^{33}S splittings of some sulphur centres in KCl and NaCl

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Abstract. A new sulphur centre has been detected in KCl by means of EPR. The defect is shown to be the same as the B centre detected already by Matthys and co-workers in NaCl. By enriching the sulphur centres with ^{33}S it is shown to be an S_2^- ion in a divacancy site, in contrast to the S_2^- ion detected two decades ago and located in a single anion vacancy by Vannotti and co-workers. In KCl both varieties of S_2^- may coexist. Further experimental evidence is also presented to identify the earlier reported A centre as an interstitial S$^-$ ion.

1. Introduction

A few years ago our EPR group reported on some new sulphur centres in NaCl and KCl [1–2]. In both NaCl and KCl the low-temperature spectrum (A spectrum) was assigned to an S$^-$ centre. Recent theoretical work [3] confirmed this identification. In addition, a high-temperature spectrum (B spectrum) was detected in these NaCl specimens [1] and ascribed to a substitutional S_2^- centre. Since the latter has not previously been found in NaCl, in contrast to KCl, the discovery of the B spectrum apparently added NaCl to the series of host crystals wherein S_2^- could be introduced [4].

The purpose of the present experiments was to check the hypotheses mentioned above by introducing the corresponding ^{33}S-enriched defects in NaCl and KCl.

2. Experimental details

The NaCl and KCl single crystals were again grown by the Bridgman method [1]. Instead of adding a corresponding polysulphide, however, sulphur and the alkali metal were now introduced separately. Sulphur enriched to 25.54% (KCl) and 17.46% (NaCl) in the isotope ^{33}S ($I = \frac{3}{2}$) was purchased from Oak Ridge National Laboratory, and used in order to study the ^{33}S hyperfine interactions. Samples thus grown were routinely quenched from 575 °C to room temperature (RT) and x-irradiated at RT for typically 30 min with a tungsten anticathode Philips x-ray tube, operated at 60 kV and 40 mA. However, the quenching did not affect the detection conditions of the defects discussed below.

The EPR spectra were recorded using a Bruker ESP300 X-band spectrometer. The magnetic field was modulated at 100 kHz with a peak-to-peak amplitude of 10^{-4} T.

Table 1. g- and A-tensor of the A spectrum in NaCl and KCl (Φ is the tilting angle of the y and z axes with respect to [001] and [1$\bar{1}$0] respectively).

	NaCl	KCl
g_x [110]	2.3602 ± 0.0008	2.7665 ± 0.001
g_y ([001] + Φ)	2.2700 ± 0.0008	2.1502 ± 0.001
g_z ([1$\bar{1}$0] + Φ)	1.9574 ± 0.0008	1.7071 ± 0.001
Φ (deg)	14.2 ± 1.0	27.8 ± 1.0
A_x (MHz)	55.2 ± 1.0	143.3 ± 2.0
A_y (MHz)	46.9 ± 1.0	103.5 ± 2.0
A_z (MHz)	131.2 ± 1.0	101.7 ± 2.0
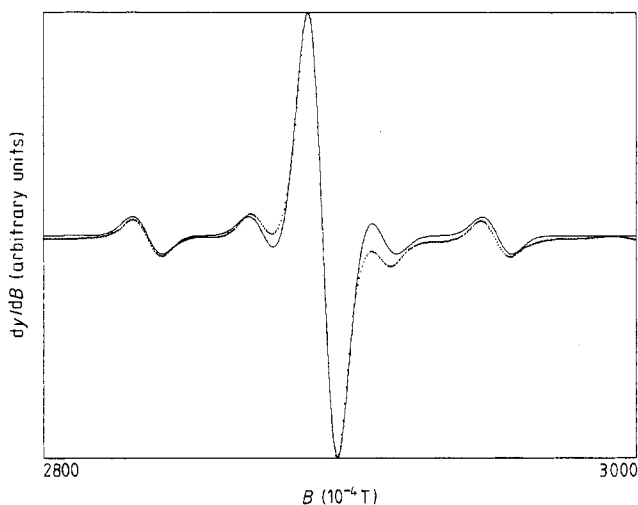
Figure 1. Computer simulation of the EPR spectrum of an S$^-$ defect in KCl together with the low-field part of the experimental A spectrum in the [001] orientation. . . . . . ., experimental curve at 4 K and 200 mW; ———, simulation with a Gaussian line shape and an intensity ratio of 12 between the central line and each of the HF lines.

