

## $^{19}\text{F}$ ENDOR for $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ in alkaline earth fluorides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 7537

(<http://iopscience.iop.org/0953-8984/2/36/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 22:29

Please note that [terms and conditions apply](#).

## $^{19}\text{F}$ ENDOR for $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ in alkaline earth fluorides

J M Baker and L J C Bluck

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

Received 16 February 1990, in final form 20 June 1990

**Abstract.** A careful analysis of ENDOR data for both ligand and second-neighbour  $^{19}\text{F}$  nuclei in alkaline earth fluorides reveals small discrepancies with previous work on these materials. For  $\text{Eu}^{2+}$  reasonable and explicable displacements of second-neighbour  $\text{F}^-$  ions are measured. For  $\text{Gd}^{3+}$  much fewer data are available, and they are not easily explained.

### 1. Introduction

In their accounts of measurements of ENDOR of the  $S$ -state ions  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in crystals with the fluorite structure, Baker and Christidis (1977) and Baker and Wood (1979) pointed out two effects that rendered inaccurate some of the earlier measurements in these systems.

First, Baker and Christidis found that it was necessary to augment the usually used hyperfine spin Hamiltonian describing the interaction with a ligand whose bond axis is in the  $z$  direction

$$H = A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) = A_s \mathbf{S} \cdot \mathbf{I} + (A_p + A_d)(3S_z I_z - \mathbf{S} \cdot \mathbf{I}) \quad (1)$$

by adding a term

$$A_{\parallel} [S_z^3 I_z - \frac{1}{5} S_z I_z (3S^2 + 3S - 1)] \quad (2)$$

where we have corrected the term in the final bracket, which was incorrectly quoted both by Baker and Christidis and by Baker and Wood. We have extended this analysis to the other readily obtainable crystals of the series. The additional term has the effect of changing the values of  $A_{\parallel}$  and  $A_{\perp}$  found by previous workers. In equation (1),  $A_d = gg_N \mu_B \mu_N / R^3$  represents the dipolar interaction between the  $^{19}\text{F}$  nuclear moment and the compact spherically symmetrical unpaired  $4f^7$  electrons centred on the lanthanide nucleus, separated by distance  $R$ , and  $A_s$  and  $A_p$  represent the contribution of unpaired  $s$  and  $p$  electrons on the  $\text{F}^-$  ion.

Secondly, Baker and Wood, investigating the transferred hyperfine interaction for second-neighbour  $\text{F}^-$  ions in the  $\text{PbF}_2:\text{Gd}^{3+}$ , pointed out that distortion of the position of these neighbours relative to the  $\text{Gd}^{3+}$  site could be both radial and angular, and that omission of the angular distortion by earlier workers had produced misleading results. We have measured these distortions for several other crystals of the series.

Much of the detailed background of experiment and theory of the interactions between the unpaired electrons and  $^{19}\text{F}$  neighbours is discussed by Baker (1979), Baker

**Table 1.** Hyperfine parameters for  $^{19}\text{F}$  ligands,  $A/h$  (MHz).

Crystal	$A_{\parallel}/h$	$A_{\perp}/h$	$A'_{\parallel}/h$	$A_s/h$	$(A_p + A_d)/h$
$\text{CaF}_2:\text{Eu}$	5.854(27)	-6.293(15)	-0.002(1)	-2.244(3)	4.049(12)
$\text{SrF}_2:\text{Eu}$	5.535(10)	-5.742(7)	-0.003(1)	-1.983(4)	3.759(3)
$\text{BaF}_2:\text{Eu}$	5.362(16)	-5.201(9)	-0.000(1)	-1.680(2)	3.521(7)
$\text{CaF}_2:\text{Gd}$	8.295(12)	-7.037(12)	-0.012(1)	-1.926(3)	5.111(9)
$\text{BaF}_2:\text{Gd}^\dagger$	7.488(5)	-6.446(4)	-0.010(1)	-1.815(4)	4.631(3)

† Baker and Allsopp (1988).

and Christidis (1977) and by Baker and Wood (1979), and references therein: in the interest of brevity we shall not repeat this discussion.

## 2. Experimental details

ENDOR was measured at 4.2 or 20 K and 35 GHz, with 115 kHz modulation of the steady magnetic field applied, and frequency modulation of the radio frequency. Measurements were made with  $\mathbf{B}$  in the  $\{110\}$  plane, whose orientation could be set to  $\sim 0.1^\circ$  using the fourfold coincidence of ligand ENDOR for  $\langle 100 \rangle$  and the threefold coincidence for  $\langle 111 \rangle$ .

A least squares fitting procedure was used to find the spin Hamiltonian parameters which gave the best fit with the measured ENDOR line frequencies. In the tables of parameters the numbers in brackets represent the change in the parameters which double the RMS deviation between calculated and experimental line positions.

