Dangling-bond defect in a-Si:H: Characterization of network and strain effects by first-principles calculation of the EPR parameters

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The performance of hydrogenated amorphous silicon (a-Si:H) solar cells is severely affected by the light-induced formation of metastable defects in the material (Staebler-Wronski effect). The common notion is that the dangling-bond (db) defect, a threefold coordinated silicon atom, plays a key role in the underlying mechanisms. To support the characterization of this defect by electron paramagnetic resonance (EPR), we present in this work a first-principles study of the EPR parameters for a structural ensemble of the db defect. We show that the a-Si:H dangling bond is a network defect for which charge and spin localization substantially depend on the actual coordination of the db atom and the local geometric and electronic structure of the immediate surrounding. It consequently differs by its very nature from its crystalline counterpart, which is typically related to the presence of a vacancy. The application of hydrostatic strain to our models yields further insights into the dependence of the hyperfine interaction on the structural characteristics of the defect. The observed trends are shown to result from the interplay between delocalization and *sp* hybridization.

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I. INTRODUCTION

Thin-film amorphous silicon (a-Si:H) is an established material for flexible, low-cost, and nontoxic solar cells. However, the major drawbacks of a-Si:H solar cells are their low conversion efficiency η and—related to that—the degradation over time due to light exposure—the Staebler-Wronski effect[1] (SWE). Due to the SWE, a single-junction solar cell loses about 30% of its initial efficiency after 1000 h of illumination.[2] The SWE is metastable and annealing at 100–250 °C restores the conversion efficiency within a few minutes.[3] Similarly, one observes seasonal fluctuations in real-life a-Si:H solar cells, with a partial recovery of η in the summer months.[4]

The SWE is related to structural changes in the material, i.e., the formation of metastable defects. However, a full understanding of the relevant processes has not been obtained so far. One of the reasons is that the notion of a structural defect is conceptually complicated in the amorphous phase. Initially, it is only characterized by the corresponding deviation from the ideal nearest-neighbor coordination $N = 4$ (see Fig. 1). However, the complex local structure often makes a clear distinction between different kinds of defects (e.g., dangling bond, broken bond, floating bond) difficult. Commonly, the SWE is believed to be related to the creation of a dangling bond (db), i.e., a threefold coordinated silicon atom with the remaining electron being unpaired and strongly localized.[5–7] But there is no consensus on the specific defect-creation mechanism. Several models have been suggested over the years as reviewed elsewhere.[8,9] Besides the db defect, there are indications that strained regions contribute to the Staebler-Wronski effect as well.[8,10–12]

Atomistic-scale information about the defect is crucial for a better understanding of the Staebler-Wronski effect. Experimentally this can be obtained by electron paramagnetic resonance (EPR), which probes for the local atomic structure of defects with unpaired spins,[13] such as the silicon dangling bond. In the case of a-Si:H, the resulting absorption spectrum is mainly characterized by the interaction of the unpaired spin with the external magnetic field (Zeeman interaction, g tensor) and with the nuclear dipole moment of the defect atom (hyperfine interaction, A tensor). However, structural disorder of the material leads to a broad spectral distribution,[5–7,14] which cannot be assigned to a specific defect structure. Further insights into the relevant features can only be obtained by comparing experimental results with theoretical calculations.[14–19]

Simple molecular db systems such as the tetrasilyl-radical $(SiH_3)_3Si\bullet$ are able to capture the experimental notion of a strongly localized defect wave function.[5–7] Both EPR tensors ($\boldsymbol{g}$ and $\boldsymbol{A}$) are uniaxial, which means that there is a rotational symmetry (at least threefold) about a unique axis.[13] The hyperfine interaction is directly connected to the local defect geometry.[17,19] For example, the variation of the dangling-bond bond angle (to its backbond neighbors) yields trends in the hyperfine parameters, which can be reasoned by the *s*- and *p*-like character of the db orbital. In the crystalline (c-Si) environment, dangling bonds are created from vacancy-impurity complexes[19–22] or hydrogen complexes in vacancies, at surfaces,[19–21,23] and at interfaces.[24–26] The structural network of these systems can be crucial for the hyperfine interaction, which overall reflects the interplay between *sp* hybridization of the db orbital and spin delocalization.[19]

In this work we present a first-principles study of the EPR parameters of the dangling bond in a-Si:H. By this approach we are able to characterize the local defect structure and the effect of the network. Most notably, we find that the latter exerts a

