Observation of Dipolar-Induced Spin Dephasing in Ionic Solids Using Coherent Optical-Microwave Spectroscopy

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The observation of spin dephasing in an ensemble of dipolar coupled A and B spins is reported. In CaO crystals, the A-spin species are photoexcited $S=1$, F_2^{2+} centers and the group of B spins consists of $S=\frac{1}{2}$, F^+ centers. Measurements were made at different temperatures and magnetic field strengths with use of coherent optical-microwave spectroscopy. For the first time, the results show that the A-spin dephasing is influenced by exchange narrowing in the B-spin ensemble.

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Spin dephasing within a system of randomly distributed spins, when caused by magnetic dipolar coupling with fluctuating neighboring spins, has been of considerable theoretical[1-3] and experimental[4] interest in the past. Basically, one considers the spins under observation, called A spins, as isolated from the lattice; secular dipolar interaction with a second ensemble, comprising of fluctuating B spins, is the source for the loss of the phase memory in the A-spin ensemble. Up until now, only so-called T_1 samples have been considered in the literature, i.e., the time dependence of the B-spin magnetic moments is thought to arise from spin-lattice relaxation in the B-spin ensemble. In the present paper we demonstrate the use of coherent optical-microwave spectroscopy to probe dephasing by a new, other than T_1, mechanism. The results, obtained for photoexcited ionic solids, indicate the direct role of the phenomenon of exchange narrowing in the B-spin ensemble which in turn reveals itself by a *slowing down* of the A-spin dephasing rate as the temperature is raised from 1.2 to 10 K.

In our experiments, the group of A spins is formed by F_2^{2+} centers, in the phosphorescent $^3B_1$ state, in CaO crystals. The main spectroscopic data of the center are summarized in Fig. 1; for more details, the reader is referred to the work of Gravesteijn and Glasbeek.[5] In addition to these F_2^{2+} centers, the crystals contain an abundant amount of F^+ centers ($S=\frac{1}{2}$), i.e., single-oxygen-anion vacancies at which one electron is trapped. We consider these F^+ centers to form the B-spin ensemble.

The A-B system discussed in this work offers several advantages that we desire for probing spin dephasing. Firstly, the A-spin dephasing as a function of temperature is not determined by the direct coupling of A spins with lattice vibrational modes (up to 10 K), but instead is primarily governed by the temperature effect on the B-spin dephasing (see later discussions). The experimental procedure in this work is to detect the A-spin echo decay at zero (or low) magnetic fields. It follows that the experimental approach makes the B-spin dynamics amenable to experimental investigation in *zero* magnetic field, which is an advantage in the sense that T_1 relaxation of the B spins may be suppressed considerably. Secondly, as also shown later, exchange narrowing in the B spin can be controlled not only by varying the temperature but also by applying a magnetic field. It should be emphasized that techniques which directly measure the B-spin–echo decay in the microwave region cannot yield similar data due to the isotropy of the $S=\frac{1}{2}$ ESR sig-

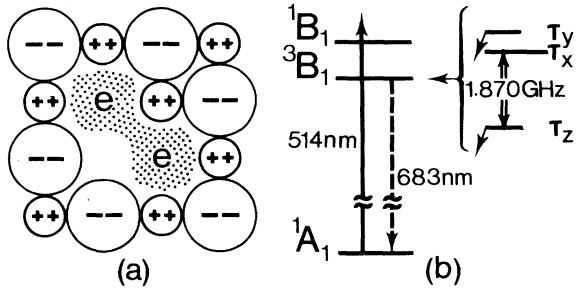

FIG. 1. F_2^{2+} center in CaO crystal. (a) model in (100) plane; (b) optical cycle for probing coherence between τ_z and τ_x sublevels.

nal and also because T_1 processes might dominate in the dephasing at high magnetic fields.

