An electron–nuclear double-resonance study of the F centre in CsBr

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Abstract. Electron–nuclear double-resonance (ENDOR) measurements were performed on the F centre in CsBr using the stationary ENDOR method. Five Cs and three Br shells could be resolved. The observed superhyperfine interactions cannot be explained by a spherically symmetric F-centre wavefunction. Lattice-ion overlaps and an admixture of $|g\rangle$-type functions ($L = 4$) have to be included in the description of the F-centre wavefunction.

1. Introduction

F centres in alkali halides have long been regarded as a model system for electronic defects in insulators. The interest in them has been renewed by the discovery of an E–V energy transfer from the electronic excitation into the vibrational stretch mode of a molecular neighbour (e.g. CN^- and OH^-) [1]. The efficiency of this process is particularly high in crystals with the CsCl structure. In these host materials (CsCl, CsBr, and CsI) the F centre has not been studied in much detail. In particular, the F-centre electron distribution has not been determined accurately by magnetic resonance techniques. So far only the electron paramagnetic resonance (EPR) has been measured. In CsBr only a broad unresolved EPR line at $g = 1.996$ with a peak-to-peak derivative linewidth of 70 mT has been detected, indicating a fairly large superhyperfine (shf) interaction with the neighbouring Cs nuclei [2]. In CsCl the EPR spectrum shows structure due to shf interactions with the nearest Cs neighbours [3]. As a basis for any model of the E–V transfer mechanism, a more detailed study by means of electron–nuclear double-resonance (ENDOR) is necessary, which we present for CsBr in this communication.

2. Experimental results

The CsBr crystals were grown by the Czochralski method and oriented along a (100) plane by x-ray diffraction (the Laue technique). The high F-centre concentrations necessary for ENDOR ($>10^{18}$ cm^{-3}) have been produced by additive coloration in Cs vapour (200 Torr) for which the sample was kept at 630 °C close to its melting point.

Stationary ENDOR experiments were performed with a custom-built, computer-controlled X-band EPR/ENDOR spectrometer. The best stationary ENDOR spectra were obtained at $T = 15$ K.

The immediate neighbourhood of the F-centre electron in CsBr is depicted in figure 1. It consists of eight nearest-neighbour Cs_I nuclei in the eight [111] directions and of six
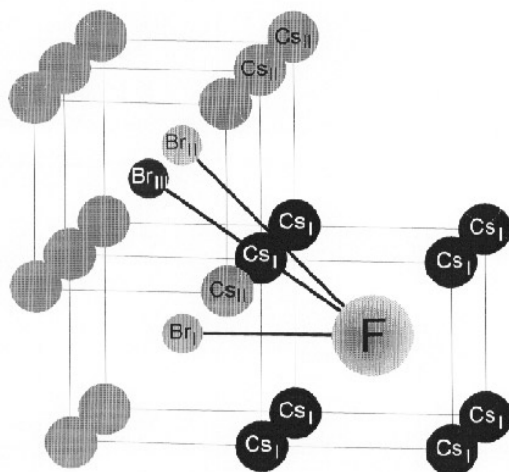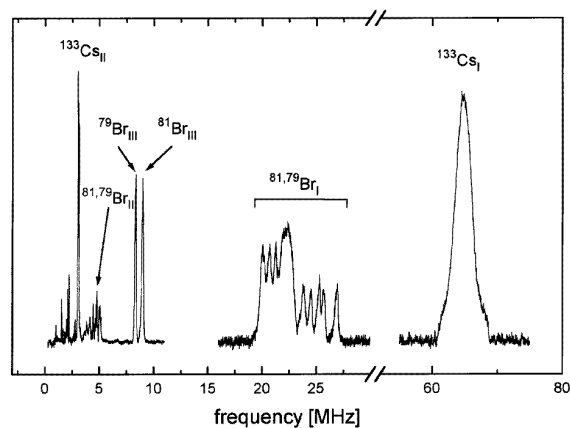
Figure 1. Local surroundings of the F centre in CsBr.

