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Annealing of vacancy-related defects in semi-insulating SiC

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The annealing of $P6/P7$ centers (V_CC_{Si} pairs) in the presence of carbon vacancies in high concentrations typical for semi-insulating (SI) silicon carbide (SiC) is studied theoretically. The calculated hyperfine parameters support the suggestion of a negatively charged divacancy as the most stable SI-5 center. A possible correlation of the SI-1 and SI-2 spectra with metastable configurations of this divacancy reveals a rather complicated equilibrium of several defect configurations that might be responsible for the large number of electron paramagnetic resonance signals observed in high-purity semi-insulating SiC.

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Silicon carbide (SiC) is suitable for many high power, high-frequency, and high-temperature electronic applications.[1] Devices like metal-semiconductor field-effect transistors (MESFET) designed for increased power densities require high-purity semi-insulating (HPSI) SiC substrates. These can be grown by physical vapor tranport (PVT)[2] and also by high-temperature chemical vapor deposition (HTCVD).[3] The defect or defects giving rise to the semi-insulating (SI) character of these HPSI materials are still discussed controversially. Residual vanadium contamination, several kinds of vacancies, or complexes thereof, are considered as possible candidates. A high concentration of carbon vacancies V_C^+ is observed, but clearly the number of different centers in electron paramagnetic resonance (EPR) measurements exceeds the number that could be explained by isolated carbon vacancies alone.

However, the concentrations of the various defects observed in different HPSI substrates vary strongly:[4] Whereas in PVT material grown at moderate temperatures the $P6/P7$ centers (V_CC_{Si} pairs) are dominating,[5–7] these $P6$-like signals are practically absent in all substrates grown by HTCVD processes at high temperatures (HT). Instead, several signals (labeled SI-1 to SI-9) are observed with different signature, which can be found exclusively in SI material,[4,6] e.g., a broad isotropic line labeled SI-1, as well as a very anisotropic spectrum SI-2 within C_{1h} symmetry.

The $P6/P7$ centers, in contrast, are well known from irradiated material: they represent the first annealing products of the silicon vacancy[8,9] and are proposed to anneal out at temperatures above 1200 °C via the emission of V_C, resulting in a carbon antisite or a $Si_C(C_{Si})_2$ antisite complex, respectively. The latter, isolelectronic defect is an excellent candidate to cause the prominent D_I luminescence which is observed in *n*-type doped, as well as in *p*-type SiC, after high-temperature annealing up to 1700 °C.[10] This luminescence, however, has not been detected in SI material. Instead, the EPR signal of the so-called SI-5 centers remains visible after annealing at temperatures above 1600 °C.[4] In some HTCVD samples, this SI-5 line is already dominating without additional annealing, whereas the prominent V_C^+ signal appears significantly weaker. In PVT 4H–SiC substrates the SI-5 line can only be detected under illumination above 1.75 eV. Obviously, the annealing behavior of vacancy-related centers depends crucially on the doping and growth conditions.

In this work, we calculate how carbon vacancies in high concentrations influence the annealing of the $P6$-like centers. The hyperfine parameters calculated for different defect models confirm in part the assumption of Son *et al.*, that a negatively charged divacancy is the origin for the most stable SI-5 center.[4] We further show that there is a rather complicated equilibrium of several metastable configurations of the divacancy which might cause the large number of EPR signals observed in high-purity SI–SiC grown by HTCVD.

We use a combination of two theoretical methods to investigate the origin of the SI-5 signal: For the computationally demanding dynamical calculations, i.e., geometry optimization and calculation of activation energies, the self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method is used.[11] Various supercell models [up to a $(4\times4\times4)$ supercell with 512 atoms in 3C–SiC] have been used together with the Γ-point approximation. For the geometry optimization with a common conjugate gradient scheme, all atoms were permitted to relax freely. Using the relaxed geometries obtained by the SCC-DFTB calculations, *ab initio* calculations of the electronic structure and the hyperfine (hf) interactions were carried out within a Green's-function-based approach, the linear muffin-tin orbital method within the atomic spheres approximation (LMTO-ASA),[12] which allows us to investigate isolated charged defects in an otherwise infinite perfect crystal. Further details of the methods, e.g., an adjustment of the fundamental gap to the experimental value by the scissors operator technique[13] and the scalar relativistic treatment of the valence electrons, can be found elsewhere.[11,12]

