

An EPR study and spin-Hamiltonian analysis of a new $S\text{Se}^-$ defect in NaCl

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

1994 J. Phys.: Condens. Matter 6 8065

(<http://iopscience.iop.org/0953-8984/6/39/025>)

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

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:39

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

An EPR study and spin-Hamiltonian analysis of a new SSe^- defect in NaCl

F Maes, S Van Doorslaer, F Callens, P Moens, P Matthys and E Boesman
Vakgroep Vaste-Stofwetenschappen, Universiteit Gent, Krijgslaan 281-S1, B-9000 Gent,
Belgium

Received 3 May 1994

Abstract. An EPR study of a new S–Se defect in NaCl is presented. The paramagnetic centre is formed after appropriate doping and exposure to x-rays at room temperature. By enriching the SSe^- centre with either ^{33}S or ^{77}Se it is shown that the defect involves one S and one Se nucleus. Theoretical expressions for the \mathbf{g} and hyperfine tensors are derived and compared to the experimental results.

1. Introduction

Chalcogen impurity ions have been studied by means of EPR in a number of alkali-halide matrices. Since 1959 many different homogeneous chalcogen defects have been observed and it has been shown that several types of monatomic X^- ($X = \text{O}, \text{S}, \text{Se}$) [1–17], diatomic X_2^- [10, 14, 16, 18–27], triatomic X_3^- [17, 28–30] and tetra-atomic X_4^- [28] defect exist.

So far the SSe^- ion is the only mixed chalcogen centre that has been investigated, cursorily by Vannotti and Morton [23]. The discovery that it is possible to introduce the S_2^- [10] and the even larger Se_2^- centres into NaCl [16] prompted us to attempt to form the mixed SSe^- centre in NaCl in an analogous way. This paper deals with the SSe^- centre investigated by means of EPR and presents a theoretical analysis of the \mathbf{g} and hyperfine tensors.

2. Experimental details

Single crystals were grown by the Bridgman method [16]. The growth capsule contained NaCl powder (p.a. UCB) and about 0.1 wt% of S, Se and pure Na metal. The NaCl powder was dried in vacuum for one week at 250 °C. The Na metal, the S and the Se were added to the NaCl powder under an Ar atmosphere in a plastic bag (Aldrich Chemie) fitted with gloves. S enriched to 17% was used in order to study the ^{33}S ($I = \frac{3}{2}$) (Oak Ridge National Laboratory) hyperfine interaction and Se enriched to 87% in order to study the ^{77}Se ($I = \frac{1}{2}$) (AEA Technology) hyperfine interaction. Unenriched crystals, crystals enriched in ^{33}S and crystals enriched in ^{77}Se were grown. Samples thus grown were routinely quenched from 600 °C to room temperature (RT). The crystals were then x-irradiated at RT for typically 30 min with a W-anticathode Philips x-ray tube, operated at 60 kV and 40 mW.

All EPR spectra were recorded with a Bruker ESP300 X band spectrometer, equipped with an Oxford Instruments ESR10 flow cryostat, and normalized to 9.47 GHz. The magnetic field was modulated at 100 kHz with a peak-to-peak amplitude of 10^{-4} T. The

samples could be rotated about a vertical axis perpendicular to the magnetic field B . Crystals cleaved to rotate around a $\langle 001 \rangle$ direction were prepared and an angular dependence was determined. The best detection conditions were relatively high temperature (30 K) and high microwave power (200 mW).

3. EPR results

Resonances originating from S_2^- , Se_2^- and the new SSe^- defect were all visible at 30 K and 200 mW. Exact alignment of the crystal, so that B was parallel to $\langle 100 \rangle$ or $\langle 110 \rangle$, was carried out by observing the coincidence of certain lines in the S_2^- and Se_2^- spectra. The angular variation of the $S^{77}Se^-$ lines is shown in figure 1. Some lines are not indicated because of the overlap with the EPR resonances of the S_2^- and Se_2^- defects.

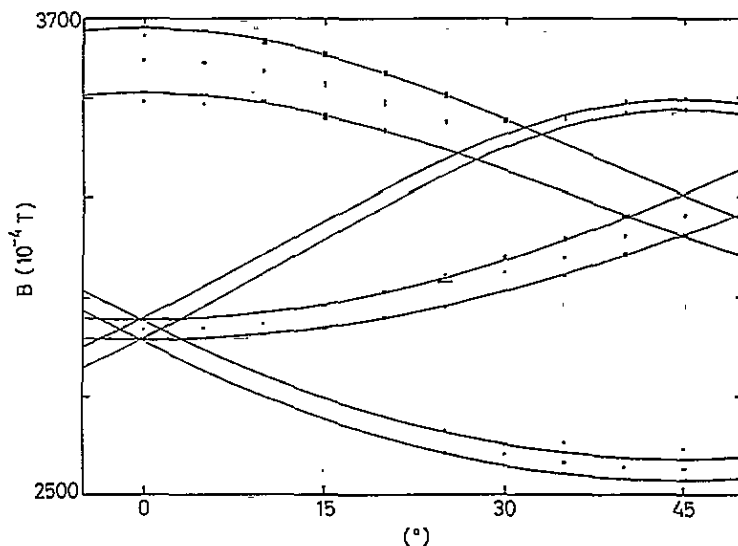


Figure 1. The angular variation of the $S^{77}Se^-$ defect (0° corresponds to $B \parallel \langle 100 \rangle$, 45° corresponds to $B \parallel \langle 110 \rangle$).

In table 1 the g and hyperfine tensors are listed for this new SSe^- centre. No indications were found for non-coinciding hyperfine- and g -tensor principal axes.

Table 1. The g and A tensors for the SSe^- centre in NaCl (hyperfine principal values in megahertz).

