A proposed new route to $d^0$ magnetism in semiconductors

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Here we propose to induce magnetism in semiconductor utilizing the unique properties of the interstitial defect to act as the magnetic impurity within the $\alpha$-PbO crystal structure. The Pb$_i$ interstitial generates the $p$-localized state with two on-site electrons to obey the Hund’s rule for their ordering. It is demonstrated that instead of Pb interstitial other non-magnetic impurities of $s^2p^x$ outer shell configuration can be applied to induce $d^0$ magnetism with possibility to tune the local magnetic moments $\mu_B$ by varying a number of electrons $1 \leq x \leq 3$. The magnetic coupling between such defects is found to be driven by the long-range order interactions that in combination with high defect solubility promises the magnetic percolation to remain above the room temperature.

Spintronics has recently emerged as a widely successful technology that exploits the principles of magnetism, but the classical metal ferromagnets are not applicable there. That has led to the creation of a new branch of research directed at semiconductors exhibiting magnetism at room temperature [1]. The first success in this regard was with the so-called ”diluted magnetic semiconductors” created by doping semiconductors with magnetic ions whose inner 3$d$ or 4$f$ shells being partially filled that allows the ferromagnetic spin alignment [2–5]. A keen interest on ferromagnetic semiconductors also arose when ‘non-magnetic’ materials were discovered to demonstrate magnetism [6–9]. Origin of so-called ’non-magnetic’ materials was found to demonstrate the long-range order between such defects can demonstrate the magnetic percolation [9].

Here we propose to induce magnetism in semiconductor utilizing the unique properties of the interstitial defect to act as the magnetic impurity within the $\alpha$-PbO crystal structure. The Pb$_i$ interstitial generates the $p$-localized state with two on-site electrons to obey the Hund’s rule for their ordering: the magnetic coupling occurs [9]. Ordering of the localized $sp$ states: vacancies create a network of unpaired electrons and as interaction between such defects can demonstrate the long-range order, their magnetic coupling occurs [9].

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Here we propose to induce $d^0$ magnetism by forming the interstitial defect Pb$_i$ ($\text{Pb}_i; 6s^26p^2$ outer shell) within the crystal structure of the tetragonal lead oxide $\alpha$-PbO. It generates the state occupied by two $p$-unpaired electrons $\text{Pb}_i; 6p^2$. Ordering of the localized electrons $\text{Pb}_i; 6p^2$ obeys the first Hund’s rule thus resulting in formation of the stable local magnetic moment of 2.0 $\mu_B$. The spin-polarization energy of such state is $E_M = E_{\text{AFM}} - E_{\text{FM}} = 0.235$ eV, where $E_{\text{AFM}}$ and $E_{\text{FM}}$ are the total energies of the anti-(AFM) and ferromagnetic states (FM), respectively [10]. Therefore, otherwise than magnetism occurs due to the partially filled $p$ shell instead of the 3$d$ or 4$f$ shells, Pb$_i$ works exactly as the magnetic impurity. It demonstrates the high on-site spin stability, its $p$ electrons are localized on impurity site showing a weak perturbation with the host (an interaction with the host occurs through Pb$_i; 6s^2$ electrons) and in addition, the interstitial defect is almost non-invasive to the electronic and crystal structures of the host. We have established that any impurity of the $s^2p^x$ outer shell embedded as the interstitial defect into the $\alpha$-PbO crystal structure would act as magnetic. The $p$-shell occupation, $p^1 \leq x \leq 3$, can be used to control the spin ordering between impurities and also to tune the local magnetic moments: $x = 2$ works for 2.0 $\mu_B$, while $x = 1$ or $x = 3$ for 1.0 $\mu_B$. From the technological point of view, the layered crystal structure of $\alpha$-PbO promises the superior advantages in achievement of the magnetic percolation and more importantly, a practical way for its control: i) the crystal structure of PbO type grows in polycrystalline form whose large surface area offers enormous potential for doping (on surface the impurities can be placed on the nearest-neighbours); ii) the dopant solubility and long-range order interactions can be manipulated with the impurity atomic radius; iii) any compounds of the tetragonal PbO type can be used as a semiconductor matrix.

