Mechanisms for p-type behavior of ZnO, Zn$_{1-x}$Mg$_x$O and related oxide semiconductors

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(Dated: January 12, 2017)

Possibilities of turning intrinsically n-type oxide semiconductors like ZnO and Zn$_{1-x}$Mg$_x$O into p-type materials are investigated. Motivated by recent experiments on Zn$_{1-x}$Mg$_x$O doped with nitrogen we analyze the electronic defect levels of point defects N$_{O}$, v$_{Zn}$, and N$_{O}$-v$_{Zn}$ pairs in ZnO and Zn$_{1-x}$Mg$_x$O by means of self-interaction-corrected density functional theory calculations. We show how the interplay of defects can lead to shallow acceptor defect levels, although the levels of individual point defects N$_{O}$ are too deep in the band gap for being responsible for p-type conduction. We relate our results to p-type conduction paths at grain boundaries seen in polycrystalline ZnO and develop an understanding of a p-type mechanism which is common to ZnO, Zn$_{1-x}$Mg$_x$O, and related materials.

PACS numbers: 71.23.-k,71.55.Jv,71.20.Mq

I. INTRODUCTION

Zinc oxide is a prominent example of an intrinsically n-type semiconductor. Its abundant availability, its low-cost production, and its wide electronic band gap of approximately 3.4 eV make ZnO attractive for transparent and conducting oxide layers in consumer-electronics devices. However, a breakthrough of ZnO-based transparent electronics has not been achieved so far due to the lack of sufficiently conductive and long-term stable p-type ZnO layers. The problem of p-type doping of ZnO has by now been a scientific challenge for more than two decades. Besides the doping with single elements like N, P, As, or Sb, substituting O and Li, Na, K, Cu, Ag or Au, substituting Zn or co-doping was discussed as well.3-9 Apparently, the most promising candidate so far is still nitrogen. However, it was shown theoretically10-12 that the substitutional defect of N on O sites (N$_{O}$) cannot be responsible for the p-type conduction which has been observed in some experiments,11 since it creates a defect level which is located too high above the valence band (VB) edge with respect to thermal excitation energies.

Recent theoretical and experimental studies consider more complicated defect complexes which involve zinc vacancies (v$_{Zn}$) or co-doping, like the N$_{O}$-v$_{Zn}$ or N$_{O}$-v$_{Zn}$-H defect complexes, as potential sources of p-type conduction.14,15

For polycrystalline ZnO it has been proposed that conduction channels of p-type can be found along grain boundaries.12,16 Here it is an interplay of grain boundaries, their depletion regions, and point defects that results in the desired low lying acceptor levels.

It has been reported by Hierro et al.17 that the use of ternary ZnO-based alloys like Zn$_{1-x}$Mg$_x$O (denoted by ZMO in the following) facilitates the p-type conductivity due to lower net electron concentrations than in pure ZnO. These authors relate the reduced net electron concentration to two deep lying Mg-related defects which act as electron traps. ZMO retains the wurtzite crystal structure of ZnO for Mg substituting Zn for concentrations up to $x \approx 40\%$, and also the lattice parameters change only slightly. Hence combining ZMO with n-type ZnO layers leads to negligible lattice misfits.17

Up to now it is not yet clear which atomic or extended defects provide the key to promote p-type conductivity in ZnO and related materials like ZMO. An understanding of this defect physics would allow a targeted development of experimental routes to synthesize materials having these particular acceptor states.

In this paper we present a density functional theory (DFT) study determining the electronic defect levels of the defects N$_{O}$, v$_{Zn}$, and N$_{O}$-v$_{Zn}$ in ZnO and ZMO. We discuss our results in the context of the accumulated experimental and theoretical knowledge, and thereby we shed light on the question of why some experimental routes recently taken have lead to p-conduction but others not. Are the defect states that originate from N$_{O}$ indeed too deep in the band gap? What changes when N$_{O}$ forms a defect complex with a Zn vacancy, and how do Mg atoms nearby affect its defect level position? For the determination of the electronic defect levels we use a self-interaction corrected (SIC) local-density approximation (LDA) approach12 that is capable to give far better results than both commonly used approximations, the LDA and the generalized gradient approximation (GGA). The latter two have limited predictive power for wide band gap semiconductors due to their inherent significant underestimation of the band gap due to their self-interaction error. SIC-LDA overcomes this limitation and yields electronic band structures with band gaps that are in good agreement with experiments12,18 and in particular for ZnO a correct separation of the Zn-3d and O-2p bands.19 By means of this approach, the defect levels in various amorphous oxide semiconductors based on In, Sn, and Zn have been predicted reliably.20,21