Figure 2. The ENDOR spectrum of the F centre in CsBr. $B = 350$ mT, $B \| [100]$, $T = 15$ K, $\nu = 9.387$ GHz.

Br_I nuclei in the six [100] directions. An ENDOR spectrum measured with $B \| [100]$ is shown in figure 2. The assignment of the ENDOR lines to the different isotopes can be performed by measuring the shift in frequency of the ENDOR line when the magnetic field is varied over the width of the EPR line. This shift is due to the nuclear Zeeman interaction which in turn depends on the nuclear g-factor. The symmetry of the shells can be found by evaluating the angular dependence of the ENDOR line positions as shown in figure 3 for the first Cs shell and in figure 4 for the first three Br shells (see e.g. [4]). The exact values of the shf and quadrupole interaction constants can then be obtained by comparing the data on the angular dependence with a calculation of ENDOR frequencies performed using the appropriate spin Hamiltonian (see below). We found that the ENDOR lines corresponding
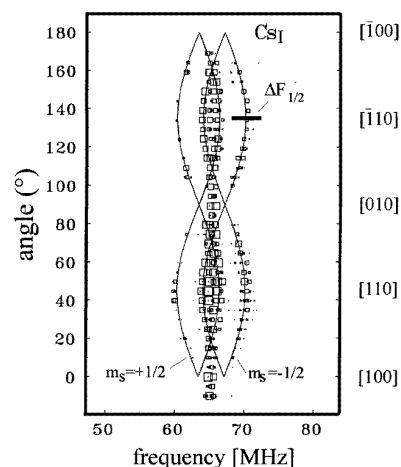
Figure 3. The ENDOR angular dependence of the F centre in CsBr showing the first ^{133}Cs shell. The magnetic field is rotated in a (100) plane. The horizontal bar indicates the approximate ENDOR linewidth.
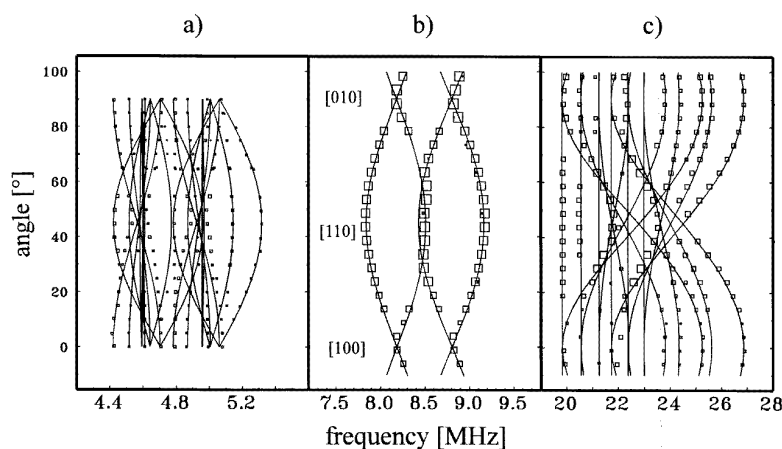
Figure 4. The ENDOR angular dependence of the F centre in CsBr showing the first three ^{81,79}Br shells. The magnetic field is rotated in a (100) plane (0° corresponds to $B\|[100]$): (a) Br$_{III}$; (b) Br$_{II}$; (c) Br$_{I}$.

to $m_S = 1/2$ are lower in intensity by more than an order of magnitude than the ones observed for $m_S = -1/2$. In the following we will discuss only the latter ones.

The lines due to the ^{133}Cs nuclei of the first shell (Cs$_I$) appear at around 70 MHz (see figure 2). This corresponds to a shf interaction W_{shf}/h of about 130 MHz. The ENDOR lines are very broad ($\Delta f_{1/2} = 2.5$ MHz). A quadrupole interaction with the ^{133}Cs nuclei ($I = 7/2$) is not resolved. The ENDOR linewidth can partly be explained by the splitting of the seven allowed NMR transitions of the ^{133}Cs nucleus ($I = 7/2$) which occurs even in the absence of quadrupole interaction when the shf interaction is not very small compared to

the electron Zeeman interaction. In second-order perturbation theory this splitting is given by [4]:

$$\Delta f = \frac{(W_{shf})^2}{2g_e\mu_B B_0}. \tag{1}$$

With $W_{shf}/h \approx 130$ MHz the splitting is about 0.5 MHz. If the ENDOR line is regarded as an envelope of these seven NMR transitions, the resulting $\Delta f_{1/2}$ is about 2 MHz, in good agreement with the experimental linewidth. This sets an upper limit on the possible broadening by quadrupole interaction. The upper limit for the quadrupole interaction constant q/h (see below) is 0.1 MHz.