In irradiated SiC, a combination of these two methods has been previously applied to investigate the annealing of the silicon vacancy and its follow-up products (e.g., V_CC_{Si}).[9,10] Usually, the local-density approximation (LDA) of DFT is known to give rather accurate values for total energies. However, the LDA underestimates the polarization of the core electron by up to a factor of 2, also if these electrons are treated fully relativistically.[14] In Ref. 10, it was shown that a self-interaction-corrected optimized effective potential (SIC-OEP) method[15,16] improves the description of the core electrons and their contribution to the hf interactions. Using this

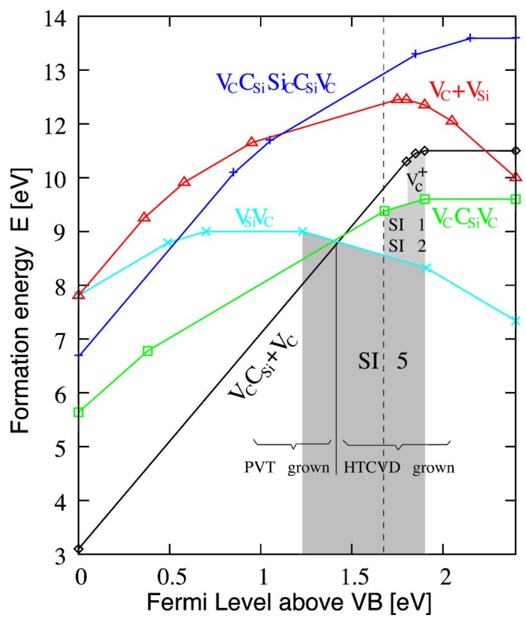

FIG. 1. (Color online) Formation energies of the divacancy and stochiometric equivalent configurations in 3C–SiC with respect to the Fermi level. Note that the various structures are separated by energy barriers (see also Fig. 2, taking $E_F = E^{2+/+}(V_C C_{Si} V_C) = 1.68$ eV as an example).

functional, which goes beyond usual LDA but is no more time consuming, the comparability with experimentally observed hf splittings is improved significantly. We, therefore, shall adopt it for our present calculation of hf parameters as a fingerprint of the SI centers.

Despite the rather complicated appearance of defects in different HPSI samples, it is quite obvious that the *P*6/*P*7 centers are not observed if the so-called SI signals are present and vice versa. Our total-energy calculations indicate that the *P*6/*P*7 centers can be transformed into some of the SI centers. Since in semi-insulating SiC high concentrations of carbon vacancies are available, they can, in principle, form larger complexes with $V_C C_{Si}$ pairs, ending up in $V_C C_{Si} V_C$. However, as can be taken from the calculated formation energies of $V_C C_{Si} + V_C$ and possible follow-up products in Fig. 1, the energy gain and, thus, the appearance of these complexes, strongly depends on the position of the Fermi level with respect to the valence bands. For a Fermi level below midgap, the *P*6-like centers are expected to appear in its isolated form as observed for SI substrates grown by PVT. For Fermi levels above $E_{VB} + 1.4$ eV, in contrast, the additional carbon vacancies tend to form complexes with the *P*6-like centers. Also in the case of the *P*6′ and *P*6″ centers ($V_C C_{Si} Si_C C_{Si}$ complexes, recently identified in electron irradiated 6H–SiC),[10] this scenario ends within $V_C C_{Si} V_C$ aggregates. Apparently no activation energy is required and the gain by this (multi-atom) jump process amounts to 1–3 eV. However, from this $C_{Si}(V_C)_2$ complex the formation of *divacancies* ($V_C V_{Si}$) is possible. The concentrations and relative stability of these defects depends crucially on the position of the Fermi level, and moreover, on the energy barriers separating the different atomic configurations. In Fig. 2, this is shown for $E_F = 1.68$ eV as an example. Fortunately, and in

