Frequency-dependent optical dephasing and the nature of inhomogeneous broadening in crystals

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We present a theory of frequency-dependent optical dephasing as measured by narrow-band photon echo experiments. We consider a substitutionally disordered crystal with inhomogeneous broadening (diagonal disorder) and electronic interactions between occupied sites. We include the possibility of site-energy correlations. We find that the frequency dependence of the dephasing rate $1/T_2$ is very sensitive to the ratio ξ/a, where ξ is the correlation length and a is the lattice spacing. When $\xi/a \to \infty$, and there are macroscopic domains of resonant ions, $1/T_2$ becomes frequency independent. In the other limit when $\xi/a \to 0$, and the site energies are uncorrelated (microscopic broadening), $1/T_2$ is proportional to the inhomogeneous line shape. We have compared our results to experiments by Macfarlane and Shelby on Y_2O_3:Eu^{3+} (2 at. %) and EuP_5O_{14}. We find reasonable agreement with experiment when ξ is less than a few lattice sites. Thus, for these systems the model of microscopic broadening is more appropriate than that of macroscopic broadening.

I. INTRODUCTION

Optical transitions of ions or molecules in crystals are inhomogeneously broadened. If the concentration of the optically active ions or molecules is sufficiently dilute so that they are noninteracting, then the inhomogeneous broadening is due to imperfections in the host crystal. Homogeneous broadening, which can be measured by line narrowing[1] or coherent transient[2-4] techniques such as the photon echo, results from coupling of the optically active ions or molecules to nuclear spins[5] or to phonons.[6] If the optically active ions or molecules are not dilute, then phonon-assisted energy transfer[7] or quasiresonant (purely electronic) interactions among the excited impurities can also lead to homogeneous broadening.

We,[8] and others,[9,10] have formulated a theory of photon-echo decay due to quasiresonant interactions. We find that the dephasing rate is very sensitive to the *nature* of the inhomogeneous broadening. We discussed[8] the two limiting cases of "macroscopic" and "microscopic" inhomogeneous broadening. In the limit of macroscopic broadening the system consists of large domains of resonant ions (or molecules); dephasing is produced by resonant interactions within domains. In the opposite limit of microscopic broadening, one assumes that the site energies are completely uncorrelated. In this case dephasing is due to quasiresonant interactions with nearby (in space and frequency) ions. More generally, if ω_i and ω_j are the excitation frequencies at sites i and j, and $\langle \omega \rangle$ is the average frequency, we might suppose that

$$\langle (\omega_i - \langle \omega \rangle)(\omega_j - \langle \omega \rangle) \rangle = \langle (\omega - \langle \omega \rangle)^2 \rangle e^{-r_{ij}/\xi}, \quad (1)$$

where r_{ij} is the distance between ions and ξ is a correlation length. In the limit $\xi \to 0$, this becomes

$$\langle (\omega_i - \langle \omega \rangle)(\omega_j - \langle \omega \rangle) \rangle = \langle (\omega - \langle \omega \rangle)^2 \rangle \delta_{ij}, \quad (2)$$

corresponding to the case of random uncorrelated site energies or microscopic broadening. In the other limit of macroscopic broadening when $\xi \to \infty$, there is complete correlation and all sites are resonant.

Information on the degree of correlation of site energies in inhomogeneously broadened crystals is essential for an understanding of energy-transfer processes. For example, the usual model of the Anderson transition[11,12] from localized to extended electronic eigenstates assumes random variation in the site energies. If there is some correlation of site energies, one would expect the Anderson transition for a diagonally disordered system to occur at lower intersite coupling strength, or for a substitutionally disordered system to occur at a lower critical concentration. Experimentally the degree of site-energy correlation is unclear, although there seems to be some evidence[13] that in ruby the broadening is not microscopic. Because the features of the photon echo decay are so sensitive to the nature of inhomogeneous broadening, one might hope to learn something about the correlation length from photon echo experiments.

Recently Shelby and Macfarlane have performed narrow-band photon echo experiments at 2 K on the $^7F_0 \leftrightarrow ^5D_0$ transition of Eu^{3+} in the stoichiometric material EuP_5O_{14} (Ref. 14) and 2 at. % Y_2O_3:Eu^{3+}.[15] In both cases, they found that the dephasing rate, $1/T_2$, depended on laser frequency and was greater near the center of the inhomogeneous line. $1/T_2$ was temperature independent (at low T), apparently ruling out the interaction with thermal phonons. Thus they argued that the effect must *not* be due to varying coupling to phonons through the inhomogeneous line,[16] or to phonon-assisted Eu^{3+}-Eu^{3+} energy transfer.[7] One must also consider spontaneous emission of phonons. This would produce a large $1/T_2$ on the high-energy side of the line since there are many acceptor ions with lower energy, but a small $1/T_2$ on the low-energy side of the line since in this case there are few acceptors with lower energy. Inasmuch as this asymmetry

was not observed, we can discount this effect. In addition, Shelby and Macfarlane found that $1/T_2$ was magnetic field independent, and therefore ruled out nuclear spin interactions.[5] They attributed the frequency-dependent dephasing to quasiresonant Eu^{3+}-Eu^{3+} interactions.

The dependence of the dephasing rate on laser frequency is significant in that it would seem to discount the possibility of the existence of large domains of resonant ions. In the macroscopic-broadening limit dephasing results from interactions within a domain and is independent of the domain energy. Thus while the total echo *intensity* would be frequency dependent, since there are more domains near the center of the line and fewer in the wings, the dephasing *rate* would be frequency independent.