$\langle 110 \rangle$	$\langle 001 \rangle$	$\langle 1\bar{1}0 \rangle$
$g_x = 1.9421$	$g_y = 1.8818$	$g_z = 2.6393$
$A_x^S \ll A_z^S$	$A_y^S = 80$	$A_z^S = 60$
$A_x^{Se} = 69$ (?)	$A_y^{Se} = 432$	$A_z^{Se} = 200$

The ^{33}S hyperfine tensor could only be determined incompletely and only estimates were obtained for this hyperfine tensor due to the rather low ^{33}S enrichment available. The ^{77}Se hyperfine tensor could be evaluated fairly well although the obtained A_x value is not very accurate.

From the line-intensity ratios it can be shown that the spectra are due to a centre containing only one S and one Se atom. There is consequently little doubt that the centre under investigation is the $S\text{Se}^-$ centre. This will be further substantiated by the g - and hyperfine-tensor analysis.

4. Theoretical formulas for the g tensor

In this and the next sections we develop a theory to acquire a quantitative understanding of the g and hyperfine tensors. The formulas were derived in an analogous way to the formulas for the g and hyperfine tensors of the homogeneous diatomic O_2^- centre by Zeller and Känzig [19].

The $S\text{Se}^-$ molecule has 51 electrons. For the calculations, we consider the following part of the molecular configuration for the free $S\text{Se}^-$ ion (figure 2):

$$\dots (1\sigma)^2 (1\pi)^4 (2\pi)^3 (2\sigma)^0$$

with a $^2\Pi$ ground state. In contradistinction to the homonuclear chalcogen molecules, the u and g classification does not apply since there is no inversion symmetry. The indices 1 and 2 distinguish between the orbitals. The σ levels are twofold and the π levels fourfold degenerate when spin is considered for the free $S\text{Se}^-$ molecule. For the free molecular ion the symmetry is $C_{\infty v}$.

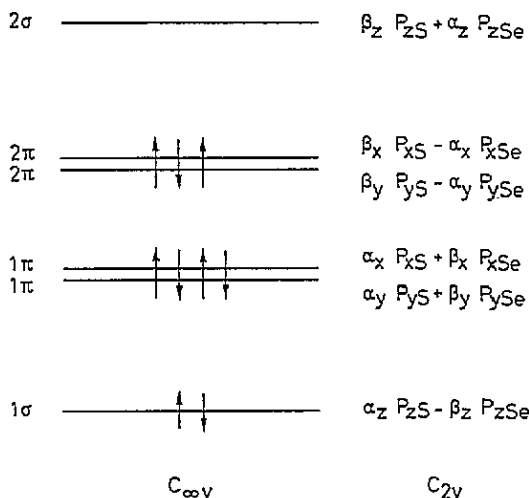


Figure 2. The energy-level scheme of the free $S\text{Se}^-$ ion.

When the molecule is placed in an orthorhombic crystal field, then the symmetry group of $S\text{Se}^-$ and its surroundings is lowered from $C_{\infty v}$ to C_{2v} and the degeneracy of the π orbitals is lifted.

4.1. The ground state of the $S\text{Se}^-$ centre

In this section we determine the theoretical formulas for the \mathbf{g} tensor of the $S\text{Se}^-$ centre in an orthorhombic crystal field. The centre exhibits C_{2v} symmetry in such a field.

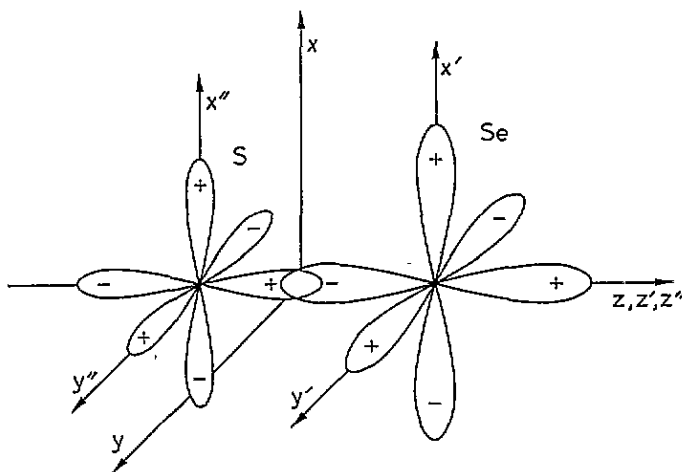


Figure 3. A pictorial representation of the p_x , p_y and p_z lobes of the $S\text{Se}^-$ ion and the definition of the X , Y and Z axes.

Using group theory and considering figure 3, we find for the MO-LCAOs

$$\begin{aligned}
 |a_1^*\rangle &= \alpha_{2z}p_{zS} + \beta_{2z}p_{zSe} && \text{anti-binding} \\
 |b_1^*\rangle &= \alpha_{2x}p_{xS} - \beta_{2x}p_{xSe} && \text{anti-binding} \\
 |b_2^*\rangle &= \alpha_{2y}p_{yS} - \beta_{2y}p_{ySe} && \text{anti-binding} \\
 |b_1\rangle &= \alpha_{1x}p_{xS} + \beta_{1x}p_{xSe} && \text{binding} \\
 |b_2\rangle &= \alpha_{1y}p_{yS} + \beta_{1y}p_{ySe} && \text{binding} \\
 |a_1\rangle &= \alpha_{1z}p_{zS} - \beta_{1z}p_{zSe} && \text{binding.}
 \end{aligned}$$

The α and β are connected by the following orthonormality relations, neglecting the overlap between the AOs ($3p_S$ and $4p_{Se}$) of different nuclei:

$$\alpha_{1x}^2 + \beta_{1x}^2 = 1 \quad \alpha_{2x}^2 + \beta_{2x}^2 = 1 \quad \alpha_{1x}\alpha_{2x} - \beta_{1x}\beta_{2x} = 0 \quad (\text{cycl. } y, z).$$

