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Abstract. The observed zero-field splitting parameter D of the triplet self-trapped excitons in alkali fluorides is negative, while in alkaline-earth fluorides of the fluorite structure it is of comparable magnitude but positive. D in these materials is almost completely due to spin–spin interaction. Analysis of D allows an estimate of the separation between the hole and electron charges. These are found to be in satisfactory agreement with the results of recent calculation which predicted the off-centre character of the self-trapped exciton in alkali halide crystals. As for the alkaline-earth fluorides with the fluorite structure, the analysis explains the positive sign of D in this structure and also identifies which of the proposed nearest-neighbour F–H pair configurations corresponds to the observed self-trapped exciton.

1. Introduction

Of the many spectroscopic methods employed for the study of defects in crystals, electron spin resonance explores the symmetry around the defect most directly. It is no wonder that this technique has played an important role in the study of the self-trapped excitons (STEs) in ionic halides. The lowest state of the STE in ionic halides is a spin triplet state with a lifetime in the range between 10^{-5} and 10^{-3} s depending on the material. The selection rule for the recombination luminescence becomes relaxed as a result of the spin–orbit interaction which mixes various spin states. The electron spin resonance is studied through optical detection. As the magnetic field splits the triplet sublevels and microwave absorption connects these sublevels, the lifetime and intensity of luminescence are modified. This is the principle of optically detected magnetic resonance (ODMR), which has been very important in the study of defects with short lifetimes.

In alkali halide crystals of the NaCl structure, the STE has been considered to be equivalent to a self-trapped hole (also called the V_k centre, which is a pair of halogen ions sharing a hole in the form of an X_2^- molecule) having captured an excited electron in an s-like orbital. There is now a growing body of experimental evidence (see, e.g., [1]) which indicates that this 'on-centre' V_k + e system is strongly unstable against the translational motion of the X_2^- molecule along the (110) axis. As a consequence, the electron splits away from the V_k core and occupies a nascent anion vacancy, thereby becoming an F centre, while the molecule ion X_2^- occupies a single anion site. In this

'off-centre' configuration, the STE closely resembles a primitive F–H pair, very similar to the STE in the fluorite structure. There has been considerable discussion regarding this structure [2–4]. The experimental work most directly relevant to the off-centre structure has been the ENDOR measurement of KCl by Block *et al* [5]. They found from analysis of the quadrupolar interaction term that the two chlorine ions are inequivalent. Apart from an earlier analysis [6] of the ENDOR data for KCl, the magnitude of this off-centre shift of the V_k core (or the separation of the electron and hole charges) has not been deduced from experiment.

ODMR data of the triplet state STE are available for most of the alkali halides and alkaline-earth fluorides. In the fluorides of the NaCl structure and CaF_2 structure the parameter D is of comparable magnitude (about 1000 G), but of opposite sign. D is negative in LiF, NaF and KF [7] and positive in CaF_2, SrF_2 and BaF_2 [8]. In these materials the parameter D is almost entirely due to the magnetic dipole–dipole interaction term D_{ss} and the other term D_{so} originating from the spin–orbit coupling is negligible. It is possible in this circumstance to gain important information about the defect geometry and dimensions [9]. The other parameter E of zero-field splitting measures the deviation from cubic symmetry about the z axis. The values of E for the fluorites are large and comparable with those of D. This reflects the fact that the symmetry around the axis of the H centre is low [8].

In this paper we present a semi-quantitative analysis of the zero-field splitting parameter D for the STE in alkali fluorides (LiF, NaF and KF) and in the alkaline-earth fluorides (CaF_2, SrF_2 and BaF_2). We deduce the separation between the electron (on the F centre site) and the hole (on the H centre site) for the six fluorides mentioned above and show that the values obtained are in fairly good agreement with the recent theoretical predictions. In addition we are able to explain the reversal of sign of D_{ss} of the STE between the NaCl and CaF_2 lattices. At the same time we identify the geometry of the STE in the fluorite structure among the several possible configurations of the nearest-neighbour F–H pair previously suggested [10]. We also show that D_{ss} is most probably very small if the STE is in the $V_k + e$ configuration.

2. Derivation of an approximate expression for D_{ss}

The zero-field splitting parameter D contains two components: $D = D_{ss} + D_{so}$, where D_{ss} describes the magnetic dipole–dipole interaction and D_{so} is due to the spin–orbit coupling. In this work, we are only concerned with the fluorides where the spin–orbit coupling is weak so that we can neglect D_{so}.