In this paper we present a theory of frequency-dependent optical dephasing due to quasiresonant interactions. The theory is closely related to the theory of the concentration dependence developed previously by us.[8] We find that the magnitude and frequency dependence of $1/T_2$ depend strongly on the correlation length ξ, introduced above. When $\xi \to \infty$ (large resonant domains) we find that $1/T_2$ is frequency independent. When $\xi \to 0$ (random broadening) we find that $1/T_2(\omega) \propto P(\omega)$, where $P(\omega)$ is the probability distribution for the site energies, which in the limit of weak ion-ion interactions is simply the (inhomogeneous) absorption line shape. For intermediate ξ, our results show a weaker frequency dependence. The theory is consistent with both Eu^{3+} experiments of Shelby and Macfarlane[14,15] when the correlation length ξ is on the order of a few lattice spacings or smaller. Thus for these experimental systems the model of microscopic broadening is more appropriate than that of macroscopic broadening.

II. FORMULATION OF THE MODEL

The model we adopt is that considered previously by us:[8] a host crystal lattice randomly substituted by guests (impurities) with a fractional concentration f. We consider transitions between two electronic states of the guest ions, and assume that these states are isolated from other electronic states, so that each impurity can be treated as a two-level system. The transition frequencies of the guests are inhomogeneously broadened as discussed in the Introduction. We assume that the transition frequencies of the host ions are sufficiently different from those of the impurities that interactions between guests and hosts can be neglected. The guest ions are coupled by a distance-dependent interaction. Since the impurities are randomly distributed spatially, the coupling strengths J_{ij} are random variables. We do not consider phonons, since here we are interested only in purely electronic interactions among the guests.

The model Hamiltonian is then

$$H = \sum_i \hbar \omega_i a_i^\dagger a_i + \sum_{ij} \hbar J_{ij} a_i^\dagger a_j - \sum_i (a_i^\dagger + a_i) \mu E(t) \cos(\Omega t) .$$

$$(3)$$

The summations are over all lattice sites occupied by

guests. ω_i is the electronic transition frequency at impurity site i. The transition frequencies are characterized by the normalized inhomogeneous distribution $P(\omega)$. $a_i^\dagger (a_i)$ creates (annihilates) an electronic excitation at site i. J_{ij} is the coupling matrix element between sites i and j. For the experimental systems considered in this paper the appropriate intersite interaction is the dipole-dipole interaction.[17] The last term in Eq. (3) describes the interaction with an applied laser pulse of frequency Ω, and μ is the transition dipole. We have neglected a spatially dependent phase factor which only determines the directional characteristics of the echo. We assume square pulses, so that $E(t) = E$ during a pulse, 0 otherwise.

This Hamiltonian describes one realization of the system. Results for observables must be averaged over the energetic and, if $f \neq 1$, the substitutional disorder. To facilitate the average over the substitutional disorder we write (3) in the equivalent form

$$H = \sum_i' \xi_i \hbar \omega_i a_i^\dagger a_i + \sum_{ij}' \xi_i \xi_j \hbar J_{ij} a_i^\dagger a_j$$
$$- \mu \sum_i' \xi_i (a_i^\dagger + a_i) E(t) \cos(\Omega t) .$$

$$(4)$$

Here $\sum'$ denotes a sum over *all* lattice sites. The ξ_i's are occupational variables: $\xi_i = 1$ if site i is occupied by a guest, 0 if it is occupied by a host. The ξ_i's are characterized by the probability distribution

$$P(\xi) = f\delta(1-\xi) + (1-f)\delta(\xi) .$$

$$(5)$$

In a photon echo experiment one applies a laser pulse of length τ_1, lets the system evolve freely for a time t_1, applies a pulse of length τ_2, and lets the system evolve freely for a time t_2. The echo appears at $t_2 \approx t_1$. The observable is the echo intensity, which is measured as a function of the time t_1 between the pulses. The echo intensity is given by[2-4]

$$I(2t_1) \propto |\langle p(2t_1) \rangle_{\omega,\xi}|^2 ,$$

$$(6)$$

where

$$p(t) = \mu \, \text{Tr} \left[\sum_i (a_i^\dagger + a_i) \rho(t) \right]$$

$$(7)$$

is the total polarization of the sample and $\rho(t)$ is the density operator. As indicated, $p(t)$ must be averaged over the inhomogeneous distribution and over the substitutional disorder.

The equation of motion for the density operator is the Liouville equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] .$$

$$(8)$$

Transferring to a rotating frame and making the rotating-wave approximation, we obtain[8]

$$\frac{\partial \tilde{\rho}}{\partial t} = \frac{-i}{\hbar}[H_\delta + H_1, \tilde{\rho}] + \frac{i\chi}{2} \left[\sum_i (a_i^\dagger + a_i), \tilde{\rho} \right] .$$

$$(9)$$

Here

$$\tilde{\rho}(t) = \exp(iH_0 t/\hbar) \rho \exp(-iH_0 t/\hbar) ,$$

$$(10)$$

$$H_0 = \hbar\Omega \sum_i a_i^\dagger a_i \ , \tag{11}$$

$$H_\delta = \sum_i \hbar(\omega_i - \Omega) a_i^\dagger a_i \ , \tag{12}$$

$$H_1 = \sum_{ij} \hbar J_{ij} a_i^\dagger a_j \ , \tag{13}$$

and $\chi = \mu E / \hbar$ is the Rabi frequency.

