Optically detected magnetic-resonance studies of oxygen vacancy defects in the phosphorescent spin quartet state in CaO

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A new zero-phonon line emission at 638 nm is observed from photoexcited additively colored calcium oxide crystals. By means of optically detected magnetic resonance it is established that the emission arises from a localized spin-quartet state with the following spin Hamiltonian parameters $|D| = 1030 \pm 5$ MHz, $|E| = 463 \pm 3$ MHz, and $g = 2.00 \pm 0.05$. The fine-structure principal axes are parallel with the [001], [$\bar{1}$10], and [110] crystallographic directions. It is proposed that the emission is from defects which comprise three adjacent oxygen vacancies which have trapped three electrons.

Localized phosphorescent states in additively colored alkaline-earth-metal oxides have been extensively studied.[1] Two-electron F-type defects with photoexcited triplet states have been proposed to account for most of the long-lived emissions. Very recently, the existence of a localized phosphorescent spin-quartet state was demonstrated after photoexcitation of yellow-colored CaO.[2] The photoexcited $S = \frac{3}{2}$ state gives rise to a zero-phonon line (ZPL) emission peaking at 657 nm. From the results of optically detected magnetic resonance (ODMR)] experiments the presence of an F-O_2^- hole center pair with a phosphorescent quartet state was invoked.

In this paper, optical and ODMR studies of yet another long-lived emissive spin-quartet state in additively colored calcium oxide are presented. The emissive state gives rise to a ZPL peaking at 638 nm and is attributed to an F^+-center aggregate which consists of three neighboring oxygen vacancies which have trapped three electrons.

The yellow-colored calcium oxide crystals were the same as in previous experiments.[3] The crystal was mounted in a slow-wave helix immersed in a pumped liquid-helium bath at a temperature of 1.4 K. Optical excitation of the crystal was by means of a Coherent Ar$^+$-ion laser pumping a dye laser (rhodamine 6G as a dye). Details of the experimental setup have been described elsewhere.[4]

Upon laser excitation near 569 nm, the crystal showed luminescence as displayed in Fig. 1(a). A ZPL peaking at 638 nm and peaks in the phonon sideband at 643, 646, 656, and 670 nm are observed. The excitation spectrum detected at 647 nm [cf. Fig. 1(b)] peaks sharply at 571 nm and has a broad weakly structured band at lower wavelengths. After chopping the exciting light, the time dependence of the emission intensity decay was measured. The experimental decay curve fitted a sum of two exponential functions with decay times of 7 and 23 ms, respectively. The slow radiative decay is suggestive of a spin-forbidden optical transition to the electronic ground state. Subsequently, zero-field and low-field ODMR experiments were performed. In these experiments, the microwaves were amplitude modulated (at 30 Hz) and phase-sensitive photodetection was applied. To improve the signal-to-noise ratio of the ODMR spectra, signal averaging over repeated scans was performed. At zero

field the ODMR spectrum detected at 647 nm shows a single transition as displayed in Fig. 1(c). The line occurs at a frequency of 2610 MHz, its width is 6 MHz [full width at half maximum (FWHM)]. The signal corresponds to a microwave-induced light increase. From microwave recovery experiments, the lifetimes of the sublevels involved in the zero-field ODMR transition were determined. While optically pumping the emissive state, a resonant microwave pulse was applied and the resulting phosphorescence transient was measured. The transient was well fitted with a biexponential function having characteristic time constants of 7 and 23 ms, respectively.

In the presence of a small external magnetic field $(H \leq 60$ G), the single ODMR signal is observed to split into several lines. The magnetic-field strength dependence for $\mathbf{H} \| [010]$ and the angular variations in a (001) plane for $H = 10$ G of the ODMR lines are shown in Figs. 2(a) and 2(b), respectively. All our ODMR data could be accounted for by computer simulations based on the following spin Hamiltonian:

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

where $S = \frac{3}{2}$, $|D| = 1030 \pm 5$ MHz, $|E| = 463 \pm 3$ MHz, and $g = 2.00 \pm 0.05$. The principal fine-structure axes x, y, and z were found along [001], [$\bar{1}$10], and [110], showing that the excited spin-quartet state is of orthorhombic I symmetry.[5] The absence of the ODMR lines near 2.61 GHz in our spectra is readily explained when the influence of the polarization of the applied microwaves of our experiments is considered more explicitly. Then, with the direction of the microwave field vector linearly polarized along [001] and the applied state magnetic field along [110], the transition moments of the resonances predicted near 2.61 GHz are calculated to be negligibly small.

