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SCIENCE DIRECT

Solid State Communications 132 (2004) 787–790

solid state communications

www.elsevier.com/locate/ssc

Density functional theory investigation of S_2^- in KCl: evidence for the existence of a di-vacancy site

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Received 13 August 2004; received in revised form 14 September 2004; accepted 14 September 2004 by M. Grynberg

Abstract

Electron paramagnetic resonance experiments have shown that, depending on the doping procedure, two different S_2^- centers may coexist in KCl. These centers have the $^2B_{2g}$ ($g_x[\bar{1}10] < g_y[001]$) and the $^2B_{3g}$ ($g_x[\bar{1}10] > g_y[001]$) ground state, respectively. As no experimental ligand hyperfine data are available, it could not be determined whether the S_2^- molecular ion replaces a single halide ion (mono-vacancy site) or two nearest neighbor halide ions (di-vacancy site). Also, other defect models could a priory be considered. In this work, cluster in vacuo density functional theory calculations of the g and ^{33}S hyperfine tensors show that the S_2^- ion at a mono-vacancy site has the $^2B_{2g}$ ground state, whereas S_2^- in a di-vacancy exhibits a $^2B_{3g}$ ground state. For the latter center, the possibility of charge compensation by a cation vacancy is also considered. The calculations indicate that a possible vacancy is not in the direct vicinity (nearest or next-nearest neighbor) of the S_2^- ion.

PACS: 31.15.E

Keywords: E. Electron paramagnetic resonance

1. Introduction

In order to determine the microscopic structure of the introduced defects, chalcogen-doped alkali halide lattices have been thoroughly studied by means of electron paramagnetic resonance (EPR). Using this technique, both mono- [1–4], di- [5–9], tri- [10–12] and tetra-atomic [10] chalcogen defects could be identified. For the di-atomic MZ:XY$^-$ (X, Y = O, S, Se and M = Na, K, Rb and Z = Cl, Br, I) defect structures, different orientations for the paramagnetic lobes of the unpaired electron are found depending on the chalcogen size and the lattice environment, leading to a $^2B_{2g}$ ($g_x[\bar{1}10] < g_y[001]$) or $^2B_{3g}$ ($g_x[\bar{1}10] > g_y[001]$) ground state, while g_z, the molecular ion axis, is along a [110] direction. In both cases, the direction of the smallest g value corresponds to the direction of the paramagnetic lobes which contain the unpaired electron [6]. For symmetry reasons, two defect structures are compatible with these observations: the mono-vacancy model in which the XY$^-$ molecular ion replaces a single halide ion, e.g. (Fig. 1(a)) and the di-vacancy model in which XY$^-$ replaces two nearest neighbor halide ions, e.g. (Fig. 1(b)). For both defect models, either ground state is in principle possible. Using density functional theory methods, [13,14] the experimental ground states for the MZ:XY$^-$ defect structures could be reproduced, assuming a mono-vacancy configuration. For the KCl:S_2^- defect structure, for which both the $^2B_{2g}$ and $^2B_{3g}$ ground state are observed experimentally, the $^2B_{2g}$ ground state was obtained theoretically assuming the mono-vacancy model.

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doi:10.1016/j.ssc.2004.09.030