The model investigated here differs from that of Ref. 8 in that we now consider the case of narrow-band excitation. In Ref. 8 we assumed short, intense laser pulses, so that the entire inhomogeneous line was excited. In this paper we focus on the opposite limit of a very narrow excitation profile, in order to investigate the frequency dependence of $1/T_2$. In this case we solve Eq. (9) as follows. When the laser field is on, we can neglect H_1 compared to the driving term if $J \ll \chi$. Thus after a pulse of length τ,

$$\rho(t_0 + \tau) = U(\tau)\rho(t_0)U^\dagger(\tau) \ , \tag{14}$$

where

$$U(\tau) = \exp\left[i\left[\frac{\chi}{2} \sum_i (a_i^\dagger + a_i) - H_\delta/\hbar \right] \tau \right] \ . \tag{15}$$

Although exact expressions for the matrix elements of $U(\tau)$ can easily be found,[9] the resulting analysis is so much more complex that here we make a rather crude approximation, but one which should not qualitatively affect our results. The argument is as follows. For those molecules exactly on resonance, $\omega_i - \Omega = 0$, and only the driving term remains in Eq. (15). For those molecules near resonance, with $|\omega_i - \Omega| \leq \chi/2$, the off-resonance contribution should be retained. However the major effect of this term, which describes dephasing during the pulse, is the production of a delay in the echo,[4] which does not concern us here. Therefore if $|\omega_i - \Omega| \leq \chi/2$, we simply neglect the off-resonance term, and hence treat these near-resonant molecules as if they are in perfect resonance. For those molecules far off-resonance, with $|\omega_i - \Omega| \gg \chi$, the driving term can be neglected in Eq. (15). These molecules are not excited and thus cannot directly contribute to the echo. Moreover, it can be shown[18] that the contribution to the echo decay due to energy transfer from ions initially excited to those initially unexcited (spectral diffusion) is negligible compared to the contribution due to interactions among excited ions. Therefore we can completely ignore the unexcited ions. The second part of our approximation consists of treating all molecules with $|\omega_i - \Omega| > \chi/2$ as if they are far off-resonance, and hence can be ignored. Thus we approximate Eq. (15) by

$$U(\tau) = \exp\left[\frac{i\theta}{2} \sum_i {}^* (a_i^\dagger + a_i) \right] \ , \tag{16}$$

where $\theta = \chi\tau$ and the asterisk ($*$) restricts the sum to those impurity molecules with $|\omega_i - \Omega| \leq \chi/2$.

When the laser is off, the solution to Eq. (9) is

$$\tilde{\rho}(t + t_0) = V(t)\tilde{\rho}(t_0)V^\dagger(t) \ , \tag{17}$$

where

$$V(t) = \exp[-i(H_\delta^* + H_1^*)t/\hbar] \ , \tag{18}$$

$$H_\delta^* = \sum_i {}^* \hbar(\omega_i - \Omega)a_i^\dagger a_i \ , \tag{19}$$

and

$$H_1^* = \sum_{ij} {}^* \hbar J_{ij}(a_i^\dagger a_j) \ . \tag{20}$$

As discussed above, we only consider the ions sufficiently near resonance to be excited. Finally in Eq. (6), $p(t)$ may be replaced by

$$p(t) = \mu \, \mathrm{Tr}\left[\sum_i {}^* (a_i^\dagger + a_i)\rho(t) \right] \ . \tag{21}$$

III. INHOMOGENEOUS BROADENING AND FREQUENCY-DEPENDENT DEPHASING

Within the approximations outlined above, the calculation of the echo amplitude $\langle p(t) \rangle_{\omega,\zeta}$ follows closely that of Ref. 8, and thus we will not repeat the analysis. The only difference between the two calculations is that here we need to focus only on those ions with $|\omega_i - \Omega| < \chi/2$. This modification has interesting and important consequences which we describe below. As discussed in the Introduction, we want to consider the effect of different models of inhomogeneous broadening on the echo decay. We first consider the case of macroscopic broadening.

A. Macroscopic broadening

In the case of macroscopic broadening, the correlation length of Eq. (1) is infinite: all molecules have the same site energy. Actually, in order to produce the observed inhomogeneous broadening, one must postulate the existence of *near*-macroscopic domains. Within each domain the site energies are all equal, but there is a distribution of domain energies.

In a narrow-band photon echo experiment, one would excite only a subset of domains. The dephasing within each domain can be calculated exactly as in Ref. 8. There we found that for a $\pi/2$-π pulse sequence and $f \ll 1$, the photon echo decay was exponential, with a dephasing rate constant

$$\frac{1}{T_2} = \frac{8\pi^2}{9\sqrt{3}}fJ \ , \tag{22}$$

where $J = \mu^2/a^3\hbar$, and a is the lattice spacing. In the above, for simplicity we assumed dipole-dipole interactions on a simple cubic lattice, with all the transition dipoles in the $\hat{z}$ direction. We also noted[8] that this result was only valid for "intermediate" times. The important point is that $1/T_2$ is independent of laser frequency because dephasing within a domain does not depend upon the domain energy. Thus macroscopic broadening predicts a frequency-independent optical-dephasing decay rate. It might be noted that of course the overall echo intensity is frequency dependent. For example, at the wings of the inhomogeneous line, there are many fewer domains to excite, and thus the signal is smaller.