The radiative properties of the quartet spin sublevels were investigated by measurement of the *polarization* of the microwave-induced light changes in the presence of an external magnetic field. For example, in the experimental configuration shown in Fig. 3, the resonance frequency of the $|a\rangle \leftrightarrow |d\rangle$ ODMR transition due to sites 3 and 4 is expected to be 2636 MHz when $H = 10$ G. However, a weak ODMR signal is observed when *unpolarized*-light changes are detected in the [010] direction. On the other hand, with a polarizer in the detection pathway, a

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microwave-induced phosphorescence intensity increase is monitored for light polarized parallel to the [100] direction and, simultaneously, a decrease (of a little less intensity) of the light polarized along [001]. These and all other data are consistent with the idea that both the upper and the lower spin-level pairs of the quartet state are radiative: one pair (lifetime 7 ms) emitting x-polarized and the other (lifetime 23 ms) z-polarized light, x and z being the molecular axes as given in Fig. 3.

The results of the low-field ODMR experiments show that the new emission reported here is due to a localized defect of nonaxial symmetry ($E \neq 0$). From the fact that the orientation of the quartet fine-structure main axis is along a [110] direction, it seems likely that the defect in the fcc CaO crystal involves neighboring oxygen sites. We now discuss a model implying a stabilized F^+-center aggregate which comprises three electrons trapped in three neighboring (colinear) oxygen vacancies (cf. Fig. 4).
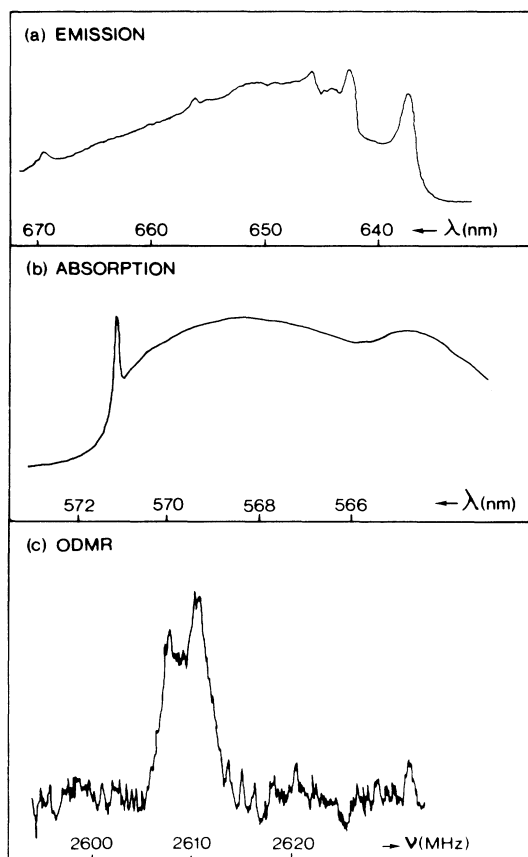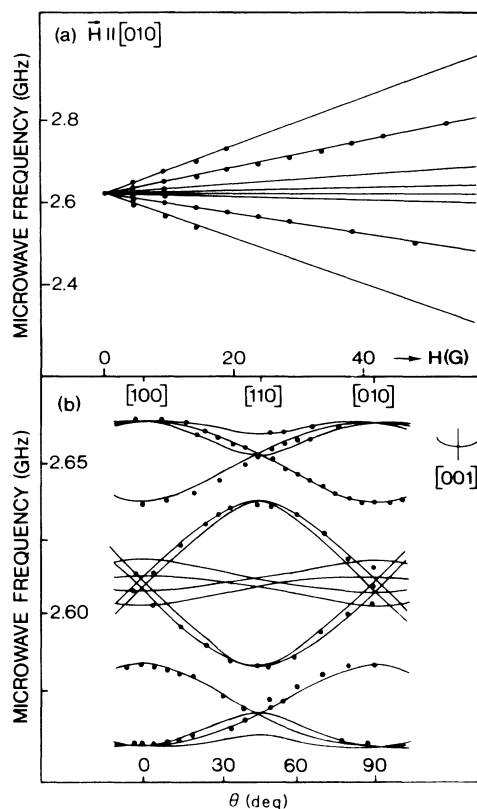