To probe the spin dephasing, we followed the behavior of the *optically* detected A-spin-echo decay[5] of one of the triplet-state transitions (zero-field frequency of the latter: 1.870 GHz) as a function of temperature and magnetic field. In zero field and at 1.2 K, the F_2^{2+} (A-) spin echo decays almost exponentially with $T_M(A) = 140$ μsec (see inset to Fig. 3). Compared with other known electron-spin dephasing times, $T_M(A)$ is unusually long. The phenomenon arises because for $S = 1$ spins, in nonaxial local crystalline fields, the magnetic moment is quenched in zero field.[6] Therefore, the loss of A-spin coherence, which results from magnetic dipolar coupling to fluctuating B spins, is a higher-order process. When a dc magnetic field is applied the situation is different: The A-spin magnetic moment becomes unquenched and dephasing in the A-spin ensemble is enhanced. Quantitatively this is seen as follows.

In general, the echo amplitude is related to the in-phase component of the magnetic polarization, i.e., the r_1 component of the Feynman-Vernon-Hellwarth representation. To determine the decay characteristics we need the time evolution of r_1. Starting with the Liouville–von Neumann equation for the density operator, one can derive[7,8] the equation of motion for the observable S_1, where S_1 is defined by $\langle S_1 \rangle = r_1$. In the lowest Born approximation of the A-B dipolar interaction we obtain for S_1^*, i.e., S_1 in the A-spin interaction representation,

$$\frac{\partial \langle S_1^* \rangle}{\partial t} = -\int_0^t dt' \, \frac{(S_1|\hat{\mathcal{H}}^*(t)(1-P)\hat{\mathcal{H}}^*(t')|S_1)}{(S_1|S_1)} \langle S_1^*(t') \rangle , \tag{1}$$

where $\mathcal{H}^* = U\mathcal{H}_{DD}{}^{AB}U^{-1} + \mathcal{H}^B$, $U = \exp(i\mathcal{H}^A t)$, $\mathcal{H}^A$ and $\mathcal{H}^B$ denote the spin Hamiltonians, including Zeeman interactions, for the ensembles of A and B spins respectively, and $\mathcal{H}_{DD}{}^{AB}$ represents the dipolar interactions between all A and B spins. The projection operator, P, is here defined as $P = |S_1)(S_1|S_1)^{-1}(S_1|$ in Liouville space. We note that the dipolar interaction, $\mathcal{H}_{DD}{}^{AB}$, is between unlike A and B spins for which the resonance frequencies differ by orders of magnitude. Then, the expression for the secular part of $\mathcal{H}_{DD}{}^{AB}$ (this being the only part in $\mathcal{H}^*$ not containing an explicit time dependence for the A spins) is readily derived in a manner given previously for the case of nuclear spin coupling.[9] Substitution of this $\mathcal{H}_{DD}{}^{AB}$ (secular) in Eq. (1) eventually leads to the following integrodifferential equation

$$\frac{\partial \langle S_1^*(t) \rangle}{\partial t} = -g_A{}^2 g_B{}^2 \mu_B{}^4 \int_0^t dt' \sum_{A,B} \frac{(1-3Z_{AB}{}^2)^2}{r_{AB}{}^6} \frac{z^2}{1+z^2} \frac{1}{n_A} C_B(t',t) \langle S_1^*(t') \rangle , \tag{2}$$

in which $z = g_A H_z' |E|^{-1}$, $H_z' = (H_{\rm loc}{}^2 + H_z{}^2)^{1/2}$, $H_{\rm loc}$ being the effective local field at A-spin sites, n_A is the number of A triplet spins and, finally, $C_B(t',t)$ is the B-spin time autocorrelation function. It is noted that Eq. (2) relates $\langle S_1^*(t) \rangle$ to values at all earlier times and may reflect non-Markoffian behavior in the A-spin dynamics. We now make the following crucial assumptions: (i) $C_B(t',t)$ decays exponentially with time, i.e., $C_B \sim \exp[-R|t'-t|]$, where R denotes the B- spin dephasing rate, and (ii) the characteristic B-spin decay time, R^{-1}, is small compared with $T_M(A)$. Having in mind these assertions and the statistical averaging procedure of Ref. 3, Eq. (2) can be integrated to give for the echo amplitude[7]

$$\langle S_1^*(2\tau) \rangle \propto \exp\{-k d_B [z/(1+z^2)^{1/2}] B(\tau)^{1/2}\}, \tag{3}$$

in which $k = \frac{8}{27}(3\pi^3)^{1/2} g_A g_B \mu_B{}^2$, d_B is the density of B spins and $B(\tau) = 4R^{-2}\{R\tau - [1 - \exp(-R\tau)] - \frac{1}{2}[1 - \exp(-R\tau)]^2\}$. Equation (3) allows us to quantitatively test the model by verifying the z dependence of $\langle S_1^* \rangle$.