B. Microscopic broadening

In this case the correlation length of Eq. (1) is zero, and all site energies are uncorrelated. The echo decay from narrow-band excitation can be calculated in the manner of Ref. 8, Sec. IV. The sole modification is that the sums are over only those molecules with $|\omega_i - \Omega| < \chi/2$. An intermediate result from that calculation, modified by the

above, is

$$\langle \tilde{p}(2t_1) \rangle_{\omega,\xi} \propto \exp[-K_2(t_1)/2] , \tag{23}$$

where $\tilde{p}(t)$ is defined by

$$p(t) = \tilde{p}(t)e^{-i\Omega t} + \tilde{p}(t)^* e^{i\Omega t} , \tag{24}$$

and

$$K_2(t_1) = \left[\frac{2}{N_g^*}\right] \int_0^{t_1} d\tau_1 \int_0^{t_1} d\tau_2 \Big\langle 2\sum_{ij}^{*} (J_{ij})^2 e^{i\delta_{ij}(\tau_1-\tau_2)} + \sum_{ijk\neq}^{*} J_{ij}J_{jk} e^{i\delta_{ij}\tau_2}(e^{i\delta_{jk}\tau_1} - e^{-i\delta_{jk}\tau_1})\Big\rangle_{\omega,\xi} . \tag{25}$$

Here N_g^* is the number of guest sites at which $|\omega_i - \Omega| \leq \chi/2$, $\delta_{ij} = \omega_i - \omega_j$, and $\sum_{ijk\neq}^{*}$ denotes $\sum_{ijk}^{*}$ with $i\neq j\neq k$. As shown in Ref. 8, the echo intensity can be calculated directly from $\tilde{p}(2t_1)$ rather than $p(2t_1)$, and is in fact given by Eq. (6) with $p(2t_1)$ replaced by $\tilde{p}(2t_1)$. Defining

$$g(\tau) \equiv \int_{\Omega-\chi/2}^{\Omega+\chi/2} d\omega\, P(\omega)e^{i\omega\tau} \tag{26}$$

and recalling that in the limit of microscopic inhomogeneous broadening the ω_i's vary independently, one can perform the average over ω to obtain

$$K_2(t_1) = \left[\frac{2}{N_g^*}\right] \int_0^{t_1} d\tau_1 \int_0^{t_1} d\tau_2 \Big\langle 2\sum_{ij} (J_{ij})^2 g(\tau_1-\tau_2)g(\tau_1-\tau_2)^*$$
$$+ \sum_{ijk\neq} J_{ij}J_{jk}[g(\tau_1)^* g(\tau_2)g(\tau_1-\tau_2) - g(\tau_1)g(\tau_2)g(\tau_1+\tau_2)^*]\Big\rangle_\xi . \tag{27}$$

The summations now are over *all* impurity sites.

The function $g(\tau)$ decays on the timescale of χ^{-1}, which is just the inhomogeneous dephasing time for the subset of guests that is excited. We are interested in times t_1 of the order of the homogeneous dephasing time, which is long compared to the inhomogeneous dephasing time. We are therefore interested in the limit $t_1 \gg \chi^{-1}$. In this limit the first term is clearly linear in t_1, since the integrand depends only on the difference $\tau_1-\tau_2$, while the second term is a constant, independent of t_1. The second term can therefore be neglected compared to the first, so that

$$K_2(t_1) = \left[\frac{4}{N_g^*}\right] t_1 \int_{-\infty}^{\infty} d\tau |g(\tau)|^2 \Big\langle \sum_{ij} (J_{ij})^2 \Big\rangle_\xi . \tag{28}$$

It is easily shown that (assuming all possible impurity sites are equivalent)

$$\Big\langle \sum_{ij} (J_{ij})^2 \Big\rangle_\xi = N_g f \sum_j{}' (J_{ij})^2 , \tag{29}$$

where N_g is the number of guest sites. Then substituting Eqs. (26) and (29) into Eq. (28) yields

$$K_2(t_1) = 8\pi f \left[\frac{N_g}{N_g^*}\right] t_1 \sum_j{}' (J_{ij})^2 \int_{\Omega-\chi/2}^{\Omega+\chi/2} d\omega[P(\omega)]^2 . \tag{30}$$

Since the excitation profile is very narrow, χ is small compared to the range over which $P(\omega)$ varies, and we may approximate the integral as

$$K_2(t_1) = 8\pi f t_1 \left[\frac{N_g}{N_g^*}\right] \sum_j{}' (J_{ij})^2 \chi[P(\Omega)]^2 . \tag{31}$$

Since $P(\omega)$ is normalized,

$$\frac{N_g^*}{N_g} = \int_{\Omega-\chi/2}^{\Omega+\chi/2} d\omega\, P(\omega) \approx \chi P(\Omega) . \tag{32}$$

Equation (23) together with Eqs. (31) and (32) shows that the echo amplitude decays exponentially,

$$\langle \tilde{p}(2t_1) \rangle_{\omega,\xi} \propto \exp\left[-2\pi f P(\Omega)\sum_j{}'(J_{ij})^2 2t_1\right] , \tag{33a}$$

with a dephasing rate constant

$$\frac{1}{T_2} = 2\pi f P(\Omega)\sum_j{}' (J_{ij})^2 . \tag{33b}$$

For definiteness we evaluate this for a simple cubic lattice with parallel dipoles pointing along $\hat{z}$ to obtain

$$\frac{1}{T_2} = 2\pi(13.3)fJ^2 P(\Omega) . \tag{34}$$

Thus, we find that the dephasing rate is proportional to the height of the inhomogeneous distribution at the exci-

tation frequency. The enhanced dephasing near the center of the line is due to the "effective concentration" argument of Shelby and Macfarlane;[14] that is, an ion at the center of the line has more nearly resonant neighbors than do ions in the wings.