In our study we applied the generalized gradient approximation (GGA) with the PBE parametrization [11] provided by WIEN2k package for the density functional calculations [12]. The supercell approach ($R_{\text{cell}}^\text{max}=7$) with sufficiently large supercell of 108-atom size ($3 \times 3 \times 3$ array of the primitive unit cells) for single impurity and of 160-atom size ($5 \times 4 \times 2$) for two interacting impurities have been used. The Pb,5p, 5d, 6s, 6p and O:2s, 2p electrons have been treated as the valence electrons. For integration of the Brillouin-zone, the Monkhorst-Pack scheme using a ($5 \times 5 \times 4$) k-mesh was applied. The localization of the impurity wavefunction has been additionally examined with HF applied directly to the unpaired electrons that allows to preserve accuracy provided by DFT but in the same time to correct the unpaired electrons self-interaction [13].

The tetragonal lead oxide $\alpha$-PbO possesses the layered structure leading to formation of platelets upon compound growth and each platelets is considered as a single crystal. The layers within such crystal are held together by the interlayer interaction of Pb:6s$^2$ electrons [14]. In terms of electronic properties, these interactions induce a deepening of the conduction band at $\text{M}^*$ point [15] and the gap shrinks as interactions enhance. GGA tends to overestimate the interlayer separation in the layered structures but in the same time it also well known to
underestimate the band gap size. For α-PbO system it results in compensation effect [17], for the lattice parameters optimized with GGA the band gap is only slightly underestimated as 1.8 eV against the experimental value of 1.9 eV [10] (application of the experimental value of the lattice parameters causes the band gap to shrink by 0.22 eV). The correct band gap size is important in investigation of the magnetic impurities: when the band gap size is underestimated the hole-carrying impurity orbital occurs closer to the the conduction band in turn forcing a delocalization of the defect tails. In order to avoid the spurious long-range order interactions all band structure calculations have been performed for the lattice parameters optimized with GGA. However, since an incorporation of the interstitial becomes easier as interlayer distance increases, the interlayer distance has also crucial impact on the defect formation energy. In order to make correct evaluation of the formation energy, the experimental value of the lattice parameters has been applied for those calculations.

The interstitial defects have never been considered in origin of d$^9$ magnetism because they do not belong to a class of most common defects in crystalline materials as they induce a significant perturbation of the host lattice resulting in their large formation energy [18]. The layered structure of α-PbO is different, as it allows the foreign atoms to squeeze between layers inducing a minimal lattice deformation to the host immediate neighborhood (see Fig. 1 (a)). As a result, the formation energy of Pb$_i$ is not too high. For the Pb rich conditions/vacuum the neutral charge state is characterized by the formation energy of 1.23 eV (for methods see [17]).

The band diagram and the density of states (DOS) for α-PbO containing Pb$_i$ are presented in Fig. 1 (b) and (c), respectively. The Pb interstitial makes a bond with Pb atom from the host generating the defect state inside the band gap. The defect-induced spin-up and spin-down bands (1$^u$ and 1$^d$ in Fig. 1 (b) and (c)) both show dominant Pb$_i$:6$p_{x+y}$ character but demonstrate a different behavior. The spin-up band is filled with two electrons and appears just above the midgap at 0.99 eV + $E_V$, where $E_V$ is a top of the valence band (VB). In contrast, the spin-down band (1$^d$) is unoccupied and appears at the edge of the conduction band (CB). In order to understand an asymmetry in filling of the spin-up and spin-down states, bonding of Pb$_i$ with the host lattice has to be considered.

The integration of the Pb interstitial into the crystal lattice requires excitation of its ground state 6$s^2$6$p^2$ to 6$s^1$6$p^3$. The Pb$_i$:6$s^1$ and Pb$_i$:6$p^1_z$ electrons participate in bond formation with the Pb atom from the host which shares its Pb:6$s^2$ electrons (see Fig. 1 (c)). The bonding orbital appears inside VB, while the antibonding forms the CB bottom (see 2$^u$ and 2$^d$ bands and notations of 'bonding' and 'antibonding' at B and C panels to DOS). The length of the Pb$_i$-Pb bond is fairly short, 2.9 Å, that is indicative of a double bond formation. An out-of-plane displacement of 0.54 Å occurs for the Pb atom involved in bonding. Because participation of the host Pb:6$s^2$ orbitals in bonding interferes with interlayer interactions, it alters a behavior of the conduction bands near the CB top: in analogy with the band behavior in a single layer [15], the band deeping at the M$^*$ point is suppressed.

