Brief Reports

Nitrogen-related defect in CaO

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(Received 8 June 1994)

A center in thermochemically reduced CaO crystal associated with nitrogen has been characterized with electron paramagnetic resonance. The electron paramagnetic resonance spectrum of this center displays axial symmetry with a threefold hyperfine splitting. The spin-Hamiltonian parameters for this center are $S = \frac{1}{2}$, $I = 1$, $g_\perp = 1.9702(2)$, $g_\parallel = 1.9436(2)$, $|A_\perp| = 5.4(1)$ MHz, and $|A_\parallel| = 3.0(1)$ MHz, with symmetry axis along the $\langle 100 \rangle$ direction. A plausible candidate for this center is the $[F_N]^0$ center—an F^+ center next to a nitrogen substitutional impurity. This center is stable from 13 to 140 K.

Nitrogen is a common substitutional impurity in the covalent lattice of diamond.[1] Nitrogen associated molecular ion defects, such as NO, NO_2, etc., have also been reported in alkaline halides.[2] Here, we report on a nitrogen-related defect in ionic calcium oxide crystal. It was investigated with electron paramagnetic resonance (EPR) technique.

The CaO crystals used in the present study were grown at Oak Ridge National Laboratory using the arc-fusion method. The samples were further subjected to thermochemical reduction (additive coloration) by being heated in high temperature and under high pressure of calcium vapor. This produces F center (anion vacancy with two electrons) concentrations of the order of $10^{17}/cm^3$.[3]

The EPR spectra were taken with a Bruker Associates SRC 200 spectrometer operating at 9.76 GHz. Sample temperatures were controlled by an Airproducts (Model DMX-1A/15) closed-cycle helium refrigerator.

In Fig. 1(top), when the static magnetic field H is parallel to one of the cube axes—say [100], two sets of three lines are seen. In a general orientation three sets of three equally spaced lines of equal intensity are observed (Fig. 1, middle). One of these three sets has its resonance position remain fixed, while the other two sets moving toward each other as the H depart from the [100] direction. A coalescence is attained when the H is parallel to the [110] crystal direction (Fig. 1, bottom). These signals are stable from 13 to 140 K and the intensities show no dependence upon bleaching with light from 300 to 600 nm.

The orientation dependence of the resonances on crystal rotation around a $\langle 100 \rangle$ axis with respect to the magnetic field exhibit axial symmetry for both g and A tensor [Figs. 2(a) and 2(b)]. The EPR spectra were fitted to the following spin Hamiltonian:

$$H = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y)$$
$$+ A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) \tag{1}$$

with $S = \frac{1}{2}$, $I = 1$, and the following spin-Hamiltonian constants: $g_\perp = 1.9702$ and $g_\parallel = 1.9436$, $|A_\perp| = 5.4(1)$ MHz and $|A_\parallel| = 3.0(1)$ MHz.

Candidates for having $I = 1$ with considerable natural abundance are Li^6 (7.5%) and N^{14} (99.63%) only. Hyperfine interaction with Li^6 (7.5%, $I = 1$) nuclei should appear with the resonance of Li^7 (92.5%, $I = \frac{3}{2}$) nuclei. Therefore, we describe that this EPR spectrum (Fig. 1) corresponds to a $S = \frac{1}{2}$ defect having a hyperfine
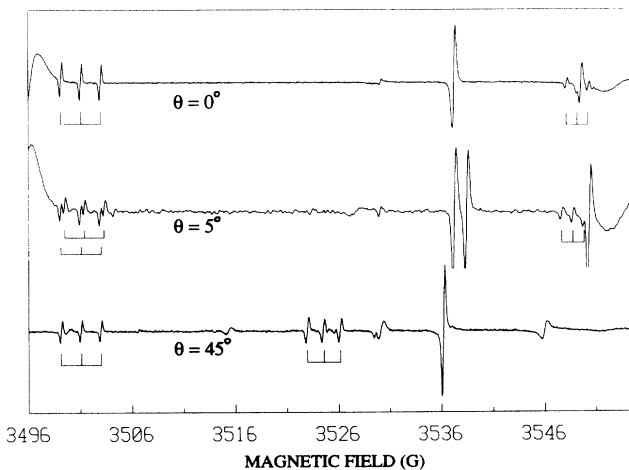

FIG. 1. The EPR spectra of CaO:N^+. θ is the angle between the magnetic field and the $\langle 100 \rangle$ crystal axis. Temperature: 13 K.

$$a = (A_\parallel + 2A_\perp)/3 \text{ and } b = (A_\parallel - A_\perp)/3 , \tag{2}$$

we obtain the hyperfine value of $a = 4.6$ MHz and $b = 0.8$ MHz.

The isotropic hyperfine constant a is related to the unpaired electron wave function at the N^{14} nucleus through the Fermi contact term

$$a = (8\pi/3h)[g_e\beta_e][g_N\beta_N]|\varphi(0)|^2 , \tag{3}$$

where $|\varphi(0)|^2$ is the electron-spin density at the N^{14} nucleus. Hence, $|\varphi(0)|^2$ is 980×10^{20} cm^{-3}.