In practice, the observed spin-echo decay curves were computer fitted to a function of the form $\exp[-C(z)B(\tau)^{1/2}]$ yielding the two parameters $C(z)$ and R. As an example, the results for $C(z)$ and R obtained at 1.2 K are plotted in Fig. 2

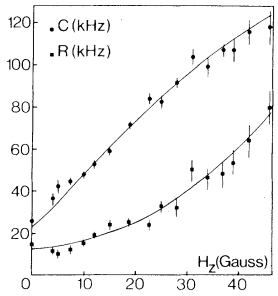

FIG. 2. Magnetic field dependence of $C(z)$ (circles) and R (squares) when the $F_2{}^{2+}$-center spin-echo decay is fitted to the form $\exp[-C(z)B(\tau)^{1/2}]$, where $B(\tau)$ is defined in the text. Drawn curves represent best fits, namely $C(z) \propto z/(1+z^2)^{1/2}$ and $R \propto H_z{}^2$.

as a function of H_z. Clearly, the complete linear proportionality between $C(z)$ and $z/(1+z^2)^{1/2}$ is strong evidence that the dipolar coupling between A and B spins determines the A-spin dephasing. Also, the $R \propto H_z^2$ dependence is a significant result. If $C_B(t',t)$ was determined solely by T_1 processes in the B system, one would expect at low temperatures direct one-phonon processes to yield $R \propto H_z^4$.[10] Apparently, the observed R vs H_z behavior excludes the classification of the system as a T_1 sample. The latter is confirmed in the analysis of the interesting effect of temperature on R at zero-magnetic field.

Raising the temperature from 1.2 K up to 10 K we find that the A-spin–echo decay attains a pronounced nonexponential shape approaching the form $\exp[-(2\tau/T_M)^x]$ with $x = 1.5$ and $T_M(A) = 200$ μsec at 10 K. The result is typical for the limit in which $R\tau \ll 1$, i.e., as the temperature is increased, the B spin dephasing rate, R, is decreased. The phenomenon can be explained by invoking an exchange coupling among the spin transitions of the B-system. In other words, in addition to the usual dephasing of B-spin transitions (due to direct spin-bath coupling) there exists a dipolar coupling which motionally narrows transitions of the B-spin ensemble. An alternative mechanism for the retarded A-spin dephasing would be exchange narrowing involving *only* A spins. This possibility, however, could be rejected from a study of the A-spin ensemble prepared in an ordered state.[11,12] Using optical-microwave techniques similar to those of Ref. 12, we could determine how long the local fields, which cause the inhomogeneous broadening of the A-spin signal, persist. The characteristic decay time for the A-spin ordered state turned out to be 3 msec (up to 10 K). This result shows that the spin ordering is limited by the lifetime of the $^3B_1$ state and that rapid A-spin flips do not occur. Consequently, the A-spin ensemble itself does not exhibit exchange narrowing and the lengthening of the A-spin phase memory must be dominated by B-spin exchange narrowing.

From the numerical analysis of the echo decay curves the B-spin density could be determined [cf. Fig. 2 and Eq. (3)]. We find $d_B \simeq 10^{17}/\mathrm{cm}^3$, which means that the B spins, because of their dipolar coupling, effectively experience a local field of ~1 mG. At high field ($H = 3300$ G) the inhomogeneous linewidth of the F^+ center electron paramagnetic resonance signal is 0.2 G. It follows that at *zero field* the residual strain broadening would be $\sim 10^{-4}$ mG, i.e., negligible compared to the dipolar broadening. It is therefore not surprising that at zero field exchange narrowing in the B ensemble is observed owing to the extremely small inhomogeneous broadening!