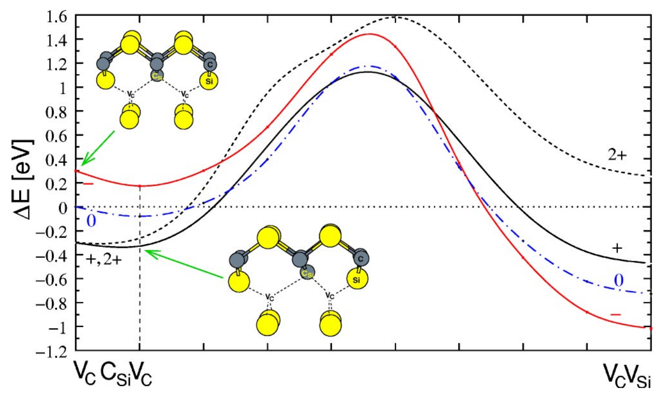

FIG. 2. (Color online) Metastability of the divacancy in SiC assuming a Fermi level $E_F = E^{2+/+}(V_C C_{Si} V_C) = E_{VB} + 1.68$ eV. Note that for the different charge states the migration paths are almost identical. At elevated temperatures starting from the $V_C C_{Si} V_C$ complex in its doubly positive charge state several charge transitions can take place resulting in a negatively charged divacancy as the most stable configuration.

contrast to many other examples in defect physics, the migration path between the $C_{Si}(V_C)_2$ complex and the divacancy practically does *not* depend on the charge state for charge states from 2+ to 2−. Thus, a charge transition during the migration of the carbon atom can be taken into account explicitly. Starting from the doubly positive charged $C_{Si}(V_C)_2^{2+}$ complex with C_{2v} symmetry, the carbon antisite moves slightly towards one of its (2,2,0) silicon next-nearest neighbors in the $(1\bar{1}0)$ plane. This lowering of the symmetry towards C_{1h} symmetry is accompanied by an energy gain of about 0.1 eV and a change of the charge state into single positive. From this position, the carbon atom has to overcome an energy barrier of about 1.5 eV, while the length of the bond between the C_{Si} and its two carbon neighbors increases from 1.6 Å (typical for C–C bondlengths like in diamond) to about 2.2 Å near the saddle-point configuration, before the carbon atom takes the position of the neighboring carbon vacancy. During this last part of the migration a multiple recharging process from + to the neutral state, and back again, takes place before finally a divacancy in its negative charge state within C_{1h} symmetry is reached. In other words, for Fermi levels lying in the upper half of the band gap, both alternatives, the $C_{Si}(V_C)_2$ aggregate defect in the C_{2v} configuration as well as with C_{1h} symmetry, are metastable configurations of the divacancy.

The $V_C V_{Si}^-$ divacancy comes out to be a very stable defect pair in SI-SiC. A dissociation into isolated vacancies requires to pass a barrier of at least 5 eV, whereby the formation energy of the dissociated parts is several eV higher than that of the defect pair. Thus, from the energetical point of view the divacancy provides a perfect candidate for the SI-5 center, which is known to remain stable after annealing above 1600 °C. In addition, a formation of the SI-5 center from *P*6/*P*7 and a nearby V_C^+ explains that the SI-5 spectrum dominates in some HTCVD samples, whereas simultaneously the V_C^+ signal is essentially reduced. The requirement of illumination to observe the SI-5 line in PVT-grown samples indicates that this material provides a lower Fermi

TABLE I. Calculated hf parameters (MHz) for the divacancy in SiC in comparison with the experimentally observed hf splittings for the SI-5 center (values deduced from Ref. 4).

Center	Symmetry	Nuclei	$A_\parallel$ (MHz)	$A_\perp$ (MHz)	a (MHz)	b (MHz)
SI-5		$3\times{}^{29}$Si	11.8	12.1	12.4	−0.30
		$3\times{}^{13}$C	**40.7**	**31.8**	34.8	2.97
$V_{Si}V_C^+$	C_{3v}	$3\times{}^{29}$Si	9.16	9.79	9.58	−0.21
		$3\times{}^{13}$C	**74.44**	**21.01**	38.82	17.81
$V_{Si}V_C^-$	C_{3v}	$3\times{}^{29}$Si	9.94	10.51	10.32	−0.19
		$3\times{}^{13}$C	**82.44**	**29.91**	47.43	17.51
$V_{Si}V_C^-$	C_{1h}	$2\times{}^{29}$Si	14.32	15.89	15.49	−0.41
		$1\times{}^{29}$Si	16.80	17.72	17.42	−0.31
		$2\times{}^{13}C_2$	**46.45**	**12.30**	23.70	11.38
		$1\times{}^{13}C_1$	155.14	62.74	93.87	31.13

level (see also Fig. 1). It is important to note here, that our results calculated for the divacancy in 3C–SiC can be transfered to the hexagonal polytypes obviously: e.g., the charge transition level $(-/2-)=1.91$ eV is in good agreement with previously reported values for 4H–SiC in the range of 1.76–1.84 eV, depending on the lattice sites.[17]