As pointed out in Ref. 8, this result for $\bar{p}(t)$ is based on a truncation of the cumulant expansion, and is therefore only rigorously valid in the limit $J/\sigma \ll 1$, where σ is the width of the inhomogeneous distribution. For the systems considered in this paper, this condition is satisfied. While this result is valid for times long compared to the inhomogeneous dephasing time, it is not valid in the long-time asymptotic limit, as terms in the cumulant expansion which have been neglected become significant at very long times. Thus this result should be thought of as an "intermediate" time result.

C. Partial correlation of site energies

Finally we examine the case of partial site-energy correlation, when ξ is neither zero nor infinite. In this case we

again begin with Eq. (25). As long as the site energies are not completely correlated ($\xi \neq \infty$), then at large t_1 the second term will be constant, while the first will be linear in t_1. Retaining only the first term gives

$$K_2(t_1) = \frac{4}{N_g^*} t_1 \int_{-\infty}^{\infty} d\tau \left\langle \sum_{ij}{}^* (J_{ij})^2 e^{i(\omega_i - \omega_j)\tau} \right\rangle_{\omega,\xi} . \quad (35)$$

Performing the time integral and the ξ average gives

$$K_2(t_1) = 8\pi t_1 f \frac{N_g}{N_g^*} \sum_j{}' (J_{ij})^2 \langle \Theta(\chi/2 - |\omega_i - \Omega|)$$

$$\times \Theta(\chi/2 - |\omega_j - \Omega|) \delta(\omega_i - \omega_j) \rangle_\omega . \quad (36a)$$

This can be written in terms of the *joint* probability function $P(\omega_i, \omega_j; r_{ij})$, which, as indicated, depends on the distance between sites i and j:

$$K_2(t_1) = 8\pi t_1 f \frac{N_g}{N_g^*} \sum_j{}' (J_{ij})^2 \int_{\Omega - \chi/2}^{\Omega + \chi/2} d\omega_i \int_{\Omega - \chi/2}^{\Omega + \chi/2} d\omega_j P(\omega_i, \omega_j; r_{ij}) \delta(\omega_i - \omega_j) . \quad (36b)$$

Using Eqs. (32) and (23) and the fact that $P(\omega,\omega;r)$ is slowly varying we obtain

$$\frac{1}{T_2} = 2\pi f \sum_j{}' (J_{ij})^2 P(\Omega,\Omega;r_{ij})/P(\Omega) . \quad (37a)$$

For interaction matrix elements J_{ij} that fall off as $1/r^2$ or faster, the first shell makes a predominant contribution to the lattice sum, and therefore we can replace $P(\Omega,\Omega;r_{ij})$ by $P(\Omega,\Omega;a)$ to obtain

$$\frac{1}{T_2} = 2\pi f [P(\Omega,\Omega;a)/P(\Omega)] \sum_j{}' (J_{ij})^2 . \quad (37b)$$

Performing the sum for dipole-dipole interactions on a cubic lattice we then obtain

$$\frac{1}{T_2} = 2\pi (13.3) f J^2 P(\Omega,\Omega;a)/P(\Omega) . \quad (38)$$

If the site energies are completely uncorrelated ($\xi = 0$), then $P(\Omega,\Omega;a) = P(\Omega)^2$ and Eq. (34) is recovered. If $\xi \neq 0$, then it is clear that $P(\Omega,\Omega;a) > P(\Omega)^2$, and $1/T_2$ will be larger.

To obtain a quantitative description in the case of partial correlation, we assume that the inhomogeneous broadening is Gaussian, so that[19]

$$P(\omega) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left[-\frac{\Delta\omega^2}{2\sigma^2} \right] , \quad (39)$$

where $\Delta\omega = \omega - \langle\omega\rangle$, $\sigma^2 = \langle\Delta\omega^2\rangle$, and

$$P(\omega,\omega';r) = \frac{1}{2\pi\sigma^2(1 - e^{-2r/\xi})^{1/2}} \exp\left[-\frac{\Delta\omega^2 + \Delta\omega'^2 - 2\Delta\omega \Delta\omega' e^{-r/\xi}}{2\sigma^2(1 - e^{-2r/\xi})} \right] . \quad (40)$$

We have assumed that the site-energy correlation function is given by Eq. (1).