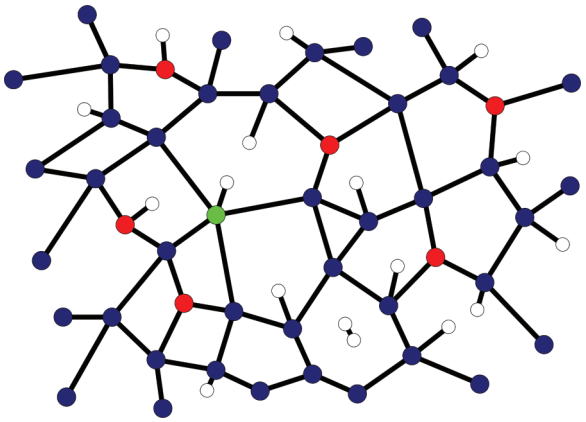


FIG. 1. (Color online) Random-network model of a-Si:H illustrating various local structural characteristics. The colors indicate coordination [white: 1 (hydrogen), red: threefold (dangling bond), blue: fourfold, green: fivefold (floating bond)]. In this work we use periodic-boundary conditions and a supercell approach for the modeling of the amorphous structure.

much more important influence than in the crystalline matrix. We then apply hydrostatic strain to our a-Si:H db models to gain insights into their structural stability, which is required for elaborating the differences to other kinds of possible defect mechanisms such as strained regions.[8,10–12] This study reveals the different nature of the c-Si and a-Si:H dangling bond, and can also in part explain the remaining discrepancies between theoretical and experimental findings.

II. COMPUTATIONAL METHODS

In this work we employ periodic-boundary conditions and a supercell-based approach. For the creation of the db models we start from defect-free a-Si:H models, which were either created by releasing hydrogen into Wooten-Winer-Weaire models of a-Si,[27] or by heating and gradually annealing of c-Si:H models followed by structural relaxation.[28,29] The dangling bond is then created by removing one hydrogen atom from the supercell with a subsequent relaxation of the atoms. We note in passing that in some cases the network rearranges so that the dangling bond moves away from the site where the hydrogen atom has been taken out. For our investigation we use 26 small (64Si-7H) as well as 28 large db models (216Si-29H). The generation of the structures as well as the computation of the EPR parameters (most notably, the g tensor) is resource demanding, and we can therefore only simulate a subensemble of realistically occurring defect configurations (10^{15}–10^{19} defects/cm^3 in experiment[30]). Second, the ratio between silicon and hydrogen atoms yields a hydrogen concentration on the order of 11–13%. Experimentally it can have a much larger fluctuation on the order of 7–30%.[7,14]

For the *ab initio* calculation of the EPR parameters, we have used the plane-wave DFT code QUANTUM ESPRESSO[31] (v4.2.1), in which the GIPAW formalism[32] has been recently implemented. We employ the Perdew-Burke-Ernzerhof functional[33] and norm-conserving pseudopotentials[34] with a scalar-relativistic correction for silicon.[35,36] We use the same plane-wave cutoff (30 Ry), and **k**-point mesh[37] ($6 \times 6 \times 6$ for the small supercells and $4 \times 4 \times 4$ for the large supercells) as established in a previous work on c-Si db models.[21] Here also a good agreement between theory and experiment was found, specifically the deviation for the g tensor is on the order of a few 10^{-3} and up to 3% for the hyperfine parameters. Thus our approach is able to accurately characterize the defect structure of localized dangling bonds in silicon.

Experimentally, only the absolute value of the hyperfine couplings can be determined from powder spectra. In our calculations we keep the negative sign due to the negative gyromagnetic ratio of silicon, but follow the experimental notion that the magnitude of the coupling is determined by the absolute value.

