An $O_2^-$ molecule ion in CaF$_2$: Structure and dynamical features

H. Bill

Department of Physical Chemistry, Sciences II, University, 1211 Geneva 4, Switzerland
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This experimental study reports EPR and ENDOR results of an $O_2^-$ molecule ion in natural yellow fluorites. The $O_2^-$ is associated with a sodium neighbor and a calcium neighbor. This cluster performs a rapid switching movement between energetically equivalent positions. The resulting dynamical features in the EPR spectrum are investigated with the aid of the stochastic Liouville equation.

INTRODUCTION

A few years ago an $O_2^-$ center was identified in natural yellow fluorites. Its electron paramagnetic resonance (EPR) spectrum recorded at 78 K and an optical absorption band peaking at 2300 Å correlates with the EPR spectrum of paramagnetic molecules. This experimental study reports EPR and ENDOR results of an $O_2^-$ molecule ion in natural yellow fluorites. The $O_2^-$ is associated with a sodium neighbor and a calcium neighbor. This cluster performs a rapid switching movement between energetically equivalent positions. The resulting dynamical features in the EPR spectrum are investigated with the aid of the stochastic Liouville equation.

EXPERIMENTAL TECHNIQUES

Natural yellow fluorites were obtained from several sources. The crystals were cut into pieces and the homogeneous parts were selected. Samples were then cut to shape from these latter parts. The EPR investigation was performed on an X band spectrometer (Varian V-4500) in conjunction with the necessary low temperature equipment of our design. The sample temperature was monitored with a calibrated germanium resistance thermometer at temperatures below 30 K and with an Au-0.3% Fe vs chromel thermocouple above this temperature.

The ENDOR spectrometer has been built in the laboratory. The device is fully computer controlled giving the possibility to do signal averaging. This feature has been used extensively because the intensity of the signals was rather weak due to the relatively short relaxation times caused by the motional effects. Furthermore, the available concentration of the centers was not a free parameter.

EXPERIMENTAL RESULTS

Structural information

The detailed experimental study confirmed that the center involves an $O_2^-$ molecule ion. But the model proposed in the preliminary note has to be supplemented. A sodium ion and probably a Ca$^{+}$ neighbor are associated with the $O_2^-$. A highly schematic drawing is presented in Fig. 1. It does not represent the real model but is only intended to be an aid during the subsequent discussions.

The center is not paraelastic. It does, however, reorient between energetically equivalent positions as discussed later in the paper.

$g$ values

The EPR spectrum is orthorhombic above 15 K. The principal axes of the $g$ tensor are those labeled $x$, $y$, $z$ in Fig. 1. Typical records are shown in Figs. 2 and 3. This latter figure presents the evolution of the EPR spectrum observed with $B || [101]$ when the crystal is cooled from 15 to 4.2 K. A detailed investigation of the angular dependence of the spectrum at 4.2 K proved...
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![Schematic representation of the O$_2^-$ center in CaF$_2$.](image)

The coordinate system in the upper right corner defines the orientation of the $g$ tensor in the low temperature spectrum.

![EPR spectrum, $T=78$ K, B parallel to a $C_4$ crystal axis.](image)

The structure of the component labeled $g_{22}$ is due to the hyperfine interaction with four equivalent F neighbors. The same spectral component $g_{22}$ but recorded at 4.2 K. The four F neighbors form two inequivalent sets. Also appearing in the spectrum are lines due to cubic Gd$^{3+}$ and due to the O$_2^-$ molecule ion always present in the yellow fluorites.

![Experimental ENDOR spectra. B parallel to z, $T=4.2$ K.](image)

The label $\mu$ sums over the fluorine neighbors. The principal values of $g$ have been determined at 78 K (high temperature spectrum) and at 4.2 K (low temperature spectrum). Table I summarizes the experimental parameters.

