Dephasing-Rephasing Balancing in Photon Echoes by Excitation Induced Frequency Shifts

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The excitation dephasing in solids resulting from the interaction with neighboring species' excitations is investigated. The frequency shifts due to these interactions are identified by the observation of partial dephasing-rephasing balancing in bichromatic photon-echo experiments applied to rare-earth ion doped crystals. The experimental observations are in good agreement with the predictions obtained from a model which accounts for the disorder in the crystal and for the stochastic nature of the excitations.

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Photon-echo techniques are well established in the studies of various coherence phenomena in ordered and disordered systems. The optically induced coherence is extremely sensitive to small fluctuations in the medium and can thus be applied to investigate weak effects. Because of their frequency selectivity rare-earth ion doped inorganic crystals have been found to be very appropriate for these investigations [1–11]. Very small perturbations in the environments of the excited species lead to changes in the transition frequencies which in turn cause a dephasing strong enough for detection. These perturbations may arise from stationary thermally activated processes, such as phonons or spin flips, or from nonthermal perturbations originating from the presence of the excitations involved in the echo forming process. This excitation induced dephasing can result from excitation induced frequency shifts (EFS). The local electrostatic and magnetic fields at a probe species are modified by excitations of nearby species, such that spectral diffusion results which give rise to a dephasing [2–6,9,10]. Dephasing due to EFS was first considered by Taylor and Hessler [2] who were motivated in their analysis by analogous observations in NMR [11]. Recently, Huang *et al.* reported on two-pulse photon-echo experiments in which the intensities of the pulses relative to each other were varied or a third perturbing "scrambler" pulse was applied [5]. They concluded that EFS definitely contribute to the dephasing process. Related to EFS are the frequency shifts induced by an external electrical field; as a function of the field strength the Stark shifts lead to a modulation of the echo intensities [12].

The EFS are thought to result from the diagonal interactions between impurities; these contrast with the off-diagonal, resonance interaction [13]. If the frequencies of the echo forming and of the scrambler excitations are identical or close to each other, the off-diagonal interactions may contribute to the excitation induced dephasing. This has to be considered particularly in "pure" two-pulse photon-echo experiments. Furthermore, by the nonradiative decay of the excitations large amounts of electronic energy are dissipated into lattice vibrations; these vibrations can also cause a phase randomization in the coherently prepared system [7,8]. Since all three effects depend on the excitation density, it is difficult to discriminate between the different contributions.

To corroborate previous results on EFS [4,5,9] and to gain detailed insight into the EFS mechanism, we have performed bichromatic measurements of two-pulse photon echoes in multiple rare-earth ion doped crystals. With two lasers two different ion species are excited. With the first laser the photon echo of the probe ions (A ion) is triggered; with the pulse of the second laser another ion species (B ion) is excited. This pump-probe scheme allows for an independent control of the two-pulse photon echoes and of the dephasing due to EFS [9]. By choosing well separated A- and B-ion transition frequencies the dephasing by resonance interaction can be avoided. From a stochastic point of view the B-ion excitations survive for times t_f dictated by the lifetime of the excited state. Because of the random decay times t_f the EFS fluctuate. The fluctuations are different in the dephasing and rephasing periods of the echo process; this imbalance causes an attenuation of the echo intensity which has been termed *echo demolition* [10]. By choosing excited states of the B ions with appropriate lifetimes a further experimental parameter is at our disposal.

The echo attenuation depends on the time delay between the scrambler and the echo-pulse sequence; three situations arise. (a) If the scrambler pulse is applied at times t_s before the first echo pulse, the EFS are larger in the dephasing than in the rephasing period. (b) If t_s is located in the time range of the rephasing period, only the rephasing process is perturbed; in both cases an echo attenuation results. (c) If, however, the time t_s is in the range of the dephasing period between the first and the second echo pulse, the phase perturbations in the dephasing and rephasing periods can be balanced; thus the echo intensity is partially regained. This is more obvious from

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Fig. 1 where the three situations (a) to (c) are schematically illustrated.

