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The $(CO_3Li)^{2-}$–Li^+ Defect in Synthetic Calcite: Wave Function and Model

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EPR spectra of the $(CO_3Li)^{2-}$–Li^+ defect in X-irradiated single-crystal calcite were observed at RT immediately after irradiation. From the resolved hyperfine structure due to the coupling of the unpaired electron spin and the nuclear spin $I = \frac{1}{2}$ of ^{13}C we were able to evaluate the O–C–O bond angle. Using the LCAO–MO method we have established the wave function of the single electron. This permitted us to propose a model for the $(CO_3Li)^{2-}$–Li^+ center.

Introduction

Single crystals of γ-, X-, and neutron-irradiated naturally occurring calcite ($CaCO_3$), which belongs to the $D_{3d}^6R\bar{3}c$ space group, contain a great variety of paramagnetic defects. Electron paramagnetic resonance (EPR) has been used by Marshall *et al.* at the Argonne National Laboratory to identify many of these radiation-induced centers. We shall only quote here the ionized carbonate ions which are axially symmetric along the crystalline *c*-axis (*1*).

We have reported on the existence of the CO_3^{3-}–Li^+ center (*2*) created by X irradiation at RT of specimens of synthetic single-crystal calcite grown by means of the traveling solvent melting zone method where Li_2CO_3 was used as a solvent (*3*). Later (*4*) we determined the bond angle and the wave function of this defect which also has C_{3v} axial symmetry along the calcite ⟨111⟩ axis. The ionized carbonate ion with its 25 valence electrons was found to be the main constituent of this defect. The associated Li^+ ion is located at an interstitial site in the Ca^{2+} plane above the vertex of the pyramidal CO_3^{3-} ion. Here and in the following, the terms "above" and "below" the C atom are used as defined in Fig. 1.

In the same crystal we also observed a CO_3^{3-} defect associated with three Li^+ ions. Its spectrum was only measured with the magnetic field direction parallel to the *c*-axis (*4*), and we have not attempted any further study of this defect.

Immediately after the irradiation one can also observe a CO_3^{3-} ion defect associated with two Li^+, which is unstable at room temperature (*5*). This paper is devoted to a closer study of this defect.

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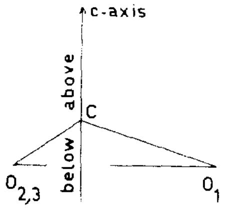

FIG. 1. Projection of the pyramidal ("up" distortion) CO_3^{3-} ion on a plane containing the oxygen O_1 and the c-axis, explaining what we mean by above (or below) the carbon atom.

Experimental and Spin Hamiltonian

Samples of dimensions $3\times3\times3\ \mathrm{mm}^3$ were X-irradiated at RT for about 10 hr, and then immediately studied at the same temperature. The defect of interest decays with a half-life of 2 days at 300 K. Its spectrum exhibits very narrow lines ($\Delta H \sim 20$ mG) which are easily saturated.

In our preliminary measurements made in X-band using a conventional 100-kHz field modulation spectrometer we were unable to observe the satellites originating from the coupling of the unpaired electron with the $^{13}C(I=\frac{1}{2})$ nucleus due to the low signal to noise ratio. The use of a more sensitive Varian E 109 spectrometer enabled us to see such satellites for $H\|c$ as well as for $H\perp c$. The use of 10-kHz field modulation increased the resolution.

When the Zeeman field vector is either parallel or perpendicular to the crystalline c-axis, the main spectrum consists of four sets of quadruplets (^{7}Li–^{7}Li pairs) and of three sets of quadruplets, the intensity of which is much weaker (^{6}Li–^{7}Li pairs). The maximum spread of each quadruplet is 0.5 G. As no angular dependence was found in a plane parallel to that containing the host ion, this defect must also have C_{3v} symmetry along the calcite ⟨111⟩ axis. This implies that the two Li^+ ions in question are located on the c-axis with respect to the ionized carbonate ion.

During the rotation about any axis perpendicular to c, it was not possible to follow the three quadruplets originating from ^{6}Li–^{7}Li pairs which are hidden by the CO_3^{3-}–Li^+ spectrum. Within each of the four sets due to ^{7}Li–^{7}Li pairs, the quadruplets collapse in a unique line $(55.7\pm0.5)°$ away from the c-axis.