### Hyperfine interaction

**High temperature spectrum**

The EPR spectra recorded with $B$ parallel to a $C_4$, $C_3$, or a $C_2$ crystal axis present components which split into a partly resolved structure due to the hyperfine interaction with the first-neighbor fluorine ions. A par-

![Diagram showing the coordinate system in the upper right corner defines the orientation of the g tensor in the low temperature spectrum.](image)

The symmetry is now $C_s$. The corresponding EPR spectrum shall be termed the low temperature spectrum whereas the former one is the high temperature spectrum. The EPR and ENDOR results were fitted by the following spin Hamiltonian (the symbols have their usual meaning):

$$\mathcal{H} = \beta_e B g S + \sum_{\mu} (S A_{\mu} I_{\mu} - g_{\mu} g_{Na} B I_{Na}) + S A_{Na} I_{Na} + I_{Na} P I_{Na}$$

$$- g_{Na} g_{Na} B I_{Na} = \gamma_S + \sum_{\mu} \gamma_{\mu} + \gamma_{Na},$$

(1)

where $S = 1/2$, $I_{Na} = 1/2$, $I_{Na} = 3/2$.

The label $\mu$ sums over the fluorine neighbors. The principal values of $g$ have been determined at 78 K (high temperature spectrum) and at 4.2 K (low temperature spectrum). Table I summarizes the experimental parameters.

### Table I. EPR experimental $g$ values of the high temperature spectrum (a) and the low temperature spectrum (b).$^*$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>Average $g$ over $\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>2.0069</td>
<td>1.9994</td>
<td>2.1124</td>
<td>2.1124 $^*$</td>
</tr>
<tr>
<td>4.2</td>
<td>2.0054</td>
<td>1.9991</td>
<td>2.1136</td>
<td>2.1136 $^*$</td>
</tr>
</tbody>
</table>

$^*$Errors: $g$ values $\pm 0.003$, angle $\pm 0.4^\circ$; the $g$ values (b) are considered to be the "true" ones of the center in this paper.
neighbors, neighbors,neighbors. Suppose we consider the Table II. (a) B was rotated parallel to \((x', z')\). The ordinate gives the frequency of the transitions. Only the high line position and the free precession frequency of the sodium nucleus.

particularly well resolved structure is shown in Fig. 2(a). For other directions of B a second derivative recording was necessary.

The observed structures are consistently explained in terms of the hyperfine interaction if the \(F^-\) neighbors, labeled 2, 3, 4, 5 in Fig. 1, are equivalent within the resolution of the EPR experiments (0.6 G).

Low temperature spectrum

A detailed ENDOR study has been performed.

Na+. The ENDOR investigation made possible the identification of this nucleus and it showed that the Na+ is a neighbor of the \(O^2^-\) molecule ion. The three interaction terms in the spin-Hamiltonian [Eq. (3)] are small with respect to the EPR line width for this ion. For this reason all three quadrupolar components of the Na+ ENDOR spectrum are observed simultaneously. An experimental record is shown in Fig. 3(a).

Figure 4 gives the angular dependence of this spectrum observed when B rotates in the \((x', z')\) plane and the \((y, z)\) plane, respectively. The latter plot demonstrates that \((x', z')\) as defined in Fig. 1 is also a symmetry plane of the Na+ interaction tensors. The spectra have been parametrized with the part \(3CQ + 3C_n^0\) of the total spin Hamiltonian. The experimental constants are collected in Table II and the Appendix furnishes some indications regarding the parameterization. It is noteworthy that \(A_n^0\) is not parallel to \(P\) and that both tensors are oriented differently from the \(g\) tensor. The signs of the quadrupole constants have been determined experimentally by taking advantage of the fact that the three transitions are observed simultaneously in the ENDOR spectrum. Is there only one Na+ involved per center? This question seems trivial. Let us recall, however, that it is not possible under the usually applied growth methods and treatment techniques to produce the center in the laboratory. A detailed search for a second sodium neighbor has been performed—without success. The only remaining possibility is that there are two magnetically equivalent nuclei. Such a pair could only be identified by ENDOR due to the mutual magnetic coupling between the partners through the electronic wave function. This effect is of second order in the hyperfine interactions and produces a splitting of the order \(|\langle x|x\rangle|8\omega_n \approx 1\) kHz. This corresponds to approximately 10% of a typical ENDOR line width. Although the experimental lines showed no structure which could be traced back to this effect the possibility of two equivalent nuclei cannot be ruled out totally (see also the discussion at the end of the paper).