The results presented in this paper may solve the controversial problem that individual N$_{O}$ defects are indeed creating levels lying too deep inside the band gap even though nitrogen doping has been observed to lead to p-type ZnO and ZMO, probably due to an interplay with...
other defects. Moreover, we relate our present results to
the p-type conduction effects which have been observed
for grain boundaries in ZnO, and we relate all this to one
common origin. The emerging theoretical picture will
presumably be useful for the experimental optimization
of p-type conduction in ZnO and ZMO.

II. COMPUTATIONAL APPROACH

A. Supercell models

For the study of defect complexes we have chosen a
supercell model of the wurtzite crystal structure of ZnO
containing 72 atoms and consisting of \(3 \times 3 \times 2\) primitive
unit cells. Since \(\text{Zn}_{32}\text{Mg}_{4}\text{O}_{36}\) retains the wurtzite struc-
ture for Mg concentrations \(x \leq 40\%)\), the corresponding
supercells were generated by randomly substituting Zn
atoms by Mg atoms. For the study of the bulk crystal
properties like lattice parameters and band gap as func-
tion of the Mg concentration we compared several real-
izations of random Mg distributions within the 72-atoms
supercell, and we find a negligible dependency of these
properties on the Mg distribution. For comparison, we
have also examined results from a 36-atom supercell in
the study of bulk properties. For the subsequent study
of defects we have chosen the specific Mg concentration
of \(x = 1/9 \sim 11\%\) (i.e. replacing 4 of 36 Zn atoms by Mg
atoms in the 72-atom supercell) which is representative
for typical experimental concentrations.\(^{24}\) Furthermore,
the defect analysis concentrates on specific realizations
of the Mg distribution which differ in the number of Mg
atoms that cluster in the direct neighborhood of the \(N_{0}\)
point defect under study. Two such realizations are dis-
played in Fig. 1.

B. Structure optimization

The structure optimization of all the constructed
supercell models was carried out using the projector
augmented-wave (PAW) method\(^{25,26}\) as implemented in the
VASP code.\(^{25,26}\) The LDA was used for the exchange-
correlation functional, and PAW potentials describing
the Zn-(3d,4s,4p), Mg-3s, and O-(2s,2p) as valence elec-
trons. All VASP calculations were carried out with a
plane-wave energy cutoff energy of \(400\) eV, a \(3\times3\times3\) Monkhorst-
Pack k-mesh, and a Gaussian broadening of 0.1 eV.

For all bulk structures the volume optimization was
carried out by fitting the universal equation of state\(^{25}\) to
a dataset of minimal total energies calculated at differ-
cent cell volumes. Optimization of the lattice parameter
ratio \(c/a\) and internal relaxation of the atomic positions
were achieved by minimizing the elastic stress and the
forces acting on the atoms, respectively. The supercells
containing defects were internally relaxed at fixed volume
and \(c/a\) ratio.

C. Electronic-structure calculations

The electronic-structure calculations on the basis of
the SIC-LDA were performed using the computational
mixed-basis pseudopotential (MBPP) method\(^{29,30}\) with
the same calculation setup as reported in previous papers.\(^{12,33,34}\) We have taken the LDA for exchange
 correlation as parametrized by Perdew and Zunger.\(^{35}\)
For Zn, Mg, and O optimally smooth norm-conserv-
ing pseudopotentials\(^{36}\) were constructed, and a mixed ba-
sis of plane waves and non-overlapping localized orbitals
were used. Due to the localized orbitals a plane-wave
cutoff energy of \(20\) Ry (\(1\)Ry = 13.606 eV) is sufficient for
obtaining well converged results. For the k-point sam-
ping of the Brillouin-zone integrals a Monkhorst-Pack
mesh of \(3 \times 3 \times 3\) and a Gaussian broadening of \(0.2\) eV
were used. The DOS of the supercells were evaluated
with the same mesh and a Gaussian broadening of 0.1 eV.