It follows that we can put without loss of generality

$$\beta_{2x} = \alpha_{1x} = \alpha_x \quad \beta_{1x} = \alpha_{2x} = \beta_x \quad (\text{cycl. } y, z).$$

Using these results we find

$$\begin{aligned}
 |a_1^*\rangle &= \beta_z p_{zS} + \alpha_z p_{zSe} && \text{anti-binding} \\
 |b_1^*\rangle &= \beta_x p_{xS} - \alpha_x p_{xSe} && \text{anti-binding} \\
 |b_2^*\rangle &= \beta_y p_{yS} - \alpha_y p_{ySe} && \text{anti-binding} \\
 |b_1\rangle &= \alpha_x p_{xS} + \beta_x p_{xSe} && \text{binding} \\
 |b_2\rangle &= \alpha_y p_{yS} + \beta_y p_{ySe} && \text{binding} \\
 |a_1\rangle &= \alpha_z p_{zS} - \beta_z p_{zSe} && \text{binding.}
 \end{aligned}$$

Using these molecular orbitals we can describe the ground state of the SSe^- centre by defining the four following Slater determinants (the + and - signs indicated are associated with $M_S = +\frac{1}{2}$ and $M_S = -\frac{1}{2}$):

$$\begin{aligned} |0+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle & |0-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle \\ |1+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_2^* b_2^*\rangle & |1-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_2^* \bar{b}_1^* b_2^*\rangle. \end{aligned}$$

In an orthorhombic crystal field the fourfold degeneration of the free-ion ${}^2\Pi$ state is removed. The paramagnetic electron is then located either in a $|b_1^*\rangle$ or $|b_2^*\rangle$ orbital, yielding a 2B_1 or 2B_2 ground state respectively. From now on we will assume that the paramagnetic electron is localized in $|b_2^*\rangle$; the other case will be summarized at the end of the calculations. The energy splitting between $|0\rangle$ and $|1\rangle$ is determined by the crystal-field Hamiltonian H_c , which transforms according to A_1 and hence only has diagonal matrix elements. We define

$$\langle 0 | H_c | 0 \rangle = 2V_{a_1} + 2V_{b_1} + 2V_{b_2} + 2V_{b_1^*} + V_{b_2^*} = V_1$$

$$\langle 1 | H_c | 1 \rangle = 2V_{a_1} + 2V_{b_1} + 2V_{b_2} + V_{b_1^*} + 2V_{b_2^*} = V_2$$

$$V_{b_1^*} < V_{b_2^*} \Rightarrow V_2 > V_1$$

where V_{a_1} , V_{b_1} , V_{b_2} , $V_{b_1^*}$ and $V_{b_2^*}$ are one-electron crystal-field energies (figure 4).

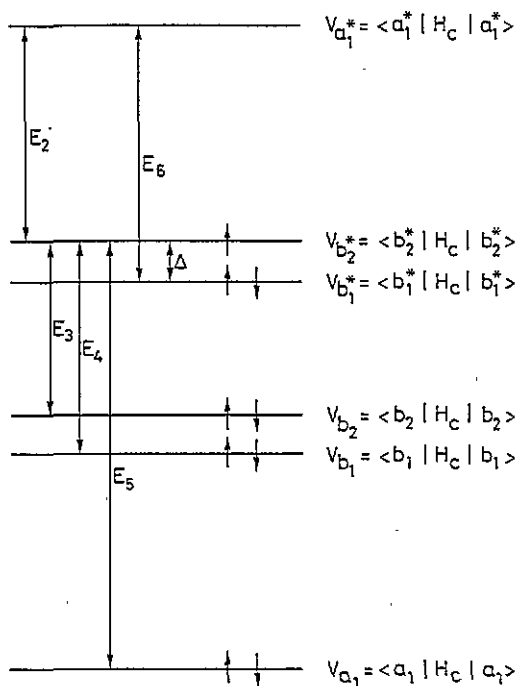


Figure 4. The energy-level scheme of SSe^- in NaCl in the case of a 2B_2 ground state.

So far, we have not used the spin-orbit interaction H_{SO} . An exact relativistic theory of polyelectronic systems is not known. In the Pauli approximation the relativistic correction H_{SO} is

$$H_{SO} = \sum_{i=1}^9 \zeta_{Sl_{iS}} \cdot S_i + \zeta_{Se l_{iSe}} \cdot S_i.$$

ζ_X ($X = S, Se$) is the spin-orbit coupling constant for a valence electron of the $X^{-1/2}$ ion; we use this average because the SSe^- ion is built up primarily from S and Se^- or S^- and Se valence electrons, so it is a reasonable approximation to construct the SSe^- ion from $S^{-1/2}$ and $Se^{-1/2}$ (see e.g. [31]). l_{iX} is the orbital-angular-momentum operator of electron i referred to nucleus X . We used a one-electron description and hence each ζ is positive. The summation goes over the nine electrons of the paramagnetic system. The ζ_X and $\zeta_S = 161 \text{ cm}^{-1}$ [32] and $\zeta_{Se} = 918 \text{ cm}^{-1}$ [33]; these represent the average of the ζ values of the X^- ion and X^0 atom ($\zeta_X = \frac{1}{2}(\zeta_{X^0} + \zeta_{X^-})$).

