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Optically detected magnetic resonance and spin coherence of self-trapped hole centers in an excited spin-quartet state in calcium oxide

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A new defect in additively colored calcium oxide is studied by means of optically detected magnetic resonance and spin-coherence experiments. It is established that the defect shows emission from a spin-quartet state with spin-Hamiltonian parameters $|D| = 1950 \pm 2$ MHz, $|E| = 550 \pm 2$ MHz, and $g = 2.00 \pm 0.05$. The fine-structure principal axes are along $[110]$, $[1\bar{1}0]$, and $[001]$. We argue the existence of a vacancy-interstitial hole, the F center- O_2^- pair, that can be photoexcited in the phosphorescent quartet state. Time-resolved microwave recovery experiments at zero field yielded the lifetimes of the radiative and nonradiative quartet sublevels to be $230 \mu\text{s}$ and 3.8 ms, respectively. From optically detected spin-coherence decay measurements at 1.4 K a phase memory time of $38 \mu\text{s}$ was found, showing that irreversible spin dephasing is not determined by population relaxation.

In studies of excited states in solids, techniques for the optical detection of magnetic resonance (ODMR) and spin-coherent transients are widely applied nowadays.¹ Elaborate investigations have been reported for luminescent triplet states,² self-trapped triplet excitons,³ and electron-hole recombination reactions.⁴ To our knowledge, defects in phosphorescent excited spin-quartet states have not yet been studied. In this Rapid Communication, a zero-field and low-field ODMR study of a new long-lived emissive state in additively colored calcium oxide is reported. The localized state [which gives rise to a zero-phonon line (ZPL) emission peaking at 657 nm] is identified as due to a self-trapped hole, adjacent to an F center, in a phosphorescent spin-quartet state. Also, it appeared possible to create spin coherence in the excited spin-quartet state. Preliminary results of time-resolved experiments show that pure dephasing (and not population relaxation) is responsible for the measured spin-coherence decay.

Yellow-colored calcium oxide single crystals were the same as in previous experiments.⁵ The experimental setup has been described in detail elsewhere.⁶ The sample was mounted inside a slow-wave helix immersed in a pumped liquid-helium bath. All measurements were conducted at 1.4 K. Optical excitation was by means of a cw Ar^+ -ion laser pumping a dye laser (rhodamine 6 G as a dye).

Laser excitation of the calcium oxide crystal near 611 nm resulted in a narrow zero-phonon emission peaking at 657 nm. Upon chopping the exciting light, the radiative level was found to decay exponentially with a characteristic decay time of $230 \mu\text{s}$. The slow radiative decay is suggestive of a spin-forbidden transition to the electronic ground state. Subsequently, zero-field ODMR experiments⁶ were undertaken in which the microwave frequency was swept in the range from 0.1 up to 12 GHz. The zero-field ODMR spectrum obtained with amplitude modulation of the microwaves and phase-sensitive detection (at 30 Hz), is displayed in Fig. 1. A narrow ODMR transition is found at a frequency of 4340 MHz, the width being 10

