k_BT)$ [see Eq. (8)]. Hence, the value of $T_{1,\min}$ for the gadolinium glass at 13 mK as deduced from our measurement at 25 mK is 70 μsec,

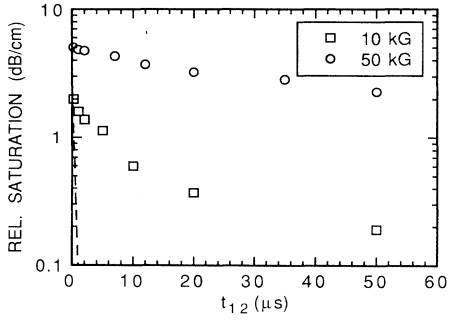

FIG. 10. Attenuation variation of a probing acoustic pulse as a function of its delay with respect to a first saturating acoustic pulse, for two values of the magnetic field, in a 10.1% gadolinium-doped glass. The acoustic frequency is 620 MHz and the temperature 25 mK. The dashed line holds for zero magnetic field (see text).

which is of the same order of magnitude as the one for the lanthanum glass. Thus, we can conclude that the effect of the magnetic ions has almost disappeared. The interpretation of these results is clear: The fast relaxation we have found in low magnetic field is due to the magnetic TS associated with the Gd ions on their anisotropy axis, which they cannot leave because the thermal energy around 20 mK is much lower than the anisotropy energy. In high magnetic field (i.e., $g_J\mu_B JB \gg DJ^2$), the Gd ions remain no longer on their anisotropy axis but orient themselves along the magnetic field (at 50 kG, the Zeeman energy of the Gd ions is 25 K and their anisotropy energy is of the order of a few K). So, the magnetic TS as defined in Sec. II B are destroyed and the sample behaves acoustically as an usual glass.

C. Saturation recovery in an europium-doped glass

Figure 11 shows the results of a saturation recovery experiment in a 1.5% europium-doped glass at 12 mK, for two magnetic fields. In zero magnetic field the desaturation is fast. From the initial decay of the saturation the value of $T_{1,\min}$ can be determined and is found to be 4 μsec. This value is larger than the one obtained in the other magnetic glasses. However, it must be pointed out that the ion concentration is lower than in the preceding cases. Moreover, the proportion of Eu^{2+} ions as compared to Eu^{3+} ions is unknown (Sec. V C). Hence, the concentration of magnetic ions is certainly smaller than 1% in the present case. At 50 kG the desaturation is slowed down (Fig. 11). From the initial decay of the saturation the value $T_{1,\min}=22$ μsec is deduced. It remains shorter than in the nonmagnetic sample. That means that a magnetic field of 50 kG is not sufficiently high to destroy the magnetic TS associated with Eu^{2+} ions, which is not the case for Gd^{3+} ions. We assign this difference to the anisotropy energy which must be higher for Eu^{2+} (which is twofold coordinated) than for Gd^{3+} (which is threefold coordinated). Hence, a much higher magnetic field would be necessary to destroy completely the magnetic TS associated with the Eu^{2+} ions.

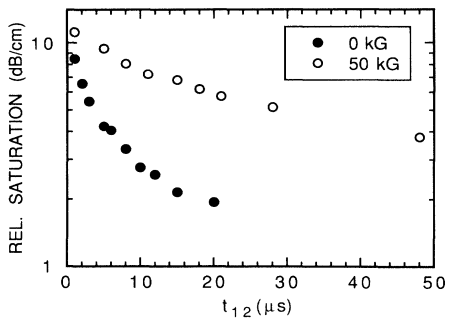

FIG. 11. Attenuation variation of a probing acoustic pulse as a function of its delay with respect to a first saturating acoustic pulse, for two values of the magnetic field, in a 1.5% europium-doped glass. The acoustic frequency is 600 MHz and the temperature 13 mK.

D. Stimulated phonon echo in a dysprosium-doped glass

Figure 12 shows the amplitude of the stimulated echo as a function of the delay $t_{13}=t_3-t_1$, for two values of the magnetic field, in the 1.5% dysprosium-doped sample. The amplitude of the stimulated echo for the lanthanum-doped glass is also reported in Fig. 12. It can be seen that the decay is nonexponential, as usual.[14] However, such as for the saturation recovery, the initial exponential decay, which can be seen in the nonmagnetic glass, no longer appears in the magnetic one. About the magnetic field, its only effect is to multiply by 2 the amplitude of the stimulated echo (6 dB). Indeed, the two curves of Fig. 12 can be deduced from one another by a vertical translation. This phenomenon cannot be explained by a direct contribution of the magnetic TS which have a density of states decreasing with increasing magnetic field. Nevertheless, it can be explained by taking into account the strong interaction of the elastic TS with the magnetic TS, already considered (see Sec. V A). The mechanism could be the following: There are in the sample some elastic TS with very short relaxation times, due to their interaction with the magnetic TS. They are first saturated by the third acoustic pulse, and then, during the time t_{12} before the stimulated echo, their saturation rate changes. This leads to an attenuation of the stimulated echo propagating in the sample. This attenuation depends on the saturation rate, which changes with the magnetic field (see Sec. VI A).