All spectra were normalised to 9.47 GHz. The best detection conditions were low temperature (2 K) and high microwave power (200 mW) for the A spectra and high temperature (50 K) and intermediate microwave power (1 mW) for the B spectra (see also references [1] and [2]).

3. EPR results

3.1. A spectra

For both NaCl and KCl the A spectra described earlier [1, 2] were found together with their ^{33}S lines. The g- and A-tensor values are listed in table 1.

From the line intensity ratios the result that the A spectrum in KCl is due to a centre containing only one sulphur atom (figure 1) can be unambiguously derived. For KCl the

Table 2. g- and A-tensor of the B spectrum in NaCl and KCl (values in parentheses are only rough estimates).

	NaCl	KCl
g_x [110]	2.0107 ± 0.0005	1.9708 ± 0.0005
g_y [001]	1.9860 ± 0.0005	1.9491 ± 0.0005
g_z [1$\bar{1}$0]	2.2531 ± 0.0005	2.4548 ± 0.0005
A_x (MHz)	$<A_y$	(19.4)
A_y (MHz)	108.5 ± 2.0	99.9 ± 2.0
A_z (MHz)	$<A_y$	(32.8)

expected ratios between the central (i.e. the largest line) and the second-largest line for a centre containing one, two or three equivalent sulphur atoms are 11.66, 6.00, 4.11, whereas for NaCl we calculate 18.9, 9.56 and 6.44. In this calculation we took into account that a centre containing two ^{33}S nuclei also contributes to the central line intensity (neglecting the second-order corrections, which are small compared to the linewidth). Due to lower ^{33}S enrichment the experimental error is larger for NaCl than for KCl. Nevertheless all ratios determined for NaCl are fairly close to 18.9. This confirms the one-sulphur model for this centre.

3.2. B spectra

In KCl a new spectrum was found with g-tensor properties, saturation and thermal behaviour completely analogous to the B spectrum in NaCl (see also reference [1]). Hence it is also denoted as B spectrum. In table 2 both g-tensors are compared. It is interesting to note that within a few hundredths the principal g-values of the B spectrum in KCl are identical to those of the O_2^- molecular ion in KCl [5]. However this is not the case for NaCl.

The ^{33}S hyperfine (HF) tensors could only be determined incompletely. Except for the [001] orientation the linewidths are too large with respect to the HF splittings to yield reliable A-values. The A_x- and A_z-values mentioned in table 2 for KCl have been extrapolated and ought to be considered as rough estimates.

An important matter to be checked is again the intensity ratio between the central and HF lines. For KCl there is no doubt that the centre contains 2 sulphur atoms since all determined ratios are close to 6. In figure 2 a computer simulation for $\bar{B} \parallel y$ is compared with the experimental curve. Due to the lower ^{33}S enrichment, deviations up to 10% from 9.56 are found in NaCl, although again a model incorporating two sulphur atoms is by far the most probable.