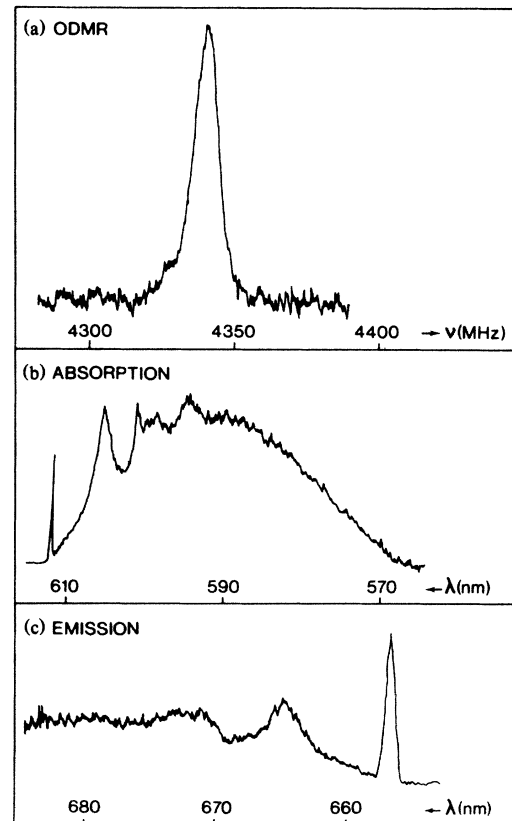


FIG. 1. (a) Optically detected magnetic resonance spectrum at zero field of the F - O_2^- pair defect, in CaO, in the photoexcited phosphorescent spin-quartet state. $T = 1.4$ K. Excitation wavelength: 604 nm; detection wavelength: 672 nm. Phase-sensitive detection was at 30 Hz. (b) Excitation wavelength dependence of the ODMR intensity at $\nu = 4340$ MHz. Everything else as in (a). (c) Phosphorescence microwave double-resonance (PMDR) spectrum for the F - O_2^- defect, optically pumped at 595 nm, in the spin-quartet state. Everything else as in (a).

TABLE I. Main characteristics of the phosphorescent states of the $F-H$ and F_A centers in CaO. Data for the $F-H$ defect are from this work; data for the F_A center are from Refs. 5 and 7.

	Absorption (nm)	No-phonon emission (nm)	Fine-structure parameters (MHz)	Orientation magnetic axes	Lifetime of radiative (τ^r) and nonradiative (τ^{nr}) spin levels at 1.4 K
$F-H$	611 (ZPL)	657	$D = 1950$ $E = 550$	$x \parallel [110]$ $y \parallel [1\bar{1}0]$ $z \parallel [001]$	$\tau^r = 230 \mu\text{s}$ $\tau^{nr} = 3.8 \text{ ms}$
F_A	460 (Broad band)	657	$D = 1369$ $E = 0$	$z \parallel [001]$	$\tau^r = 9.5 \text{ ms}$ $\tau^{nr} = 475 \text{ ms}$

MHz (FWHM). The optical spectral dependence of the ODMR signal was monitored by scanning the wavelength of the exciting light (or the detected emission) while keeping the microwave frequency on resonance. The results representative of the optical absorption (or emission) spectrum belonging to the new defect are shown in Fig. 1 also. The absorption is seen to be sharply peaked at 611 nm, the weakly structured band absorption has its maximum near 595 nm. In emission, a narrow ZPL peaking at 657 nm is observed; weak-phonon side bands occur at 665 and 671 nm. It is remarked that the no-phonon emission coincides with the ZPL-emission characteristic of the F_A center in CaO.⁷ However, apart from this resemblance, all other properties of the emissive state under study here differ significantly from those of the F_A -center $^3A_{1u}$ state (cf. Table I). Evidently, the possibility that the results of Fig. 1 are due to the F_A center can be excluded.

In an externally applied magnetic field, the ODMR signal is split in a multitude of lines [up to 12 lines were observed for the sample in a small field of 32 G, arbitrarily oriented in the (100) plane]. The angular variations of the ODMR peak positions for a small field in the (100) and (110) planes are shown in Fig. 2. All of the lines in the low-field ODMR spectra (fields up to 100 G were used) and their anisotropic behavior are accounted for by computer fittings based on a spin Hamiltonian given by

$$H = g\mu_B \mathbf{H} \cdot \mathbf{S} + D(S_z^2 - \frac{1}{3}S(S+1)) + E(S_x^2 - S_y^2), \quad (1)$$

where $S = \frac{3}{2}$ (a spin quartet), $g = 2.00 \pm 0.05$, $|D| = 1950 \pm 2$ MHz, and $|E| = 550 \pm 2$ MHz. The principal axes x , y , and z of the fine-structure tensor were found along $[110]$, $[1\bar{1}0]$, and $[001]$, showing that the quartet state is of rhombic I symmetry in Kaplyanskii's notation.⁸ No hyperfine splittings were resolved. The solid curves in Fig. 2 show the computed angular dependences for the six equivalent orthorhombic centers as deduced with the above-mentioned parameter values. The lack of resonances for certain orientations could well be reproduced numerically simply by taking the intermixing of the sublevels and the microwave field polarization into account.⁹ Further, level-crossing effects were observed which could also be explained on the basis of the parameters of Eq. (1)

given above.⁹ In conclusion it is well established that (i) the emissive state is a spin-quartet state of nonaxial symmetry and (ii) the zero-field split sublevels have different radiative properties.