It is interesting to look at the behavior of the stimulated echo for large t_{13}, because it is very peculiar. We have plotted in Fig. 13 the amplitude of the stimulated echo in the 1.5% dysprosium sample as a function of t_{13}, in high magnetic field (50 kG). It can be seen that the experimental points fit very well a straight line in logarithmic scales, and this in a wide delay range. The solid line in Fig. 13 corresponds to the following law:

$$A(t_{13})=A_0(t_{13})^{-1/3} . \tag{24}$$

Firstly, it must be pointed out that this phenomenological

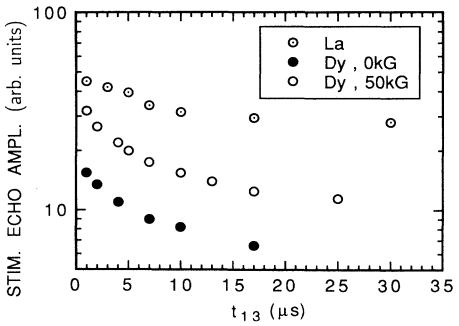

FIG. 12. Amplitude of the stimulated phonon echo as a function of the delay t_{13} between the first and the third acoustic pulse, for two values of the magnetic field, in a 1.5% dysprosium-doped glass. The acoustic frequency is 655 MHz and the temperature 13 mK. The echo amplitude in the 10.1% lanthanum-doped glass is shown as reference to the nonmagnetic glass.

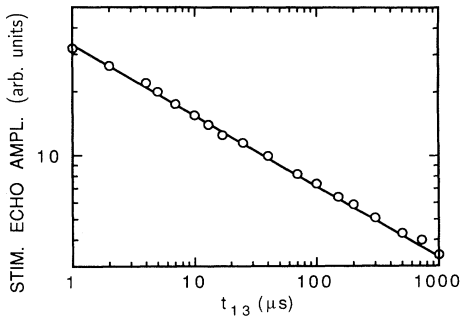

FIG. 13. Amplitude of the stimulated phonon echo as a function of the delay t_{13} between the first and the third acoustic pulse, in a 1.5% dysprosium-doped glass, in a magnetic field of 50 kG. The solid line is the theoretical curve obtained from Eq. (24). The acoustic frequency is 655 MHz and the temperature 13 mK.

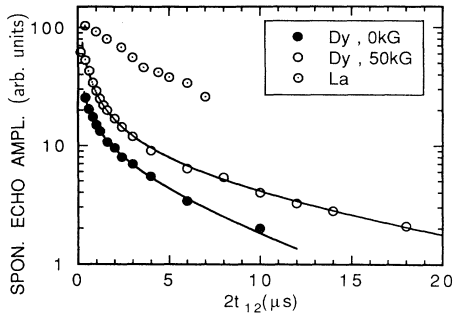

FIG. 14. Amplitude of the spontaneous phonon echo as a function of the delay between the first and the second pulse, in a 1.5% dysprosium-doped glass, for two magnetic fields. The acoustic frequency is 655 MHz and the temperature 13 mK. The solid lines are the theoretical curves obtained from Eq. (25). The echo amplitude in the 10.1% lanthanum-doped glass is shown as reference to the nonmagnetic glass.

law cannot apply to the whole range $(0, +\infty)$, since it diverges at $t_{13}=0$. There is necessarily a lower limit $t_{\min}$ of the validity range. However, the validity range is very wide (three decades), and this behavior is meaningful. It has not been found in insulating glasses, and seems to be peculiar to our magnetic glasses. This phenomenological law is quite different from the expected behavior of the stimulated echo by taking into account spectral diffusion[16] and is not explained presently.

VII. PHASE MEMORY TIME

So far, we have reported on experiments that allow the determination of the relaxation time T_1. This one characterizes the interaction of the TS with the lattice. There is another relaxation time T_2 which characterizes the interaction of the TS with each other (see Sec. II A). This relaxation time, also called phase memory time, can be obtained from phonon-echo experiments or free-precession experiments.