The self-interaction of the LDA is corrected by an in-
corporation of the SIC in the pseudopotentials.\(^{12,37}\) The
SIC procedure uses weight factors \(w = (w_{s}, w_{p}, w_{d})\) ac-
counting for the occupations of the individual s, p and
d valence orbitals. We corrected the Zn 3d semi-core
orbitals by 100\%, i.e. \(w_{\text{Zn}}=(0, 0, 1)\). The localized O-
2s semi-core orbitals are also corrected by 100\% while
for the spatially more extended O-2p valence-band or-
bitals we have taken 80\% which implies the weight factors
\(w_{\text{O}}=(1, 0.8, 0)\). We did not apply a SIC to the almost
unoccupied Mg-3s, 3p and Zn-4s, 4p conduction-band or-
bitals of the almost fully ionic compounds \(\text{Zn}_{1-x}\text{Mg}_{x}\text{O}\).
For the adjustment of the atomic SIC to the crystal field
in the solids, a scaling factor \(\alpha = 0.8\) is applied.
The functional dependencies of the lattice parameters $a$ and $c$ on the Mg content are displayed in Fig. 2. Our results underestimate the experimental values by about one percent, which is a typical systematic deviation for LDA results. The increase of $a$ and the decrease of $c$ with increasing Mg content are quantitatively correct and just slightly shifted with respect to previous experimental and theoretical findings. This good agreement on the structural parameters is the prerequisite for the electronic structure calculations which are the focus of this work. Note that the deviations from Vegard’s rule in some of the values of the experimentally observed lattice constants is probably related to the quality of the thin films and maybe due to the presence of compensated defects or residual strain as discussed, e.g., by Ryoken et al. \cite{Ryoken:2007}.

### B. Band gap of ZMO

Theoretical and experimental values of the band gap of Zn$_{1-x}$Mg$_x$O as function of the Mg content $x$ are displayed and compared in Fig. 3. The results obtained by the SIC-LDA approach do not only show the rising trend correctly, but also the calculated values agree quantitatively well to the experimental data. The dependency of the band gap on the specific distribution of Mg atoms within the supercell is small, e.g. for the sample structures with $x \sim 22\%$ we find an energy scatter of only $\delta E \sim 10\text{meV}$.

The wide scatter of experimental results in Fig. 3 is probably due to the varying quality of the thin films but also due to different experimental approaches of determining the band gaps. \cite{Ryoken:2007,Park:2000,Gosh:2009} Above the thermodynamical solubility limit of $x \sim 5\%$ a non-equilibrium solid solution is formed. Depending on the route of synthesis, this results in compositional non-uniformity which then leads to the generation of non-equilibrium compensated defects or even structural inhomogeneity and residual elastic stress. Naturally, all of this is reflected in the measured physical properties of the films, as discussed in the respective articles.

For our investigation the calculation of the band gap as function of the Mg content serves as a validation that the SIC-LDA describes the electronic structure of the Zn-Mg-O system rather well.

The total density of states (DOS) of a representative Zn$_{32}$Mg$_4$O$_{36}$ sample calculated with the SIC-LDA approach is shown in Figure 4. The upper part of the VB is mainly formed by the O 2p valence orbitals while the lower part is dominated by the Zn 3d semicore orbitals. Experimentally, the average d-band energy of ZnO was determined to be at -7.8 eV relative to the VB edge. \cite{Park:2000} This is almost unchanged when Mg is introduced. The SIC-LDA approach reproduces this experimental observation in contrast to LDA, GGA and several commonly used hybrid functionals which place the Zn 3d levels too high in energy and therefore overestimate their hybridization with the O 2p levels. The latter can lead to wrong positions of defect levels in the band gap. \cite{Park:2000} Thus these results validate our approach to analyze individual electronic levels of point defects by using the SIC-LDA approach.
FIG. 4: (Color online) Comparison of the total DOS of \( \text{Zn}_3\text{Mg}_4\text{O}_{36} \) without (bulk) and with \( \text{N}_\text{O}, \text{v}_\text{Zn}, \) and \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defects. The inset magnifies the region close to the VB maximum. Small colored arrows on the energy axis mark the highest occupied levels. The curves are aligned with respect to the valence band and the energy of the bulk VB edge is set to zero.