FIG. 2. (a) Magnetic-field dependence of the microwave-resonance frequency for the F_3^{3+} defect in its phosphorescent quartet state. The magnetic field is oriented parallel to the crystallographic [010] axis. (b) Angular dependence of the ODMR transitions when the magnetic field is rotated in the (001) plane. $H = 10$ G. All other experimental conditions as in Fig. 1(c). Solid lines in (a) and (b) show fittings calculated from Eq. (1) and the spin Hamiltonian parameters given in the text.
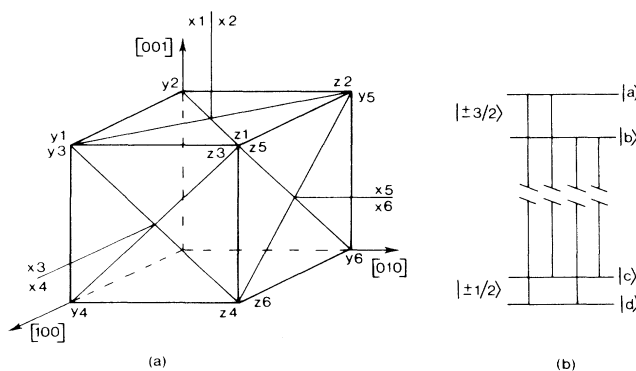

FIG. 1. (a) Luminescence spectrum of the F_3^{3+} defect in yellow-colored CaO after photoexcitation at 569 nm, $T = 1.4$ K. (b) Excitation spectrum of the F_3^{3+} defect as detected at 647 nm. (c) Optically detected magnetic-resonance spectrum at zero field of the F^+ trimer. Excitation wavelength, 569 nm; detection wavelength, 647 nm; phase-sensitive detection was at 30 Hz; $T = 1.4$ K.

FIG. 3. (a) Labeling, for each site, of the F_3^{3+}-defect fine-structure main axes. The magnetic-field vector and the excitation are along the [100] direction. Photodetection is along the [010] direction. (b) Labeling of zero- and low-field quartet state spin sublevels.
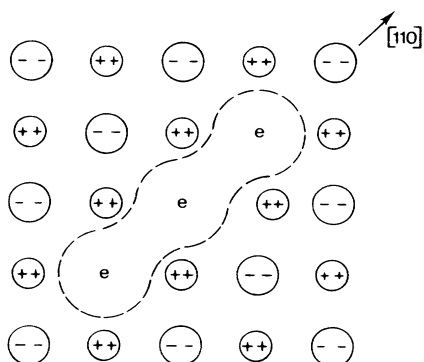
FIG. 4. Schematic picture of the $F_3{}^{3+}$ defect in a (001) plane of the CaO crystal.

In a simple Heitler-London approximation, the F^+-center trimer has a $(1s_a 1s_b 1s_c)$ ground state and $(1s_a 1s_b 2p_c)$-type lowest excited configurations.[6] For the latter, total-spin quantum numbers of $\frac{3}{2}$ or $\frac{1}{2}$ are possible, the quartet states having the lower energies. For a covalent quartet $(1s^2 2p_y)$ configuration, it is straightforward to show that

spin-orbit couplings cause admixtures with $(1s^2 2p_z)$ and $(1s^2 2p_x)$ doublet configurations.[7] Radiative decay from the excited quartet state to the $(1s_a 1s_b 1s_c)$ doublet ground-state configuration is then partially allowed for the $|\pm\frac{3}{2}\rangle$ sublevels (z polarized) and $|\pm\frac{1}{2}\rangle$ sublevels (x polarized). Furthermore, in the approximation of a point dipolar coupling between three electron spins, localized at the centers of oxygen vacancies along [110], 3.39 Å apart in CaO, we estimate $D = 1423$ MHz, which is to be compared with the experimental value of $D = 1030$ MHz.

In summary, from optical and low-field ODMR experiments we have found a new localized phosphorescent state in additively colored calcium oxide. The new emission is due to a long-living spin-quartet state of nonaxial local symmetry. It is proposed that the emission arises from a photoexcited F^+-center aggregate consisting of three adjacent oxygen vacancies containing three electrons.

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