From the anisotropic hyperfine interaction b, if we assume that is solely due to dipole-dipole interaction, we obtain an electron-nucleus distance of 1.92 Å, by using

$$b = (1/h)[g_e\beta_e][g_N\beta_N](1/R^3) , \tag{4}$$

where R is the separation of the two dipoles.

The signals from this center are too weak for the detection of superhyperfine interactions with Ca^{43} ($I = 7/2, 0.13\%$ abundance) or O^{17} ($I = 5/2, 0.038\%$ abundance) ion. Such interactions would be very useful for the development of a model for this nitrogen defect.

We can, however, suggest a model based on the symmetry and the magnitudes of the spin-Hamiltonian parameters relative to those of known defects in CaO crystal. Also, during the thermochemical reduction of the sample, a large concentration of anion vacancies were generated. Since no nitrogen centers have been reported for the stoichiometric CaO crystal, we assume that the nitrogen centers in our samples are associated with the anion vacancies and a plausible model is the $[F_N]^0$ center.

An electron trapped at an oxygen vacancy with a N^{1+}($1s^2, 2s^2, 2p^2$) ion replacing an adjacent Ca^{2+} ion would have the observed axial symmetry along the [100] crystal direction. In addition, the g value being $g_\parallel < g_\perp < g_e$ is typical of F-type centers. Since this center possesses local electrical neutrality, requiring no charge compensation, it would not trap any electrons liberated during bleaching into the F band of CaO and this would be stable under light illumination.

Finally, we compared the electron-spin densities at the N^{1+} nucleus and the electron-nucleus dipole-dipole distance with the same parameters of other known perturbed CaO F centers[4,5]—(Mg^{2+}, Li^{1+}). This comparison shows a reasonable consistency, that is
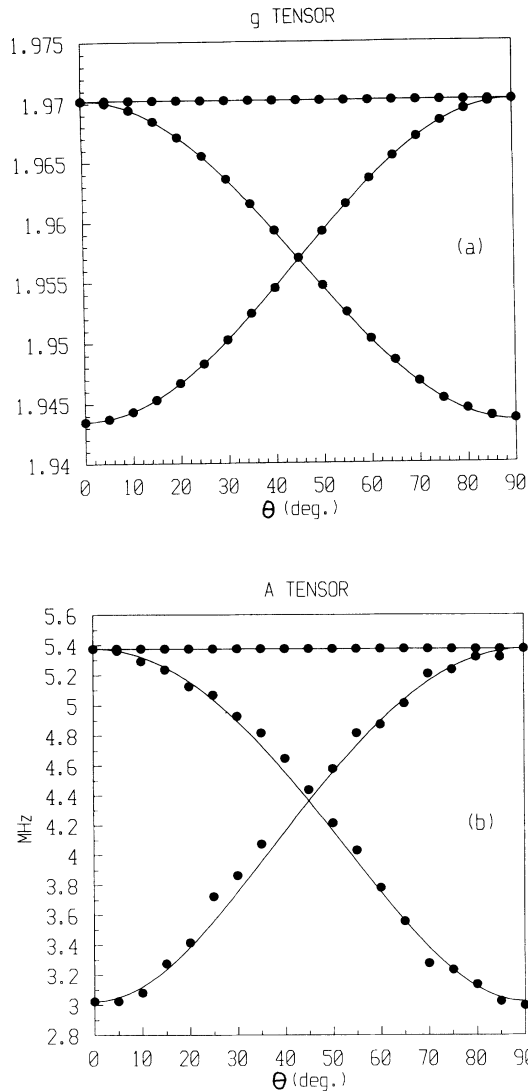

FIG. 2. (a), (b) Fully angular variation study of g and A tensor. Solid lines are calculated dependence. ● are experimental values.

interaction with the N^{14} ($I = 1$, 99.63%) ion. The hyperfine interaction with the N^{15} ($I = \frac{1}{2}$, 0.37%) isotope was not detected.

If we decompose the axial hyperfine A tensor into its isotropic and anisotropic components a and b, defined by

	$[F_{Li}]^0$		$[F_N]^0$		$[F_{Mg}]^+$
Dipole-dipole distance:	2.94	>	1.92	>	1.87 Å
Spin density at nuclei:	2.54	<	980	<	2040 ($\times 10^{20}$ cm^{-3}).

In summary, we have identified a nitrogen-involved defect center in CaO crystal and a plausible model for this defect is the $[F_N]^0$ center.

The CaO crystal was kindly supplied by Dr. Y. Chen of the Oak Ridge National Laboratories.

[1]W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. B **115**, 1546 (1959).

[2]Claude Jaccard, Phys. Rev. **124**, 60 (1961).

[3]R. Gonzalez, G. P. Summers, and Y. Chen, Phys. Rev. B **30**, 2112 (1984).

[4]J. F. Boas, T. P. P. Hall, and A. E. Hughes, J. Phys. C **6**, 1639 (1973).

[5]M. M. Abraham, Y. Chen, D. N. Olson, V. M. Orera, T. M. Wilson, and R. F. Wood, Phys. Rev. B **23**, 51 (1981).