C. Electronic defect levels near the VB

From the total density of states (DOS) in Fig. 4 it can be seen that the defects \( \text{N}_\text{O}, \text{v}_\text{Zn}, \) and \( \text{N}_\text{O}+\text{v}_\text{Zn} \) create energy levels close the VB edge. However, a closer inspection – which is provided in the inset – shows that the defect levels that originate from \( \text{N}_\text{O} \) are separated from the VB with a peak at about 0.25 eV. In the left panel of Fig. 4 the position of the \( \text{N}_\text{O} \) defect level is shown as function of the number of nearest Mg neighbors (NN). Here, NN-1Mg indicates a \( \text{Zn}_{32}\text{Mg}_4\text{O}_{35}\text{N} \) (or \( \text{Zn}_{31}\text{Mg}_4\text{O}_{35}\text{N} \)) supercell in which one Mg atom is adjacent to the \( \text{N}_\text{O} \) (or \( \text{N}_\text{O}+\text{v}_\text{Zn} \)) defect, respectively, while in the NN-2Mg and NN-3Mg supercells, two and three Mg atoms are nearest neighbors of the defect.

An increasing number of NN Mg atoms leads to an up-shift of the defect level. Therefore, concerning p-type conductivity, Mg doping makes \( \text{N}_\text{O} \) defects less attractive since the level becomes more narrow and moves deeper into the band gap. On the other hand, the energy level position of the \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defect complex remains almost unchanged for different numbers of NN Mg atoms.

The substitution of Zn by Mg in ZnO does not help to make the acceptor levels of individual \( \text{N}_\text{O} \) defects shallow, which would facilitate p-type conductivity at room temperature, but rather provokes the contrary. Moreover, it has been reported that the presence of Mg atoms in the neighborhood of a \( \text{N}_\text{O} \) defect increases the defect formation energy considerably and therefore reduces the respective defect concentration in the material. Our calculations are in line with the findings of Ref. 48, see discussion in the Appendix.

Zinc vacancy defects alone create very shallow defect levels (see inset of Fig. 4), which is a well known result from previous studies. Experimentally, defect levels at either 130meV\(^\text{13}\), 160 meV\(^\text{24}\), or 190 meV\(^\text{25}\) are reported, depending on the specific experiment. According to Fig. 5 the levels of the \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defect complex lie higher above the VB edge than that of the individual \( \text{v}_\text{Zn} \) defect and fit to the experimentally determined values rather well. We thus propose to assign the experimentally found acceptor levels to a \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defect complex. This complex is very promising since it provides shallow defect levels that are not separated in energy from the VB edge, and thus continuous low energy excitation are possible. The position of the defect level varies only slightly with the number of Mg atoms near the defect complex (see right panel of Fig. 4).

D. Spatial distribution of \( \text{N}_\text{O} \) and \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defect levels

In order to analyze the spatial distribution of the defect levels we have evaluated the atom-projected local densities of states (LDOS) for the most relevant atoms involved in the defect (complex). Figure 6 displays their contributions to the defect levels while the relative locations of these atoms are sketched in Fig. 7a. A contribution of an individual neighbor atom to a defect level is evaluated by integrating the LDOS of the respective atom in the relevant energy interval and subsequent division by the sum of the LDOS of all atoms in the supercell, integrated for the same energy range. The energy interval [-0.1, 0.5]eV was chosen for the analysis of the \( \text{N}_\text{O} \) defect, while the analysis of the \( \text{N}_\text{O}+\text{v}_\text{Zn} \) defect complex is carried out separately for the intervals [-0.2, 0.0]eV (VB edge) and [0.0, 0.4]eV (unoccupied states above the VB edge), c.f. Fig. 6.
Contributions are shown. The left in Fig. 7. For the oxygen and metal ions the summed contributions of the NN metal atoms (numbered 4–6 in Fig. 7a) only contribute \( \approx 2\% \) (Zn) and \( \approx 1\% \) (Mg), each. For the VB edge (right panel in Fig. 6), reminiscent of the \( v_{Zn} \) defect, the 3 oxygen atoms are more important (\( \approx 20\% \)), but the N-atom still contributes on average with \( \approx 20\% \). A change in the number of NN Mg atoms has only little effect on this spatial distribution with a small shift of weight from the NN metal atoms to N.