A. Spontaneous phonon echo in dysprosium-doped glasses

Figure 14 shows the amplitude of the spontaneous echo as a function of the delay $t_{12}=t_2-t_1$ in a 1.5% dysprosium-doped sample, for two magnetic fields. A preliminary report on this observation has been published.[23] The amplitude of the spontaneous echo in the lanthanum-doped glass (which is nonmagnetic) is also reported in Fig. 14. Its variation is exponential as a function of $2t_{12}$, as usual in nonmagnetic glasses.[14] From this variation the value $T_2=6$ μsec is deduced for the lanthanum glass. This value is shorter than in fused silica.[14] For the dysprosium glass, the decay of the spontaneous echo as a function of $2t_{12}$ is not exponential, in zero field as well in 50 kG. Moreover, the initial decay is much faster than in the nonmagnetic sample. Our previous results can help us to understand this behavior. Indeed, we know that the TS-lattice relaxation is much shorter in dysprosium-doped glasses than in nonmagnetic ones. To explain our results, we assume, as in Sec. V A, the existence of two groups of TS: the first one contains the standard TS and the second one contains the TS which are strongly coupled to the Dy^{3+} ions and which have very short relaxation times. Hence, these ones do not give rise to a phonons echo (because the phase memory is very short), but they attenuate the phonon echo generated by the TS of the first group. This attenuation depends on the saturation rate of the TS of the second group. Hence, assuming an exponential decay for the TS of the first group alone, we can write the amplitude of the spontaneous echo

$$A(t_{12})=A_0\exp(-t_{12}/T_2-\beta\ln t_{12}) , \tag{25}$$

where the second term in the exponential arises from Eq. (23). The solid lines in Fig. 14 are the curves obtained from Eq. (25) for the best fit parameters. We can see that the agreement is very good. Moreover, β can be compared to the value we have obtained from the saturation recovery experiment [Eq. (23) in Sec. VI A]. Within 15%, we obtain the same value in the two cases. This is very satisfactory and validates our assumption of very short relaxation times. In consequence of this agreement we can assert now that $T_{1,\min}$ is even shorter than 0.2 μs, which is the minimum value of t_{12} used in this experiment. Lastly, from the numerical fits the following phase memory times are obtained:

$$\begin{cases} T_2=10\ \mu\text{s} & \text{for } B=0\text{ kG} \\ T_2=25\ \mu\text{s} & \text{for } B=50\text{ kG} . \end{cases}$$

One can see that the effect of the magnetic field is weak. Nevertheless, it is surprising to obtain longer characteristic times than in the lanthanum glass, but it is not obvious that this difference is significant. As compared with the very strong effect of the magnetic ions on T_1, we can say that the effect of the magnetic ions on T_2, if any, is quite small.

We have found a similar behavior of the spontaneous phonon echo in samples with higher dysprosium content: the magnetic field does not change significantly the dephasing time T_2. However, the 3.38% and 6.7%

dysprosium-doped glasses have a characteristic time T_2 shorter than the lanthanum glass, unlike the 1.5% dysprosium-doped glass (we have found T_2 around 2 μs for these two glasses). The effect of the increase of the dysprosium content on the spontaneous-phonon echo is to reduce the amplitude. This is not surprising, since we know that the number of TS with long relaxation times (those which give rise to the spontaneous phonon echo) decreases for the benefit of the fast TS, as the dysprosium concentration increases [see Sec. V A].

B. Spontaneous phonon echo in gadolinium and europium glasses

These two glasses are especially interesting because a high magnetic field suppresses the magnetic TS almost completely. In the gadolinium-doped glass, no spontaneous echo could be detected in zero magnetic field, just like in the 10.1% dysprosium-doped glass. This is not surprising, since we have seen that the medium get back to the thermal equilibrium in less than 1 μs (Sec. VI B). So, the spontaneous echo is expected to disappear very quickly. When a high magnetic field (50 kG) is applied, the spontaneous echo reappears due to the suppression of the magnetic TS (Sec. VI B). The decay of the echo amplitude as a function of t_{12} is exponential as usual and T_2 is found to be of the same order of magnitude as in the lanthanum-doped glass ($T_2=2.5$ μsec at 13 mK).

In the europium-doped glass, the behavior is similar. In zero field, the relaxation is slower than in the gadolinium-doped glass, and the spontaneous echo can still be detected (this is due to the low concentration of magnetic ions as explained in Sec. V C). Here, we can get a better comparison between the fast relaxation regime and the slow one, which can be found in nonmagnetic glasses. We have reported in Fig. 15 the amplitude of the spontaneous echo as a function of $2t_{12}$ for the two values 0 and 50 kG of the magnetic field. We can see that the decay is exponential in the two cases. T_2 is almost the same for the two field values (1 μsec in zero field and 2 μsec at 50 kG). The main difference concerns only the amplitude of the spontaneous echo which increases by a factor of 3 as the magnetic field is set up. This implies that the number of TS having a T_2 long enough to generate a spontaneous echo is multiplied by a factor of 9.