In discussing the origin of the spin-quartet excited configuration we first note that it gives rise to a narrow ZPL emission (at 657 nm) and thus must be characterized as a

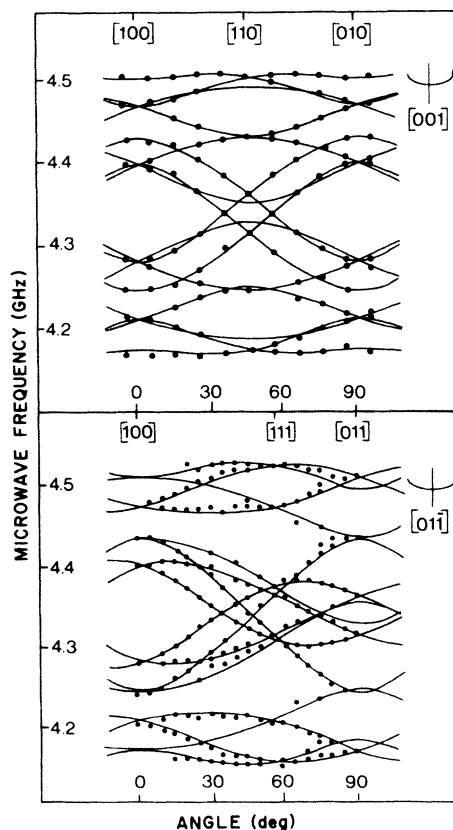


FIG. 2. Angular dependence of the ODMR spectrum of the $F-O_2^-$ pair in the presence of a magnetic field of 32 G in a (a) (100) plane and (b) (110) plane. Solid lines show the angular dependence as computed from Eq. (1) and the spin-Hamiltonian parameters given in the text.

deep (localized) state. From the orientation of the fine-structure main axes (along $[110]$, $[1\bar{1}0]$, and $[001]$), it is inferred that the localized defect in the fcc CaO crystal involves adjacent oxygen sites. A three-particle spin state is readily conceived for a O_2^- hole center in the excited $\sigma_g^2\pi_u^4\pi_g^2\sigma_u$ quartet state.¹⁰ The O_2^- molecular ion has been extensively studied as an impurity in alkali halides¹¹ but has not yet been reported in oxides.¹² In alkaline earth oxides, the O_2^- defect is expected to be analogous to either the V_k center, i.e., the self-trapped X_2^- hole in alkali halides, or the H center in alkali halides, i.e., interstitial X_2^- substitutional for a single halide anion (X^-). Very recently, theoretical arguments have been put forward¹³ implying that in simple oxides the F center is equivalent to an oxygen vacancy defect having bound two electrons in a level below the valence-band states. In this picture it is very likely that hole trapping in the crystal takes place near F -center sites. Extending this model to our system, we tentatively propose that the optical and ODMR data reported here were obtained for a nearest-neighbor oxygen vacancy-interstitial pair, i.e., an F - H pair, which can be excited into a luminescent spin-quartet state (cf. Fig. 3). It is remarked that the proposed structure is the analog in simple oxides of the F - H pair defect well studied in alkali halides.^{14,15} For the defect in Fig. 3 a spin-doublet electronic ground state is anticipated (as derived from the $\sigma_g^2\pi_u^4\pi_g^3$ ground-state configuration for the O_2^- ion) and thus the slow radiative decay of the excited quartet state is readily understood because, in first order, the electronic dipole transition from the excited quartet to the doublet ground state is spin forbidden. Furthermore, the model correctly predicts the disparity in the radiative properties of the $|\pm \frac{1}{2}\rangle$ and $|\pm \frac{3}{2}\rangle$ levels, respectively. Spin-orbit interactions selectively effect a coupling among the $|\pm \frac{1}{2}\rangle$ quartet sublevels and the spin-doublet $\sigma_g^2\pi_u^4\pi_g^2\sigma_u$ configuration (which is radiative), whereas no such spin-orbit-induced mixings are calculated for the $|\pm \frac{3}{2}\rangle$ sublevels.

