Spin Coherence and the Stark Modulation Effect in the Excited State of FA-Mo Centers in CaO

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Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.39.105

cause large ρ values occur when $2k_F$ overlaps the peak in $\tilde{S}'(q)$. This same condition produces a decrease in ρ on heating because of the peak reduction. As in the case of amorphous alloys, the room-temperature value of α is determined by the Debye-Waller factor only so that $|\alpha| \sim 10^{-4}$ K^{-1} is predicted in agreement with observed values.

In conclusion, extended Ziman-Evans theory provides a unified framework for the description of transport in glassy metals and disordered crystalline alloys as well as in liquid metals. Moreover, the procedure described does not depend on any particular model for $S(q, \omega)$ but is valid for any system whose structure factor $S_0(q)$ is a continuous function of q. Thus, the predicted temperature dependences will be universal features of such systems.

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Spin Coherence and the Stark Modulation Effect in the Excited State of F_A-Mo Centers in CaO

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(Received 26 May 1977)

Optically detected electron-spin coherence effects in the photoexcited triplet state of a new defect, the F_A-Mo pair in CaO, are presented. They include a Stark-field-stimulated modulation of the Hahn-echo decay.

Spin alignment in emissive triplet states of defect centers in ionic solids is known to occur[1] and, therefore, the zero-field double-resonance techniques that have been so valuable in spin coherence studies of excitations in molecular solids[2] are expected to be applicable in colar centers too. Our experiments concern the lowest emissive $S = 1$ state of a new color center in CaO, the F_A-Mo pair. It will be shown that spin coherence in the phosphorescent state can be achieved and that by analogy to spin-echo experiments on paramagnetic systems in the ground state,[3] a modulation of the optically detected echo-decay envelope can be induced by an electric field. As a result, the experiments illustrate that the method offers a powerful means of studying small electric field effects in excited non-Kramers states with the sensitivity of optical detection. Furthermore, the dynamical cause for the loss of phase coherence in the triplet spin ensemble is briefly considered. A pseudo-Jahn-Teller coupling between excited $^3A_1$ and ^3E states of the pair center has been invoked[4] on the basis of optically detected magnetic-resonance data. It turns out that the decay factor for the envelope of of the spin-echo signals reported here can be satisfactorily related to the vibronic nature of the excited states.

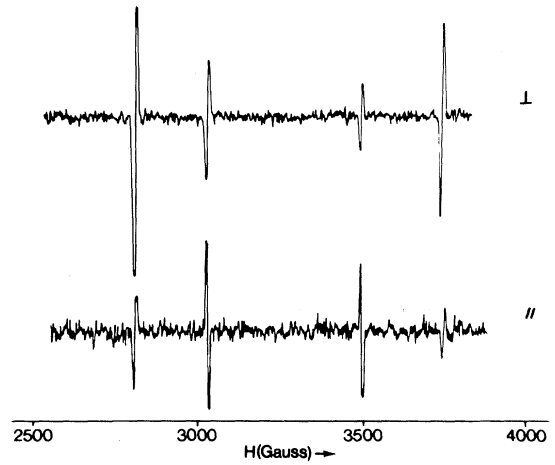

FIG. 1. Optically detected EPR spectra at X-band frequencies of the F_A-Mo pair in CaO. $\vec{H}$ is oriented along the [001] direction of the crystal, the detection wavelength is 684 nm, $T = 1.6$ K. The light changes are detected perpendicualr to $\vec{H}$, and of σ polarization (upper part) and π polarization (lower part).

Yellow colored CaO crystals purchased from Spicer Ltd. were used in the experiments. Illumination of the crystals with light in the blue or near uv allowed the optical detection of magnetic resonance (ODMR) spectra of the center at 1.5 K. The X-band ODMR spectra showed anisotropy characteristic of three equivalent tetragonal centers in an $S = 1$ state. In addition to the fine structure, an isotropic hyperfine interaction due to an isotope with $I = \frac{5}{2}$ in a 25% abundance was observed. A representative spectrum is given in Fig. 1. The hyperfine lines have intensity $\simeq \frac{1}{25}$ relative to the main line and were observed at a higher gain than shown in the figure. The spin Hamiltonian parameters were obtained as $g_{\parallel} = 1.998 \pm 0.001$, $g_{\perp} = 2.006 \pm 0.001$, $D = 4.56 \times 10^{-2}$ cm^{-1}, whereas $a_{iso} = 17.8 \times 10^{-4}$ cm^{-1} for the hyperfine coupling constant of the $I = \frac{5}{2}$ isotope.