The eigenvalues and eigenfunctions of the molecular centre are determined in a first-order approximation by the matrix $\mathbf{H} = \mathbf{H}_c + \mathbf{H}_{SO}$, calculated between the four Slater determinants mentioned before. We now label the following parameter:

$$\lambda_{\beta_x\beta_y} = \zeta_S\beta_x\beta_y + \zeta_{Se}\alpha_x\alpha_y.$$

The 4×4 representation matrix of $\mathbf{H} = \mathbf{H}_c + \mathbf{H}_{SO}$ is then

	$ 0+\rangle$	$ 1+\rangle$	$ 0-\rangle$	$ 1-\rangle$
$\langle 0+ $	V_1	$(i/2)\lambda_{\beta_x\beta_y}$	0	0
$\langle 1+ $	$-(i/2)\lambda_{\beta_x\beta_y}$	V_2	0	0
$\langle 0- $	0	0	V_1	$-(i/2)\lambda_{\beta_x\beta_y}$
$\langle 1- $	0	0	$(i/2)\lambda_{\beta_x\beta_y}$	V_2

An eigenvalue W of this Hamiltonian satisfies the equation

$$\{(V_1 - W)(V_2 - W) - \lambda_{\beta_x\beta_y}^2/4\}^2 = 0.$$

So the eigenvalues are

$$W_1 = (V_1 + V_2)/2 + \frac{1}{2}\sqrt{(V_1 - V_2)^2 + \lambda_{\beta_x\beta_y}^2} = V_2 + \frac{1}{2}\lambda_{\beta_x\beta_y} \tan \phi$$

$$W_2 = (V_1 + V_2)/2 - \frac{1}{2}\sqrt{(V_2 - V_1)^2 + \lambda_{\beta_x\beta_y}^2} = V_1 - \frac{1}{2}\lambda_{\beta_x\beta_y} \tan \phi$$

and the corresponding eigenfunctions

$$W_1 : |H+\rangle = \cos \phi |1+\rangle - i \sin \phi |0+\rangle \quad |H-\rangle = \cos \phi |1-\rangle + i \sin \phi |0-\rangle$$

$$W_2 : |G+\rangle = \cos \phi |0+\rangle + i \sin \phi |1+\rangle \quad |G-\rangle = \cos \phi |0-\rangle - i \sin \phi |1-\rangle$$

in which we used

$$\tan 2\phi = \lambda_{\beta_x\beta_y}/\Delta$$

$$\Delta = V_2 - V_1 = V_{b_2} - V_{b_1} > 0.$$

The energy-level scheme of the SSe^- centre is given in figure 4.

The \mathbf{g} tensor is the expectation value of the Zeeman Hamiltonian within the ground state $|G\rangle$:

$$\mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} = \mu_B \mathbf{B} \cdot \langle G | \sum_{i=1}^9 l_{iS} + l_{iSe} + g_e s_i | G \rangle.$$

Following Zeller and Känzig [19] we introduce (in the next formula l_z is an adjustable parameter and not the operator l_z)

$$\langle 0 | \sum_{i=1}^9 l_{iZS} + l_{iZSe} | 1 \rangle = i \{ \beta_x \beta_y l_{zS} + \alpha_x \alpha_y l_{zSe} \} = i \tilde{l}_z.$$

For the free molecular ion l_{zS} and l_{zSe} are equal to one. The deviation of l_{zS} and l_{zSe} from one is a measure of the orthorhombic distortion of the eigenfunction of the centre.

This leads to the following expressions for the principal values of the \mathbf{g} tensor:

$$g_x = g_e \cos 2\phi \quad g_y = g_e \cos 2\phi \quad g_z = g_e + 2l_z \sin 2\phi.$$

From these formulas, we see that the largest g value is found along the bounding axis of the SSe^- ion. Using first-order theory one sees that g_x and g_y are equal and both less than the free-electron value. The latter agrees with experiment; the former does not.

4.2. Mixing of higher energy levels

Until now, we have only used $|0\rangle$ and $|1\rangle$ in the calculations of the \mathbf{g} tensor. However other energy levels can be mixed with the ground state due to the H_{SO} Hamiltonian. The effect of this mixing seems to be large enough to explain the slight difference between g_x and g_y . The mixing of other levels is given by

$$|\Psi\rangle = |g\rangle - \sum_j \frac{\langle j | H_{SO} | G \rangle}{\epsilon_j - W_2} |j\rangle.$$

The ground state becomes, after mixing with other states, using first-order perturbation theory

$$\begin{aligned} |\Psi+\rangle &= |G+\rangle - \frac{i}{2} \frac{\lambda_{\beta_x \beta_y}}{E_2} \cos \phi |2-\rangle - \frac{1}{2} \frac{\lambda_{\beta_x \alpha_y}}{E_3} \sin \phi |3+\rangle + \frac{i}{2} \frac{\lambda_{\alpha_x \beta_y}}{E_4} \cos \phi |4+\rangle \\ &\quad - \frac{i}{2} \left(\frac{\lambda_{\beta_y \alpha_z}}{E_5} \cos \phi - \frac{\lambda_{\beta_x \alpha_z}}{E_5} \sin \phi \right) |5-\rangle - \frac{1}{2} \frac{\lambda_{\beta_x \beta_y}}{E_6} \sin \phi |6-\rangle \\ |\Psi-\rangle &= |G-\rangle - \frac{i}{2} \frac{\lambda_{\beta_y \beta_z}}{E_2} \cos \phi |2+\rangle - \frac{1}{2} \frac{\lambda_{\beta_x \alpha_y}}{E_3} \sin \phi |3-\rangle - \frac{i}{2} \frac{\lambda_{\alpha_x \beta_y}}{E_4} \cos \phi |4-\rangle \\ &\quad - \frac{i}{2} \left(\frac{\lambda_{\beta_y \alpha_z}}{E_5} \cos \phi - \frac{\lambda_{\beta_x \alpha_z}}{E_5} \sin \phi \right) |5+\rangle + \frac{1}{2} \frac{\lambda_{\beta_y \beta_z}}{E_6} \cos \phi |6+\rangle \end{aligned}$$