\(F^+\) neighbors. The low temperature EPR spectrum still shows partly resolved structure of some of its components. But this structure is of lower symmetry and indicates that all of the \(F^+\) neighbors are no longer equivalent.

ENDOR experiments performed at 4.2 K show that they form two inequivalent sets. The following geometrical relationship can be established between the orientation of the \(O_2^-\) center and the position of the different \(F^+\) neighbors. Suppose we consider the \(O_2^-\) having its magnetic axes oriented as shown in the insert of Fig. 1. Then, the nuclei labeled 3 and 5, respectively, form one set. They are associated with the ENDOR line labeled \(a\) in Fig. 3(b). The other set embracing the nuclei labeled 2 and 4, respectively, produces the line labeled \(b\).

This correspondence can be established for the following reasons: (i) The EPR spectrum is of low symmetry and the \(g\) tensor is rather strongly anisotropic. (ii) The ENDOR investigation furnished the principal values and the orientation of the hyperfine structure tensors. (iii) For particular directions of B it was possible to determine the number of equivalent \(F^+\) neighbors from the EPR spectrum.

Great care was taken to align the static field properly parallel to the principal crystal axes. The misalignment was smaller than 0.3° for the EPR experiments and smaller than 0.1° for the ENDOR experiments. The ENDOR results have been parametrized by using the appropriate terms of Eq. 1 as described in the Appendix. The results are collected in Table II.

MOTIONAL EFFECTS

The EPR results suggest that the molecule possesses two distinguishable equilibrium orientations of its magnetic moment and that it jumps between them. The movement is limited to the \((x', y')\) plane because no effects are observed in the spectra which correspond to a movement perpendicular to this plane. The two config-
TABLE II. ENDOR results with the following orientation of the $g$ tensor: Euler angles are $\alpha' = 0, \beta' = 3.6^\circ$, and $\gamma' = 0$ with respect to the axes $x, y, z$ of Fig. 1. a

<table>
<thead>
<tr>
<th>Center</th>
<th>T(K)</th>
<th>Nucleus</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_s$</th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>Ref. b</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_{2}^-</td>
<td>4.2</td>
<td>Na$^+$</td>
<td>2.123</td>
<td>-1.006</td>
<td>-1.117</td>
<td>-3.103</td>
<td>-0.435</td>
<td>+0.355</td>
<td>+0.08</td>
<td>180</td>
<td>2.7</td>
<td>180</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.3</td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td>$F$</td>
<td>2.5</td>
<td>+11.48</td>
<td>5.71</td>
<td>5.78</td>
<td>5.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-67.1</td>
<td>60.5</td>
<td>59.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>+5.79</td>
<td>3.242</td>
<td>3.53</td>
<td>3.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83.6</td>
<td>116.8</td>
<td>-70.3</td>
<td></td>
</tr>
<tr>
<td>$V_F$</td>
<td>4.2</td>
<td>+1.64</td>
<td>-1.03</td>
<td>-0.67</td>
<td>-3.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.15</td>
<td>0</td>
<td>0</td>
<td>(b)</td>
</tr>
</tbody>
</table>

aEuler angles $\alpha, \beta$, and $\gamma$ refer to the axes $x, y, z$ of Fig. 1 for the sodium nucleus. They refer, however, to the three four-fold axes of the figure for the $F$ neighbors. The $V_F$ center data have been included for convenience comparison with this geometrically somewhat similar center.

bReferences: (a) this paper, (b) Ref. 7.

The stochastic Liouville equation reads for our center

$$\delta \rho(\theta) = - (i/\hbar) [\mathcal{H}(\theta), \delta \rho(\theta)] - \mathcal{T} \delta \rho(\theta).$$

(2)

$\delta \rho(\theta) = \rho(\theta) - \rho_{eq}(\theta)$ is the difference between the density matrix and its Boltzmann equilibrium value. $\mathcal{H}(\theta)$ is the electronic Zeeman part of the spin Hamiltonian embodying the contributions of both equilibrium positions. The associated Liouville operator is defined $\mathcal{L}(\theta) = [\mathcal{H}(\theta), \ldots]$. The transition matrix $\mathcal{T}$ is defined by the Markov equation

$$\frac{d}{dt} \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \left(\mathcal{T}\right) \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \begin{pmatrix} 0 & 0.5 & -0.5 \\ 0.5 & -0.5 & 0 \end{pmatrix} \begin{pmatrix} P_1 \\ P_2 \end{pmatrix},$$

(3)

where $\omega_e$ is the jump frequency.