To study the effect of hydrostatic strain we change the lattice constant of the model, and then relax the atomic positions within the cell. We only consider the smaller 64Si-7H supercells. However, we do not expect drastic differences for the larger supercells, because the EPR-parameter statistics of both are quite similar, which agrees well with previous findings for other key properties such as the radial distribution function, the band gap, and tail states.[28,29]

III. RESULTS AND DISCUSSION

A. EPR parameters of the whole ensemble

The most natural assumption is that the described generation of the models indeed creates a dangling bond in the amorphous matrix, even though network rearrangements occurring during relaxation may strongly modify the character of the defect. The statistical average of our models should therefore correspond to a metastable dangling bond at a random position in the a-Si:H network. From this unbiased approach, previous studies draw the following conclusions.[14,38] The theoretical g tensor has rhombic symmetry and it is in good agreement with experimental results. The A tensor is axial, and the experimentally observed redshift of the isotropic contribution a from the crystalline ($a_{\text{c-Si}} \sim -300$ MHz) to the a-Si:H matrix ($a^{\text{exp}}_{\text{a-Si:H}} \sim -200$ MHz) can only be reproduced by our calculations in part with a remaining discrepancy on the order of 70 MHz. This indicates a selection of dangling bonds in experiments, which needs to be clarified by complementary studies of possible mechanisms. The g and A tensor have different symmetry properties since the g tensor reflects the global electronic defect structure, while the A tensor is exclusively determined by the local spin-density distribution in the vicinity of the nucleus of interest. Consequently, in some cases one obtains similar g values for models with a quite different degree of spin localization. This implies that the g tensor holds little information about the local defect geometry, and we will therefore put our focus on the hyperfine interaction in the following.

B. Classification by coordination and spin localization

Going beyond the statistical picture, one has to establish criteria according to which one can classify the a-Si:H db models. We regard the atom with the largest hyperfine interaction as the central atom of the defect, i.e., the db atom. First, it is necessary to check for the coordination at this atom, i.e., that it is indeed bonded to exactly three defect neighbors. To investigate this question, we consider two parameters,

the number of atoms within a certain distance r_{cut} and the bonding to hydrogen. We find that 43 models (80%) are triply coordinated for the reasonable cut-off bond length of 2.42 Å, and only four models (7%) do have a hydrogen as a backbond neighbor. Within our limited ensemble it is therefore more likely that the dangling bond has only silicon neighbors in accordance with recent experimental studies.[39,40]

Another important aspect is the degree of spin localization, which we quantify by looking at the largest and second largest a_{2nd} value for each db model. For crystalline models, the a_{2nd} value is relatively constant at around −30 MHz, and it always occurs at the second-nearest backbond neighbor.[19,21,24] In the amorphous case, the situation is far more complex, and some models even have $a_{2nd} > -100$ MHz. Clearly in these cases the spin is delocalized. In order to draw a line in between the localized and delocalized db models, we chose that a model belonging to the former category must not have an a_{2nd} larger than −80 MHz. According to this criteria, 38 db models (70%) are localized. A common feature of the delocalized models is that the a parameter at the dangling bond is usually smaller than −250 MHz and the anisotropic b parameter[13] is not larger than −30 MHz. This is again consistent with our picture of spin delocalization, which becomes apparently much more important in the amorphous environment.

C. The characteristics of strongly localized dangling bonds

As mentioned, the common notion of the amorphous db defect is that it is indeed threefold coordinated and that the spin is strongly localized on the central defect atom. In the following we take this into account by applying the mentioned criteria and only considering the subensemble of 33 models (61%) corresponding to a strongly localized, threefold coordinated db defect either bond to three silicon atoms or two silicon and one hydrogen atom. This procedure has also the advantage that we can work out the structural differences between the defect in the crystalline and the amorphous matrix.