Note that the contributions for the oxygen ions (red line) and metal ions (green line) shown in Fig. 6 are the sums for the 3 O-atoms (numbered 1–3 in Fig. 7a) and the 3 or 4 metal atoms (numbered 4–7 in Fig. 7b), respectively. The metal atoms at positions 4–6 can be either Zn or Mg, while position 7 corresponds to either a Zn atom or a Zn vacancy. The relative positions of these atoms, which are the ones most involved in the defect complex, are sketched on the left in Fig. 7. For the oxygen and metal ions the summed contributions are shown.

FIG. 6: (Color online) Relative LDOS contributions to the total DOS of the \( N_O \)-defect level (left), the unoccupied part of the \( (N_O-v_{Zn}) \)-defect level (middle) and the respective VB edge (right), shown for the \( N_O \) atom and its most relevant neighbors. The relative positions of these atoms, which are the ones most involved in the defect complex, are sketched on the left in Fig. 7. For the oxygen and metal ions the summed contributions are shown.

FIG. 7: (Color online) (a) Sketch of the most relevant atoms involved in the defects \( N_O \) and \( N_O + v_{Zn} \). Metal atoms on positions 4–6 can be either Zn or Mg. Position 7 corresponds to either a Zn atom or a Zn vacancy. (b) Dependency of the \( N_O \) atom position (height \( h_{N} \)) above the atomic plane defined by the metal atoms 4–6 on the number of Mg atoms involved.

E. Defect-complex mechanism for p-type conduction mechanism

For p-type conduction a Fermi level close the VB edge and shallow acceptor levels in sufficiently high concentration are needed. Since the thermal excitation energy at room temperature is only about 25 meV, p-type conduction with a significant hole concentration can at best be achieved by acceptor defect levels which are distributed continuously right above the VB edge. Our SIC-LDA analysis of the most relevant defects in N-doped ZMO shows that \( v_{Zn} \) and \( N_O-v_{Zn} \) indeed provide such defect levels.

Our results support the hypothesis that co-doping of ZnO with Mg and N can be a possible route to obtain p-type conductivity. The \( (N_O-v_{Zn}) \) defect complex yields shallow acceptor levels which can be activated by the experimentally reported lowering of the net electron concentration in ZMO. This carrier compensation effect increases linearly with the Mg content and can be explained by deep-lying Mg-related defects which act as charge traps.

Zinc vacancies are low lying energy defects which exist also in pure ZnO. However, pure ZnO usually is an intrinsically n-type semiconductor since donor defects dominate. Only grain boundaries in polycrystalline ZnO
may provoke p-type conducting films under oxygen rich conditions. In general the addition of oxygen is thought to reduce the number of oxygen vacancies which are supposed to be the key donor defects. We believe that an understanding of the effect of oxygen addition has to be extended to take the grain boundaries into account. Under oxygen rich conditions the percentage of grain boundaries with undercoordinated oxygen atoms increases. In previous work,\cite{12,18} we have shown that such grain boundaries contribute shallow levels above the VB edge. These are an equivalent to the defect levels of v\textsubscript{Zn} in bulk-like ZnO or ZMO discussed here, since the oxygen atoms at the grain boundaries are undercoordinated due to local Zn deficiencies. Furthermore, nitrogen at grain boundaries can form shallow defect levels which are very similar to those shown in Fig. 8 (see Fig. 11 in Ref. \cite{12}). We argue therefore that all these shallow levels are activated due to the depletion zones near grain boundaries.\cite{16,52} Zhang et al. interpret their experimental results along this line,\cite{16} and Wang et al. even suppose that oxygen excess causes the formation of a quasi two dimensional hole gas which could explain the very high mobilities seen in some experiments (see Ref. \cite{16} and references therein).

Putting all from above together, this rather general defect-complex mechanism for promoting p-type conductivity in ZnO, ZMO, and related materials emerges: defect complexes which are connected to the zinc vacancies in the bulk interior or at grain boundaries provide shallow defect levels which can serve as acceptor defects. The activation of these defects by lowering the net electron concentration is provided either by co-doping (e.g. N and Mg\cite{17}) or by depletion zones around grain boundaries.