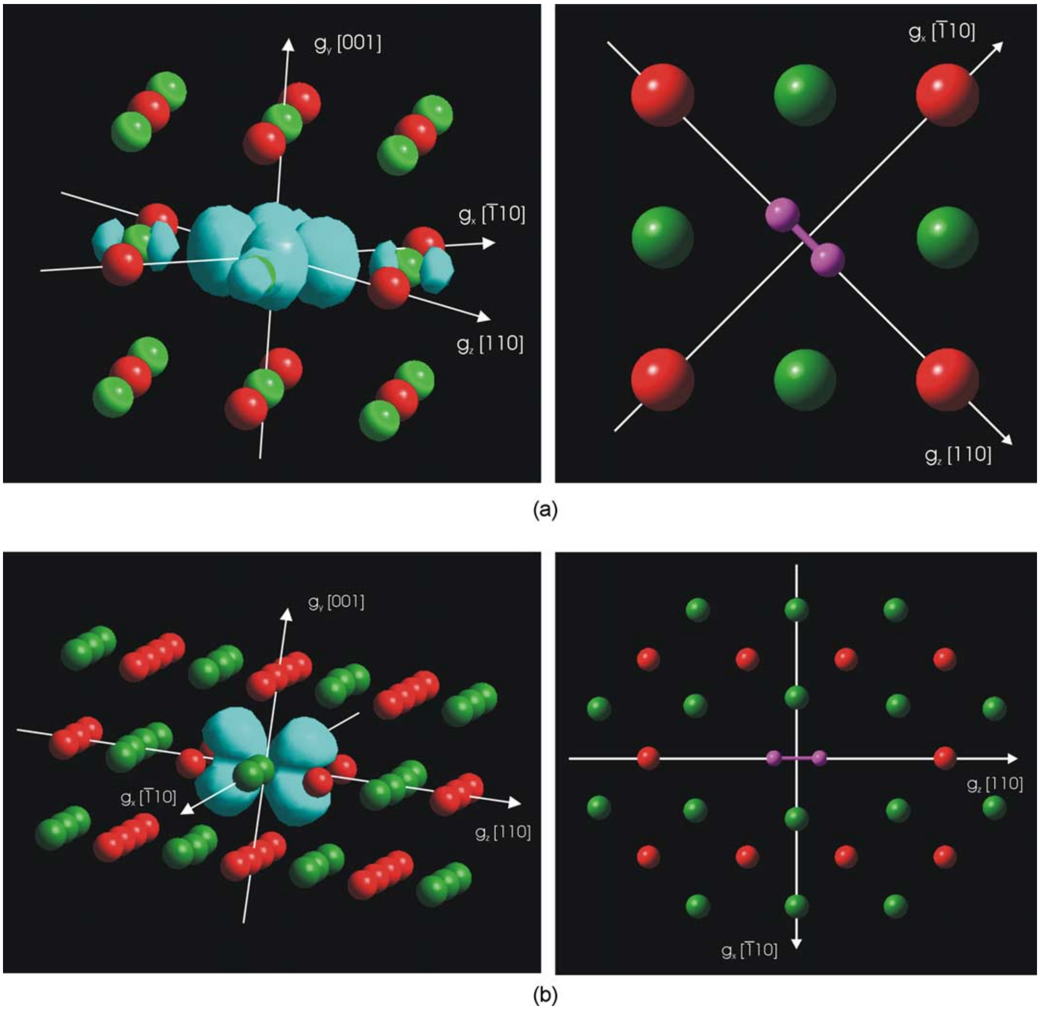

Fig. 1. Spin density for the S_2^- molecular ion in the KCl lattice when located in a mono- (a) and di-vacancy (b) configuration. Additionally, the cross section of both defect models is given. The alkali and halide ions are colored green and red, respectively.

The first EPR measurements on KCl:S_2^- were performed by Vannotti et al. [8]. In this work, a $^2B_{2g}$ ground state was found and a mono-vacancy model was proposed. The second S_2^- center with the $^2B_{3g}$ ground state was observed in KCl by Callens et al. [9]. In view of the specific doping procedure favoring anion vacancy formation, a di-vacancy model was proposed. Although in both cases it could be unambiguously shown that a S_2^- ion was observed, no final conclusions concerning the defect structure could be made due to the absence of experimental ligand hyperfine data.

In the present paper, we want to validate to which extent the di-vacancy model for the S_2^- center in KCl is able to account for the $^2B_{3g}$ ground state. As this model implies an effective positive charge in the lattice, the possibility of charge compensation by a cation vacancy is also explored.

2. Calculation scheme

All calculations, both geometry optimization and EPR calculations, are performed using the Amsterdam density functional (ADF) program package, version 2003 [15]. Calculations using the VWN [16] and Bp86 [17,18] functional form led to essential the same results. Therefore, only the Bp86 results are reported. In all calculations a TZP (triple-ζ plus additional polarization function) basis set, as implemented in ADF2003 was used. For the description of the mono-vacancy model, an 88 atoms cluster was used as described in Ref. [13]. For the simulation of the di-vacancy model, a cluster as shown in Fig. 1.(b) was used. This cluster consists of 72 atoms and has a charge of +1. When cation vacancies are considered, the cluster is neutral. For both defect structures, the central molecular ion and the nearest alkali and halide lattice shells were allowed to relax during the optimization, while all other ions were kept fixed at their lattice positions. The frozen core approximation was applied for all lattice atoms (up to the 3p shell for K(+) and up to 2p for Cl(−)) except for the central S_2^- ion and the nearest alkali ions [14].

3. Computational results

In Table 1, experimental g and hyperfine values for both ground states are compared with theoretical data obtained using the mono- and di-vacancy configuration for the KCl:S_2^- defect structure. Because for both ground state configurations no precise defect model was proposed experimentally due to the absence of ligand hyperfine data, the validation of the theoretical defect structures is mainly based on (i) the reproduction of the experimental ground state and (ii) quantitative agreement with experimental g and hyperfine data.

As is clear from Table 1, the mono- and di-vacancy model give rise to two different ground states for the KCl:S_2^- defect structure. As previously reported [13], a $^2B_{2g}$ ground state is observed theoretically when using a mono-vacancy configuration. When the S_2^- molecular ion is located in a di-vacancy environment, the computed g values correspond to a $^2B_{3g}$ ground state. While for the $^2B_{2g}$ ground state fair agreement with the experimental data is obtained, the experimental g values for the $^2B_{3g}$ ground state are reproduced almost exactly.