D_{ss} is given by

$$D_{ss} = \tfrac{3}{4}(g\beta)^2 \langle \Psi_{12} | (r_{12}^2 - 3z_{12}^2)/r_{12}^5 | \Psi_{12} \rangle \tag{1}$$

with

$$\Psi_{12} = (1/\sqrt{N_{12}})[\psi_1(r_1)\psi_2(r_2) - \psi_2(r_1)\psi_1(r_2)]\alpha_1\alpha_2 \tag{2}$$

(D in tesla is obtained by multiplying equation (1) by $4\pi 10^{-7}/g\beta$).

Here ψ_1 and ψ_2 are respectively the wavefunctions of the hole and electron of the STE. We assume that the hole is in a σ_u-like orbital formed by 2p orbitals of the two

fluorine ions A and B at positions A and B, and the electron is in an s-like orbital centred at R:

$$\psi_1(r) = \sigma_u(r) = (1/\sqrt{N})[\varphi_A(r-A) - \varphi_B(r-B)]$$
$$\psi_2(r) = \varphi(|r-R|) = (1/\sqrt{N_0}) \exp(-\alpha|r-R|^2).$$

(3)

We now make two approximations. First, we retain only the Coulomb-like terms in equation (1) since the other exchange-like terms are generally smaller and become negligible at large distance [9]. Second, recognising that the wavefunction of the hole is much more compact than that of the excited electron, we approximate the hole charge density $|\psi_1|^2$ as a sum of two delta functions:

$$|\psi_1|^2 = q_A\delta(r-A) + q_B\delta(r-B)$$

(4)

where q_A and q_B are the fractions of the hole charge on the two ions which form the V_k centre. With these approximations, we obtain

$$D_{ss} = \tfrac{3}{4}(g\beta)^2 \sum_i q_i \int \varphi^2(|r-R|) \frac{r_i^2 - 3z_i^2}{r_i^5} \, d\tau.$$

(5)

Here $i \equiv A$ (or B) and $r_i = r - A$ (or $r - B$).

The above expression is very similar to that of the hyperfine interaction term between an electron and a nuclear spin. The integral can best be calculated by making use of a multipolar expansion of φ^2 about A (or B). Since $(r_i^2 - 3z_i^2)/r_i^2$ transforms as the spherical harmonics Y_2^0, only the term containing Y_2^0 in the multipolar expansion contributes to the integral, giving

$$\int \varphi^2(|r-R|)(r_i^2 - 3z_i^2) \frac{1}{r_i^5} \, d\tau = \frac{2\pi(R_i^2 - 3Z_i^2)}{R_i^2} \int F_2(r_i, R_i) \frac{dr_i}{r_i}$$

(6)

with

$$F_2(r_i, R_i) = \int \varphi^2(|r_i - R_i|)P_2(\cos\Omega_i) \, d(\cos\Omega_i).$$

(7)

Here for $i \equiv A$ (or B), $R_i = R - A$ (or $R - B$), P_2 is the Legendre polynomial of order 2 and Ω_i is the angle between r_i and R_i. We remark that the factor $(R_i^2 - 3Z_i^2)/R_i^2$ depends on the geometry between the molecular axis (the z axis in the spin Hamiltonian) and the position of the electron charge relative to A (or B).

The final expression for D_{ss} is

$$D_{ss} = \tfrac{3}{4}(g\beta)^2 \sum_i \left(q_i \frac{1}{R_i^3} \frac{R_i^2 - 3Z_i^2}{R_i^2} \right) f(\sqrt{\alpha}R_i)$$

(8)

where the expression inside the large parentheses is the classical limit for well separated electron and hole and shows the well known R^{-3} dependence on the separation R. f is a scaling factor given by

$$f(\sqrt{\alpha}R) = 2\pi R^3 \int F_2(r, R) \frac{1}{r} \, dr.$$

(9)

We have also studied the limiting values of f. In the case of large separation $(\sqrt{\alpha}R \to \infty)$,

$$f = 1 - \tfrac{3}{4}/\alpha R^2$$

(10)

and, for small separation $(\sqrt{\alpha}R \to 0)$,

$$f = (64/15)\sqrt{2\pi}(\sqrt{\alpha}R)^5 \exp - (2\alpha R^2).$$
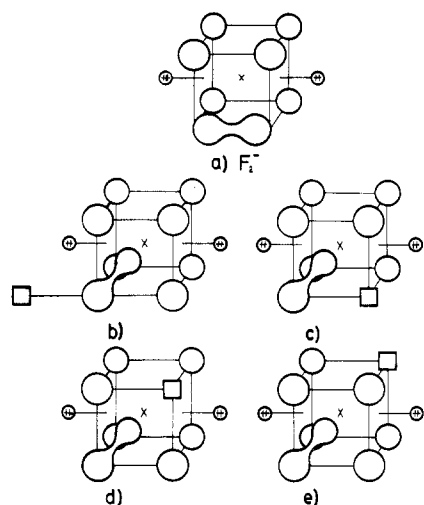
(11)

Figure 1. Four possible nearest-neighbour F–H pair configurations proposed earlier [10] as the structure of the STE in the fluorite structure: (a) the V_k centre before the electron capture; (b) configuration 1 in [10]; (c) configuration 2 in [10]; (d) configuration 3 in [10]; (e) configuration 4 in [10]. The circles represent F^- ions, the squares the F centre and the dumb-bell the F_2^- molecule ion.