The spectra due to ^{7}Li–^{7}Li pairs were fitted to the following spin Hamiltonian:

$$\mathcal{H}=\mu_B H\cdot\tilde{g}\cdot S+\sum_{i=1}^{3} S\cdot\tilde{A}_i\cdot I_i \qquad (1)$$

where $S=\frac{1}{2}$, $I_1=I_2=\frac{3}{2}$, and $I_3=\frac{1}{2}$, and with the constants listed in Table I. In this table we also report the constants describing the $H\|c$ and $H\perp c$ spectra due to ^{6}Li–^{7}Li pairs which could be determined. It is worthwhile to note that the exact sign of the various $^{(1)}A$ to $^{(3)}A$ components is not known. Nevertheless we know that if $^{(1)}A_\|$ and $^{(1)}A_\perp$ have the same sign (as also $^{(3)}A_\|$ and $^{(3)}A_\perp$), then $^{(2)}A_\|$ and $^{(2)}A_\perp$ will have different signs.

Spin Density on the Various Atoms

Each of the hyperfine tensors arising in the spin Hamiltonian (*1*) can be written as

$$\tilde{A}_i=A_{\mathrm{iso}}^{(i)}+\tilde{T}^{(i)}, \qquad (2)$$

where each $\tilde{T}^{(i)}$ is a traceless tensor. This leads to

$$^7A^{(1)}=34.93+\left|\begin{matrix}-4.51 & & \\ & -4.51 & \\ & & +9.02\end{matrix}\right|\mathrm{MHz},$$

$$^7A^{(2)}=0.013+\left|\begin{matrix}-0.277 & & \\ & -0.277 & \\ & & +0.555\end{matrix}\right|\mathrm{MHz},$$

and

$$^{13}A=309.9+\left|\begin{matrix}-52.6 & & \\ & -52.6 & \\ & & +105.2\end{matrix}\right|\mathrm{MHz}.$$

TABLE I

SPIN-HAMILTONIAN CONSTANTS FOR THE $(CO_3Li)^{2-}$–Li^+ CENTER IN $CaCO_3$

Defect	$g_\parallel$	$g_\perp$	$^{(1)}A_\parallel$ (MHz)	$^{(1)}A_\perp$ (MHz)	$^{(2)}A_\parallel$ (MHz)	$^{(2)}A_\perp$ (MHz)	$^{(13)}A_\parallel$ (MHz)	$^{(13)}A_\perp$ (MHz)
$(CO_3\,{}^7Li)^{2-}$–$^7Li^+$	2.00147 ±0.00003	2.00344 ±0.00003	43.95 ±0.09	30.42 ±0.07	0.568 ±0.004	−0.264 ±0.004	415.1 ±0.8	257.3 ±0.6
$(CO_3\,{}^6Li)^{2-}$–$^7Li^+$	2.00147 ±0.00003	2.00344 ±0.00003	16.68 ±0.05	11.54 ±0.05	0.568 ±0.004	−0.264 ±0.004	Not observed	Not observed

For an unpaired electron fully localized in the lithium atom 2*s* orbital, the Fermi contact term

$$K=\frac{8\pi}{3}gg_N\mu_B\mu_N|\psi_{2s}(o)|^2$$

was found to be equal to 289.97 MHz using the wave function given by Clementi (*6*). Comparing this value to 34.93 and 0.013 MHz we find that the unpaired electron spin density $(sd)_i$ in the two lithium 2*s* orbitals is 0.12 and 4.5×10^{-5}, respectively. In the case of ^{13}C with $K = 3102.4$ MHz the spin density in the 2*s* orbital is $^{13}(sd)\equiv\alpha'^2=0.10$. It can be seen that the spin density on what we shall define as the first Li^+ ion and that on the carbon atom are of the same order of magnitude.

Remark. The primed Greek letters stand for the coefficients of LCAO–MO in which the overlapping between the AO of the various constituents of the molecular ion *is not taken into account*. The α to δ Greek letters refer to Eq. (5).

We were unable to measure the hyperfine interaction between the electron spin $I=\frac{5}{2}$ of the ^{17}O nucleus as did Marshall *et al.* (*7*) in the case of a pure CO_3^{3-} in natural calcite. In the following we shall use $(sd)_O\equiv(\gamma_1')^2=0.012$ for the spin density on each oxygen and $(\gamma_2')^2=0.109$ for the $2p_{oi}$ character. Both these values are deduced from $^{17}A_\parallel$ and $^{17}A_\perp$ of Ref. (*7*).

O–C–O Bond Angle

The CO_3^{3-} molecular ion is the central part of the defect studied as also in the defects CO_3^{3-}–Li^+ (*2*) and CO_3^{3-} associated with three Li^+ (*4*).

Usually the bond angle θ is estimated using the equations:

$$\tan^2\phi=2\left[\frac{\lambda^2+1}{\lambda^2-2}\right],\qquad(3)$$

where ϕ is the angle subtended by the C_3 axis of the molecule with the C–O bond direction and

$$\theta=\cos^{-1}\left[\frac{1.5}{2\lambda^2+3}-0.5\right],\qquad(4)$$

where $\lambda^2=|\beta'|^2/|\alpha'|^2$ is the *p* to *s* hybridization ratio along the *z* direction (*8*) which is parallel to the calcite *c*-axis.

