HfO$_2$: a new direction for intrinsic defect driven ferromagnetism

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In view of the recent experimental reports of unexpected ferromagnetism in HfO$_2$ thin films [1], we carried out first principles investigations looking for magnetic order possibly brought about by the presence of small concentrations of intrinsic point defects. *Ab initio* electronic structure calculations using density functional theory (DFT) show that isolated cation vacancy sites in HfO$_2$ lead to the formation of high spin defect states. Furthermore these appear to be ferromagnetically coupled with a rather short range magnetic interaction, resulting in a ferromagnetic ground state for the whole system. More interestingly, the occurrence of these high spin states and ferromagnetism is in the low symmetry monoclinic phase of HfO$_2$. This is radically different from other systems previously known to exhibit point defect ferromagnetism, warranting a closer look at the phenomenon.

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Pure Hafnium oxide (Hafnia, HfO$_2$) is a wide band gap insulator with a high dielectric constant and presents no evidence of any magnetic order in the ground state. It has been heavily studied in recent times within a first-principles context [2, 3] along with several other high-k dielectrics mainly because of its potential for substituting SiO$_2$ as a gate dielectric in microelectronic devices. First-principles investigations of the physics of defects in Hafnia [4, 5] also reflect this trend.

Given the intrinsic non-magnetic nature of HfO$_2$, the discovery of ferromagnetic order in thin films which are pure except for the possible presence of intrinsic defects [1] comes as a surprise. Since the nominal valence of Hf in HfO$_2$ is 4+, which leaves Hf atoms with an empty d-shell, the phenomenon was initially termed $d^0$ magnetism. It was suggested that the magnetism probably arose from partially filled d-orbitals derived from Hafnium atoms co-ordinating Oxygen Vacancy sites (V$_O$). In this letter we present the results of our first-principles band structure calculations which clearly show that the observed ferromagnetism is most likely due to the presence of cation (Hf) vacancy sites V$_{Hf}$. These form high spin states derived mainly from the Oxygen p-orbitals co-ordinating the V$_{Hf}$.

Intrinsic point defect driven ferromagnetism in otherwise non magnetic compounds has been previously studied using first principles methods, in several systems. Notable cases include CaB$_6$ [6], CaO [7] and SiC [8]. The main characteristic of the vacancies in all these systems is the high symmetry, either octahedral or tetrahedral around the vacancy site. This invariably leads to a highly degenerate single particle spectrum, which may then present high spin states. In CaO for instance Coulomb repulsion stabilizes the two holes occupying the degenerate molecular orbital associated to V$_{Ca}$ in a triplet ground state [7]. Similarly Zywietz *et al.* showed that for a Si vacancy in cubic SiC, only the occurrence of a magnetic Jahn-Teller distortion stabilizes the spin singlet relative to the triplet state otherwise expected from the $T_d$ symmetry and the degenerate single particle spectrum. Hafnium vacancies in monoclinic HfO$_2$ however, are radically set apart by the complete lack of symmetry around the vacancy site. In a defect molecular model, the single particle spectrum is completely non-degenerate and yet, as our DFT calculations show, they have magnetic ground states. This suggests that our understanding of defect induced ferromagnetism is at least incomplete and the phenomenon deserves a closer look.

Our DFT calculations are carried out in the local spin density approximation (LSDA) using the Ceperly-Alder exchange correlation potential [9] in the numerical implementation contained in the code SIESTA [10]. Test calculations using the generalized gradient approximation (GGA), yield qualitatively similar results. We use the numerical localized atomic orbital basis set implemented in SIESTA including polarized orbitals with an energy shift of 0.01 eV [11]. The basis set consists of O 2s, 2p states and Hf 6s, 5d and 6p states. A set of two zetas and a polarized orbital are used for every shell except the 5d for which two zetas suffice. k-point sampling is done by using a fixed $k$-grid cutoff of 15.0Å which is equivalent to a 6x6x6 Monkhorst-Pack mesh for the twelve atom monoclinic unit cell. For 2x2x2 supercell containing 96 atoms the same cut-off is equivalent to a 3x3x3 Monkhorst-Pack mesh. The energy cutoff defining the equivalent planewave cutoff for the numerical grid is set at a value of 250.0 Ryd. In all cases, the systems studied are relaxed until all the forces are smaller than 0.05 eV/Å.

In order to make contact with the $d^0$ magnetism model [1] we first look at the case of Oxygen vacancies. In the monoclinic structure there are two possibilities: i) V$_O$ co-ordinated by three Hf atoms (VO3), and ii) V$_O$ co-ordinated by four Hf atoms (VO4). These are shown in Fig. 1. A description of the various defect energetics is outside the scope of our work (see reference [12]) and here...
we focus only on the electronic and magnetic structure of the defects.