where

$$\begin{aligned} |2+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* a_1^*\rangle & |2-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* a_1^*\rangle \\ |3+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle & |3-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2^* \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle \\ |4+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle & |4-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle \\ |5+\rangle &= |a_1 \bar{b}_2^* b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle & |5-\rangle &= |b_2^* \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{b}_1^* b_2^*\rangle \\ |6+\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 a_1^* \bar{b}_1^* b_2^*\rangle & |6-\rangle &= |a_1 \bar{a}_1 b_1 \bar{b}_1 b_2 \bar{b}_2 b_1^* \bar{a}_1^* \bar{b}_2^*\rangle \end{aligned}$$

$$E_2 = \epsilon_2 - W_2 = \langle 2 | H_C | 2 \rangle - W_2 = V_{a_1^*} - V_{b_2^*} + \frac{1}{2} \lambda_{\beta_x \beta_y} \tan \phi$$

$$E_3 = \epsilon_3 - W_2 = \langle 3 | H_C | 3 \rangle - W_2 = V_{b_2^*} - V_{b_2} + \frac{1}{2} \lambda_{\beta_x \beta_y} \tan \phi$$

$$E_4 = \epsilon_4 - W_2 = \langle 4 | H_C | 4 \rangle - W_2 = V_{b_2^*} + \frac{1}{2} \lambda_{\beta_x \beta_y} \tan \phi$$

$$E_5 = \epsilon_5 - W_2 = \langle 5 | H_C | 5 \rangle - W_2 = V_{b_2^*} - V_{a_1} + \frac{1}{2} \lambda_{\beta_x \beta_y} \tan \phi$$

$$E_6 = \epsilon_6 - W_2 = \langle 6 | H_C | 6 \rangle - W_2 = V_{a_1^*} - V_{b_1^*} + \frac{1}{2} \lambda_{\beta_x \beta_y} \tan \phi$$

$$\lambda_{\alpha_x \beta_y} = \zeta_S \alpha_x \beta_y - \zeta_{Se} \beta_x \alpha_y \quad \lambda_{\beta_x \alpha_y} = \zeta_S \beta_x \alpha_y - \zeta_{Se} \alpha_x \beta_y$$

$$\lambda_{\beta_x \alpha_z} = \zeta_S \beta_x \alpha_z + \zeta_{Se} \alpha_x \beta_z \quad \lambda_{\beta_y \alpha_z} = \zeta_S \beta_y \alpha_z + \zeta_{Se} \alpha_y \beta_z$$

$$\lambda_{\beta_x \beta_z} = \zeta_S \beta_x \beta_z - \zeta_{Se} \alpha_x \alpha_z \quad \lambda_{\beta_y \beta_z} = \zeta_S \beta_y \beta_z - \zeta_{Se} \alpha_y \alpha_z.$$

Now the \mathbf{g} tensor is

$$g_x = g_e \cos 2\phi + l_{\beta_x \alpha_z} \{ (\lambda_{\beta_y \alpha_z} / E_5) (\cos 2\phi + 1) - (\lambda_{\beta_x \alpha_z} / E_5) \sin 2\phi \} \\ - l_{\beta_y \beta_z} (\lambda_{\beta_y \beta_z} / E_2) (\cos 2\phi + 1) \\ g_y = g_e \cos 2\phi + l_{\beta_x \alpha_z} \{ (\lambda_{\beta_y \alpha_z} / E_5) \sin 2\phi + (\lambda_{\beta_x \alpha_z} / E_5) (\cos 2\phi - 1) \} - l_{\beta_x \beta_z} (\lambda_{\beta_y \beta_z} / E_6) \sin 2\phi \\ g_z = g_e + 2l_z \sin 2\phi - l_{\beta_x \alpha_y} (\lambda_{\beta_x \alpha_y} / E_3) (\cos 2\phi - 1) + l_{\alpha_x \beta_y} (\lambda_{\alpha_x \beta_y} / E_4) (\cos 2\phi + 1).$$

These expressions predict $g_x > g_y$ for small ϕ . Since these calculations were made with the assumption that the unpaired electron was placed in $|b_2^*\rangle = \beta_y p_{yS} - \alpha_y p_{ySe}$ we conclude that the smallest g value is found along the y axis, which is the direction of the paramagnetic p lobe, and that the ground state is 2B_2 .

When we assume that the unpaired electron is placed in $|b_1^*\rangle$, then we find the following results:

$$g_x = g_e \cos 2\phi + l_{\beta_x \alpha_z} \{ (\lambda_{\beta_x \alpha_z} / E_5) \sin 2\phi + (\lambda_{\beta_y \alpha_z} / E_5) (\cos 2\phi - 1) \} - l_{\beta_y \beta_z} (\lambda_{\beta_x \beta_z} / E_6) \sin 2\phi \\ g_y = g_e \cos 2\phi + l_{\beta_x \alpha_z} \{ (\lambda_{\beta_x \alpha_z} / E_5) (\cos 2\phi + 1) - (\lambda_{\beta_y \alpha_z} / E_5) \sin 2\phi \} \\ - l_{\beta_x \beta_z} (\lambda_{\beta_x \beta_z} / E_2) (\cos 2\phi + 1) \\ g_z = g_e + 2l_z \sin 2\phi + l_{\beta_x \alpha_y} (\lambda_{\beta_x \alpha_y} / E_3) (\cos 2\phi + 1) - l_{\alpha_x \beta_y} (\lambda_{\alpha_x \beta_y} / E_4) (\cos 2\phi - 1).$$

These expressions predict $g_x < g_y$ for small ϕ . These calculation were made with the assumption that the unpaired electron was placed in $|b_1^*\rangle = \beta_x p_{xS} - \alpha_x p_{xSe}$, the smallest g value is found along the x axis, the direction of the paramagnetic p lobe, and the ground state is 2B_1 .