In principle, our total-energy calculations confirm the defect model of Son *et al.*[4] However, in HTCVD-grown substrates these authors report hf splittings that belong to *three* ^{29}Si nuclei and to *three* ^{13}C nuclei, as appropriate for a divacancy$^-$ $(S=1/2)$ in C_{3v} symmetry. According to our total-energy calculations, in contrast, the resulting ^2E state with its $a_1^2e^3$ electronic configuration is subject to a Jahn-Teller distortion leading to a slightly distorted atomic configuration with C_{1h} symmetry, 0.05 eV lower in energy. Since the EPR spectra were measured at 77 K, a dynamic Jahn-Teller effect could give rise to motional averaged spectra with effective $\overline{C_{3v}}$ symmetry. Then, as can be taken from Table I, the divacancy in its negative charge state gives rise to a hf splitting $A_\perp=29.91$ MHz with *three* equivalent ^{13}C nuclei—a value which corresponds very well with the 31.8 MHz experimentally observed for **B** perpendicular to the c axis. However, the value $A_\parallel=82.44$ MHz exceeds the experimental value for $\mathbf{B}\parallel c$ by more than a factor of 2.[18] About the same discrepancy is found for a positively charged divacancy (which also provides a spin $S=1/2$ system).

From the hf interactions calculated for the $V_CV_{Si}^-$ divacancy in its C_{1h} configuration we propose alternatively to assign the outer carbon splittings to the *two* equivalent carbon neighbors of the distorted divacancy. A value of $A_\parallel=46.45$ MHz is in good agreement with the experimentally observed value of 40.7 MHz. In this interpretation the hf interaction with the remaining *single* ^{13}C nucleus (see also Fig. 3) would not have been resolved in the experiments. The small natural abundance of the carbon atoms with nuclear spin (1.1%) leads to less intense satellite lines with respect to the central line. In addition, the estimated splitting of $A_\parallel=155.14$ MHz would overlap with several other signals observed in the HPSI material. Further EPR measurements should aim at a confirmation of this model of a divacancy in C_{1h} symmetry via a resolved hf splitting due to a *single* ^{13}C nucleus above 100 MHz. A first hint of a C_{1h} symmetry is already visible in the EPR measurement at 77 K: the inner lines, assigned to *three* silicon neighbors, do not split but broaden for **B** perpendicular to the c axis. The calculated nearly isotropic hf splittings due to the silicon neighbors of the divacancy in C_{1h} symmetry $(1\times15.49$ and 2