An Oxygen vacancy in both the three and four fold co-ordinated case leads to the formation of a set of impurity levels, with a low lying level in the HfO\(_2\) band gap (VO\(_3\) and VO\(_4\)) and higher lying levels just below the conduction band (VO\(_3^*\) and VO\(_4^*\)), see figure 2. These impurity levels are formed from the dangling \(d\)-orbitals of Hf atoms co-ordinating the vacancy site. The level in the band gap is filled by two electrons which in the perfect crystal, would have populated O \(p\)-orbitals. In this sense \(V_O\) is an n-type defect as it results in two electrons occupying conduction band derived cation orbitals. Also from the density of states (DOS) it follows that the system is non-magnetic and remains effectively semi-conducting. If we assume for the moment that the clusters of Hf atoms co-ordinating the VO\(_4\) and the VO\(_3\) sites form a perfect tetrahedron and a perfect trigonal plane respectively, resulting in local \(T_d\) and \(C_{3h}\) symmetries, then the single particle molecular orbital ground state in each case would be a completely symmetric and non-degenerate \(a1\) and \(a1'\) singlet respectively. Similarly the higher lying \(\sigma\)-bonding single particle states would be a \(t_2\) triplet in the VO\(_4\) case and a \(e'\) doublet in the VO\(_3\) case. Deviation from perfect symmetry, as in the actual case, of course means that the degeneracies of the excited states are lifted and energy levels suitably re-ordered. Nevertheless, the ground state remains an orbital singlet. The higher lying states are well separated in energy from the low-lying singlet level. Configurations with one electron promoted to the higher lying states lie prohibitively higher in energy relative to the ground state thus ruling out electron promotion. Since two electrons occupying an orbital singlet anti-align their spins, the resulting ground state is non-magnetic.

We then investigate the effect of partial p-doping of the system, by substituting an electron acceptor like N at an O site. In figure 2 we present the DOS for VO\(_3\) only, bearing in mind that the situation for VO\(_4\) is essentially the same. In this case one electron is removed from the VO level, which therefore spin splits with a magnetic moment of 1 \(\mu_B\) per vacancy. We then check whether these localized moments interact with each other, by doubling our supercell and comparing the total energies of the ferromagnetic and anti-ferromagnetic alignment of the magnetic moments on two separate vacancy sites. We find no difference in the total energy and so we conclude that the isolated moments are not coupled. The system can at best be paramagnetic and thus the \(V_O\) themselves cannot possibly be behind the observed ferromagnetism.

We now move on to investigate the hypothesis of ferromagnetic order due to \(V_{\text{Hf}}\). In monoclinic HfO\(_2\) (baddeleyite), each Hf atom is co-ordinated by seven O atoms (see figure 1). Of the seven O atoms, three are of one type which we label ‘O1’ and the remaining four of a second type which we label ‘O2’. The two types of O atoms differ in their Hf co-ordination number in the crystal. We further label the remaining O atoms not directly co-ordinating the vacancy site as type ‘O3’. In the perfect crystal, the O 2\(p\) levels are fully filled and form the bulk of the valence band. Since Hf is a cation with a 4+ valence, the removal a neutral Hf atom introduces four empty states among the oxygen 2\(p\) levels. The spin occupation of these four states established whether or not the system is magnetic.

At this point we present our LSDA results for the ground state of Hf deficient HfO\(_2\). We consider a 2x2x2 supercell containing 96 atoms. Only one Hf vacancy is introduced in the supercell and upon relaxation the O atoms are seen to move outwards around the vacancy site
by about 0.15 Å. In figure 3 we present the DOS for the fully relaxed case. The valence band is clearly spin split, with the compensating holes mostly confined to the down spin states resulting in an almost half metallic ground state with a magnetic moment of 3.52 µB per vacancy. Prior to relaxation the system is completely half metallic with an integer magnetic moment of 4 µB per vacancy. The relaxation involves a considerable redistribution of the hole density over the O atoms around the vacancy site as shown if figure 4, with the magnetism coming predominantly from the O1 type atoms. The observed charge redistribution is driven by large scale re-hybridization, upon relaxation, of the orbitals constituting the impurity levels with the crystalline surroundings. We find that the holes clump together on and around the O1 atoms and their nearest O3 type neighbours. Figure 5 shows the localization of the magnetic moment around the vacancy site, where this outward spread in the polarization due to relaxation is evident.

Having studied the real space distribution of the magnetic moment, we now look at the symmetry aspect of the defect states. Considering the seven O atoms coordinating the vacancy site as a single molecular cluster, we find a trivial C1 point group. Thus the single particle molecular orbitals generated from combining the O atomic orbitals form a set of non-degenerate levels, and the high spin state arises from the singly occupied four topmost molecular orbitals (see insets of figure 6). Interestingly the calculated magnetic moment (~4µB) cannot originate from a single orbitally degenerate molecular level even in the most symmetric octahedral molecule. In fact the largest orbital degeneracy allowed is just three fold, and a total spin S=2 for a configuration of four spin 1/2 particles is ruled out by the Pauli principle. This means that in any case a set of non-degenerate molecular orbitals must be involved in the high spin configuration. As non-degenerate molecular orbitals differ in single particle properties (kinetic and ionic energies), the final configuration of the four spin 1/2 particles is decided not just by mutual Coulomb repulsion or exchange energy but by an interplay between all contributions in the Hamiltonian.