When we make the limiting case going from a heterogeneous to a homogeneous diatomic molecule for the case of $g_x > g_y$ then we have to replace the α and β by $1/\sqrt{2}$ and $\zeta_S = \zeta_{Se} = \lambda$ in our formulas. Doing so we find the following results:

$$g_x = g_e \cos 2\phi + (\lambda/E) \{ \cos 2\phi + 1 - \sin 2\phi \} \quad g_y = g_e \cos 2\phi + (\lambda/E) \{ \cos 2\phi - 1 + \sin 2\phi \} \\ g_z = g_e + 2l_z \sin 3\phi.$$

Comparing, one sees that these formulas are identical with those found by Zeller and Känzig [19] for homonuclear diatomic chalcogen centres.

5. Theoretical formulas for the \mathbf{A} tensor

The nuclear hyperfine structure can be expressed in terms of the following Hamiltonian:

$$H_{\text{HF}} = 2\mu_B \mu_N g_N \frac{\mu_0}{4\pi} \sum_{i=1}^9 \sum_{j=1}^2 \left\{ \frac{8\pi}{3} |\Psi(0)|_j^2 \mathbf{S}_i \cdot \mathbf{I}_j + \langle r^{-3} \rangle_i l_{ij} \cdot \mathbf{I}_j \right. \\ \left. + \langle r^{-3} \rangle_{sj} \left[3 \frac{(\mathbf{r}_{ij} \cdot \mathbf{I}_j)(\mathbf{r}_{ij} \cdot \mathbf{s}_i)}{r_{ij}^2} \mathbf{s}_i \cdot \mathbf{I}_j \right] \right\}.$$

The first term describes the Fermi contact interaction. The second term represents the contribution to the hyperfine interaction resulting from the orbital motion of the electron. The last two terms in this expression correspond to the dipolar interaction between the

electronic and nuclear spins. The first summation is over all the electrons the second is over the two nuclei.

After tedious but straightforward calculations, using the ground state $|G\rangle$, we find the following.

(i) $g_x > g_y$, for the ^{33}S hyperfine tensor:

$$A_x^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_y^2 - \beta_x^2) + (\beta_y^2 + \beta_x^2) \cos 2\phi] \right. \\ \left. - \left[\frac{\beta_y^2 + 2\beta_x^2}{5} + \frac{\beta_y^2 - 2\beta_x^2}{5} \cos 2\phi - \frac{3}{5} \beta_x \beta_y \sin 2\phi \right] \langle r^{-3} \rangle_{ss} \right\}$$

$$A_y^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_y^2 - \beta_x^2) + (\beta_y^2 + \beta_x^2) \cos 2\phi] \right. \\ \left. + \left[\frac{2\beta_y^2 + \beta_x^2}{5} + \frac{2\beta_y^2 - \beta_x^2}{5} \cos 2\phi - \frac{3}{5} \beta_x \beta_y \sin 2\phi \right] \langle r^{-3} \rangle_{ss} \right\}$$

$$A_z^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_y^2 + \beta_x^2) + (\beta_y^2 - \beta_x^2) \cos 2\phi] \right. \\ \left. - \left[\frac{\beta_y^2 + \beta_x^2}{5} + \frac{\beta_y^2 - \beta_x^2}{5} \cos 2\phi \right] \langle r^{-3} \rangle_{ss} + 2\beta_x \beta_y \sin 2\phi \langle r^{-3} \rangle_{ls} \right\}.$$

The β have to be replaced by the α in the above formula to obtain the ^{77}Se hyperfine tensor. The appropriate values of the parameters $2\mu_B\mu_N g_N (\mu_0/4\pi) \{ (8\pi/3) |\Psi(0)|_S^2 \}$, $2\mu_B\mu_N g_N (\mu_0/4\pi) \langle r^{-3} \rangle_{ss}$ and $2\mu_B\mu_N g_N (\mu_0/4\pi) \langle r^{-3} \rangle_{ls}$ have to be used in these formulas to calculate the hyperfine interaction.

(ii) $g_x < g_y$, for the ^{33}S hyperfine tensor:

$$A_x^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_x^2 - \beta_y^2) + (\beta_x^2 + \beta_y^2) \cos 2\phi] \right. \\ \left. + \left[\frac{2\beta_x^2 + \beta_y^2}{5} + \frac{2\beta_x^2 - \beta_y^2}{5} \cos 2\phi - \frac{3}{5} \beta_x \beta_y \sin 2\phi \right] \langle r^{-3} \rangle_{ss} \right\}$$

$$A_y^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_x^2 - \beta_y^2) + (\beta_x^2 + \beta_y^2) \cos 2\phi] \right. \\ \left. - \left[\frac{\beta_x^2 + 2\beta_y^2}{5} + \frac{\beta_x^2 - 2\beta_y^2}{5} \cos 2\phi - \frac{3}{5} \beta_x \beta_y \sin 2\phi \right] \langle r^{-3} \rangle_{ss} \right\}$$

$$A_z^S = 2\mu_B\mu_N g_N \frac{\mu_0}{4\pi} \left\{ \frac{8\pi}{3} |\Psi(0)|_S^2 [(\beta_x^2 + \beta_y^2) + (\beta_x^2 - \beta_y^2) \cos 2\phi] \right. \\ \left. - \left[\frac{\beta_x^2 + \beta_y^2}{5} + \frac{\beta_x^2 - \beta_y^2}{5} \cos 2\phi \right] \langle r^{-3} \rangle_{ss} + 2\beta_x \beta_y \sin 2\phi \langle r^{-3} \rangle_{ls} \right\}.$$

Again, the β have to be replaced by α in the above formulas to obtain the ^{77}Se hyperfine tensor.