ENDOR lines due to the first shell of Br nuclei (Br_I) appear at around 23 MHz. The ENDOR lines at about 8 MHz are due to the Br nuclei of the third shell (Br_{III}). This shell has the same (111) symmetry as the first ^{133}Cs shell (see figure 1). ENDOR lines due to the second Br shell (Br_{II}) appear near the Larmor frequencies of the two Br isotopes (^{81}Br, ^{79}Br). The shf interaction with these nuclei is lower than the shf interaction with the nuclei of the third Br shell, although the Br_{II} nuclei are nearer to the F centre.

The ENDOR lines at around 3.1 MHz are due to the nuclei of the second ^{133}Cs shell (Cs_{II}). Finally, the ENDOR lines due to distant ^{133}Cs nuclei (Cs_{III-V}) appear at around the Larmor frequency of ^{133}Cs. They are almost isotropic. Therefore, an assignment of these lines to specific shells on the basis of symmetry was not possible.

Table 1. Superhyperfine and quadrupole interaction parameters for the ^{133}Cs and ^{81}Br neighbours of the F centre in CsBr.

| Shell	a/h (MHz)	b/h (MHz)	q/h (MHz)	b_{dd}/h (MHz)	r_i (Å)
Cs_I	130.3 ± 0.5	6.0 ± 0.5	< 0.1	0.21	3.72
Cs_{II}	2.21 ± 0.2	0.07 ± 0.2	0	0.03	7.11
Cs_{III}	0.54 ± 0.2	$\approx 0.03 \pm 0.1$			
Cs_{IV}	0.27 ± 0.2	< 0.01			
Cs_V	0.08 ± 0.2	< 0.01			
Br_I	40.0 ± 0.1	2.25 ± 0.1	0.20 ± 0.02	0.28	4.21
Br_{II}	1.84 ± 0.02	0.18 ± 0.02	0.03 ± 0.01	0.11	6.07
Br_{III}	9.90 ± 0.02	0.73 ± 0.02	< 0.01	0.06	7.43

A quantitative analysis requires the evaluation of the following spin Hamiltonian:

$$\mathcal{H} = g\mu_B B_0 \cdot S + \sum_j (S\hat{\mathbf{A}}_j I_j + I_j\hat{\mathbf{Q}}_j I_j - g_{Ij}\mu_n B_0 \cdot I_j) \tag{2}$$

with the usual notation (see e.g. [4]). Here $S = 1/2$, $I = 3/2$ for ^{81,79}Br, and $I = 7/2$ for ^{133}Cs. The sum runs over the various Br and Cs ligands. The first term corresponds to the electronic Zeeman interaction, and the last three denote the shf, quadrupole and nuclear Zeeman interactions, respectively. The shf and quadrupole interaction constants of the resolved shells of the neighbours, obtained from the angular dependencies of the ENDOR lines (figures 3 and 4), are given in table 1.

They are given in terms of the isotropic shf constant a and the anisotropic shf constants b and b', which are related to the principal values of the shf tensor by

$$A_{xx} = a - b + b' \qquad A_{yy} = a - b - b' \qquad A_{zz} = a + 2b. \tag{3}$$
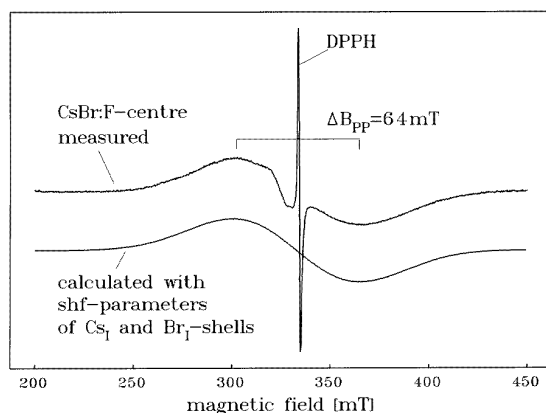
Figure 5. A comparison of the measured EPR spectrum of the F centre and a simulation of the EPR linewidth using the shf parameters of the first Cs shell and first Br shell obtained from the ENDOR analysis (table 1).