Looking at the relative energetics of different possible electronic configurations of the defect levels helps to see what stabilizes the high spin ground state. To this end, we now look at the energy aspect of the defect states.

FIG. 3: Spin resolved DOS for one V_Hf is a 96 atoms HfO2 supercell. E_F is set at 0.0 eV.

FIG. 4: Isosurface of the local density of states for the highest, minority-spin defect level of V_Hf. After relaxation the charge density (hole density) clumps mainly on the three O1 type O atoms. As a result the O2 type atoms lose most of their spin polarization. The central atom is a dummy atom included only for clarity.

FIG. 5: Localization plot for the magnetic moment inside the supercell before and after relaxation. The quantity presented is \( \text{pol}(R) = \int_{R}^{R+dR} \int d\Omega \left[ \rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r}) \right] \) against \( R \). \( \text{pol}(R) \) is the spin polarization from a shell of thickness \( dR \) at radius \( R \) where \( R \) is measured radially outward from the vacancy site. Note the redistribution of the magnetic moment towards outer shells upon relaxation.

FIG. 6: Magnetic moment per vacancy as a function of the average distance from the vacancy site of the seven coordinating Oxygen atoms. In the two insets schematic representations of the high spin \( S=2 \), and non-magnetic \( S=0 \) state.
we perform fixed spin moment calculations, for the two limiting cases of S=2 and S=0. From the calculations it emerges that the high spin configuration is expensive with regards to kinetic and Hartree energies but the gain in exchange and ionic energy is enough to stabilize it. It is likely that the higher lying molecular orbitals are strongly anti-bonding in character with the electrons in these levels being localized more on the ions. This results in higher kinetic energies and lower ionic potential energies. In fact, one expects that analogously to what happens in molecules, if the O atoms around the vacancy are artificially squeezed in towards the vacancy, thus driving the system highly kinetic, the higher lying defect levels would be emptied out accompanied by a fall in the magnetic moment. This is indeed seen to be the case as shown in figure 4. As it turns out, at the equilibrium distance in the crystal (≈2.28 Å), the magnetic moment is close to 4μB.

Next we address the question of the magnetic coupling between vacancies, by calculating the total energy of a supercell containing two V_Hf and comparing the energy for the ferromagnetic (E_PM) and antiferromagnetic state (E_AF) (see Table I). Clearly the ferromagnetic alignment is always energetically favorable, and most remarkably the coupling appears rather strong, in particular for short V_Hf – V_Hf distances. This leads us to attribute the observed ferromagnetism in HfO2 thin-films 1 to Hf vacancies. Moreover the large values of ΔE suggest Curie temperatures above room temperature at large enough concentrations.

In order to have a better understanding of the origin of this ferromagnetic ordering we have performed an extensive study of the charge distribution by means of Mulliken population analysis. The main features are: (a) the O atoms in the cell are polarized to different degrees depending on their orientation and distance relative to the vacancy site but always with the same sign, (b) the Hf atoms in the cell are also polarized but importantly, the sign of polarization is opposite to that of the O, and (c) the total polarization of all the O atoms in the cell is 3.92μB and that for the Hf atoms is -0.40μB, leaving a moment of the cell of 3.52μB. This suggests that the magnetic coupling between the O atoms in the cell is mediated by minority spin electron delocalization across the Hf bridge connecting the O atoms. This applies also to O atoms belonging to different V_Hf sites. The delocalization is larger when local moments on the two V_Hf are ferromagnetically aligned resulting in lower Kinetic and Exchange energies relative to the anti-ferromagnetic case.

In summary we have performed DFT calculations investigating the possibility of intrinsic defect driven ferromagnetism in HfO2. Oxygen vacancies form non-magnetic impurity levels unless p-type co-dopants are present. However, in this case the magnetic interaction is negligible, ruling out the hypothesis of d⁰ ferromagnetism 7. In contrast Hf vacancies show a high spin state with an associated magnetic moment of ~3.5 μB. These are ferromagnetically coupled via minority spin electron delocalization across the bridging Hf sites, with a large coupling strength suggesting high Curie temperatures. Thus a new direction for intrinsic defect ferromagnetism is evident based on the following facts: 1) symmetry driven orbital degeneracy is not a pre-requisite for the existence of a high-spin defect ground state, 2) a set of closely spaced single particle levels together with strong exchange might be sufficient for the same, 3) suitable mixing of defect states with the crystalline environment can lead to ferromagnetic inter-defect coupling. These findings suggest that a wider class of systems, not restricted by symmetry and free from the possibility of Jahn-Teller like distortions, might actually be open to intrinsic defect ferromagnetism.

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