4. Discussion

4.1. A spectra

The EPR results presented above provide evidence that the A centre contains one S nucleus. For the same reasons as given by Vannotti and Morton [6] the S^+, S^{3+} and SO^- possibilities can be disregarded. As already shown [3], the g-tensor can be fairly well explained in terms of a np^5 configuration in a crystal field with σ_d symmetry. Using this
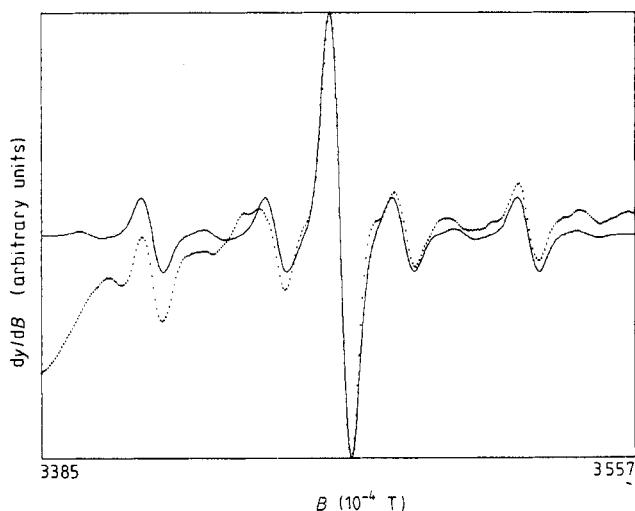
Figure 2. Computer simulation of the EPR spectrum of an S_2^- defect in KCl together with the high-field part of the experimental B spectrum in the [001] orientation. . . . . ., experimental curve at 50 K and 1 mW; ——, simulation with a Gaussian line shape and an intensity ratio of 6.00 between the central line and each of the largest HF lines. The theoretical contributions of all 11 lines are (only 9 are presented for reasons of overlapping in the experimental spectrum): 0.41, 0.82, 9.51, 1.22, 9.51, 57.07, 9.51, 1.22, 9.51, 0.82, 0.41.
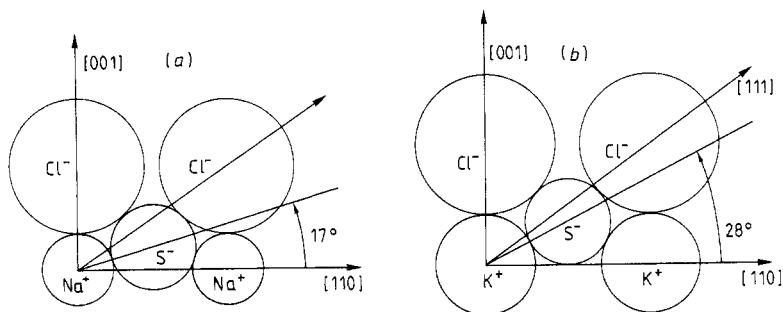
Figure 3. Model for an interstitial S^- in (*a*) NaCl and (*b*) KCl. The angles of 17 and 28 deg define the orientation of the line joining the centre of the interstitial cavity and the centre of a nearest Na^+ (or K^+) with respect to the [110] axis. The circle around S^- is the largest one that can be inscribed in the interstitial cavity by assuming a hard-sphere model for all ions involved.

hypothesis the hyperfine tensor was calculated in [6]. Assuming the following ground-state wavefunction

$$|\Phi_\beta^\alpha\rangle = \mp A|p_{x\alpha}^\beta\rangle - iB|p_{y\alpha}^\beta\rangle + C|p_{z\beta}^\alpha\rangle \tag{1}$$

they found the following principal A-values:

$$A_x = \gamma_e\gamma_N[(1 - 2A^2)8\pi|\Psi(0)|^2/3 + 4BC\langle r^{-3}\rangle_l - 0.4\langle r^{-3}\rangle_s(1 + A^2 - 3AC + 3AB)] \tag{2}$$

$$A_y = \gamma_e\gamma_N[(1 - 2B^2)8\pi|\Psi(0)|^2/3 + 4AC\langle r^{-3}\rangle_l - 0.4\langle r^{-3}\rangle_s(1 + B^2 - 3BC + 3AB)] \tag{3}$$

Table 3. Parameters A, B, C, l describing the wavefunction of the unpaired electron in an interstitial S^-. These parameters are defined in [6]. The listed HF parameters are calculated with these parameters.

	NaCl	KCl
A	0.0912	0.1845
B	0.1120	0.3106
C	0.9895	0.9324
l	0.8873	0.7791
A_x^{th} (MHz)	44.8	150.8
A_y^{th} (MHz)	36.8	99.2
A_z^{th} (MHz)	133.8	92.0

$$A_z = \gamma_e \gamma_N [(2C^2 - 1)8\pi|\Psi(0)|^2/3 + 4AB\langle r^{-3}\rangle_l + 0.4\langle r^{-3}\rangle_s(1 + C^2 - 3BC - 3AC)].$$

(4)

γ_e, γ_N have their usual meaning and the quantities $\gamma_e\gamma_N 8\pi|\Psi(0)|^2/3$, $\gamma_e\gamma_N\langle r^{-3}\rangle_l$, $\gamma_e\gamma_N\langle r^{-3}\rangle_s$ are considered to be adjustable parameters. They are introduced when a 'one-electron' wavefunction cannot account for the observed hyperfine splittings, as is the case here. The origin of $\gamma_e\gamma_N 8\pi|\Psi(0)|^2/3$ is connected with the interaction between the nuclear spin and the electron spin density at the nucleus and differs in this case from zero by the 'core polarisation' of the inner s electrons. $\gamma_e\gamma_N\langle r^{-3}\rangle_l$ and $\gamma_e\gamma_N\langle r^{-3}\rangle_s$ describe the interaction between the nuclear magnetic moment and the electron orbit and the electron spin distribution outside the nucleus, respectively [7].