## 3. Ligand $^{19}\text{F}$ ENDOR

The additional term (2) in the hyperfine spin Hamiltonian (1) is observed only for  $\mathbf{B}$  along a bond axis, leading to ENDOR frequencies:

$$h\nu(M) = g_N \mu_N B - A_{\parallel} M - A'_{\parallel} [M^3 - (M/5)(3S^2 + 3S - 1)]$$

for  $S_z = M$ . The effect of the small term in  $A'_{\parallel}$  is most easily measured using ENDOR on the  $M \leftrightarrow (M + 1)$  transition when

$$h\nu(M + 1) - h\nu(M) = -A_{\parallel} - A'_{\parallel} [3M^2 + 3M + 1 - \frac{1}{5}(3S^2 + 3S - 1)]$$

which gives frequency differences which vary with  $M$ . However, one can measure  $A'_{\parallel}$  even if only the  $M = \frac{1}{2}$  to  $-\frac{1}{2}$  transition is observable, as:

$$h\nu(\frac{1}{2}) - h\nu(-\frac{1}{2}) = -A_{\parallel} - A'_{\parallel} [\frac{1}{4} - \frac{1}{5}(3S^2 + 3S - 1)].$$

$A_{\parallel}$  may be obtained from the ENDOR frequencies for the other ligands with  $\mathbf{B}$  along  $\langle 111 \rangle$  and with  $\mathbf{B}$  along  $\langle 100 \rangle$ .

Table 1 gives the results of these measurements. The presence of the term  $A'_{\parallel}$  for  $\text{SrF}_2:\text{Eu}^{2+}$  leads to a value of  $A_{\parallel}$  which is different from that of Valentin (1969), but as  $A'_{\parallel}$  is zero for  $\text{BaF}_2:\text{Eu}^{2+}$  our data for  $A_{\parallel}$  agree with those of Baberschke (1971).

Our data is consistent with the findings of Baker and Christidis in showing considerably larger values of  $A'_{\parallel}$  for  $\text{Gd}^{3+}$  than for  $\text{Eu}^{2+}$ .

**Table 2.** Hyperfine parameters for second-neighbour <sup>19</sup>F ions,  $A_s/h$  and  $A_x/h = (A_p + A_d)/h$  (kHz).

	CaF <sub>2</sub> :Eu	SrF <sub>2</sub> :Eu	BaF <sub>2</sub> :Eu	CaF <sub>2</sub> :Gd	PbF <sub>2</sub> :Gd
$A_s^a$	-4(6)	+3(6)	+2(6)	-1(6)	+14(10)
$A_x^a$	+761(4)	+666(4)	+544(4)	+816(4)	+629(14)
$A_s^b$	+14(6)	0(6)	+4(6)	-5(6)	+5(10)
$A_x^b$	+788(4)	+671(4)	+553(4)	+817(4)	+650(15)
$A_s^c$	+5(6)	+2(6)	+3(6)	-3(6)	+9(10)
$A_x^c$	+789(4)	+669(4)	+553(4)	+817(4)	+640(10)
$A_s^d$	+5(6)	+1(6)	+3(6)	-3(6)	+10(10)
$A_x^d$	+789(9)	+669(4)	+553(4)	+817(4)	+639(10)
$\Phi^{0d}$	25.31(9)	25.36(15)	25.31(6)	25.24(6)	25.74(20)

<sup>a</sup> Deduced from measurements for **B** along  $\langle 100 \rangle$  only.

<sup>b</sup> Deduced from measurements for **B** along  $\langle 111 \rangle$  only.

<sup>c</sup> Deduced using data for both directions, but  $\Phi = 25.24^\circ$ .

<sup>d</sup> Deduced using data for both directions,  $\Phi$  unrestricted.

#### 4. ENDOR of second-neighbour F<sup>-</sup> ions

Baker and Wood (1979) have pointed out that because of the possibility of angular as well as radial displacements of the positions of second-neighbour F<sup>-</sup> ions, it can be misleading to deduce parameters from ENDOR measurements for **B** in one direction only, on the assumption that equation (1) describes the interaction for *z* along the undistorted bond direction.

Table 2 shows the parameters deduced from our ENDOR data. This demonstrates the danger of relying upon measurements for either **B** only along  $\langle 111 \rangle$  or **B** only along  $\langle 100 \rangle$ . Using data for both directions, but assuming that the bond vector **R** is in the direction ( $\Phi = 25.239^\circ$ ) appropriate to the undistorted crystal gives different parameters. Allowing  $\Phi$ , the angle between **R** and  $\langle 100 \rangle$ , to be a variable does not in fact change  $A_s$  or ( $A_p + A_d$ ), but the RMS deviation of the fit is reduced from typically  $\approx 8$  kHz to  $\approx 2$  kHz, and some angular displacements are detected.