### IV. SUMMARY

We have studied the electronic densities of states of crystalline ZnO and Zn\textsubscript{1-x}Mg\textsubscript{x}O with 0 ≤ x ≤ 0.4. We have shown that the SIC-LDA allows to calculate the electronic band gap as function of the Mg content and leads to quantitatively reasonable results with respect to experimental data. We have determined the electronic defect levels which are generated by the introduction of N\textsubscript{O} substitutional defects. They are at 0.25 eV above the VB or higher. An increasing number of neighboring Mg atoms to the N\textsubscript{O} site shifts the defect level even deeper into the band gap. On the other hand, isolated v\textsubscript{Zn} defects generate shallow levels attached to the VB edge. In combination with N\textsubscript{O}, the defect complex N\textsubscript{O}-v\textsubscript{Zn} produces low lying defect levels which emerge continuously above the VB and no detached gap states (like in the case of the isolated N\textsubscript{O} defect) appear. It is likely that these levels which are peaked at 125–140 meV are connected to experimentally determined acceptor levels which are reported at 130 meV\cite{13}, 160 meV\cite{24} or 190 meV.\cite{49} Neighboring Mg atoms to the N\textsubscript{O}-v\textsubscript{Zn} defect complex do not change the situation significantly. Apparently the role of Mg is mainly a lowering of the net electron concentration which lowers the Fermi level and therefore contributes the N\textsubscript{O}-v\textsubscript{Zn} defect complexes as acceptors.

Our presented results are consistent with those of an earlier study on ZnO grain boundaries,\cite{12,18} in which we found that at grain boundaries with local Zn deficiencies (which is equivalent to undercoordinated oxygen atoms), N\textsubscript{O} defects at the grain boundary produce shallow defect levels without gap to the VB edge and are thus promising acceptor levels.

The following conclusion emerges from this work: one condition for p-type conductivity in ZnO, ZMO, or related materials is to have enough p-type defects like for example N\textsubscript{O} which interact with v\textsubscript{Zn} point defects, or local Zn deficiencies in extended defects like grain boundaries, in order to form shallow gapless defect levels above the VB edge. Moreover, the net electron concentration has to be low enough in order to make these shallow acceptor states partially unoccupied. This second condition can be achieved by Mg\textsubscript{Zn}/N\textsubscript{O} co-doping in the bulk interior or by N\textsubscript{O} doping at grain boundaries to create depletion zones.

### V. ACKNOWLEDGMENTS

Financial support for this work was provided by the European Commission through contract No. NMP3-LA-2010-246334 (ORAMA).
VI. APPENDIX

A. Defect formation energies

The defect formation energies of the zinc vacancy and the N\textsubscript{O} substitutional defect in ZnO have recently been discussed in great detail (see e.g. Refs. 12, 13 and Refs. therein). For a discussion of defect formation energies in ZnO obtained from SIC-LDA we refer the reader to Refs. [18,34]. Here we want to focus on the effect of the Mg atoms on the defect formation energies (E\textsubscript{form}) of N\textsubscript{O} and the N\textsubscript{O}-v\textsubscript{Zn} complex. E\textsubscript{form} is found to depend strongly on the number of Mg atoms being nearest neighbor to the defect site, which can be explained by a stronger Zn-N bond compared to the Mg-N bond. Figure 8 shows the increase in E\textsubscript{form} with respect to bulk ZnO with an increasing number of next neighbor Mg atoms. Our results are in line with the findings of Gai et al. who have performed DFT simulations using cubic zinc-blende ZMO alloys. Note that the formation of a N\textsubscript{O}-v\textsubscript{Zn} complex is energetically favorable by 0.3eV compared to a pair of isolated N\textsubscript{O} and v\textsubscript{Zn} point defects without Mg atoms in direct vicinity of the N atom.

B. Supercell size effects

In order to check the influence of the finite supercell size on the defect levels obtained from our DOS calculations, we have compared calculations for three different supercell sizes, namely N=36, 72 and 108 atoms. As shown in Fig. 9 there is only very little change in level position and peak shape, when comparing the results for 72 and 108 atom supercells. On the other hand, the 36-atom supercells do not yet yield fully converged results, although the general conclusions could qualitatively also be drawn from these rather small cells. We therefore decided to use the 72-atom supercells for the results presented in the main part of the paper.

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