From their experiments Vannotti and Morton [6] derived values for the parameters $\gamma_e\gamma_N 8\pi|\Psi(0)|^2/3$, $\gamma_e\gamma_N\langle r^{-3}\rangle_l$, $\gamma_e\gamma_N\langle r^{-3}\rangle_s$ of 35, 143 and 172 MHz for KCl [6]. Using these values and the A, B and C from our g-tensor we can 'predict' the principal values of the A-tensor in table 3.

Comparing tables 1 and 3 we find that a fair agreement is obtained. From this we may conclude that the A spectrum is very probably caused by an S^- centre. The most plausible model seems to be an interstitial S^- ion. No SHF structure could be resolved but the measured linewidths are considerably larger than for the $S^-[110]$ ion associated with an anion vacancy (20.1 G compared to 6.1 G). The smaller l-values for the presented centres referred to the $S^-[110]$ ion also point to a larger overlap with neighbouring ions and hence support the interstitial model.

For the O^- centre in KCl and RbCl [8], and for the A centre discussed here, the small size of the interstitial cavity may account for the tilting angle of two g- and A-tensor axes. Finally we may try to elucidate the values of these tilting angles: 15° in NaCl and 28° in KCl. It may be interesting to note that these angles are, within the experimental error, equal to the angle of [110] and the line formed by the centre of the interstitial cavity and the centre of the Na^+ ion (figure 3). The centre of the interstitial cavity is calculated by assuming a hard-sphere model for Na^+, K^+ and Cl^- (ionic radii 0.97, 1.33 and 1.81 Å, respectively).

4.2. B spectra

We will show that there is strong evidence that the B spectra must be ascribed to S_2^- ions substituting for two Cl^- ions (figure 4). As mentioned in § 3.2 the B centre contains two
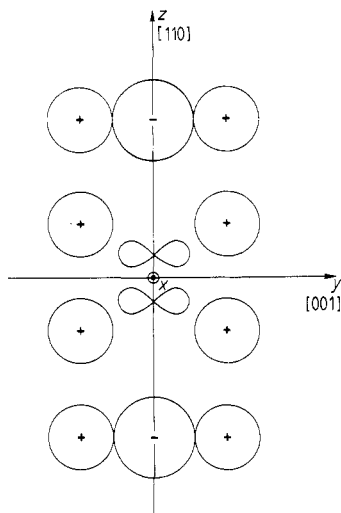
Figure 4. Model for an S_2^- ion in a divacancy site. The y axis defines the directions of the p functions.

sulphur atoms. Of course a lot of possibilities remain, e.g. S_2O^-, $S_2O_2^-$, $S_2O_3^-$ (hydrogen-containing centres can be discarded by the absence of hydrogen HF interactions). These oxygen-containing radicals are known from EPR studies on $Na_2S_2O_3$ [9]. For the latter both g- and A-values are quite different from the values for the centre in table 2, e.g. S_2O^- has all g-values larger than $g_e = 2.0023$; $S_2O_2^-$ has a nearly isotropic g-tensor again with all g-values larger than g_e, etc. In addition we do not expect that enough oxygen is present in these samples grown under the described conditions. As a result only the S_2^- ion remains plausible.

The latter assumption is further supported by the analysis of the g- and A-tensor. Applying the theory for O_2^- (or S_2^-) derived in [5], the principal values of the g-tensor are given by (here $g_x > g_y$, which means that the unpaired electron is placed in the $^2\Gamma_4^+$ ($^2\Pi_g^y$) state)

$$g_x = g_e \cos(2\alpha) + [\cos(2\alpha) + 1 - \sin(2\alpha)]l_y\lambda_y/E \tag{5}$$

$$g_y = g_e \cos(2\alpha) + [\sin(2\alpha) - 1 + \cos(2\alpha)]l_y\lambda_y/E \tag{6}$$

$$g_z = g_e + 2l_z \sin(2\alpha). \tag{7}$$

These expressions contain three independent parameters $\lambda/\Delta_0 = \tan 2\alpha$, $l_y\lambda_y/E$ and l_z which are all defined in [5]. They can be calculated to be $\lambda/\Delta = 0.1353$, $l_y\lambda_y/E = 0.0143$ and $l_z = 0.9351$ for NaCl and $\lambda/\Delta_0 = 0.2419$, $l_y\lambda_y/E = 0.0142$ and $l_z = 0.9624$ for KCl.