Table 1. Zero-field splitting parameters D and E of the STE in six fluorides of the NaCl and CaF_2 structures. Data for the NaCl structure and the CaF_2 structure are taken, respectively, from [7] and [8].

	Value for the following crystals					
	LiF	NaF	KF	CaF_2	SrF_2	BaF_2
D (G)	−1185	−803	−615	1552	1588	1397
E (G)	−160	−64	16	−587	−954	−1164

3. Results and discussion

We first present an explanation of the opposite signs of D_{ss} found for the STE in LiF, NaF and KF on the one hand ($D_{ss} < 0$) and CaF_2, SrF_2 and BaF_2 on the other ($D_{ss} > 0$). By doing so we also identify the geometry of the nearest-neighbour F–H pair which is responsible for the π-band in the fluorite structure. We show that it is most likely configuration 2 of the four possible configurations (figure 1) proposed earlier [10]. Then we present the values of the separation between the hole and electron charges derived from the experimental data of D_{ss}. These are compared with the theoretical predictions [11] for the NaCl structure and with values deduced from configuration 2 of the nearest-neighbour F–H pair (figure 1(c)) for the fluorite structure. Finally we show that regarding the on-centre STE the values of D_{ss} would be too small to be compatible with the experimental data.

As shown in table 1, the sign of the observed D_{ss} is opposite for the two lattice structures: NaCl and CaF_2. The sign of this parameter can be determined in an unambiguous way by studying with circularly polarised light of left and right polarisation [12]. It is therefore of considerable interest to understand this reversal of sign. According to the new off-centre point of view, the STE should be considered more like a close F–H

Table 2. The sign of D_{ss} for the STE in four possible nearest-neighbour F–H pair configurations in CaF_2. The geometrical factor of equation (8) $(R_i^2 - 3Z_i^2)/R_i^2$ is given for the two ions $F^{-0.3}$ and $F^{-0.7}$ for each configuration. These are numbered as in [10]. R corresponds to CaF_2.

		Value for the following configurations			
		1	2	3	4
$(R_i^2 - 3Z_i^2)/R_i^2$	$F^{-0.3}$	−1.13	0.95	0.29	−2.0
	$F^{-0.7}$	0.0	0.0	−1.0	−2.0
R (au)	$F^{-0.3}$	7.8	4.3	4.8	5.3
	$F^{-0.7}$	5.2	5.2	7.3	8.9

pair. The difference with the two lattice structures is then reflected in the geometrical factor $(R_i^2 - 3Z_i^2)/R_i^2$ of equation (8).

In the NaCl structure, the hole is found to be shared about equally between the two F ions, i.e. $q_A = q_B = 0.5$ [4]. Taking the molecular axis as the z axis of the spin Hamiltonian, it is clear that the geometrical factor $(R_i - 3Z_i^2)/R_i^2 = -2.0$ for both ions of the V_k core, thereby giving a negative D_{ss}.

For the STE in the fluorite structure, the 'H centre' is aligned approximately about a $\langle 111 \rangle$ axis and the 'F centre' is occupying one of several possible anion sites [10]. For an H centre in the fluorite lattice the fluorine ion which occupies an interstitial position carries about 70% of the hole charge, while the substitutional F ion carries only about 30% [13]. This means that the F ions are respectively $F^{-0.3}$ (interstitial at $(2.1, 2.1, 2.1)$ in atomic units) and $F^{-0.7}$ (substitutional at $(0, 0, 0)$). We have assumed here that the F_2^- bond length is 3.6 au for all fluorides. In earlier work on ODMR, symmetry analysis alone could not discriminate between the three possible nearest-neighbour F–H pairs [10]. We have included also configuration 4 for completeness. Our analysis of the sign of D_{ss} allows us to identify the geometry that is compatible with experiment. The F centre is located at $(-1, 0, 0), (1, 0, 0), (1, 0, 1)$ and $(1, 1, 1)$, respectively, for configurations 1, 2, 3 and 4 (the coordinates are in units of F–F distance). Figures 1(b), 1(c), 1(d) and 1(e) show these four configurations, respectively.