In the limit $r/\xi \to \infty$,

$$P(\omega,\omega';r) = P(\omega)P(\omega') , \quad (41)$$

and the sites are uncorrelated; in the limit $r/\xi \to 0$ they are completely correlated:

$$P(\omega,\omega';r) = P(\omega)\delta(\omega - \omega') . \quad (42)$$

With Eqs. (38) and (40) we can write for the dephasing rate

$$\frac{1}{T_2} = 2\pi (13.3) f J^2 P(\Omega) \frac{1}{(1 - e^{-2a/\xi})^{1/2}}$$

$$\times \exp\left[-\frac{(\Delta\Omega)^2(e^{-2a/\xi} - e^{-a/\xi})}{\sigma^2(1 - e^{-2a/\xi})} \right] . \quad (43)$$

In the limit $a/\xi \to \infty$ we recover Eq. (34), while in the limit $a/\xi \to 0$ we obtain

$$\frac{1}{T_2} = 13.3(\pi)^{1/2} f \frac{J^2}{\sigma} (\xi/a)^{1/2} . \tag{44}$$

It is interesting that this is no longer frequency dependent. This is because dephasing only depends on local environments, which in the limit of large ξ are well correlated. Therefore the effective concentration argument of Sec. III B is no longer appropriate.

One should note that it is not possible to recover the macroscopic-broadening result of Eq. (22) by setting $\xi = \infty$ in the above—indeed, if this is done one obtains a divergent result. This is because the limit $\xi = \infty$ is inconsistent with the requirement that the integrand in Eq. (25) decay. However, a simple calculation shows that as long as $\xi/a \ll \sigma^2/fJ^2$ (which can be very large indeed), Eq. (44) is valid. If, in fact, ξ is infinite, then $\delta_{ij} = 0$ in Eq. (25) and $K_2(t_1) \sim t_1^2$. This is the first term in an infinite cumulant expansion, which when summed[8] leads to Eq. (22).

D. Additional remarks

Our results for complete or partial site-energy randomness from Secs. III B and III C, Eqs. (33b) and (37b), are not particularly sensitive to the range of the interaction. This is, for an interaction that falls off as $1/r^2$ or faster, the lattice sums are dominated by the first shell, and the resulting dephasing rates differ only by a numerical factor. This insensitivity to the interaction range might seem surprising in view of Anderson's prediction[11] that for interactions falling off as $1/r^3$ or slower, some of the eigenstates are always extended, while for shorter-range interactions, all states are localized if the interaction strength is much less than the width of the site-energy distribution (as assumed in Secs. III B and III C). Thus one might expect that the dephasing rate for long-range interactions should be substantially larger than that for short-range interactions, or at least should be less sensitive to the correlation length. This puzzle can be understood by distinguishing between transport and dephasing experiments. In a transport experiment one measures population migration, which is sensitive to the nature of the eigenstates. (If the eigenstates are all localized, there is no long-range transport.) On the other hand, dephasing can occur without any substantial population transfer, and is primarily sensitive to the local environment and not to the asymptotic character of the eigenfunctions. We should also reiterate, however, that our results are only valid for intermediate times. It is, in fact, quite possible that the asymptotic form of the photon echo decay is sensitive to the range of the interaction. Finally we remark that for the case of macroscopic broadening discussed in Sec. III A, the results are sensitive to the range of the interaction. Our result of Eq. (22) was derived for the case of dipole-dipole coupling. Other multipolar interactions produce somewhat different time dependences for the photon echo decay.[20]

IV. APPLICATION TO EXPERIMENTS

A. Y_2O_3:Eu^{3+} (2 at. %)

In narrow-band photon echo experiments on Y_2O_3:Eu^{3+} (2 at. %), Macfarlane and Shelby[15] found that the dephasing rate varied with position in the inhomogeneous line, being larger near the center of the line than in the wings. This is the behavior predicted by the present theory for the case in which the correlation length is not infinite.

Since inhomogeneous broadening greatly exceeds homogeneous broadening in this system, the absorption spectrum reflects the inhomogeneous distribution. The absorption spectrum of this crystal is approximately Gaussian (Fig. 1).[21] Thus we can apply the results of Sec. III C for the case of partial site-energy correlation, which assumed a Gaussian inhomogeneous distribution. We can then obtain an estimate of the correlation length ξ in this crystal. Figure 1 shows the absorption spectrum and the Gaussian by which we approximate it, with $\sigma = 2.4 \times 10^{10}$ sec^{-1}.

Figure 2 shows the experimentally measured dephasing rates[22] with the theoretically predicted rates for various values of ξ/a (a is the lattice constant). The squares are the photon echo data, and the curves are from Eq. (43) with J determined by the best least-squares fit to the data. The baseline is given by $1/(2\pi T_1) = 185$ Hz.[15] Although there is appreciable scatter in the data, the curves for $\xi/a = 1$ or 2 seem the most reasonable, the curve for $\xi/a = 0$ seems a little narrow, and the curve for $\xi/a = 5$ seems too broad. For $\xi/a > 5$ the theoretical curves are even broader and clearly do not represent the data well. Thus we can place an upper bound of several lattice spacings on the correlation length ξ in this crystal. The present theory also yields a value for J, the nearest-neighbor coupling strength. From Eq. (43) with $f = 0.02$, for the fits shown in Fig. 2, we find $J = 1.5 \times 10^7$ sec^{-1} for $\xi/a = 0$, $J = 1.4 \times 10^7$ sec^{-1} for $\xi/a = 1$, and $J = 1.2 \times 10^7$ sec^{-1} for $\xi/a = 2$.