The dephasing by EFS contrasts with the dephasing due to nonequilibrium phonons generated by nonradiative relaxation of electronic energy. The thermalization of these phonons is fast compared to the electronic excitation lifetime, and their density is thus governed by the density of the electronic excitation. Despite this fact, a dephasing-rephasing balancing by nonequilibrium phonons cannot take place. In a stochastic picture the scattering processes of nonequilibrium phonons at species involved in the echo process induce phase jumps in the electronic excitation. Because the scattering processes are stochastic and uncorrelated events also take place, the phase jumps are uncorrelated. A balancing of the accumulated phase jumps in the dephasing and rephasing periods can thus be ruled out. The dephasing-rephasing balancing results primarily from reversible frequency shifts and, if observed, is a strong indication for the dephasing by EFS. The experimental technique based on two species excitations provides fortuitous conditions for discriminating between the competing effects.

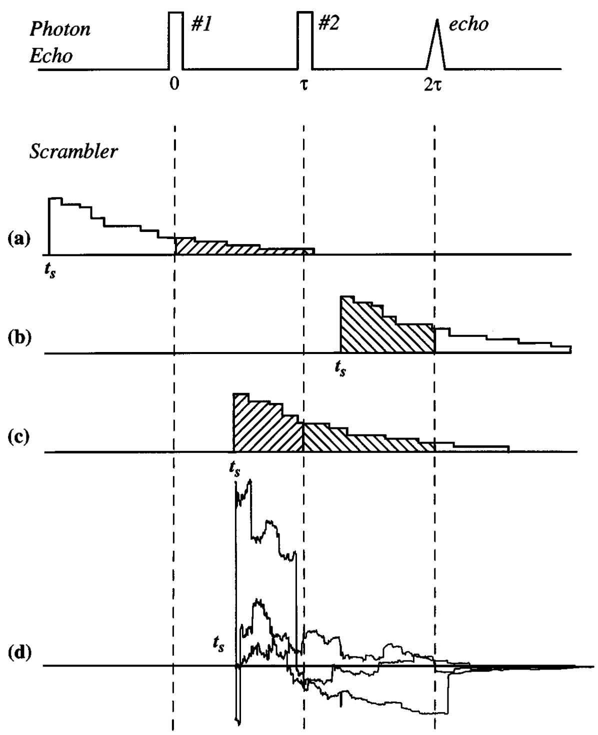

FIG. 1. EFS trajectories and the dephasing-rephasing balancing. (a)–(c) demonstrate schematically the three different cases discussed in the text. The lines, following staircases, denote $\omega_j(t)$ and depict the temporal relaxation of the EFS. The shaded areas indicate the contributions to the phase shift; the areas of the rephasing period contribute with a negative sign. A dephasing-rephasing balancing can occur in case (c). (d) EFS trajectories obtained from computer simulations for dipolar interactions with $p = 10^{-2}$ and for a cubic lattice spherically restricted to 10^5 sites.

The purpose of this Letter is to investigate the effect of dephasing-rephasing balancing and to give theoretical and experimental evidence for its reality. We consider a stochastic approach for the description of the perturbing B-ion excitations [9] and make use of the sudden-jump model [14]. For the time-dependent electronic transition frequency $\omega_j(t)$ of the jth A ion we write

$$\omega_j(t) = \omega_{j0} + \sum_k \epsilon(\mathbf{r}_{jk})\xi_k u_k(t)\,, \tag{1}$$

where $\epsilon(\mathbf{r}_{jk})$ is the frequency shift of the A-ion transition induced by the excitation of a B ion at a displacement $\mathbf{r}_{jk}$. The $\xi_k u_k(t)$ term is introduced to account explicitly for the randomness of the spatial configuration and for the stochastic nature of the B-ion excitations. ξ_k is an indicator variable indicating whether the kth site is occupied by an excited B ion at time $t = t_s$. Thus ξ takes the value 1 with probability p and the value 0 with probability $1 - p$; i.e., the probability of ξ is $P_\xi = \delta_{0\xi}(1 - p) + \delta_{1\xi}p$, where p depends on the probability of a lattice site to be occupied by a B ion and on the excitation probability. The sum in Eq. (1) runs over all lattice sites of possible B-ion positions. Finally, $u(t)$ indicates the stochastic aspect of the model with the excitation initiated at t_s and surviving until time t_f, so that $u(t; t_s, t_f)$ is 1 for times $t_s < t < t_f$ and zero otherwise. An exponential decay is considered for the B-ion excitations so that t_f is distributed according to the probability density $P_{t_f} = \gamma e^{-\gamma(t_f - t_s)}$ with a uniform decay rate γ for all B ions. Basic in this description is the independence of the B ions so that P_ξ and P_{t_f} apply independently to all possible lattice sites. Figure 1(d) shows typical realizations of EFS trajectories. They are characterized by sudden jumps on many scales; this behavior is reminiscent of Lévy flights [15], or, more specifically, of Lorentzian diffusion [11]. Comparing the trajectories in Fig. 1 we notice that the schematic trajectories (a)–(c) are caricatures, yet the effect of dephasing-rephasing balancing persists as we show below.