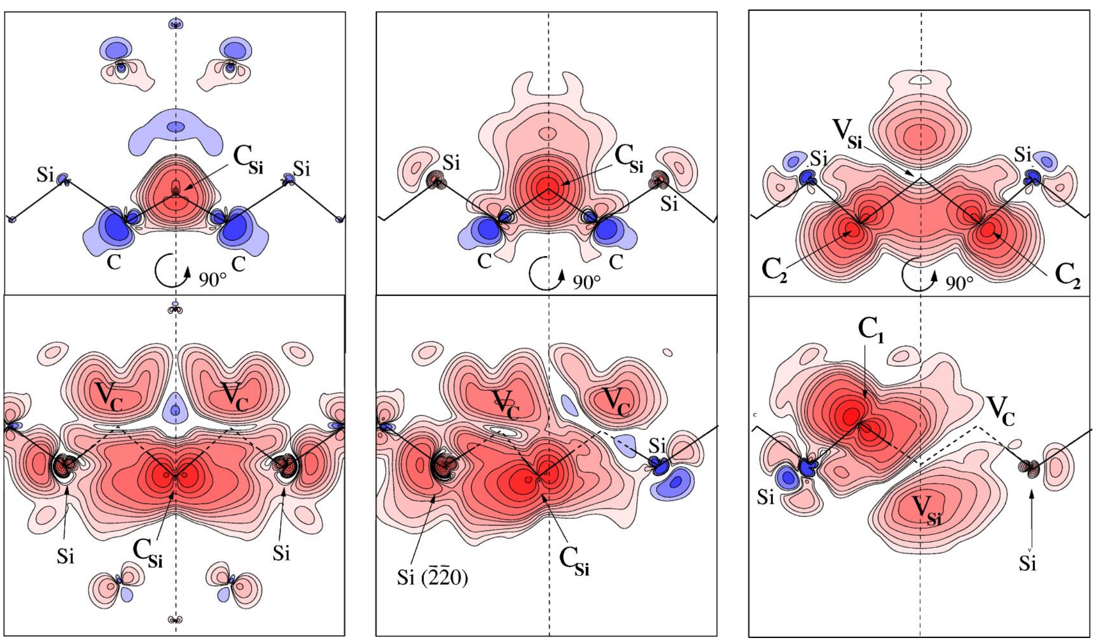

FIG. 3. (Color online) Spin density of $(S=1/2)$ configurations of the divacancy in 3C–SiC: the metastable configuration $V_CC_{Si}V_C^+$ in C_{2v} symmetry (left) and in C_{1h} symmetry (middle), as well as the nearest-neighbor configuration $V_CV_{Si}^-$ in the C_{1h} ground-state configuration. The lower parts describe the $(1\overline{1}0)$ mirror planes, the upper parts are perpendicular to these planes.

$\times 17.42$ MHz), fit very well with this experimental finding of three almost equivalent ^{29}Si nuclei.

The metastable configurations $V_C C_{Si} V_C^+$ of the divacancy provide $S=1/2$ spin systems and, thus, are likely candidates to explain the isotropic SI-1 and the strongly anisotropic SI-2 signals. The C_{1h} configuration (lower structure in Fig. 2) can explain a slight deviation of the principal axis of the g factor from the c axis by 3° in case of the SI-2 center. Alternatively, this structure can contribute to the broad signal of the SI-1 center. The metastable character and the rather small energy differences between the various atomic configurations with different orientations would lead to an inhomogeneous superposition of several similar signals. A broad, rather isotropic, signal is the consequence. In the hexagonal polytypes the number of different configurations which might contribute to the broad SI-1 signal is increased by inequivalent lattice sites. In Table II the calculated hf parameters for the two configurations possible in 3C–SiC are given. In both cases, the estimated spectrum is dominated by a strongly anisotropic splitting due to the carbon antisite $^{13}C_{Si}$ nucleus accompanied by up to 10 silicon-related rather isotropic splittings in the range between 20 and 70 MHz. As can be taken from Fig. 3, the relaxation of the C_{Si} to one of its silicon next-nearest neighbors [the Si$(\bar{2},\bar{2},0)$ nucleus in the left-hand side of the lower density plots] leads to a transfer of spin density to this site at the expense of the previously (in C_{2v} symmetry) equivalent silicon nuclei around the Si(2,2,0) site.

TABLE II. hf parameters (MHz) of the $V_C C_{Si} V_C$ complex calculated for its $^3A'$ ground state in C_{1h} symmetry and for the symmetric metastable $^3B_2$ state (C_{2v} symmetry).

		$^3B_2$ (C_{2v} symmetry)		$^3A'$ (C_{1h} symmetry)	
$V_C C_{Si} V_C^+$	Atoms per shell	a (MHz)	b (MHz)	a (MHz)	b (MHz)
$^{13}C_{Si}$	1	13.97	23.08	11.26	23.85
$^{13}C(1,\bar{1},\bar{1})$	2	−8.74	1.69	−5.29	2.48
$^{13}C(\bar{3},\bar{1},\bar{1})$	2	−0.79	0.59	4.92	1.41
$^{29}Si(\bar{2},\bar{2},0)$	1	−20.16	−2.63	**−68.51**	**−5.94**
$^{29}Si(2,2,0)$	1	−20.16	−2.63	8.30	1.06
$^{29}Si(0,\bar{2},\bar{2})$	2	−41.34	−3.10	−46.56	−3.25
$^{29}Si(0,2,\bar{2})$	2	−41.34	−3.10	**−20.98**	**−2.49**
$^{29}Si(0,2,2)$	2	−56.41	−5.71	**−28.23**	**−2.85**
$^{29}Si(0,\bar{2},2)$	2	−56.41	−5.71	−53.96	−6.91