The formal solution of Eq. (2) is introduced into the expression of the correlator of the magnetic moment $G(t) = \text{Tr} \left[ M_s(t) M_s \right]$. The Fourier integral expressing the susceptibility within linear response theory by $G(t)$ is solved by a Laplace transform. The resulting expression is

$$\frac{M_s}{B_s} = \chi_{\text{ex}}(\omega, B) = \frac{C \omega}{(2S + 1)kT} \text{Tr} \left\{ P_s S_s \frac{1}{[\omega - \mathcal{H}(\theta)] - (\mathcal{T} + \gamma) S_s} \right\}. $$

(4)

$B_s$ is the microwave field acting along an $x$ axis perpendicular to $B$. The trace is over the spin space and the two dimensional orientational space. The matrix $\gamma$ is diagonal and represents the static (ad hoc) line width contribution due to the usual relaxation mechanisms.

The matrix resulting from Eq. (4) was written down in the operator basis $\{ \frac{1}{2} M_{Jx} \}$ times the two-dimensional orientational basis labeled by $j$. It was then evaluated on a computer and the results directly plotted by a graphic plotter.

A set of computed spectra is reproduced in Fig. 5(b). They have been calculated with $B$ being oriented as given in the figure and by using the parameters of Table I. The jump frequency is an adjustable parameter. It was
chosen for each spectrum to obtain closest fit with the corresponding experimental record of Fig. 5(a). The agreement between the two sets is quite good when the evolution of the spectrum with temperature is considered. Detailed comparison of the shape of the spectra, however, reveals some discrepancy. The calculated lines are essentially Lorentzians whereas the experimental spectra consist of nearly Gaussian components both in the low temperature and in the high temperature region. They are inhomogeneously broadened by the unresolved hyperfine interaction. In addition the width of the individual homogeneous packet is not only determined by the motional relaxation but also by the more usual spin–phonon relaxation mechanisms which prevail in the low temperature limit. This is taken into account by the matrix $\gamma$ in Eq. (4).

Possible improvements of the model (4) include the rather simple but unsatisfactory possibility to convolve the calculated line shape with a Gaussian envelope function. A better way to follow is probably the introduction into (4) of as many hyperfine structure interaction terms as possible with respect to available computer space. This procedure is actually in progress. This latter approach might also give a solution to another discrepancy. The experimental line labeled 9.3 K in Fig. 5(a) is not symmetrical because of the anisotropic hyperfine interaction. In spite of these objections the model (4) seems to account qualitatively correctly for the motional effects observed.

A word is in order here concerning the way the experimental lines have been fitted by the calculated ones. Above the transition region the line intensity is a good criterion as it depends quite strongly on the jump frequency. In the low temperature limit this criterion is useful near to the transition region. The calculated line intensities were plotted as a function of the jump frequency parameter from the low temperature to the high temperature limit. The experimental intensities were suitably fitted to this curve yielding the results shown in Fig. 5. The experimental line intensities were corrected for the intrinsic temperature dependence.

The relation $\omega_0 = \omega_0(T)$ thus obtained was fitted by an Arrhenius type relation $\omega_0 = \omega_0 \exp(-E/kT)$ with $E/k = 8.8$ K and $\omega_0 = 1.5 \times 10^8$. The confidence of this fit to the results of the Fig. 5 is 99%. The same results were in addition fitted by the relation $\omega_0 = c/T$ with $c = 6.3 \times 10^8$ K sec$^{-1}$. The confidence is 97% for this relation. The Arrhenius type relation is deduced from a model which involves thermal excitation of the molecule ion over a barrier whereas the second relation is typical for a phonon assisted tunneling process in the one phonon limit. A supplementary detailed theoretical and experimental investigation would be needed to decide between the two processes. Nevertheless, the low transition temperature observed in the EPR spectrum suggests a rather shallow barrier height of the double well potential.