Replacing the α and β by $1/\sqrt{2}$ and $\lambda_S = \lambda_{Se} = \lambda$ in our formulas, we find for a homogeneous diatomic molecule (for $g_x > g_y$)

$$A_x = 2\mu_B\mu_N g_N(\mu_0/4\pi) \left\{ (8\pi/3)|\Psi(0)|^2 \cos 2\phi + \frac{1}{10}[\cos 2\phi - 3 + 3 \sin 2\phi] \langle r^{-3} \rangle_s \right\}$$

$$A_y = 2\mu_B\mu_N g_N(\mu_0/4\pi) \left\{ (8\pi/3)|\Psi(0)|^2 \cos 2\phi + \frac{1}{10}[\cos 2\phi + 3 - 3 \sin 2\phi] \langle r^{-3} \rangle_s \right\}$$

$$A_z = 2\mu_B\mu_N g_N(\mu_0/4\pi) \left\{ (8\pi/3)|\Psi(0)|^2 - \frac{1}{5} \langle r^{-3} \rangle_s + \sin 2\phi \langle r^{-3} \rangle_l \right\}.$$

Comparing, one sees again that these formulas are identical with those found by Zeller and Känzig [19].

Table 2. Values of $2\mu_B\mu_N g_N(\mu_0/\pi)\{(8\pi/3)|\Psi(0)|^2\}$, $2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_s$ and $2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_l$ in megahertz [16, 22].

	³³ S	⁷⁷ Se
$2\mu_B\mu_N g_N(\mu_0/4\pi)\{(8\pi/3) \Psi(0) ^2\}$	47	143
$2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_s$	173	915
$2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_l$	143	685

6. Theoretical analysis

Considering table 1, we find the smallest g value along $\langle 001 \rangle$, which is the direction of the paramagnetic p lobe. Due to the symmetry in x and y of the formulas for the \mathbf{g} tensor we can *a priori* choose which set of formulas to use. Choosing always g_y along $\langle 001 \rangle$ we find a 2B_2 ground state and apply the appropriate equations for \mathbf{g} and hyperfine tensors.

Examining the formulas of the hyperfine tensor we see that only three parameters (β_x , β_y and ϕ) are necessary to explain the hyperfine values. The S_2^- and Se_2^- parameters $2\mu_B\mu_N g_N(\mu_0/4\pi)\{(8\pi/3)|\Psi(0)|^2\}$, $2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_s$ and $2\mu_B\mu_N g_N(\mu_0/4\pi)\langle r^{-3} \rangle_l$ are taken from Vannotti and Morton [22] for the ³³S and from Maes *et al* [16] for the ⁷⁷Se hyperfine tensor. These parameters are listed in table 2.

We used the experimental A_y and A_z values of the ³³S and of the ⁷⁷Se hyperfine tensors to fit the parameters. The results are

$$\beta_x = 0.7355(\alpha_x = 0.6775) \quad \beta_y = 0.6797(\alpha_y = 0.7335) \quad \lambda_{\beta_x\beta_y}/\Delta = 0.3829.$$

From the β_y value one can deduce that the electron is more localized near the Se nucleus than near the S nucleus. This is in agreement with the fact that Se is more electronegative than S.

These parameters were tested by calculating all the hyperfine values for the ³³S and ⁷⁷Se hyperfine tensor. The results are listed in table 3. Comparing the calculated values with the experimental hyperfine tensors, we find a fair agreement.

In order to check whether the parameters β_x , β_y and $\lambda_{\beta_x\beta_y}/\Delta$ are also compatible with the observed g values, we calculated g_x , g_y and g_z , using these parameters in the equations for $g_x > g_y$. A value of $1/\sqrt{2}$ was used for α . For l_z the values of $l_{zS} = 0.9351$ and $l_{zSe} = 0.8745$ were used [14, 16]. The effective spin-orbit splittings of S and Se are $\zeta_S = 161 \text{ cm}^{-1}$ and $\zeta_{Se} = 918 \text{ cm}^{-1}$. Using these values we find the following data:

$$g_x = 1.87 + 883/E_5 - 29/E_2 \quad g_y = 1.87 + 163/E_5 + 6/E_6$$

$$g_z = 2.65 - 2/E_3 + 64/E_4.$$

For the g_x and the g_y value the largest correction originates from the second term in the formula. An estimate for the energy E_5 is the mean value of $E_5 \simeq 11\,000\text{ cm}^{-1}$ [14] and $E_{\text{Se}} \simeq 10\,000\text{ cm}^{-1}$ [16], yielding $E_5 \simeq 10\,500\text{ cm}^{-1}$. This leads to a correction of 0.08 for g_x and 0.01 for g_y . The last term in these formulas can be neglected because of the relatively large values for the energies E_2 and E_6 (which are still of the order of a few 1000 cm^{-1} , since $\Delta \simeq 1400\text{ cm}^{-1}$) and the small coefficient of this term. For the g_z value the second term can be omitted for the same reason as we neglected the last term for g_x and g_y . A small contribution can arise from the last term, this correction being probably of the order of 0.01. So we finally find the following estimates for the \mathbf{g} tensor:

$$g_x = 1.95 \quad g_y = 1.88 \quad g_z = 2.66.$$

Comparing these values with the experimental ones of table 1, we find a fair agreement.

Table 3. Experimental and calculated ^{33}S and ^{77}Se hyperfine parameters in megahertz for $S\text{Se}^-$ in NaCl.

	^{33}S		^{77}Se	
	experimental	theoretical	experimental	theoretical
A_x	$A_x \ll A_z$	25	69 (?)	41
A_y	80	85	432	433
A_z	60	62	200	200

7. Discussion and conclusion

Comparing the S_2^- , Se_2^- and $S\text{Se}^-$ defects in NaCl, there is little doubt that the same type of defect is involved. All centres are visible at high temperature, 30–60 K for S_2^- , 20–50 K for Se_2^- and 20–50 K for $S\text{Se}^-$. The saturation behaviour of the three defects is analogous. All spectra were detectable at the same time in the crystals under investigation in this paper. Finally, having used the same doping procedure it could be expected that we could find a $S\text{Se}^-$ defect of the same type as the S_2^- and Se_2^- defects identified earlier in NaCl.