In the above fit, we have assumed that except for the lifetime contribution, all of the observed dephasing is due
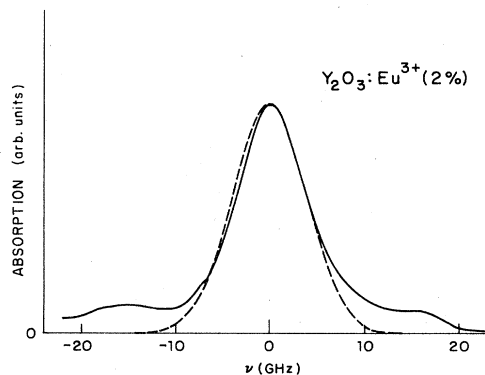

FIG. 1. Absorption spectrum of Y_2O_3:Eu^{3+} (2 at. %). The experimental data is given by the solid line (———), which we approximate by a Gaussian (— — —).
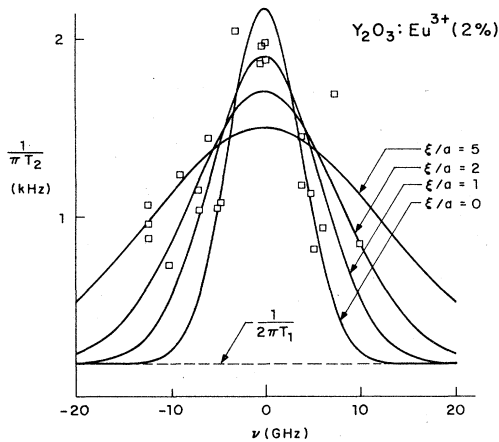
FIG. 2. Experimental points (Ref. 15) (□) and theoretical curves (———) for $1/\pi T_2$ in Y_2O_3:Eu^{3+} (2 at. %). The theoretical curves for different values of ξ/a were calculated from Eq. (43). The baseline was taken to be the lifetime-limited value of $1/(2\pi T_1) = 185$ Hz.

to Eu^{3+}-Eu^{3+} interactions. In fact there may be an additional frequency-independent contribution from several possible sources including hyperfine interactions and laser jitter.[15] To examine this possibility we simply put the baseline through the data point with the smallest $1/T_2$, which assumes that 760 Hz of the dephasing is due to some (unknown, except for the lifetime) frequency-independent mechanism. Again we consider several possible values of ξ/a; for each, the best fit to the data is shown in Fig. 3. Here we see that really only $\xi/a = 0$ gives a reasonable fit to the data. The value obtained for J is 1.2×10^7 sec^{-1}.

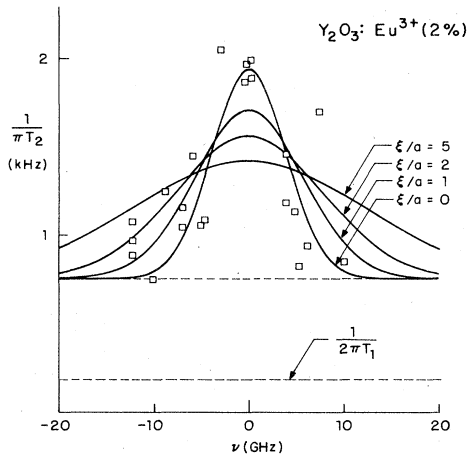In summary, we find that the frequency-dependent dephasing observed in 2 at. % Y_2O_3:Eu^{3+} can be accounted

for by quasiresonant Eu^{3+}-Eu^{3+} interactions. Furthermore, we find that the inhomogeneously broadened transition frequencies in this crystal are only correlated over distances of a few lattice spacings or less. To test further the validity of our model, it would by very interesting to have experimental results on Y_2O_3:Eu^{3+} in which the concentration dependence, as well as the frequency dependence, of the dephasing rate is investigated.

B. EuP_5O_{14}

Shelby and Macfarlane[14] also measured the photon echo decay rate as a function of position in the inhomogeneous line in the stoichiometric compound EuP_5O_{14}. In this crystal the absorption spectrum, and hence the inhomogeneous distribution, is clearly not Gaussian (Fig. 4), and therefore our general results for partial correlation are not applicable. Nonetheless, we can still determine if the model in the limit of uncorrelated site energies is consistent with the data. We first assumed that all of the observed dephasing is due to Eu^{3+}-Eu^{3+} interactions. [The lifetime contribution of $1/(2\pi T_1) = 32$ Hz is negligible in this system.] We fit the photon echo data[14] with Eq. (34), adjusting J and using the normalized experimental lineshape $P(\Omega)$. The results are unimpressive and are not reproduced here. We then examined the possibility that part of the observed dephasing is due to some other frequency-independent mechanism. We simply set the baseline at the data point with the smallest dephasing, and again fit the data with Eq. (34) using J as a free parameter. Figure 4 shows that the experimental results agree
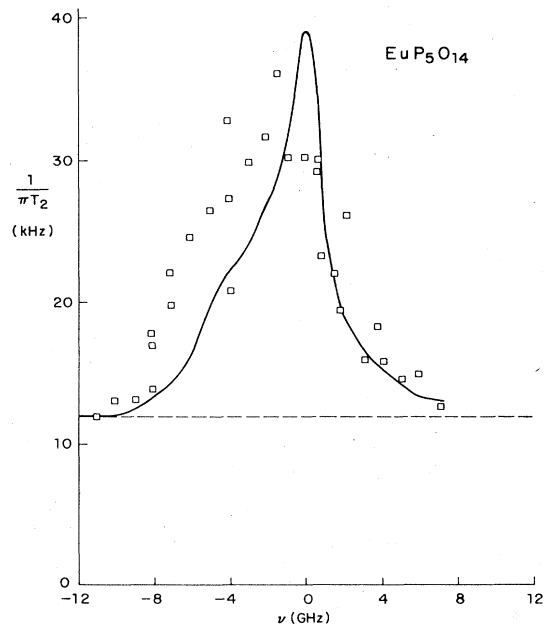

FIG. 3. Experimental points (Ref. 15) (□) and theoretical curves (———) for $1/\pi T_2$ in Y_2O_3:Eu^{3+} (2 at. %). The theoretical curves for different values of ξ/a were calculated from Eq. (43). The baseline was chosen at the data point with the lowest dephasing (760 Hz).