Using Clementi's $|2p\rangle$ wave function for the carbon we found

$$|\beta'|^2=\frac{^{13}T_{zz}}{\frac{4}{5}gg_N\mu_B\mu_N\langle r^{-3}\rangle}=\frac{105.2}{180.88}=0.582.$$

This leads to $\lambda^2\simeq5.822$ from which we have deduced the values of θ and ϕ quoted in Table II where they are compared to those corresponding to CO_3^{3-} and CO_3^{3-}–Li^+. In this table we also report the values of *h*, which represents the distance between the carbon atom and the plane of the oxygens, with the assumption that there is no displacement of the three oxygens of the carbonate ion.

TABLE II

BOND ANGLES (θ) OF VARIOUS CO_3^{3-} CENTERS OBSERVED IN $CaCO_3$

Defect	h (Å)	ϕ	θ
CO_3^{3-}–Li^+	0.369	106° 18′	112° 27′
CO_3^{3-}	0.357	105° 50′	112° 51′
$(CO_3Li)^{2-}$–Li^+	0.341	105° 09′	113° 26′

The strongest distortion of the planar CO_3^{2-} ion occurs in the CO_3^{3-}–Li^+ center, and the weakest in the $(CO_3Li)^{2-}$–Li^+ defect.

LCAO–MO Calculations and a Model of the Defect

We saw in a previous section that the spin density on the carbon and that on the first Li^+ ion have the same order of magnitude. We can then consider this lithium as a constituent of the molecular ion, the paramagnetic defect in question being $(CO_3Li)^{2-}$ associated with a second Li^+ ion.

The defect having the C_{3v} symmetry, the corresponding antibonding LCAO–MO, where some overlapping between the various AO is taken in account, can then be written as

$$|\psi\rangle = -\alpha|2s\rangle_c + \beta|2p_z\rangle_c - \frac{1}{3^{1/2}}\sum_{i=1}^{3}[\gamma_1|2s\rangle_{0i} + \gamma_2|2p_{x'}\rangle_{0i} - \gamma_3|2p_{z'}\rangle_{0i}] + \delta|2s\rangle_{Li}, \quad (5)$$

with the reference axes represented in Fig. 3.

In our previous work on CO_3^{3-}–Li^+ we have shown (*2*) that the lithium impurity is in an interstitial site in the Ca^{2+} plane above the vertex of the pyramidal CO_3 and that the spin density on it is only 0.029. Since the coefficients in Eq. (5) may be similar to those in the wave function for the CO_3^{3-}–Li^+ center given in Ref. (*4*) and since the distortion reported here is smaller, one cannot expect a larger spin density at this interstitial site in the present case.

Let us suppose now that this first lithium may be shifted toward the carbon. Then one finds that the distance $r = 0.59$ Å, where the spin density deduced from the wave function in Ref. (*4*) or from Eq. (7) is equal to the measured Li^+ spin density, is not convenient: it would be impossible for the Li^+ ion to be accommodated there.

The wave function to be determined in Eq. (7) is illustrated in Fig. 2. We see that its maximum will be reached below the carbon and will have a much larger value at the interstitial site below the original carbonate plane than at that above it. We therefore assume that the first Li^+, which has the largest spin concentration on it, is in the interstitial site in the Ca^{2+} plane below the carbon, i.e., at a distance $d = 1.42 + 0.34 = 1.76$ Å from the carbon. With such an assumption we are now able to determine the various coefficients of the defect wave function. To do this we have used the following six equations:

$$\frac{\beta}{\alpha} \equiv \frac{\beta'}{\alpha'} = 2.413, \quad (6.1)$$

$$\frac{\gamma_1}{\gamma_2} \equiv \frac{\gamma_1'}{\gamma_2'} = 0.33, \quad (6.2)$$

$$\int_v |\psi|^2\,dv = \alpha^2 + \beta^2 + \gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \delta^2 + R = 1, \quad (6.3)$$

where R stands for the overlap integrals $_c\langle 2s|2s\rangle_{0i}$ and $_c\langle 2s|2p_{x'}\rangle_{0i}$ which were evaluated using the method given by Barnett and Coulson (*9*) to solve two center integrals;

$$|\psi(o)|^2 = (\alpha')^2|\psi_{2s}^c(o)|^2 = (0.652)^2, \quad (6.4)$$

$$|\psi(l)|^2 = \frac{(\gamma_1')^2}{3}|\psi_{2s}^o(o)|^2 = (0.176)^2, \quad (6.5)$$

where l is the C–O distance,

$$|\psi(d')|^2 = (sd)_1|\psi_{2s}^{Li}(o)|^2 = (0.142)^2, \quad (6.6)$$

and d' represents the C–Li^+ distance for the first lithium. In Eqs. (6.4) and (6.5) the contribution of $|2s\rangle_{Li}$, which is very weak, was neglected.