**DISCUSSION**

**Model of the center**

Among the simple possibilities the following two models are strongly favored by the experimental results presented in this paper. One of them relies strongly on the structure depicted in Fig. 1 and consists of a Ca$^{2+}$–O$_2$–Na$^+$ cluster. This structure performs a kind of switching motion between two equilibrium positions. The justification stems from the following facts. The distance between the Ca$^{2+}$ ion and the Na$^+$ is probably smaller than the regular lattice spacing. From the sodium hyperfine data a distance Na$^+$–O$_2$ of 1.7 Å was estimated. In addition the crystal radii of the two ions are of very similar magnitude. By assuming crudely that the Ca$^{2+}$ is at the same distance as the sodium ion with respect to O$_2$ one obtains 3.4 Å instead of the 3.84 Å between the corresponding regular lattice points.

The Ca$^{2+}$ ion is likely to be more strongly stabilized near its normal equilibrium position by the Madelung potential because of the higher charge state. Therefore, the Na$^+$ end of the cluster has room to move and it approaches for instance the F$^-$ neighbors labeled 2 and 6 until the electronic correlation effects lead to the stabilization of the cluster in a slightly rotated position. Necessarily a second and equivalent equilibrium position of the cluster is attained when its Na$^+$ end approaches the F$^-$ ions labeled 3 and 7, respectively, in our specific case. The movement is probably limited to the $(x', z')$ plane because it is energetically more favorably with respect to the Madelung potential.

This structure complies with the experimental information regarding the $g$ tensor and it does not contradict the ENDOR results. A different model is obtained when both cations are assumed to be sodium ions. Again, the shorter distance between the two Na$^+$ ions involved this time enables the cluster to move around. There are, however, more possible equilibrium positions in the plane than for the previously discussed model. A translational movement is possible ("up" and "down" in Fig. 1) and also rotational displacements. The "up" and "down" movement is not compatible, however, with the experimental results concerning the $g$ tensor whereas the librational movement is not in line with the ENDOR experiments. For these reasons the second model is less likely to apply than the first one.

The reason why the cluster moves away from the regular lattice sites is the same for both models. The cluster is slightly too small to fit into the space available. As the electrostatic field cannot stabilize the cluster this one moves towards the surrounding anions until the electronic correlation energy suffices to stabilize the cluster in a certain position. This phenomenon has a slight resemblance to the adsorption of a molecule on a surface.

**Electronic structure**

The electronic energy levels of the free O$_2$ molecule ion have been calculated theoretically by Krauss et al. The results demonstrate that a low symmetric ligand field of usual strength does not suffice to produce a bent bond of the O$_2$. Many published experimental results on the O$_2$ incorporated into several host matrices confirm this result. Most of them show in addition that the magnetic properties of its ground state are very well accounted for by the model of Känzig and Cohen and of
Zeller and Kanzig\textsuperscript{4} which only considers the $X^1\Pi$ and the lowest excited $^3\Sigma^+_e$ type level. In addition to the spin-orbit interaction the ligand field due to the surroundings is the perturbation acting within the three states. The $g$ values are expressed within this model as functions of an effective ligand field splitting $\Delta$, effective angular momentum matrix elements $I_a$, $I_b = I_c$ and a spin–orbit coupling constant $\lambda$. When the experimental values of the Table I are inserted into the relevant expressions\textsuperscript{16} one obtains $I_a = 0.96$, $\lambda/\Delta = 0.058$, and $I_b/E_s = 0.0035$. Therefore by choosing $\lambda = 180$ cm$^{-1}$ the splitting $\Delta = 3100$ cm$^{-1}$.\textsuperscript{15} The quantity $E_s$ is the energy separation between the unperturbed ground level and the excited level involved. The orbital of the magnetic electron is in this model almost purely $|\pi_{xy}\rangle$ type. It is parallel to $g_z$ and therefore oriented perpendicularly to the plane of the molecular motion. The splitting $\Delta$ is large compared to the corresponding values reported for the $\text{O}_2^+$ in the alkali halides\textsuperscript{15} typically by a factor of five larger. The cations of the cluster are the principal sources of this rather strong ligand field.