Equation (1) together with the probabilities P_ξ and P_{t_f} provide a sharply outlined model which allows us to calculate the dephasing due to EFS by averaging over spatial and temporal configurations. The echo intensity $I(t_s)$, normalized to the perfect rephasing case, is given as [11]

$$I(t_s) = M^* M = \left| \sum_j \exp[i\phi_j(t_s)] \right|^2, \tag{2}$$

where M stands for the corresponding moment. $\phi_j(t_s)$ is the phase shift of the jth A ion caused by the fluctuations in the frequency $\omega_j(t)$; one has

$$\phi_j(t_s) = \int_0^\tau \omega_j(t)\,dt - \int_\tau^{2\tau} \omega_j(t)\,dt = \sum_k \epsilon(\mathbf{r}_{jk})\xi_k\theta_k(t_s)\,, \tag{3}$$

with $\theta_k(t_s) = \int_0^\tau u_k(t)\,dt - \int_\tau^{2\tau} u_k(t)\,dt$, which is a random variable depending on the stochastic decay time t_f which entered through $u(t)$. It is assumed that the two echo pulses are applied at times $t = 0$ and $t = \tau$, so that the echo is expected to take place at time $t = 2\tau$. For small A-ion concentrations we find after averaging over the spatial and temporal realizations of the excitations

$$M(t_s) = N \prod_k{}' \{1 - p[1 - S_k(t_s)]\}, \qquad (4)$$

where N is the number of A ions. $S_k(t_s)$ is a short form, $S_k(t_s) = \langle \exp[i\epsilon(\mathbf{r}_k)\theta(t_s)]\rangle_{t_f}$, that was studied previously [9]. Here $\mathbf{r}_k$ denotes the relative displacement from the A ion located at the origin. Equations (2) and (4) together with the explicit form of $S_k(t_s)$ represent an exact solution of the problem within the model assumptions.

Aiming at simpler, though approximate, forms we assume p to be small which corresponds to a weak scrambler excitation or to a diluted B-ion situation. Correspondingly, Eq. (4) can be approximated by

$$M(t_s) \simeq N \exp\left\{-p \sum_k{}' [1 - S_k(t_s)]\right\}. \qquad (5)$$

We also assume dipole-dipole interactions for the induced frequency shifts [4,11]: $\epsilon(\mathbf{r}) = \epsilon_0 (r_0/r)^3 \kappa(\Omega)$, where $\kappa(\Omega)$ gives the dependence of the interaction on the angular configuration of the dipoles relative to the displacement vector and Ω denotes the corresponding set of angles. The constant ϵ_0 depends on the differences between the dipoles of the excited and the ground states of the A and B ions. Replacing the sum in Eq. (5) by an integral we arrive at

$$\ln[I(t_s)/I_0] \simeq -2Cp\langle|\theta(t_s)|\rangle_{t_f}, \qquad (6)$$

where for the constant we have $C = (2/3)\pi^2 \epsilon_0 r_0^3 \rho_0 \langle|\kappa|\rangle_\Omega$. ρ_0 denotes the site density, and the dimensionless quantity $\langle|\kappa|\rangle_\Omega$ is of the order 1. For the t_s-dependent term in Eq. (6) we obtain

$$\langle|\theta(t_s)|\rangle_{t_f} = \begin{cases} \gamma^{-1}(1 - e^{-\tau\gamma})^2 e^{t_s\gamma}, & t_s \le 0, \\ \gamma^{-1}(2e^{-(2\tau - t_s)\gamma} - e^{-2\tau\gamma} - 2e^{-\tau\gamma} + e^{-t_s\gamma})e^{t_s\gamma}, & 0 < t_s \le \tau, \\ \gamma^{-1}(1 - e^{-(2\tau - t_s)\gamma}), & \tau < t_s \le 2\tau. \end{cases} \qquad (7)$$