We now turn to the time-resolved experiments performed on the system. By means of the method of microwave-induced delayed phosphorescence¹⁶ (MIDP) the individual lifetimes of the zero-field quartet-state sublevels were determined. In these measurements, the excit-

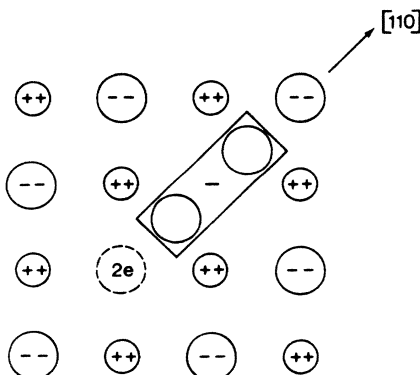


FIG. 3. Schematic structure of the F - O_2^- defect in a (100) plane of the CaO crystal.

ing laser light was chopped and in the shutoff time of the laser, a series of microwave pulses resonant with the quartet zero-field transition were applied. From the detected microwave-induced phosphorescence transients the individual decay rate constants of the two resonant spin levels could be determined.¹⁷ We find a lifetime of $230 \mu\text{s}$ for the (degenerate) pair of radiative levels and a lifetime of 3.8 ms for the (degenerate) pair of nonradiative sublevels. The observation of distinct decay times for the split zero-field sublevels implies that there is no thermal contact among the nondegenerate spin sublevels during the excited-state lifetime. Obviously, the effects of level crossing mentioned above are another manifestation of the existence of an unthermalized quartet state.

Finally, we mention preliminary results concerning the detection of spin coherent transients of the O_2^- hole defect in the excited quartet state. Microwave pulses resonant with the zero-field spin transition at 4340 MHz created a coherent superposition of the $|\pm \frac{1}{2}\rangle$ and $|\pm \frac{3}{2}\rangle$ quartet state sublevels. Spin coherence was measured optically by application of the probe pulse method.¹⁸ E.g., applying a microwave pulse sequence of the form $\pi/2$ - τ - π - τ - $\pi/2$ and scanning τ , the evolution with time of the spin-echo amplitude, at 2τ , could be monitored optically. The signal, displayed in Fig. 4, shows the echo decay. Its decay time of $38 \mu\text{s}$ is typical of the inverse homogeneous linewidth of the ODMR zero-field transition. On the other hand, the MIDP results showed that the characteristic spin-lattice relaxation time, T_1 , at 1.4 K , is longer than 3.8 ms and thus it follows that irreversible spin dephasing of the quartet spins is not determined by T_1 -type relaxation but involves a pure dephasing mechanism. Currently experiments are in progress in this laboratory to further investigate the nature of this pure dephasing process.

In summary, from optical and zero- and low-field ODMR experiments we have shown the optical, magnetic,

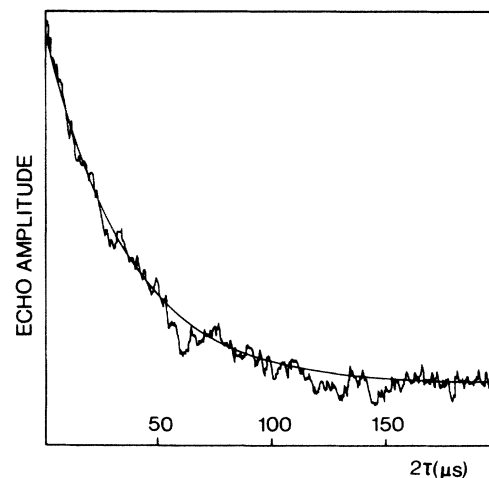


FIG. 4. Optically detected spin-echo decay for the F - O_2^- pair in the phosphorescent spin-quartet state. Microwave frequency: 4340 MHz ; photoexcitation is at 604 nm , photodetection is at 672 nm ; $T = 1.4 \text{ K}$. Solid line is best monoexponential fit with a decay time of $38 \mu\text{s}$.

and dynamical characteristics of a long-living emissive spin-quartet state in additively colored calcium oxide. The localized excitation is attributed to a vacancy-interstitial hole pair in a phosphorescent quartet state. The proposed defect structure is consistent with recently developed ideas concerning the *F*-center model in simple oxides.

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