SUPERHYPERFINE INTERACTIONS IN THE ELECTRON-SPIN-RESONANCE SPECTRUM OF SUBSTITUTIONAL Gd³⁺ IMPURITY IN CaF₂ SINGLE CRYSTALS UNDER APPLIED STRESS

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In this communication we report a superhyperfine structure in the esr spectrum of 0.001 at.% Gd^{3+} in a single crystal of CaF_2 under applied stress. The stress was applied at the polished (111) face of the CaF_2 crystal by a thin film of Ge applied as an epitaxy.[1] Differential stress was applied to the CaF_2 crystal by changing the temperature of the sample.

The esr spectrum at X band of Gd^{3+} in this crystal was examined both at room temperature and at 173°K. The spectrum consists of the seven lines of trivalent gadolinium in a cubic electrostatic field environment. The anisotropy of the spectrum shows predominantly cubic symmetry indicating that charge compensation is remote. At the lower temperature a detectable superhyperfine structure was observed, to a varying degree, superimposed on all of the fine-structure transitions. Figure 1 shows the superhyperfine structure for the transition $M_S = -\frac{1}{2} \rightarrow M_S = -\frac{3}{2}$ at 173°K and with $\vec{H}_0$ in the indicated directions. The separation of the components for the three directions is 5.7 ± 0.3 G for $\vec{H}_0 \| [100]$, 3.4 ± 0.3 G for $\vec{H}_0 \| [111]$, and 1.5 ± 0.3 G for $\vec{H}_0 \| [110]$.

In the case for which $\vec{H}_0 \| [100]$, Fig. 1(a), the separation of the outer components from the main line corresponds to one fluorine nuclear Zeeman energy. These satellite lines correspond to the forbidden transitions, $\Delta M_S = \pm 1$, $\Delta M_I = \pm 1$, whereby a fluorine nuclear spin flips because of the change in local magnetic

field induced by the electronic spin transition. The satellite lines are of the type reported by Baker, Hayes, and O'Brien.[2]

For $\vec{H}_0 \| [110]$ and $[111]$, Figs. 1(b) and 1(c), the structure is quite different, there being nine lines in both cases, and the spacing of the components is quite sensitive to angular deviations of the magnetic field direction from either of the two crystal directions. The structure entirely disappears for rotations from either direction of $\pm 15°$, leaving only the smoothed fine-structure component. There is also a strong magnetic field dependency of the separation of the superhyperfine components from one fine-structure component to the next. This superhyperfine structure, which has never been reported for Gd^{3+} in CaF_2, is believed to be stress induced. The superstructure is essentially of the type reported by Low and Ranon[3] for γ-irradiated CaF_2:Yb^{3+} and later by Ranon and Hyde[4] for CaF_2:Yb^{3+}.

The superhyperfine interaction is most adequately described by the following spin Hamiltonian:

$$H' = \vec{S} \cdot \mathsf{D} \cdot \vec{S} - g_F \beta_N \sum_{\alpha=1}^{8} \vec{H} \cdot \vec{I}^{\,\alpha} + \sum_{\alpha=1}^{8} \vec{S} \cdot \mathsf{A}^{\alpha} \cdot \vec{I}^{\,\alpha}, \quad (1)$$

where each of the three terms contributes in the same order of magnitude, but the combination gives a much smaller contribution than the Stark or electronic Zeeman term. The first term in (1) is a perturbation on the fine-structure splitting due to applied stress, and the elements of the tensor D are related to the stress components by two constants for initially cubic symmetry, which must be evaluated.[5] Because of the first term in (1), the superhyperfine tensor A^{α} is not strictly diagonalizable simultaneously for all eight fluorines as has been pointed out explicitly by Marshall and Stuart.[6]

Justification for including the first term in (1) is shown in Table I, which gives the shift at room temperature in magnetic-field position for each fine-structure component, with the
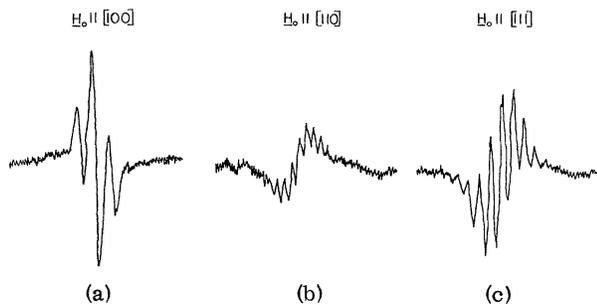

FIG. 1. The appearance of the superhyperfine structure for the fine-structure component corresponding to the transition $M_S = -\frac{1}{2} \rightarrow M_S = -\frac{3}{2}$ for $\vec{H}_0 \| [100]$, $\vec{H}_0 \| [110]$, and $\vec{H}_0 \| [111]$ at the temperature $T = 173°K$.

Table I. Magnetic field shifts of fine-structure components at room temperature upon annealing at $T = 555°C$, for $\vec{H}_0 \parallel [111]$.

$M_s \rightarrow M_s - 1$	$H_a - H_{ua}$ (G)
$\frac{7}{2} \rightarrow \frac{5}{2}$	-1.0
$-\frac{1}{2} \rightarrow -\frac{3}{2}$	0.9
$-\frac{3}{2} \rightarrow -\frac{5}{2}$	1.0
$\frac{1}{2} \rightarrow -\frac{1}{2}$	$\cdots$
$\frac{5}{2} \rightarrow \frac{3}{2}$	-0.9
$\frac{3}{2} \rightarrow \frac{1}{2}$	-1.4
$-\frac{5}{2} \rightarrow -\frac{7}{2}$	1.8

BEFORE ANNEAL

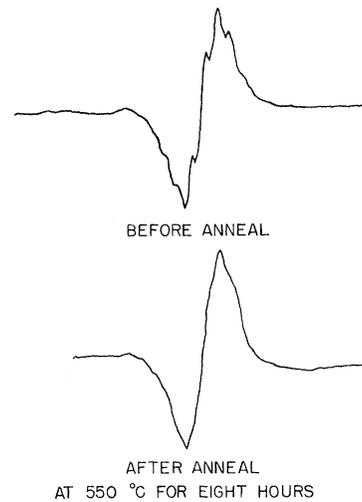AFTER ANNEAL
AT 550 °C FOR EIGHT HOURS

FIG. 2. The appearance of the superhyperfine structure for the fine-structure component corresponding to the transition $M_s = -\frac{1}{2} \rightarrow M_s = -\frac{3}{2}$ before and after anneal, for $\vec{H}_0 \parallel [111]$ at the temperature $T = 300°K$.

exception of the central one, for the crystal before and after anneal at 550°C for 8 h. In this case the Ge film had been removed. Within the experimental error of ± 0.3 G, these changes can be explained in terms of a stress-induced second-order perturbation of initially cubic-field symmetry. Furthermore, the anneal tends to reduce the superhyperfine coupling as shown in Fig. 2.

In this case, as in the case of Ranon and Hyde for $CaF_2{:}Yb^{3+}$, the superhyperfine coupling constants cannot be evaluated adequately from the esr data alone. Rather, complete information must be obtained from the combined esr and ENDOR measurements. Even so, interpretation in terms of the Hamiltonian (1) suggests that the components of the interaction tensor A^α are coupled to those of the tensor D and hence to the applied stress components.

Further work is being done using the ENDOR technique, and also to determine explicitly the relationship between the applied stresses and the superhyperfine coupling.

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