The dependence of the echo intensity on t_s through $\langle|\theta(t_s)|\rangle$ exhibits a specific behavior, as shown in Fig. 2, which reflects the underlying process. For the time regimes $t_s < 0$ and $\tau < t_s < 2\tau$ the logarithm of the intensity follows a behavior dictated by one exponential. In the intermediate regime $0 < t_s < \tau$, the behavior is more complicated and shows a local maximum

$$t_{s,\max} = \gamma^{-1} \ln[(1 + 2e^{\tau\gamma})/4], \qquad \tau\gamma > \ln(3/2), \quad (8)$$

independently of the excitation density p. We point out that the occurrence of the echo recovery characterized by the local maximum gives striking evidence for the dephasing-rephasing balancing by reversible frequency shifts.

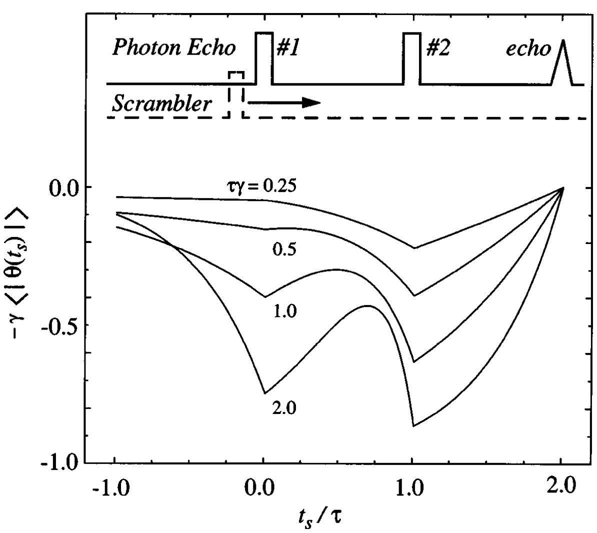

FIG. 2. Theoretical echo intensities as a function of the time delay t_s of the scrambler pulse. For clarity the function $-\gamma\langle|\theta(t_s)|\rangle$ of Eq. (7) is plotted for various $\tau\gamma$ values as indicated.

In our experimental studies we used an Y_2SiO_5 crystal doped with Pr^{3+}, Nd^{3+}, and Eu^{3+} ions at concentrations of 0.01%, 0.01%, and 0.1%, respectively. A setup was applied similar to the one used in Refs. [9,10]. In order to induce photon echoes, pulses of 1.5 μs were gated from a beam of a single mode Coherent Radiation CR-699 dye laser by a tandem of acousto-optic modulators. The laser was tuned to the Eu^{3+} (site 1) $^7F_0$-$^5D_0$ transition at 579.879 nm with a lifetime of $T_1^{\mathrm{Eu}} = 1860$ μs [6], and was frequency scanned repetitively over 150 MHz in 2 s to reduce the effects of persistent spectral hole burning. The temperature of the sample was stabilized at $T =$ 6.5 K, and the signals were recorded by a photomultiplier and fed into a boxcar averager. Counterpropagating short pulses (4 ns FWHM) from a Spectra-Physics/Quanta Ray pulsed dye laser system (DCR 3 Nd:YAG pump laser and PDL 2 dye laser) were used to create an environment of excited state neighboring ions. This laser was tuned to the comparatively strong transition from the $^4I_{9/2}$ state to the lowest energy Stark level $^4G_{5/2}$ of Nd^{3+} (site 1) at 594.5 nm with a lifetime of $\gamma^{-1} = T_1^{\mathrm{Nd}} = 245$ μs [16]. Experiments with other Nd^{3+} or Pr^{3+} transitions led to equivalent results.