**Hyperfine interactions**

This section presents qualitative arguments which justify the signs of the Na$^+$ hyperfine interaction constants as given in the Table II. The anisotropic part of $A_{Na}$ is remarkably axial with the symmetry axis pointing towards the $\text{O}_2^+$. This contribution seems to be almost purely dipolar because the $|ns\text{Na}\rangle$ and $|np_{\pi}\text{Na}\rangle$ orbitals ($i = x, y, z$) are almost orthogonal to the magnetic orbital. This relation would be exact if the symmetry of the ligand field were exactly $C_{3v}$. The classification is as follows:

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$C_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2^+$</td>
<td>$</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>$</td>
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<td></td>
<td>$</td>
</tr>
</tbody>
</table>

Under these assumptions the signs of the anisotropic part are given in Table II. Then $A_{Na}$ is negative. This is in agreement with the geometry of the magnetic orbital which implies that configuration interaction must be acting to produce the observed isotropic spin density at the sodium nucleus.

A value of the classical dipole contribution to the hyperfine interaction has been estimated by computing averaging the dipole–dipole operator over the $|\pi_{xy}\rangle$ orbital of the $\text{O}_2^+$ molecule ion. The Na$^+$ was assumed to be at the regular lattice distance of 1.92 Å. The value $A_{Na}/2 = A_0 = 1.22$ MHz was obtained. By scaling this value to the experimental anisotropic hyperfine constant a distance of 1.7 Å is found.

The $V_F$ center in CaF$_2$ reported earlier\textsuperscript{1} involves an $\text{F}_2^-$ molecule ion interacting with a Na$^+$ neighbor. This center has a great deal of similarity with the presently reported one regarding the sodium hyperfine interaction and the mechanisms producing this effect. For this reason the relevant experimental quantities of the $V_F$ center have been included into Table II.

**ACKNOWLEDGMENT**

The author is indebted to Professor H. Stalder and to Doctor A. Chermette for the beautiful sample crystals. A discussion with Professor J. Freed, Cornell University, New York, USA is gratefully acknowledged.

**APPENDIX: PARAMETERIZATION OF THE ENDOR SPECTRA**

**Sodium nucleus**

The sub Hamiltonian from Eq. (1) is $\mathcal{H}_g + \mathcal{H}_{Na}$. $\mathcal{H}_g$ is diagonalized first. A new set of axes was then introduced with the $z''$ axis determined by the quantization axis of $S$ found by the diagonalization. The new $y'$ axis was chosen in the original $(x,y)$ plane. Each tensor of $\mathcal{H}_{Na}$ was transformed according to

$$A^\prime = (B_{p1}) (A_{Na})(A_{c})(A_{s})],$$

$$P^\prime = (A_{c}) (A_{B}(P)(A_{s}).$$

$(A_{p})$, $(A_{c})$, and $(A_{s})$ are the 3 x 3 transformation matrices from the crystal axes to the new axes, from the principal axes to the crystal axes of $A_{Na}$ and of $P$, respectively.

The nuclear spin vector $I$ was quantized along the new $z''$ axis too. Due to this fact the resulting 4 x 4 matrix also contains off-diagonal nuclear Zeeman terms. This 4 x 4 matrix represents a very good approximation for the parameterization of the spectra because the terms proportional to $S_z$ and $S_y$ of the transformed Hamiltonian contribute negligibly. A computer program was written which performs the transformations, calculates the ENDOR transitions and plots the results as a function of $B$.

The single nucleus approach is a good approximation because the coupling terms between different nuclei are very small.

**Fluorine nuclei**

The procedure is similar but simpler because of the zero quadrupole interaction. The resulting 2 x 2 matrix is diagonalized readily.

\textsuperscript{6}Doctor Chermette, Lyon, France donated fluorites from Puy de Dome France. Doctor H. Stalder, Berne, Switzerland donated fluorites from the Basler Jura, Switzerland, and from Illinois, USA.
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