In order to get a clear picture of these two ground states, the spin density for the KCl:S_2^- mono- and di-vacancy model is plotted in Fig. 1. For clarity, the cross section in the g_x-g_z-plane is also shown for both defect configurations. For both defect structures the z axis is the molecular axis. When the S_2^- molecular ion is located in a mono-vacancy configuration (Fig. 1(a)), the spin density is mainly located in the xz-plane. For a di-vacancy configuration (Fig. 1(b)), the spin density is mainly located in the yz-plane. This is consistent with the fact that the direction of the smallest g value corresponds to the direction of the paramagnetic lobes which contain the unpaired electron [6].

Before we compare experimental and theoretical hyperfine values, some remarks on the experimental $^2B_{3g}$ data have to be made. The authors of Ref. [9] noted that the ^{33}S hyperfine tensor could only be determined incompletely. Except for the [100] orientation, the linewidths were too large with respect to the hyperfine splitting to get reliable A values. For this reason, the experimental A_x and A_z values have been extrapolated and ought to be considered as rough estimates. Also, the signs of these couplings could not be determined. Therefore, the signs of the experimental data have been adjusted to the experimental ones.

Similar conclusions as for the g values can be made concerning the hyperfine values. Indeed, when using the mono-vacancy model, A_z is largest while the largest hyperfine value is found along the y direction in the di-vacancy configuration. This is in agreement with the experimental data for a $^2B_{2g}$ and $^2B_{3g}$ ground state, respectively. Quantitatively, the confrontation between experimental and theoretical hyperfine values is satisfactory.

We have to keep in mind that the di-vacancy model, as used up to now, has an effective positive charge, so charge compensating defects like, e.g. a cation vacancy needs to be considered. If the cation vacancy is located close to the S_2^- molecular ion, it needs to be placed in such a way that the orthorhombic symmetry is not broken, i.e. on the g_x axis. Due to the limited size of the cluster taken into consideration, only a nearest neighbor (nn), which leads to a tri-vacancy configuration, and a next nearest neighbor (nnn) vacancy position are considered. As is clear from Table 1, the inclusion of a cation vacancy highly affects the theoretical EPR data, although the $^2B_{3g}$ ground state is obtained in all cases. Indeed, when the cation vacancy is located on an nn position, large deviations from the experimental g values are obtained, while the results for

Table 1
Comparison between experimental g and ^{33}S hyperfine values observed for the KCl:S_2^- defect structure and theoretical EPR data using the mono- and di-vacancy configuration. Additionally, computational results for nearest neighbor (nn) and next nearest neighbor (nnn) charge compensation (CC) are listed. The tilt of the A tensor axes away from the g tensor axes in the xz-plane is defined as β_A

	Experimental		Theoretical			
	Ground state		Mono-vac	Di-vac	Di-vac	
	$^2B_{2g}$	$^2B_{3g}$			CC:nn	CC:nnn
g_x	0.9484[a]	1.9708[b]	1.5413	1.9778	1.6604	1.9275
g_y	0.9500	1.9491	1.6251	1.9498	1.6447	1.9016
g_z	3.4303	2.4548	3.1346	2.4518	3.1173	2.6115
A_x	$<A_z$	19.4	14.6	7.6	−8.0	−22.9
A_y	$<A_z$	99.9	19.8	73.5	85.1	67.4
A_z	137	32.8	156.4	−28.1	42.2	26.2
β_A	0	0	0	0	3.9	1.3

[a] Ref. [8].

[b] Ref. [9].

an nnn cation vacancy agree better with experiment. Also, an additional tilting of the theoretical hyperfine axes is obtained when introducing cation vacancies: the *A* tensor axes will be tilted away from the g tensor axes in the *xz*-plane by an angle β_A. For both the nn and nnn vacancy configuration, this tilting angle is too small to be experimentally observable and decreases when the vacancy is located further away from the central molecular ion. These results suggest that charge compensating defects are not located in the close vicinity of the central molecular ion.

4. Conclusion

The occurrence of two ground states for the KCl:S_2^- defect structure has been fully characterized. In particular, the calculations undoubtedly show that these two ground states can be attributed to two different defect structures: a mono- and a di-vacancy configuration.

Some features were already observed in our previous work. Indeed, previous calculations showed that the $^2B_{2g}$ ground state could be reproduced using a mono-vacancy configuration. In the present paper, the $^2B_{3g}$ ground state for the KCl:S_2^- defect structure was attributed to a di-vacancy configuration. This was validated by the following observations: (i) using the di-vacancy structure, the $^2B_{3g}$ ground state was obtained theoretically and (ii) the quantitative agreement with experimental g and hyperfine values was good. The calculations also showed that charge compensating defects, like a cation vacancy, are not located close to the central molecular ion.

Acknowledgements

The authors would like to thank the Fund for Scientific Research (FWO-Flanders, Belgium) for financial support. H. Vrielinck thanks the Fund for Scientific Research—Flanders for a postdoctoral fellowship.

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