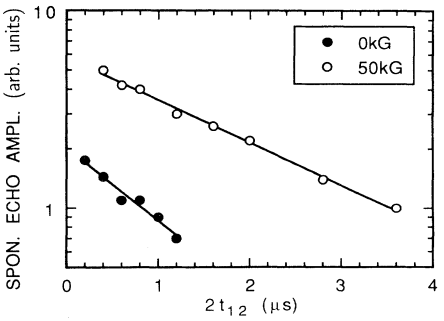

FIG. 15. Amplitude of the spontaneous phonon echo as a function of the delay between the first and the second pulse, in a 1.5% europium-doped glass, for two magnetic fields. The acoustic frequency is 900 MHz and the temperature 13 mK.

C. Free precession in a dysprosium-doped glass

The free-precession signal provides another means to evaluate T_2. To use this method, the pulse sent in the sample must be long enough to drive the TS into their steady states. Because of the very short relaxation times in our magnetic glasses, this regime can be reached with pulses of about 1 μs duration. Figure 16 shows the results obtained in the 3.38% dysprosium-doped glass, in a magnetic field of 50 kG, for different acoustic powers. All the curves have been normalized to 1 to enable comparison. We can see that the steady state is achieved after 1 μs in all the cases, and that the free-precession signal decay depends strongly on the input power. We have fitted the free-precession signal to a simple exponential law, and the agreement was very good in all the cases. A characteristic time τ is obtained from this fit. It must be pointed out that in the case of the highest power, the characteristic decay time is of the same order of magnitude as the damping time of the quartz transducer (20 nsec). However, below -25 dB, the decay becomes much slower than the damping of this one and characterizes the free-precession of the TS alone. Theory predicts the following law for the dependence of τ on the acoustic power[24]

$$\tau=\frac{T_2}{1+\sqrt{1+I/I_c}}\ , \tag{26}$$

where I_c is the critical acoustic power. It is difficult to measure the acoustic power sent in the sample. Nevertheless, it is possible to obtain precisely the quantity I/I_c as a function of the electric power supplied to the quartz transducer by studying the power-dependent attenuation.[1,2] Thus, we have obtained $I/I_c=10$ for the curve labeled -35 dB in Fig. 16. Knowing I/I_c and τ, the value of T_2 can be deduced from Eq. (26). This leads to $T_2=0.5$ μs. This is much shorter than the value deduced from the spontaneous-echo experiment (2 μsec). Presently, we have no explanation for this discrepancy.

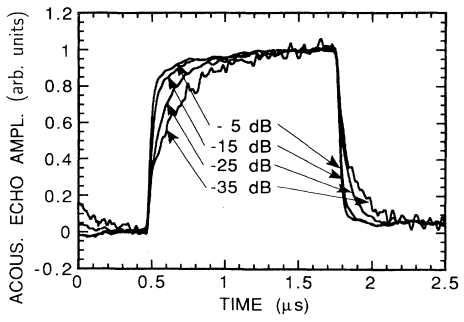

FIG. 16. Free-precession signal in a 3.38% dysprosium-doped glass, in a magnetic field of 50 kG, for different acoustic powers. The acoustic frequency is 350 MHz and the temperature 19 mK. All the echo amplitudes have been normalized to 1.

VIII. CONCLUSION

We have investigated the properties of glasses doped with Kramers rare-earth ions (Gd^{3+}, Dy^{3+}, Eu^{2+}). We have found many features attributable to these magnetic ions. Our results can be divided into two groups: firstly, we have obtained information about the behavior of the magnetic ions. Secondly, we have found properties of the elastic TS due to the presence of these ions.

The explanation of our experimental results implies the existence of another type of TS (which add to the usual elastic ones). We have identified them with the ions, whose the magnetic moment is confined on an anisotropy axis. The behavior of these magnetic TS (particularly the disappearance of these ones in the gadolinium-doped glass as a high magnetic field is applied) and their density of states are well explained by the theory. Moreover, our experiments have revealed that these magnetic TS have very short relaxation times at low temperatures. This behavior is not explained by one-phonon processes (prevailing at low temperature), which give relaxation times much longer by several orders of magnitude.[10]

Concerning the elastic TS, we have found that the introduction of Kramers ions has a very strong effect on their relaxation: The lower limit of the T_1 distribution becomes much shorter (at least by two order of magnitude in the less concentrated samples). We have found a relaxation process, much more efficient than the usual one-phonon process at low temperature. Moreover, this effect cannot be reduced to a T_1 shortening of all the TS, and there remains TS which are almost not disturbed by the magnetic ions. That means the mechanism of this relaxation process is to be found in some local interactions. It must be pointed out that the intrinsic characteristics of the TS, such as the density of states P or the coupling parameter γ, are not disturbed by the magnetic ions. Concerning the phase memory time T_2, the situation changes also with the introduction of the magnetic ions. This is expected since the spectral diffusion involves the TS-lattice relaxation of the surrounding TS.[16]

ACKNOWLEDGMENTS

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