In a similar way, the quadrupole interaction constants are related to the quadrupole tensor by

$$Q_{xx} = -q + q' \qquad Q_{yy} = -q - q' \qquad Q_{zz} = 2q. \tag{4}$$

For the first shell of Cs neighbours and for the first and third Br shell, $b' = q' = 0$ due to the axial symmetry of the shells. In the case of the second Cs and Br shells the lower local symmetry requires that all parameters in (3) and (4) have to be considered. However, within experimental accuracy no deviation from axial symmetry was found.

The width of the F-centre EPR spectrum should be determined by the shf interactions of the nearest Cs and Br shells (Cs_I, Br_I). Figure 5 shows a comparison of the experimental EPR spectrum with a calculated spectrum using the parameters of the nearest Cs and Br shells from table 1. A linewidth of 1 mT was assumed for the individual EPR lines of each shf transition. The sharp line in the experimental EPR spectrum is due to DPPH. The agreement of the experimental and simulated lineshapes of the F centre is excellent.

3. Discussion

The value of $a/h = 130.3$ MHz for the isotropic part of the Cs_I hyperfine interaction is similar to the value of 140 MHz for the F centre in CsCl [3]. In addition, the a- and b-values agree very well with theoretical values for CsBr calculated by Harker [5] ($a_{th}/h = 157$ MHz; $b_{th}/h = 5.8$ MHz). The isotropic hyperfine interaction with ^{133}Cs nuclei of the second shell is lower by almost two orders of magnitude. The anisotropic part is largely due to the point dipole–dipole interaction.

In the point dipole–dipole approximation the magnetic moment of the unpaired spin of the F-centre electron is replaced by a point dipole moment and the magnetic interaction between this dipole moment and the magnetic moment of the neighbouring nuclear spin can be calculated (see e.g. [4]) for a given distance r_i using

$$\frac{b_{dd}}{h} = \frac{\mu_0}{4\pi} \frac{\mu_e \mu_n}{r_i^3} \tag{5}$$

where μ_e and μ_n represent the magnetic moments of the electron and the nucleus respectively. The calculated values are given in table 1 along with the distances between the F centre and the nuclei of the corresponding shells.

However, the *a*- and *b*-values of the first Br shell differ considerably from the values calculated by Harker ($a_{th}/h = 113$ MHz; $b_{th}/h = 5.8$ MHz).

Moreover, the shf interaction parameters of the third Br shell are considerably higher than those of the second Br shell, although these nuclei are further away from the F centre.

A similar observation was made in the case of the F centres in the alkaline-earth fluorides [6]. In both cases a halide shell which has [111] symmetry with respect to the F centre has unusually large shf interaction values. Bartram *et al* [7] were able to explain this observation by expanding the spherically symmetric wavefunction of the F centre with admixtures of $|f\rangle$-type ($L = 3$) functions. In addition, the ion overlaps of the cations of the first shell with the anions of the third shell, which are on the same [111] axis, partly explained the high shf interaction values.

A rough estimate of the isotropic shf interaction transferred via the Cs ions of the first shell to the Br ions of the third shell gives a value of $a_{ov}(\text{Br}_{\text{III}})/h \approx 1$ MHz. Thus the ion overlap alone is not sufficient to explain the high shf interaction values of the third Br shell. Obviously the spherically symmetric F-centre wavefunctions used by Harker [5] have to be expanded by including $|g\rangle$-type functions ($L = 4$) in order to better account for the cubic (sc) symmetry and the observed shf constants.

Acknowledgment

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