1. Bonding geometry at the db atom

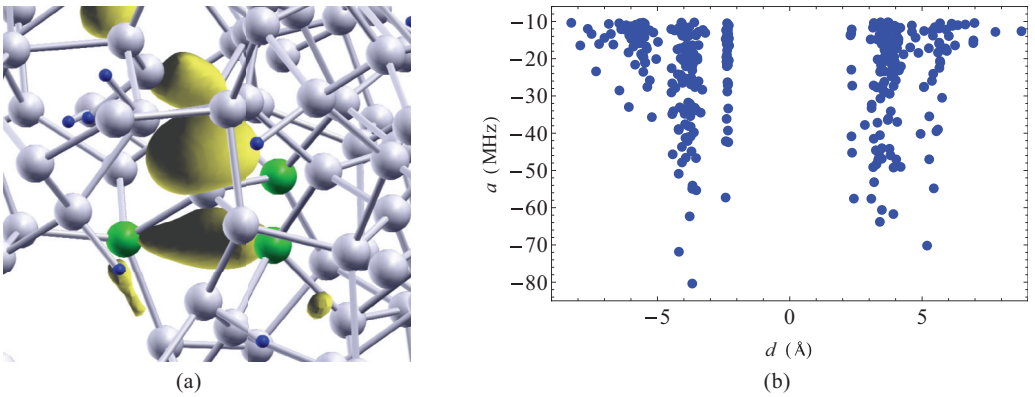
The bond lengths at the db atom are rather homogeneous with the mean value (standard deviation) $l = 2.34(0.02)$ Å. The bond angles at the db atom are close to the tetrahedral angle but do have a large variation $\alpha = 109.7°(12.6°)$. For reference, the corresponding parameters for c-Si dangling bonds[21] are on average $l = 2.35(0)$ Å and $\alpha = 110.7°(1.9°)$. On the other hand, a-Si:H models created by molecular dynamics[28] have on average the mean parameters $l = 2.38(0.05)$ Å and $\alpha = 108.9°(13.6°)$, and experimentally one typically obtains a bond length of $l = 2.35$–2.37 Å and a standard deviation for the angle distribution of 7.9°–9.6°. Most notably, this means that the theoretical angle distribution is larger than observed in experiment.[28] For our purposes, it is important to stress that these values refer to an average over a whole structural model or over the results obtained from a sample. Overall we can see that the local defect geometry of the a-Si:H dangling bond does not vary substantially neither from their crystalline counterparts nor from the rest of the network, and that the structural disorder mostly originates from fluctuations in the bond angle.

2. Hyperfine interaction

The EPR parameters of the localized db models essentially yield the same mean values compared to the overall ensemble, specifically the g values are shifted only by 0.0004 and the hyperfine parameters by $\Delta a \sim 10$ MHz, $\Delta b \sim 7$ MHz. Furthermore, the hyperfine parameters cannot be correlated unambiguously to the local bond geometry since the variation in between the smallest and the largest bond angle is typically more than 10°, and fluctuations of that order can have a drastic effect.[19] Indeed, a closer inspection reveals that there is no clear trend between the hyperfine and structural parameters.

3. Superhyperfine interaction and spin delocalization

Despite the similar bond parameters, a-Si:H dangling bonds have a smaller isotropic hyperfine coupling as their crystalline counterparts [$(\Delta a \sim -60$ MHz), $(\Delta b \sim -10$ MHz)]. This clearly indicates a stronger spin delocalization in the former case and can be understood by looking at the isotropic superhyperfine interaction of the silicon atoms. The most important difference is that the a-Si:H db models can also have strong isotropic couplings for atoms that are not second-nearest neighbors. This is illustrated in Fig. 2(a), which



(a) (b)

FIG. 2. (Color online) (a) Example of a localized dangling bond with a strong isotropic hyperfine interaction on the first neighbor (in green). (b) The dependence of the isotropic hyperfine coupling a on the distance d from the db atom. We only consider significant couplings, chosen to be larger than −10 MHz, and we distinguish between opposite (positive parameter range) and backbond (negative parameter range) atoms. Details of this classification scheme are described in the text.

shows a dangling bond with a significant spin density at the first backbond neighbor. To quantify the complexity of the spin distribution in the network, we depict in Fig. 2(b) the dependence of the isotropic superhyperfine coupling on the distance from the db atom. In doing so, we apply a criteria to distinguish between the backbond and the opposite db side. First we compute the centroid of the triangle spanned by the three nearest neighbors, the backbond atoms. Then we compare the distance $d_{\mathrm{db},n}$ between an atom (with $a >$ 10 MHz) and the db atom with the distance $d_{c,n}$ between the centroid and the atom. If the atom is closer to the centroid, $d_{c,n} < d_{\mathrm{db},n}$, we consider it as on the backbond site, and as opposite otherwise. In the former case we assign a minus to the distance, and in the latter case a plus, respectively. Overall this gives us the following basic notion of the spatial spin distribution in the supercell, which reflects the shell structure of the network. As expected from the crystalline db models, the strongest couplings occur around the second-nearest neighbor distance, even though there is no difference between opposite and backbond since for both cases the superhyperfine interaction is similar in magnitude. This again indicates that in our simulations dangling bonds appear rather randomly at sites with an appropriate geometric distortion in the network with a rather homogeneous distribution of neighbors. They differ in this aspect from their crystalline counterparts, which are typically related to the presence of a vacancy[19,21] or an interface.[24–26] In this context it is reasonable but still interesting that the superhyperfine coupling is on average larger than in the crystalline environment. Apparently this is another manifestation of the delocalization, which is—as we have seen—a characteristic feature of a-Si:H dangling bonds.