In summary, total-energy calculations confirm the divacancy to be one of the most stable defects in SI-SiC. Calculated hf parameters suggest an assignment of its ^{3}A′ state in C_{1h} symmetry to the thermally stable SI-5 center important for the SI properties of the HTCVD-grown substrates. Moreover, the existence of several metastable configurations of the divacancy in the form of $V_C C_{Si} V_C$ complex could explain the large number of different EPR signals observed in HPSI-SiC. Unfortunately, no further hf splittings have been resolved experimentally and, thus, an unambiguous assignment of the SI-1, SI-2 centers to these metastable states is not yet possible. However, from our calculations we propose the following procedure for future EPR measurements: Using a second microwave frequency, part of the occupation of the broad inhomogeneous SI-1 line can be inverted.[14] By this spectral hole burning, it should be possible to discriminate the different atomic configurations. If the hf interactions thus obtained happen to agree with the calculated hf parameters listed in Table II, we could make a major step towards an unambiguous assignment of one or even several configurations of the $V_C C_{Si} V_C^+$ aggregate defect.

[1] *Recent Major Advances in SiC*, edited by W. J. Choyke, H. Matsunami, and G. Pensl, (Springer-Verlag, Berlin, 2004), p. 437.
[2] St. G. Müller, M. F. Brady, W. H. Brixus, R. C. Glass, H. McD. Hobgood, J. R. Jenny, R. T. Leonard, D. P. Malta, A. R. Powell, V. F. Tsvetkov, S. T. Allen, J. W. Palmour, and C. H. Carter, Jr., Mater. Sci. Forum **433**, 39 (2003).
[3] A. Ellison, B. Magnusson, N. T. Son, L. Storasta, and E. Janzén, Mater. Sci. Forum **433**, 33 (2003).
[4] N. T. Son, B. Magnusson, Z. Zolnai, A. Ellison, and E. Janzén, Mater. Sci. Forum **457**, 437 (2004).
[5] W. E. Carlos, E. R. Glaser, B. V. Shanabrook, and T. A. Kennedy, Bull. Am. Phys. Soc. **48**, 1322 (2003).
[6] N. T. Son, B. Magnusson, Z. Zolnai, A. Ellison, and E. Janzén, Mater. Sci. Forum **433**, 45 (2003).
[7] W. E. Carlos, E. R. Glaser, and B. V. Shanabrook, Mater. Sci. Forum **457**, 461 (2004).
[8] E. Rauls, T. Lingner, Z. Hajnal, S. Greulich-Weber, T. Frauenheim, and J.-M. Spaeth, Phys. Status Solidi B **217**, R1 (2000).
[9] Th. Lingner, S. Greulich-Weber, J.-M. Spaeth, U. Gerstmann, E. Rauls, Z. Hajnal, Th. Frauenheim, and H. Overhof, Phys. Rev. B **64**, 245212 (2001).
[10] M. V. B. Pinheiro, E. Rauls, U. Gerstmann, S. Greulich-Weber, J.-M. Spaeth, and H. Overhof, Phys. Rev. B (to be published).
[11] Th. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz, Phys. Status Solidi B **217**, 41 (2000).
[12] O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983).
[13] G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 3460 (1984).
[14] J.-M. Spaeth and H. Overhof, *Point Defects in Semiconductors and Insulators* (Springer, Berlin, 2003).
[15] J. B. Krieger, Yan Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
[16] Chung-Yuan Ren, Hong-Tay Jeng, and Chen-Shiung Hsue, Phys. Rev. B **66**, 125105 (2002).
[17] L. Torpo, T. E. M. Staab, and R. M. Nieminen, Phys. Rev. B **65**, 085202 (2002).
[18] Note that this discrepancy even increases when using plain LDA instead of SIC-OEP, since the isotropic part a of the hf splitting would be increased by a factor of 1.5 in LDA.