In the "normal" phosphorescence spectrum, the defect emission remains hidden due to overlap with the F-center emission which extends up to 700 nm. When one uses the technique of zero-field phosphorescence microwave double resonance (PMDR)[5] however, the defect spectrum can can be produced distinctly. It consists of a narrow zero-phonon line peaked at 657.1 nm and a broad sideband with its maximum near 684 nm. Uniaxial stresses up to 25 kg/mm^2 caused linear splittings of the PMDR zero-phonon line; however, changes in the relative intensities of the induced components were not observed. Thus the stress causes a removal of orientational degeneracy between static deformations rather than a lifting of vibronic degeneracy.[6] A plausible model for the color center is the F_A-Mo pair, i.e., two electrons captured in an oxygen vacancy neighboring a Mo impurity substitutional for Ca^{2+}.

Obviously, the observation of linear Stark shifts either in the optical or microwave region would confirm the noncentrosymmetric nature of the center. In practice the very small linewidth of the PMDR zero-phonon line (< 4 cm^{-1}) already illustrates the low susceptibility of the defect for interaction with other defect point charges and therefore very high electric field strengths will be necessary to resolve line shifts. In our experiments advantage was taken of the resolving power that can be obtained with double-resonance techniques for the measurement of electron spin echoes in zero field.[2] The method relies on the detection of electric-field-induced changes in the coherence in an ensemble of triplet spins. In fact, it is the zero-field analog of the spin-echo method used by Mims for measuring paramagnetic Stark effects.[3]

For triplet spins, the optically detected Hahn-echo experiment in zero field implies a $\pi/2$ pulse, after a time τ, and finally the coherence sampling $\pi/2$ pulse at 2τ.[2] When the triplet levels are thermally isolated and the microwaves are resonant with the $\tau_y \rightarrow \tau_x$ transition, where τ_y is taken as a nonemissive state, then the phosphorescence decays as the spin echo, e.g., of the type proportional to $\exp(-2\tau/T_M)$, T_M being the homogeneous coherence relaxation time. The result is conveniently derived in a density matrix formulation in which each step in the pulse sequence is taken care of by a unitary transformation of the density matrix in the interaction representation.[7] Consider now the effect of an electric field, E_x, applied along the x direction as a step function in the time interval between τ and 2τ. For an $S = 1$ system in C_{4v}, the added term in the spin Hamiltonian will be $H_E = R_{3D} E_x [S_x^2 - \frac{1}{3} S(S+1)]$, and thus the adopted shift in the resonance frequency of all spin packets contributing to the echo signal will be $\Delta\omega = R_{3D} E_x$. In the density matrix description this effect is accounted for by including a time evolution operator of the form (in the τ_y, τ_x basis)

$$S^{-1} = \begin{bmatrix} -i\sin(\Delta\omega\tau/2) + \cos(\Delta\omega\tau/2) & 0 \\ 0 & i\sin(\Delta\omega\tau/2) + \cos(\Delta\omega\tau/2) \end{bmatrix}.$$

It can then be shown that the time-dependent density matrix in the interaction representation after the final $\pi/2$ pulse will be

$$\rho^* = \frac{1}{2}\begin{bmatrix} 1+f\cos(\Delta\omega\tau) & -if\sin(\Delta\omega\tau) \\ if\sin(\Delta\omega\tau) & 1-f\cos(\Delta\omega\tau) \end{bmatrix},$$

where $f \equiv [(N_y - N_x)/(N_y + N_x)] \exp(-2\tau/T_M)$ with N_x and N_y being the initial populations of the levels τ_x and τ_y.

Since the phosphorescence intensity is given by[7a] $I \propto (\rho_{11}^* - \rho_{22}^*)$, the Stark effect on the echo envelope is a modulation with a periodicity of $\pi/\Delta\omega$. Thus the order of the electric field effect can be extracted from the periodicity as a function of E_x. It is also seen that the electric field may induce additional coherence ($\rho_{12}^* \neq 0$). A $\pi/2$ pulse with a 90° phase shift following the second $\pi/2$ pulse should make this phenomenon observable. If, however, the crystal contains inversion image sites,[8] and the Stark effect is linear, $\Delta\omega$ will be both positive and negative and the E-field–induced coherence is not observed.

In our zero-field pulse spectrometer a three-pulse train from a clock oscillator was produced by triggering the oscillator with a 20 Hz reference frequency from a lock-in amplifier. The clock oscillator frequency, which could be swept externally, determines the time interval, τ, between the microwave pulses. In a shift register the three pulses were separated into three different channels. In each channel either a $\pi/2$ or a π pulse in a monostable multivibrator is activated. The duration of the latter pulses, typically around 200 nsec, was obtained from a transient nutation-type experiment. Finally, the echo pulse sequence was combined in an OR-gate which is in conjunction with the p-i-n diode driver. The microwaves, switched by the p-i-n diodes, were amplified by a 20-W traveling-wave tube amplifier. The microwave-induced light changes were phase sensitive detected with a lock-in amplfier. The ramp voltage of a time-averaging device was used to sweep the clock oscillator so that τ varied from 1 to 150 μsec and an electron-spin-echo decay could be monitored. Electric fields, applied as voltage step functions, up to 20 kV/cm and of 100 μsec duration were triggered synchronously with the refocusing π pulses. The CaO crystal was mounted inside a slow-wave helix immersed in a He bath at 1.5 K.