For completeness, we mention that despite their small number, dangling bonds with a hydrogen at the backbond side have rather diverse EPR parameters with a distribution comparable to dangling bonds with only silicon backbond neighbors. From the overall isotropic couplings of hydrogen we see the same features as for neighboring silicon atoms. First, it is distributed homogeneously with respect to the distance from the db atom, which is in agreement with a recent experimental observation.[39] Furthermore, hydrogen can have a significant spin polarization on the order of 30 MHz also for larger distances (5 Å) from the db atom. This implies that the point-dipole approximation[39] does not allow for a quantitative analysis of distances.

We have seen that the amorphous host matrix gives rise to a much broader spectrum of db-like defects than observed in crystalline silicon. On the one hand, the removal of a hydrogen atom from the system does not necessarily lead to the creation of a strongly localized db defect as it is largely believed in the literature.[5–7] Deviations from the threefold coordination as well as rather delocalized spin densities occur. Consequently, both aspects are characteristic for the a-Si:H dangling bond. The a-Si:H db is—in contrast to the vacancy-based c-Si db—a network defect, which most likely appears for suitable geometrical distortions with the local variation in the bond angle as the most important influence.

D. Strain

The different origins of the c-Si and the a-Si:H dangling bond can also be illustrated by considering the effect of hydrostatic strain on the hyperfine parameters. Of course, a-Si:H films are typically biaxially strained.[41] However, test calculations demonstrated the same trends as the computationally more feasible study of hydrostatic strain. This can be explained intuitively by the more or less random orientation of the dangling bond in a-Si:H. In most cases, it is not aligned to any of the axes, and consequently it is not important, in which directions strain is applied.

The amorphous db models show a large structural sensitivity to strain. In particular for large strains (tensile or compressive) one observes a redistribution of the spin density, and the dangling bond hops from one to the other atom, which again illustrates the network character of the defect. To take this into account, we consider for each model only the range in which the dangling bond is stable. Practically, this is implemented by first determining the db atom at the ideal lattice constant. Then we monitor whether it is still the atom with the largest a value as a function of the applied strain. Furthermore, since the bonding parameters of Si-H bonds cannot be compared to Si-Si bonds, we only consider those cases in which the dangling bond has three silicon atoms as neighbors.

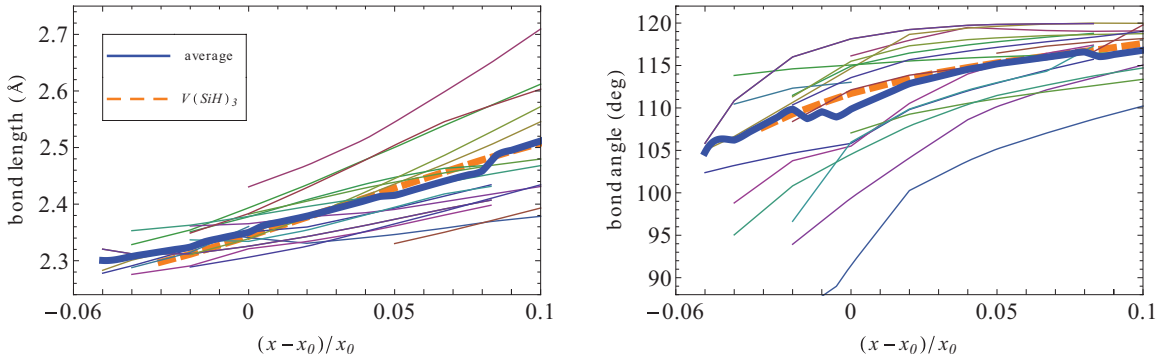


FIG. 3. (Color online) The dependence of bond length and bond angle on the elongation x from the ideal lattice constant x_0. For the rhombic supercells, x_0 corresponds to the mean lattice constant of the three axis (x_1, x_2, x_3). The bond parameters are defined by the average over the three nearest neighbors. Each thin line corresponds to one db model. The thick blue line indicates the trend for the mean value. Kinks in this curve can occur when the number of included db models changes with respect to strain. For comparison the thick dashed line shows the dependence of the crystalline $V(\mathrm{SiH_3})$ db model. Values of pressure are included for the experimentally relevant range of strains.