Both l_z-values are much closer to unity than $l_z = 0.80$ found for S_2^- in KCl [4]. This might point to a S_2^- ion that is more weakly bound to the surrounding lattice, in agreement with the greater possibility of accommodation in a divacancy site.

The equations for the principal components of the ^{33}S HF-tensor in the case of S_2^- are [6]

$$A_x = \gamma_e\gamma_N\{8\pi|\Psi(0)|^2 \cos(2\alpha)/3 + 0.1[\cos(2\alpha) - 3 + 3\sin(2\alpha)]\langle r^{-3}\rangle_s\} \tag{8}$$

$$A_y = \gamma_e\gamma_N\{8\pi|\Psi(0)|^2 \cos(2\alpha)/3 + 0.1[\cos(2\alpha) + 3 - 3\sin(2\alpha)]\langle r^{-3}\rangle_s\} \tag{9}$$

$$A_z = \gamma_e\gamma_N[8\pi|\Psi(0)|^2 \cos(2\alpha)/3 - 0.2\langle r^{-3}\rangle_s + \sin(2\alpha)\langle r^{-3}\rangle_l]. \tag{10}$$

Using again the values for the $\langle r^{-3}\rangle$-parameters calculated in [6], we calculate $A_x =$

7.0, $A_y = 96.4$ and $A_z = 19.8$ MHz for NaCl and $A_x = 11.3$, $A_y = 90.2$ and $A_z = 34.2$ MHz for KCl.

As already stated in [5] and [6], the predicted principal A-values are about 10 MHz too small since $\gamma_e \gamma_N 8\pi |\Psi(0)|^2/3$ is expected to be larger in a molecule than in an atom. Making this correction the agreement between calculated and experimental A-values can be called excellent. A_x and A_z are too small to be determined accurately. Once again the credibility of Vannotti and Morton's [6] $\langle r^{-3}\rangle$-parameters is demonstrated.

In both NaCl and KCl the direction of the largest HF splitting is the direction of the p_y wavefunction as in the case of O_2^- [5]. In the S_2^- ion detected by Vannotti and Morton [4], however, the largest HF splitting was found to correspond with the S–S bond direction [4].

The arguments given above show that very likely an S_2^- ion is responsible for the B spectrum but the problem of its location remains to be solved. Since in KCl an S_2^- ion has already convincingly been identified [4], the B spectrum in both KCl and NaCl should be ascribed to an S_2^- ion in another location. This also means that in NaCl no spectrum has been observed from an S_2^- ion replacing one Cl^- ion. We believe that the S_2^- ion described here, substitutes for two Cl^- ions as shown in figure 4. Such a defect has an effective positive charge, whereas the S_2^- ion reported by Vannotti has no effective charge. It has to be noted that the simultaneous occurrence of the A and B spectra may be related to their opposite effective charges (an interstitial S^- has a net negative charge). In a divacancy position the S_2^- ion is expected to be more loosely bound to the surrounding lattice than the S_2^- detected by Vannotti and Morton [4]. The higher l_z-values are in good agreement with this hypothesis. The saturation behaviour of the B spectrum further supports the latter. The addition of sufficient alkali metal M to the alkali halogenide salt ensures that S^{2-} is introduced with a compensating Cl^- vacancy

$$M_2S \rightarrow 2M^+ + S^{2-} + \square_{Cl^-}.$$
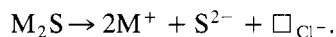
Too low a concentration of Cl^- vacancies may explain why doping procedures with polysulphide [2] or sulphur alone [4] did not give rise to the B spectrum. Finally it is remarkable that the S_2^- detected by Vannotti and Morton [4] in NaI has a g-tensor comparable to the new S_2^- in NaCl. In both cases sufficient room is available for the S_2^- ion (one I^- vacancy and two Cl^- vacancies, respectively).

5. Conclusion

The EPR results on ^{33}S-enriched KCl and NaCl samples have corroborated earlier assignments of the A and B spectra. The former has been ascribed to an interstitial S^- ion while the latter was explained in terms of an S_2^- ion in a divacancy site. Both centres are characterised by net effective charges opposite to one another. This situation is completely different from the S^- and S_2^- centres found by Vannotti and Morton [4, 6] which are both electrically neutral. Further investigations are in progress to elucidate the formation mechanisms of this kind of centres.

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