The experimental results are presented in Fig. 3; they demonstrate for the first time the dephasing-rephasing balancing effect. The data $I(t_s)/I_0$ are given for scrambler

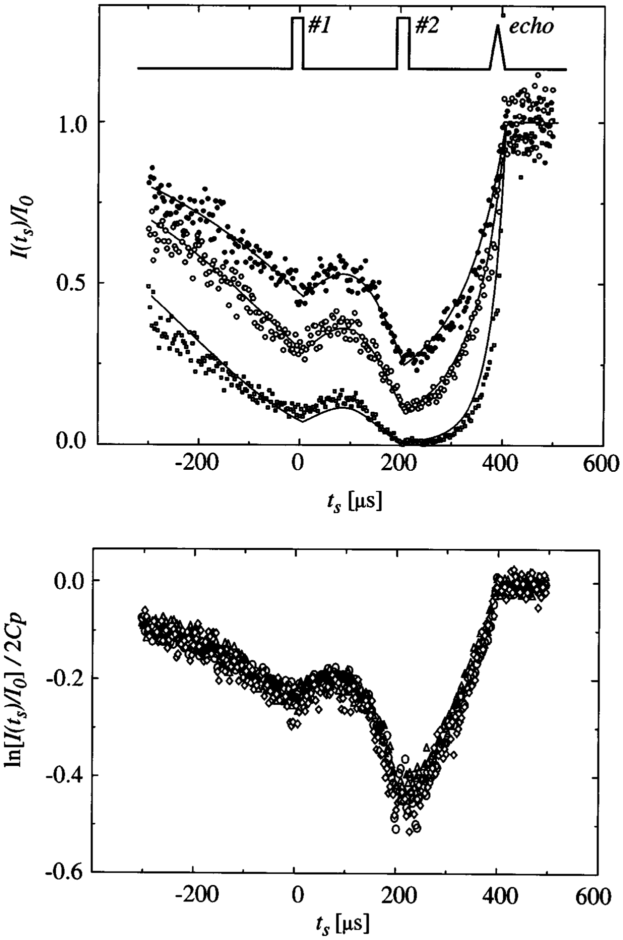

FIG. 3. Experimental echo intensities. Upper figure: The symbols give the measured data $I(t_s)/I_0$, from top to bottom for scrambler pulses of 1, 2, and 4 kW peak intensities. The full lines are the predictions of Eq. (6). Lower figure: Same data, but in the rescaled representation: $\ln[I(t_s)/I_0]/2Cp$ vs t_s.

pulses of three intensities by different symbols with the photon-echo delay kept fixed at $\tau = 200$ μs. The I_0 intensities were measured with the scrambler laser shut off. The full lines represent the predictions according to Eqs. (7) and (8) with the parameter $2Cp$ fit to the experimental data: $2Cp = 10.2$, 16.3, and 34.7 kHz for 1, 2, and 4 kW peak intensities, respectively. The ratios 10.2:16.3:34.7 of the fitted parameters are in a reasonable agreement with the corresponding ratios 1:2:4 of the scrambler pulse intensities; the deviations are attributed to experimental shortcomings. We stress that only because of the multiple-ion doping of the crystal, a pronounced echo recovery could be achieved. The long excitation lifetimes of the Eu^{3+} allows for long interpulse times τ relative to the short lifetimes of the Nd^{3+} or Pr^{3+} excitations. $\gamma\tau$ is thus clearly larger than the critical value of $\ln(2/3)$ for the detection of the local maximum while τ/T_1^A is still well below unity so that a strong echo intensity results. The rescaled presentation of the data in Fig. 3 demonstrates the unique behavior of the echo attenuation due to EFS.

The model and the derivations have been extended to describe the broadening on the same footing as the echo attenuation. From this analysis a Lorentzian line shape results for dipolar interactions with $2Cp$ being the full width at half height at the time of the B-ion excitation. We stress that from Stark-effect measurements the magnitude and the geometry of the A- and B-ion dipoles relevant for EFS can be determined so that the parameter $2Cp$ is at one's disposal from independent measurements. We have also investigated further aspects of physical importance [16]. From the convergence of $M(t_s)$ in Eq. (5) to the asymptotic value with increasing lattice size we concluded that the major amount of the attenuation results from a few close lying B-ion excitations. Furthermore, interactions different from dipole-dipole and the effect of long-range excitation density inhomogeneities present in nonideal experimental setups have been considered. We have found that the dephasing-rephasing balancing and the corresponding characteristic behavior of the echo attenuation is very robust against these modifications of the model and of the experimental conditions.

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