First let us look at the structural parameters of the db atom as depicted in Fig. 3. For the mean bond length we recognize that the amorphous db models show on average the same trends as the crystalline $V(SiH_3)$ db model.[42] In particular, for compressive strain they have a comparable range of stability, and besides that, the increase of l for tensile strain is on the same order. Significant deviations from this are only observed for $l > 2.6$ Å when the model is not triply coordinated at the ideal lattice constant. A similar correspondence is also found for the bond angle α in the case of tensile strain since the a-Si:H db models also favor a rather planar geometry. On the other hand, the diverse picture for compressive strain can be explained by inhomogeneities in the three bond angles which are not captured by the mean parameter. To exemplify this point let us look at the db model with the largest deviation from the overall trend ($\alpha = 109.6^\circ$ for $\Delta x = 0.1$). Even though the stability of the dangling bond is very sensitive to tensile strain, it is threefold coordinated and localized at the ideal lattice constant, i.e., a true db model. The bond angles at $x = x_0$ vary by $\pm 5^\circ$ from the square angle, and for large tensile strain ($\Delta x = 0.1$) this tendency is enhanced since in this case α is in between 101 and 116 deg. The large variation among the three bond angles illustrates that the mean value is indeed only an approximative measure of an actually more complex bonding geometry. Despite this deficiency, we learn from Fig. 3 that the bond parameters in general show the same trends as for the crystalline db models, and that the bond angles are more sensitive to compressive strain than the bond lengths.

The isotropic hyperfine interaction has no clear trend (Fig. 4) since we are considering all db models (despite their coordination and spin localization) on equal footing. Consequently, it can happen that the spin density at the db atom increases or decreases with applied strain, or that it is rather delocalized over the whole range. In one case, the dangling bond is only stable in between $\Delta x = [-0.004, 0]$ before it starts to bond to hydrogen. On the other hand, the trend for the b parameter is rather homogeneous for almost all models and corresponds to the one observed for the crystalline model with a constant shift of 20 MHz. The only exceptions are caused by delocalization, undercoordination, and a very small bond angle. However, the true information here is obtained again from the averaged trends. The a parameter stays rather constantly in between 200 and 250 MHz throughout the strain range, and there is no obvious dependence on the magnitude of the applied strain. This aspect distinguishes the a-Si:H dangling bonds from their crystalline counterparts,[19,21] and it might be explained by their different origins. As described, the crystalline dangling bond is related to a vacancy complex, which essentially means that it is characterized by the interplay of electronic effects (due to impurities) and the local defect geometry. On the other hand, the amorphous dangling bond is a network defect, which is consequently essentially influenced by spin delocalization into the local environment as well as structural features of the wider surrounding. Thus the trend for the a parameter can be explained by spin delocalization for small strains and the planar local db structure for large tensile strain. This picture is also consistent with the trend for the anisotropic hyperfine coupling, which shows a gradual increase in p character of the db orbital with increasing strain. Overall we learn from this that for compressive strains delocalization is important and for tensile strains the db character is enhanced. Most notably, the latter finding illustrates that spin localizes much more strongly due to a dangling bond in comparison to regions of strain, which yield rather delocalized spin distributions.[11,12]

Let us now discuss the main implication of this conceptual study for the discrepancy between theory and experiment in the a parameter. Compressive strain on the order of a few percent can lower the isotropic coupling so that the difference between both becomes reasonable. However, in this case one should also observe a corresponding shift in the b parameter, i.e., the agreement between theory and experiment should become better as well. Since this is not observed, one cannot consider strain as an exclusive explanation. But at least it gives a clear perspective that strain might have an observable influence on the hyperfine parameters, and consequently may play an important role for the defect mechanisms in the material.

Furthermore, it points out that an accurate determination of the anisotropic parameter is decisive for the experimental analysis and comparison among different samples. For example, the current deviation in between $[-39, -63]$ MHz among different experiments[6,7,14] can correspond to two opposite