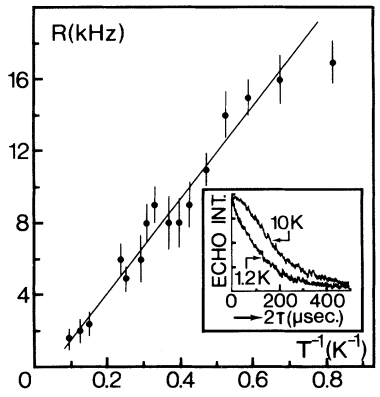

FIG. 3. Spin dephasing rate (R) of F^+ centers vs T^{-1} between 1.2 and 10 K. Drawn line is best fit for $R = 2.6 \times 10^4\, T^{-1} - 1.1 \times 10^3$ kHz. Inset shows optically detected spin-echo decays of F_2^{2+} center (microwave frequency is 1.870 GHz) at 1.2 and 10 K, respectively.

Figure 3 shows that R is almost proportional to T^{-1}. This T^{-1} dependence can now be considered by application of the recently developed theory of dephasing[13] to the aforementioned exchange mechanism. For practical purposes, we simply regard exchange within the group of B spins between just two subgroups which have slightly different resonance frequencies. In this approach, in the limit of fast exchange, the line shape is Lorentzian with a width given by

$$R = \Delta^2/(\Gamma+\gamma). \tag{4}$$

In Eq. (4), Δ is the resonance frequency difference between the two subgroups, whereas Γ and γ denote the homogeneous width of each B-spin packet and the exchange rate, respectively. In the rapid exchange limit $\Gamma = \pi \sum_{p,p'} \rho_p |T_{\mathrm{int}}|^2 \delta(\Delta + \omega_p - \omega_{p'})$, where p labels the phonon states of density ρ_p and T_{int} denotes the transition operator.[13-15] By a series expansion of the magnetic dipolar interaction between the subgroups in the phonon coordinates, it is shown straightforwardly that, at least in first order, both Γ and γ become linearly proportional to temperature. Therefore, from Eq. (4) two important conclusions can be drawn. First, for dipolar interactions between B spins we expect $R \propto \delta^2 \propto H_z^2$ which is the behavior found experimentally (cf. Fig. 2). Second, one-phonon assisted dipolar interactions are responsible for the observed $R \propto T^{-1}$ dependence.

In summary, we find that dephasing in an ensemble of dipolar coupled electron spins can be studied successfully in wide temperature and magnetic field ranges by using as a probe excited triplet spins of which the coherence decay is monitored optically. Furthermore, our results demonstrate that the dephasing mechanism in the B-spin system is consistent with a phonon-assisted random modulation of dipolar interactions in the fast exchange limit.

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Dielectric Response of a Thin-Layer Zero-Gap Semiconductor

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It is shown that the dielectric response of a thin layer of α-Sn–type semiconductor is radically different than that of the bulk material. The q^{-1} and $\omega^{-1/2}$ singularities of the bulk polarizability are absent in the layer. Instead, the dielectric response and optical absorption of the layer are highly anisotropic, and the static dielectric constant is linearly dependent on layer thickness. In the random-phase approximation, the thin-layer energy-band structure is unconditionally stable against exciton formation.

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Materials of the α-Sn type (α-Sn, HgTe, HgSe, Cd_3As_2) are of considerable interest because of their anomalous dielectric response. Their band structures are characterized by a symmetry-induced degeneracy of the extrema of the highest-lying valence band and lowest-lying conduction band.[1] At absolute zero, the zero-energy excitation at the point of contact produces a $\omega^{-1/2}$ singularity[2,3] in the frequency dependence and a q^{-1} singularity[4] in the momentum-transfer dependence of the dielectric function. This unusual behavior[5] prevents an excitonic instability,[3,6] and its effects have been seen in the transport[7-11] and optical[12,13] properties of the materials.

However, the situation in a very thin layer of zero–band-gap semiconductor will be quite different. Consider an infinite layer of zero–band-gap semiconductor, of thickness small in comparison with the electron mean free path and de Broglie wavelength, imbedded in a high–band-gap material. The electrons in the thin zero–band-gap layer will appear to be in a one-dimensional potential well in the direction normal to the layer,[14] and the conduction and valence bands will split into two-dimensional subbands. In particular, an energy gap will appear between the