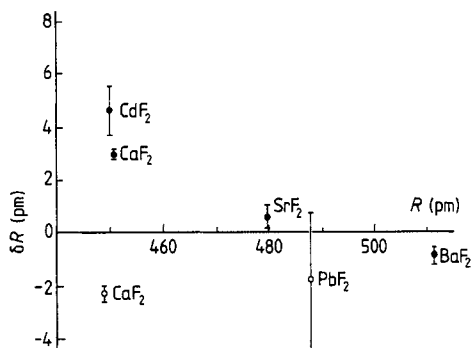
Most of these data are consistent with negligible  $A_s$ . It has been found in all well characterised examples that  $A_s$  is rather larger than  $A_p$  (Baker 1979). As  $A_s$  is negligible or very small, we can assume that  $A_p$  is zero and deduce from  $A_d$  the radial and angular displacements of the <sup>19</sup>F nucleus. Table 3 lists the displacements deduced in this way, and figure 1 plots  $\delta R$  as a function of the second-neighbour distance *R* in the undistorted lattice. For CdF<sub>2</sub> we have used the data of Valentin (1969).

For Eu<sup>2+</sup> there does appear to be a monotonic variation of  $\delta R$  with *R*, indicating zero  $\delta R$  for *R* between 480 and 490 pm. This is not very far away from the previously assumed condition that, as the ionic radii of Eu<sup>2+</sup> and Sr<sup>2+</sup> are similar, one would expect zero distortion for SrF<sub>2</sub> where *R* = 479.3 pm. Relative to the displacement for SrF<sub>2</sub>, the displacement of second neighbours is about 40% of that deduced for ligand F<sup>-</sup> ions by Baker (1979), which is a satisfactory correlation, as one would expect the distortion to damp out over a few lattice spacings. Although the fit to the data is improved by making allowance for  $\delta\Phi$ , the experimental uncertainty in all cases for Eu<sup>2+</sup> overlaps zero.

The data for Gd<sup>3+</sup> are altogether more puzzling, and for this reason it is unfortunate that the concentrations of cubic sites in our crystals of SrF<sub>2</sub>:Gd and BaF<sub>2</sub>:Gd is too small

**Table 3.** Distances  $R$  (in pm) of second to fourth neighbours deduced from transferred hyperfine interaction parameters, and the outward displacement  $\delta R$  that this indicates. Hyperfine parameters for second neighbours are given in table 2 and, below,  $A_s/h$  and  $(A_p + A_d)/h = A_x/h$  are given in kHz.

	CaF <sub>2</sub> :Eu	SrF <sub>2</sub> :Eu	BaF <sub>2</sub> :Eu	CaF <sub>2</sub> :Gd	PbF <sub>2</sub> :Gd
$R$ (2nd)	454.3(2)	479.9(5)	511.4(3)	449.0(3)	487.1(3)
$\delta R$ (2nd)	3.0(2)	0.6(5)	-0.8(3)	-2.3(3)	-2.1(3)
$A_s$ (3rd)	0(20)	2(9)	-2(8)	4(8)	
$A_x$ (3rd)	343(14)	302(6)	239(5)	355(5)	
$R$ (3rd)	599.7(8.0)	625.6(3.9)	676.4(4.8)	529.8(2.8)	
$\delta R$ (3rd)	6.5(3.0)	-4.3(3.9)	3.2(4.8)	-4.0(2.8)	
$A_s$ (4th)	-6(8)	0(3)			
$A_x$ (4th)	207(5)	177(2)			
$R$ (4th)	709.6(5.8)	747.6(3.2)			
$\delta R$ (4th)	2.5(5.8)	-3.3(3.2)			



**Figure 1.** Second-neighbour radial displacements for Eu<sup>2+</sup> (full circles) and Gd<sup>3+</sup> (open circles).

to allow satisfactory ENDOR measurements. Considering the closeness of the ionic radii of Gd<sup>3+</sup> and Ca<sup>2+</sup>, the inward displacement in CaF<sub>2</sub>:Gd is surprisingly large; it is almost as large as that deduced for ligands by Baker (1979). A rather larger displacement than expected from the ionic radii could be produced by the extra positive charge on the Gd<sup>3+</sup> ion. However, such an explanation makes the results for PbF<sub>2</sub> extremely puzzling. They are puzzling in two respects: (i)  $\delta R$  is relatively very much smaller than the inward displacement of the ligands deduced by Baker (1979), indeed it is comparable to that for CaF<sub>2</sub>; (ii) there is a large apparently significant angular displacement.

ENDOR of more distance neighbours (table 3) indicates that  $A_s$  is zero within the accuracy of measurement; and the dipolar interaction corresponds to the undistorted lattice, but measurements could not be made precisely enough to detect displacements of similar size to those of second neighbours.

## References

Baberschke K 1971 *Phys. Lett.* **34A** 41-3

- Baker J M 1979 *J. Phys. C: Solid State Phys.* **12** 4039–49  
Baker J M and Allsopp R A 1988 *Rev. Roum. Phys.* **33** 353–9  
Baker J M and Christidis T 1977 *J. Phys. C: Solid State Phys.* **10** 1059–62  
Baker J M, Christidis T, Walker P J and Wanklyn B M 1978 *J. Phys. C: Solid State Phys.* **11** 3071–80  
Baker J M and Wood R L 1979 *J. Phys. C: Solid State Phys.* **12** 4033–8  
Valentin R 1969 *Phys. Lett.* **30A** 344–5  
Wood R L 1979 *DPhil Thesis* Oxford University