In the experimental arrangement the electric field is directed along x, the microwave H_1 field is polarized (mainly) along y, optical excitation is along z, and photodetection is along y. Anticipating a one-to-one correspondence in the transition moments of the pair center and the Jahn-Teller distortions of a CaO F center, the H_1 field excites only x and z sites, i.e., sites with pair axes along x and z, respectively.[9] Emission propagating in the y direction is detected so the x and z sites are separated by their polarization, z and x, respectively.

Figure 2(a) shows the spin-echo decay detected from the x-polarized emission. The result illustrates that *spin coherence may be sampled in excited color centers in ionic solids*. The decay is exponential with a homogeneous T_M of 28 μsec. The decay is insensitive to a voltage applied in the rephasing interval, as expected for z sites. When, alternatively, in the Stark experiment the z-polarized emission is detected, the exponential decay is replaced by a damped cosine function

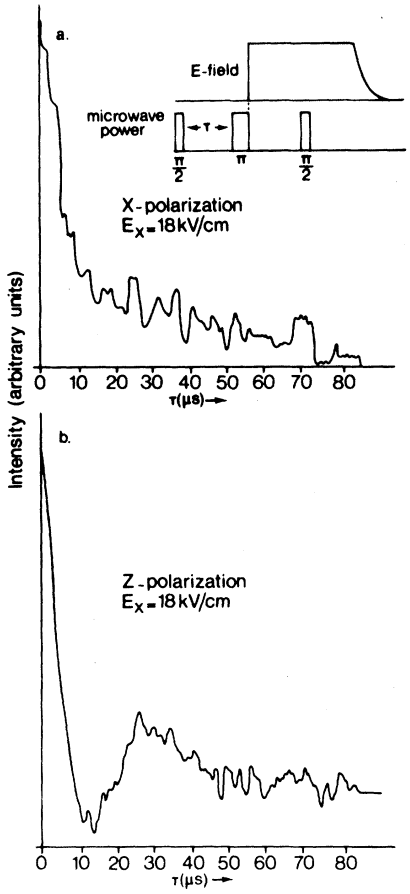

FIG. 2. Optically detected Hahn-echo decay in zero magnetic field; the electric field ($\vec{E}$) is applied after the microwave π pulse (with a duration of 240 nsec); (a) decay for x-polarized emission, no E-field effect; (b) decay for z-polarized emission, reflecting a Stark modulation effect.

[cf. Fig. 2(b)]. The periodicity of the points of zero intensity turned out to be inversely proportional to E_x. Thus the results express *a selective linear Stark effect on the spin coherence* in accordance with C_{4v}.

The sensitivity of the method is expressed by the small shift parameter, $R_{3D} = 0.37 \pm 0.05$ Hz cm/V. In zero field the ODMR signal of the F_A-Mo defect has an inhomogeneous linewidth of about 10 MHz. Therefore, when one tries to resolve Stark splittings in the ODMR resonances induced by stationary electric fields, voltages of at least 10^7 V/cm should be applied.

Another aspect of the spin-echo experiments is their relevance to irreversible loss of phase coherence in an ensemble of triplet spins. In general, the so-called spectral diffusion[10] is an important mechanism, where flippings of environmental spins are considered to be the source for fluctuations in the local field of the resonant spins. However, for diffusion-type processes nonexponential phase memory functions are expected[10-12] as have actually been observed in some cases.[12,13] The case of the F_A-Mo pair is of interest because the spin-echo signal displays an exponential decay down to 1.2 K. Spectral diffusion is therefore highly unlikely. Moreover, the CaO lattice contains very few nuclear spins (e.g., ^{43}Ca in 0.13%) and thus the mechanism appropriate in a wide class of systems, namely diffusion due to electron-spin–nuclear-spin interactions, may be disregarded indeed in our case. Alternatively, when uncorrelated jumping between different Jahn-Teller distortions can take place, an exponential spin-echo decay is expected.[14] Observed level-inversion phenomena and optical spectra[4] showed that the level scheme of the pair center is compatible with lowest excited A_1 and E states split by the axial field (as in the electronically equivalent F_t pair[15]). It could also be demonstrated that these levels are vibronically coupled by a localized mode of e symmetry. Because of this coupling the levels should possess a great tendency to undergo modulation by local lattice fluctuations and phase coherence may decay exponentially, the associated relaxation times being as short as 10^{-6} sec. In summary, the experiments illustrate that coherence in excited defects in ionic solids can be monitored optically and that its irreversible dephasing can be utilized as a sensitive tool for studies of Stark and intrinsic dynamical effects.

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