FIG. 4. Experimental points (Ref. 14) (□) and theoretical curve (———) for $1/\pi T_2$ in EuP_5O_{14}. The theoretical curve is determined from Eq. (34) and is proportional to the absorption line shape. The baseline was chosen at the data point with the smallest dephasing.

reasonably well with the theory. Of course it is quite likely that some of the "residual" broadening in Fig. 4 is actually due to quasiresonant interactions, and as in the case of Y_2O_3:Eu^{3+} could be accounted for by partial site-energy correlation. We can again obtain a value for J from the proportionality constant which gives the best fit. From Eq. (34), with $f=1$, we find $J=5.7\times10^6$ sec^{-1}.

In the case of EuP_5O_{14}, as a consistency check we evaluate J by an independent method. Since $J=\mu^2/\hbar a^3$, we can calculate J from the transition dipole μ and the lattice constant a. The photon-echo measurements were made on the $^5D_0\leftrightarrow{}^7F_0$ transition. From a knowledge of the $^5D_0$ lifetime and the relative intensity of the $^5D_0\leftrightarrow{}^7F_0$ transition[23] one finds that the lifetime of this transition is 3.36 sec. Then since[24]

$$\mu^2=\frac{3hc^3}{8\pi\omega^3\tau} , \qquad (45)$$

where ω is the frequency of the transition ($\lambda=5785$ Å) and τ is the lifetime, one finds $\mu^2=1.83\times10^{-7}D^2$. We also note that Shelby and Macfarlane[25] determined the oscillator strength of the $^5D_0\leftrightarrow{}^7F_0$ transition directly from the absolute absorption intensity, leading to a value of $\mu^2=9.00\times10^{-8}D^2$. The parameters of the EuP_5O_{14} unit cell are[26] $a=8.744A$, $b=12.949A$, $c=8.925A$, and $\gamma=90.46°$, and there are four Eu^{3+} ions per unit cell. If we assume a simple cubic lattice with the same density of Eu^{3+} ions as the actual crystal, we find that the lattice spacing a of this equivalent lattice is $6.32A$. Using the above values for μ and a we find $J=6.87\times10^5$ sec^{-1} or 3.38×10^5 sec^{-1}. This should be compared with $J=5.7\times10^6$ sec^{-1} obtained from the best fit to the data.

C. Concluding remarks

While the agreement (for EuP_5O_{14}) between the values of J determined from the echo dephasing data and independent estimates is not spectacular, it is certainly reasonable considering the several approximations in the model. For example, the theory assumes a standard $(\pi/2)$-π pulse sequence, whereas in the experiments of Macfarlane and Shelby $(\pi/2)$-π pulses were not attained.[14,15] The time dependence of the photon-echo decay is known to be highly dependent on the pulse areas,[27] but in the absence of a theory of photon echoes in multilevel systems for arbitrary pulse areas, we cannot determine the effect of this discrepancy on our results. We note, however, that the echo intensity was observed to decay exponentially,[14,15] in agreement with the predictions

of our model. Thus it seems that the assumption of $(\pi/2)$-π pulses does not qualitatively affect our results. Another rather drastic approximation in our theory is the assumption of a square excitation profile, with sites for which $|\omega_i-\Omega|\leq\chi/2$ assumed to be exactly on-resonance and other sites assumed to be completely off-resonance. Again we cannot estimate the effect of this assumption, but it seems to be a qualitatively reasonable description of the excitation profile. Optical density effects were found to be important in some experiments on concentration-dependent dephasing.[28] Macfarlane and Shelby established[15] that the crystals used in experiments on Y_2O_3:Eu^{3+} (2 at. %) were optically thin. Although they do not report[14] whether optical density effects can be similarly ruled out experimentally in the case of EuP_5O_{14}, one can argue on theoretical grounds that since $T_1\gg T_2$ these effects should be negligible.[28] The simplifying assumption of a cubic lattice with all dipoles aligned parallel is another approximation in the model. Evaluation of the lattice sum in Eq. (33b) using the actual crystal structures is straightforward, and would only change the numerical coefficient in Eq. (34). In Y_2O_3: Eu^{3+} (2 at. %) only three quarters of the Eu^{3+} sites are excited and involved in the dephasing process;[15] this again merely changes the numerical coefficient in Eq. (34).

It is not surprising, in view of the considerations discussed above, that agreement between theory and experiment is not strictly quantitative. The important point is that the predictions of the present model are in semiquantitative agreement with experimental results for both rare-earth crystals investigated. Thus we may conclude that the frequency-dependent dephasing observed by Shelby and Macfarlane can be accounted for by quasiresonant interactions among Eu^{3+} ions. Further, we have established that inhomogeneous broadening in these crystals is predominantly microscopic rather than macroscopic; for the case of Y_2O_3:Eu^{3+} we have been able to place an upper limit of several lattice spacings on the value of the correlation length ξ.

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