The geometrical factor in equation (8) is evaluated with the parameters as given above for the pure H centre. In table 2 are assembled results of the geometrical factor $(R_i^2 - 3Z_i^2)/R_i^2$ and other parameters for the four configurations which were proposed as the possible geometry of the STE in the fluorites. From table 2 it appears quite clearly that only configurations 2 and 3 can give rise to the observed positive sign for D_{ss}. Close examination shows that configuration 3 would lead to a value of D close to zero owing to a cancelling contribution from the two ions. Also, it is seen that configuration 2 corresponds to the shortest displacement of the two fluorine ions from the original V_k centre sites.

Next we evaluate the distance between the electron and the self-trapped hole from the observed value of D_{ss} for the six fluorides of the NaCl and fluorite structures. Earlier prediction indicated well separated electron and hole for the fluorides of the NaCl structure. We can therefore apply the result obtained for the limit $\sqrt{\alpha}R \to \infty$ (equation (10)). These values, presented in table 3, are in satisfactory agreement with values from the earlier prediction [11]. The classical limit with the scaling factor $f \to 1$ gives values that are larger by about 0.4 au.

Table 3. Separation R between the electron and the F ion nearest to the electron in the STE. (NA, not available.) The values of R deduced from the parameter D is compared with theoretical predictions obtained independently.

	Value for the following crystals					
	LiF	NaF	KF	CaF_2	SrF_2	BaF_2
R (from D) (au)	10.8	12.4	13.7	4.7	4.6	4.8
R (calculated) (au)	NA	7.2	8.8	4.3	4.5	4.8

As for the alkaline-earth fluorides of the fluorite structure, we shall consider only configuration 2 as the correct geometry of the STE. In this case, the separation between the F and H centres is rather small as can be seen in figure 1(c). The classical limit is far from valid, and a scaling factor should reduce it [9]. In order to do this, one requires a reliable interpolation relation between the two limits studied above. In the absence of such work with realistic wavefunctions, we relied on published results obtained for two p orbitals of identical radial functions [14]. Using $\alpha = 0.05$ au and $R = 4.5$ au, we estimated the scaling factor to be around 0.1–0.2 from [14]. Values of R obtained from the D_{ss} data using a scaling factor of 0.2 are presented in table 3, together with the values obtained directly from the geometry of configuration 2 (figure 1(c)).

As a test of the on-centre model of the STE, we have estimated the zero-field splitting for the on-centre geometry of the STE. Song and Leung [15] have argued in a recent paper that the wavefunction of the s-like state of the on-centre STE in alkali halides is quite diffuse compared with that of an F centre (or the electron of an off-centre STE). Using the limiting expression of equation (11) for a short distance R, with $\alpha = 0.01$ au, $|D_{ss}|$ was found to be about 150 G. This seems to suggest that the on-centre STE is unable to account for the observed value of $|D|$ which is typically near 1000 G. A detailed analysis of this case, including the use of a more realistic wavefunction for the hole and an exact evaluation of the integral in equation (1), is now under way.

The present analysis suggests that the ODMR measurement may provide the most direct evidence of the off-centre structure of the STE in a NaCl-type lattice. There are a number of other experimental works which imply the off-centre structure of the STE. These include the analysis of the π emission band lifetime and Stokes shift [16], analysis of the emission band shape as a function of temperature [17], resonance Raman scattering [18] and studies of F-centre formation at low and high temperatures [4]. There has been discussion about the possible experiment which could present evidence of the off-centre symmetry and also give data on the axial shift. It seems that the measurement of the zero-field splitting provides such data, at least for the fluorides and maybe also the chlorides. It is remarkable that Block and Wasiela [7] have observed that D_{ss} is correlated to the lattice constant a as $a^{-2.31}$ for the fluorides and chlorides. As the idea of the split electron and hole configuration of the STE in alkali halides was not contemplated then, they did not attach further significance to the observed correlation. It is quite clear that the observed correlation between the lattice parameter and the absolute values of D should be interpreted as indicating the structure of the STE as a system of two fairly well separated interacting dipoles.

The comparison between the values deduced from the zero-field splitting D_{ss} and obtained geometrically for configuration 2 for the fluorites is only qualitative. This is

because we do not have an accurate expression of D_{ss} for intermediate separation. We have, however, quite convincingly shown that the structure of the STE which is compatible with the ODMR corresponds to the configuration 2 nearest-neighbour F–H pair in figure $1(c)$. A similar analysis can be extended to alkali chlorides, bromides and iodides also once we have reliably evaluated the contribution of the spin–orbit interaction to D. Such work is now under way as well as a more accurate evaluation of D_{ss} for intermediate separation R.

Acknowledgments

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