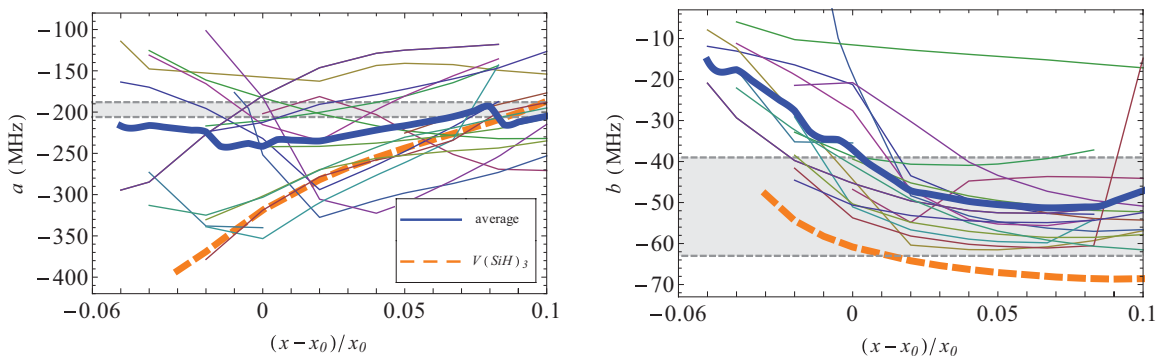


FIG. 4. (Color online) The dependence of the hyperfine parameters on the elongation x from the ideal lattice constant x_0. For the rhombic supercells, x_0 corresponds to the mean lattice constant of the three axis (x_1, x_2, x_3). The bond parameters are defined by the average over the three nearest neighbors. Each thin line corresponds to one db model. The thick blue line indicates the trend for the mean value. Kinks in this curve can occur when the number of included db models changes with respect to strain. For comparison, the thick dashed line shows the dependence of the crystalline $V(SiH_3)$ db model. Values of pressure are included for the experimentally relevant range of strains. The gray-shaded portion of the graph indicates the experimental range.[6,7,14]

strain situations. This difference is therefore too large to clearly identify the overall contribution of spin delocalization and *sp* hybridization to the defect, which would be important for a better understanding of the SWE. Our results yield a clear trend in between spin localization and structural changes due to strain. Even though the experimentally accessible range of strain is much smaller as in our study, it would be therefore interesting to carry out a corresponding experiment.

IV. CONCLUSIONS

In this work we have characterized the amorphous Si dangling bond (db), which was generated from structural models of a-Si:H by removing one hydrogen atom. This approach to creating the defect leads to a broad variety of realizations. We did not impose any constraints or weighting factors to better reflect the experimentally observed defect ensemble since we lack sufficient information on the decisive physical mechanisms. Two key characteristics are spin delocalization and the actual coordination of the db atom. Only ∼60% correspond to a strongly localized, threefold coordinated db defect as commonly assumed.[5–7] However, the EPR parameters do not indicate any distinction from the rest of the db ensemble. The mean bond length and bond angle of strongly localized dangling bonds are comparable to their crystalline counterparts, and the rest of the amorphous network. The decisive geometric parameter is the variation in the bond angles, which also makes a reasoning of the hyperfine parameters in terms of the local defect geometry ambitious.

Overall the a-Si:H db corresponds to a network defect, which is generated at suitable geometric distortions in the network. It differs in this aspect from its crystalline counterpart, which is usually related to the presence of a vacancy. The different origins of the c-Si and a-Si:H dangling bond can be also seen from the systematic study of strain effects on the hyperfine parameters. Most notably for compressive strains, we obtain in the crystalline case an increase of *s* character of the db orbital, whereas for the a-Si:H db delocalization becomes important.

Our systematic study also shows that strain can have an important effect on the hyperfine parameters with the anisotropic coupling being the decisive parameter. This is particularly interesting since the current variation among different experiments and samples is rather large.[6,7,14] An experimental investigation of the strain dependence of the EPR parameters could shed new light into the interplay between spin delocalization and *sp* hybridization of the db orbital, which is crucial for the further characterization of the db defect and the identification of its role in the Staebler-Wronski effect.