Table 4. Spin-Hamiltonian parameters for S_2^- , Se_2^- and $S\text{Se}^-$ (the hyperfine parameters are in megahertz).

	g_x	g_y	g_z	A_x	A_y	A_z	
	$\langle 110 \rangle$	$\langle 001 \rangle$	$\langle 1\bar{1}0 \rangle$	$\langle 110 \rangle$	$\langle 001 \rangle$	$\langle 1\bar{1}0 \rangle$	
S_2^-	2.0107	1.9860	2.2531	$< A_y$	109	$< A_y$	^{33}S
Se_2^-	1.8862	1.7923	2.8356	$< A_z$	347	290	^{77}Se
$S\text{Se}^-$	1.9421	1.8818	2.6393	$< A_z$	80	60	^{33}S
				69 (?)	432	200	^{77}Se

The largest g value is found along the $\langle 1\bar{1}0 \rangle$ direction and the smallest along the $\langle 001 \rangle$ direction as can be seen in table 4. From the theory derived above, we can conclude that the binding axis is along the $\langle 1\bar{1}0 \rangle$ direction and that the paramagnetic p lobe is along the $\langle 001 \rangle$ direction. The direction of the largest hyperfine splitting for $^{33}\text{S}_2^-$, $^{77}\text{Se}_2^-$, $^{33}\text{S}\text{Se}^-$ and

$S^{77}\text{Se}^-$ is the direction of the p_y wave function. The arguments given above show that very likely an SSe^- ion is responsible for the spectrum but the problem of its location remains to be solved. No direct information is available since no hyperfine structure could be resolved. Since there is no satisfactory model proposed yet (monovacancy or divacancy) for S_2^- and Se_2^- in NaCl, we cannot give a convincing model for the location of SSe^- in the crystal. A tentative model is the SSe^- ion in a monovacancy, i.e. replacing one Cl^- ion. ENDOR might supply interesting complementary information about the local environment.

Acknowledgment

This work is part of a project sponsored by Interuniversitair Instituut voor Kernwetenschappen, Belgium.

References

- [1] Sander W 1962 *Z. Phys.* **169** 353–63
- [2] Sander W 1964 *Naturwissenschaften* **51** 1–3
- [3] Hausmann A 1966 *Z. Phys.* **192** 313–28
- [4] Brailsford J R, Morton J R and Vannotti L E 1967 *J. Chem. Phys.* **45** 2237–40
- [5] Vannotti L E and Morton J R 1968 *Phys. Rev.* **171** 448–53
- [6] Brailsford J R and Morton J R 1969 *J. Chem. Phys.* **51** 4794–8
- [7] Nistor S V and Stoicescu Gh 1971 *Rev. Roumaine Physique* **16** 515–9
- [8] Bill H, Döhner D, Schwan L and Sigmund E 1980 *Solid State Commun.* **34** 383–4
- [9] Abhvani A S, Austen S P and Bates C A *Solid State Commun.* **37** 777–8
- [10] Matthys P, Callens F and Boesman E 1983 *Solid State Commun.* **45** 1–3
- [11] Callens F, Matthys P and Boesman E 1983 *Phys. Status Solidi b* **118** K35–7
- [12] Matthys P, Callens F and Boesman E 1988 *J. Phys. C: Solid State Phys.* **21** 5683–9
- [13] Matthys P, Callens F, Vekeman G and Boesman E 1988 *Phys. Status Solidi b* **149** K25–30
- [14] Callens F, Maes F, Matthys P and Boesman E 1989 *J. Phys.: Condens. Matter* **1** 6921–8
- [15] Matthys P, Maes F, Callens F and Boesman E 1990 *Solid State Commun.* **75** 17–20
- [16] Maes F, Callens F, Matthys P and Boesman E 1990 *J. Phys. Chem. Solids* **51** 1289–95
- [17] Maes F, Callens F, Matthys P and Boesman E 1991 *Radiat. Eff. Defects Solids* **116** 283–9
- [18] Känzig W and Cohen M H 1959 *Phys. Rev. Lett.* **3** 509–10
- [19] Zeller H R and Känzig W 1967 *Helv. Phys. Acta* **40** 845–72
- [20] Shuey R T and Zeller H R 1967 *Helv. Phys. Acta* **40** 873–86
- [21] Morton J R 1967 *J. Phys. Chem.* **71** 89–92
- [22] Vannotti L E and Morton J R 1967 *Phys. Rev.* **161** 282–6
- [23] Vannotti L E and Morton J R 1967 *Phys. Lett.* **24A** 520–1
- [24] Callens R, Callens F, Matthys P and Boesman E 1988 *Phys. Status Solidi b* **148** 683–8
- [25] Maes F, Callens F, Matthys P and Boesman E 1990 *Phys. Status Solidi b* **161** K1–3
- [26] Maes F, Matthys P, Callens F and Boesman E 1991 *Solid State Commun.* **80** 583–6
- [27] Maes F, Matthys P, Callens F, Moens P and Boesman E 1992 *J. Phys.: Condens. Matter* **4** 249–56
- [28] Schneider J, Dischler B and Räufer A 1966 *Phys. Status Solidi* **13** 141–57
- [29] Callens F, Matthys P and Boesman E 1988 *J. Phys. C: Solid State Phys.* **21** 3159–64
- [30] Maes F, Callens F, Matthys P and Boesman E 1989 *Phys. Status Solidi b* **155** K55–7
- [31] Schoemaker D 1973 *Phys. Rev. B* **7** 786–801
- [32] Watson R E and Freeman A J 1961 *Phys. Rev.* **123** 521
- [33] Watson R E and Freeman A J 1961 *Phys. Rev.* **123** 1117