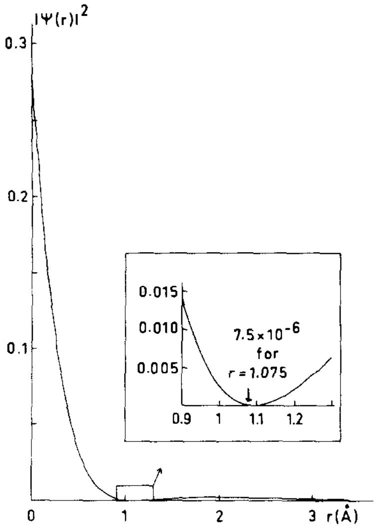

FIG. 2. Plot of $|\psi(r)|^2$. The insert, corresponding to a region around the Ca^{2+} plane above the carbon, shows the existence of a first minimum very close to zero at $r = 1.09$ Å.

Finally one obtains the following LCAO–MO:

$$|\psi\rangle = -0.215|2s\rangle_c + 0.518|2p_z\rangle_c + \frac{1}{3^{1/2}} \sum_{i=1}^{3} |0.045|2s\rangle_{Oi} + 0.137|2p_{x'}\rangle_{Oi} - 0.744|2p_{z'}\rangle_{Oi} + 0.379|2s\rangle_{Li}. \quad (7)$$

From electrostatic reasons it is evident that the second Li^+ cannot also be below the carbon. Effectively if the two lithiums were on the same side with respect to the CO_3^{2-} plane, the distortion resulting from the trapping of an extra electron would take place toward the positive charges on the two lithiums. Consequently the position of the second Li^+ ion, above the carbon, must be sought solving the equation:

$$|\psi(r_1)|^2 = (sd)_2|\psi_{2s}^{Li}(o)|^2 = 7.5 \times 10^{-6}, \quad (8)$$

where r_1 is the C–Li^+ distance.

The variation of $|\psi(r)|^2$ is shown in Fig. 2. It can be seen in the insert that there exists a minimum smaller than 7.5×10^{-6} for $r \simeq 1.09$ Å. Then three values of r are solutions of Eq. (8).

The first solution which is almost equal to 5.2 Å is less likely because this second lithium would be too far away to cause a distortion toward it. In such a situation, the distortion would take place toward the closest Li^+ leading to the CO_3^{3-}–Li^+ defect.

The two other values ($\simeq$1.11 and 1.075 Å) are close together. Nevertheless we think that $r_1 = 1.075$ Å, which almost corresponds to $h + r_1 = 1.42$ Å (the perfect interstitial site in the Ca^{2+} plane) is the most likely. Figure 3 shows the model we propose for the $(CO_3Li)^{2-}$–Li^+ center.

Discussion

When an extra electron is trapped by the CO_3^{2-} ion and creates the CO_3^{3-} paramagnetic defect, there is an equal probability for the carbon to move up (referring to Fig. 1) or down. When an interstitial Li^+ ion is located in the Ca^{2+} plane above the carbonate plane, the carbon atom with its net negative charge will be attracted by the positive impurity ion. Consequently, the distortion of the CO_3 will

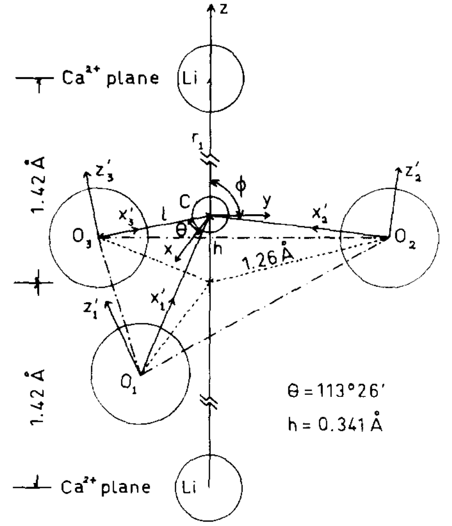

FIG. 3. Model proposed for the $(CO_3Li)^{2-}$–Li^+ center (not to scale) and reference axes used for the calculations.

be upward and greater than in the pure CO_3^{3-} case. When two lithiums are present, one on each side of the CO_3^{2-} plane, the probability for an up or down distortion is again the same. The presence of the positive charge carried by the lower lithium will then act as a restraint and the CO_3 pyramid will now be flatter than in the CO_3^{3-}–Li^+ and pure CO_3^{3-} cases.

The poor thermal stability of the $(CO_3Li)^{2-}$–Li^+ center compared to that of CO_3^{3-}–Li^+ can be explained by considering that its total negative charge is only one instead of two for the host anion and CO_3^{3-}–Li^+.

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