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[1] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[2] A. Luque and S. Hegedus, *Handbook of Photovoltaic Science and Engineering* (Wiley-VCH, New York, 2003).
[3] R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991).
[4] A. Shah, P. Torres, R. Tscharner, N. Wyrsch, and H. Keppner, Science **285**, 692 (1999).
[5] D. K. Biegelsen and M. Stutzmann, Phys. Rev. B **33**, 3006 (1986).
[6] M. Stutzmann and D. K. Biegelsen, Phys. Rev. B **40**, 9834 (1989).
[7] T. Umeda, S. Yamasaki, J. Isoya, and K. Tanaka, Phys. Rev. B **59**, 4849 (1999).
[8] A. Kołodziej, Opt. El. Rev. **12**(1), 21 (2004).
[9] T. Shimizu, Jpn. J. Appl. Phys. **43**, 3257 (2004).
[10] P. A. Fedders, Y. Fu, and D. A. Drabold, Phys. Rev. Lett. **68**, 1888 (1992).
[11] P. A. Khomyakov, W. Andreoni, N. D. Afify, and A. Curioni, Phys. Rev. Lett. **107**, 255502 (2011).
[12] L. K. Wagner and J. C. Grossman, Phys. Rev. Lett. **101**, 265501 (2008).
[13] J. A. Weil and J. R. Bolton, *Electron Paramagetic Resonance* (Wiley, New York, 2007).
[14] M. Fehr, A. Schnegg, B. Rech, K. Lips, O. Asthakov, F. Finger, G. Pfanner, C. Freysoldt, J. Neugebauer, R. Bittl, and C. Teutloff, Phys. Rev. B **84**, 245203 (2011).
[15] M. Cook and C. T. White, Semicond. Sci. Technol. **4**, 1012 (1989).
[16] A. H. Edwards and W. B. Fowler, Phys. Rev. B **41**, 19816 (1990).
[17] N. Ishii and T. Shimizu, Solid State Commun. **102**, 647 (1997).
[18] N. Ishii and T. Shimizu, J. Non-Cryst. Solids **227**, 358 (1998).
[19] G. Pfanner, C. Freysoldt, and J. Neugebauer, Phys. Rev. B **83**, 144110 (2011).
[20] P. Johannesen, B. B. Nielsen, and J. R. Byberg, Phys. Rev. B **61**, 4659 (2000).
[21] G. Pfanner, C. Freysoldt, J. Neugebauer, and U. Gerstmann, Phys. Rev. B **85**, 195202 (2012).
[22] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).
[23] B. B. Nielsen, P. Johannesen, P. Stallinga, K. B. Nielsen, and J. R. Byberg, Phys. Rev. Lett. **79**, 1507 (1997).
[24] M. Cook and C. T. White, Phys. Rev. B **38**, 9674 (1988).
[25] A. Stesmans, B. Nouwen, and V. V. Afanas'ev, Phys. Rev. B **58**, 15801 (1998).
[26] A. Stirling, A. Pasquarello, J. C. Charlier, and R. Car, Phys. Rev. Lett. **85**, 2773 (2000).
[27] P. Biswas, D. N. Tafen, F. Inam, B. Cai, and D. A. Drabold, J. Phys.: Condens. Matter **21**, 084207 (2009).
[28] K. Jarolimek, R. A. de Groot, G. A. de Wijs, and M. Zeman, Phys. Rev. B **79**, 155206 (2009).
[29] K. Jarolimek, G. A. de Wijs, R. A. de Groot, and M. Zeman, Phys. Status Solidi A **207**, 605 (2010).
[30] S. Kasap and P. Capper, eds., *Springer Handbook of Electronic and Photonic Materials* (Springer, New York, 2006).

[31]P. Giannozzi *et al*., J. Phys.: Condens. Matter **21**, 395502 (2009).
[32]C. J. Pickard and F. Mauri, Phys. Rev. Lett. **88**, 086403 (2002).
[33]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[34]The GIPAW-reconstruction data for the all-electron wave function has been generated by Ari P. Seitsonen.
[35]S. Blügel, H. Akai, R. Zeller, and P. H. Dederichs, Phys. Rev. B **35**, 3271 (1987).
[36]J. M. Spaeth and H. Overhof, *Point Defects in Semiconductors and Insulators* (Springer, New York, 2003).
[37]H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[38]C. Freysoldt, G. Pfanner, and J. Neugebauer, J. Non-Cryst. Solids **358**, 2063 (2012).
[39]M. Fehr, A. Schnegg, C. Teutloff, R. Bittl, O. Astakhov, F. Finger, B. Rech, and K. Lips, Phys. Status Solidi A **207**, 552 (2010).
[40]K. Morigaki and H. Hikita, Phys. Rev. B **76**, 085201 (2007).
[41]H. Gleskova, I. C. Cheng, S. Wagner, J. C. Sturm, and Z. Suo, Solar Energy **80**, 687 (2006).
[42]The db model corresponds to the monovacancy with three of the broken bonds passivated by hydrogen.