Therefore, out of three Pb$_i$:6$p^3$ electrons found in the excited state (6$s^1$6$p^3$), only one Pb$_i$:6$p^1_z$ participates in bonding while the two others Pb$_i$:6$p_{x+y}$ are left at the
defect site. The Hund’s rule dictates both unpaired electrons to occupy the 1\textsuperscript{st} spin-up band. The empty 1\textsuperscript{st} spin-down band is pushed up to CB that causes considerably large spin-exchange splitting of order 0.523 eV. The ferromagnetically ordered Pb\textsubscript{i}:6p\textsubscript{x+y} electrons generate the local magnetic moment of 2.0 µ\textsubscript{B}. The difference in total energy between the AFM and FM states is found to be \(E_M = E_{AFM} - E_{FM} = 0.235\) eV thus promising the FM state to be stable well above the room temperature. An application of the HF approach to the unpaired electrons induces further stabilization of the FM state to \(E_M = 0.490\) eV due to stronger on-site localization of the impurity wave function (the 1\textsuperscript{st} orbital is shifted towards the valence band by 0.5 eV thus enhancing the splitting of the 1\textsuperscript{st} and 1\textsuperscript{st} orbitals). On the other hand, reduction of the interlayer distance (the experimental lattice parameters are applied) in opposite causes delocalization of the wave function due to stronger hybridization of impurity state with the host lattice.

The 6s\textsuperscript{2}6p\textsuperscript{2} electronic configuration is a key point for the Pb interstitial to act as a magnetic impurity: filled s\textsuperscript{2} outer shell is required for bonding with the host lattice while partially filled p shell contributes in development of the local magnetic moment. Following this principle, other chemical elements possessing s\textsuperscript{2}p\textsuperscript{1}s\textsubscript{2}p\textsubscript{1} outer shell can be applied to induce d\textsuperscript{2} magnetism. Indeed, several examined impurities have shown a formation of the local magnetic moment, impurity of \(x = 1\) or \(x = 3\) induces the local magnetic moments of 1 µ\textsubscript{B}, while \(x = 2\) produces 2 µ\textsubscript{B}. The stability of the spin-polarized state is observed to grow substantially with reduction of the impurity atomic radius.

Our studies of localization of the electron density at the defect site has revealed a duality in its behavior. Since occupied band 1\textsuperscript{st} is located deep inside the band gap, the Pb\textsubscript{i}:6p\textsubscript{x+y} electrons shows strong localization on the defect site thus allowing to form the stable local magnetic moment of 2µ\textsubscript{B} (see Fig. 2(a)). However, the long defect tails appear as well but due to bonding/hybridization of the Pb\textsubscript{i}:6s\textsuperscript{1} and Pb\textsubscript{i}:6p\textsuperscript{1} electrons from the Pb interstitial and Pb:6s and Pb:6p, O:2p electrons from the host (see partial DOS in Fig. 3(c)). As a result, the electron density around the defect site is spin-polarized showing an anisotropy in its distribution: the defect tails are symmetrically polarized relative to Pb\textsubscript{i} thus contributing in stabilization of the ferromagnetic state.

Since extension of the wave function tails to the host lattice seems to be of the long-range order, it is expected to induce effective defect-defect interactions. In this respect we have investigated an interaction of Pb\textsubscript{i} with the O vacancy (V\textsubscript{O}) which formation is also favored at the Pb-rich/O-poor limit (oxygen deficiency). In its charge neutral state, V\textsubscript{O} is occupied by two electrons showing the strong localization at the vacancy site. Since the virtual hopping is allowed between the states formed by Pb\textsubscript{i} and V\textsubscript{O}, they can work as compensating centers to each other. For the defects appearing at the nearest-neighbour sites, the FM ordering of the localized spins at Pb\textsubscript{i} is found to be destroyed due to the strong interaction between defects to be accompanied by hybridization. The Pb\textsubscript{i}:6p\textsubscript{x+y} electrons from the interstitial and the Pb:6s and Pb:6p and O:2p electrons from the host lattice, all have been found to contribute equally in formation of both defect states (see manifestation of the electron density in the inter-defect region in Fig. 2(b)). The strong interactions between defects contribute in lowering of the formation energy of defect pair by 0.84 eV in comparison to the non-interacting defects. With defect separation the electronic interactions are suppressed leading to recovery of the FM state: for distance of 6.2 Å between the defects the local magnetic moment is 1.8 µ\textsubscript{B}. However, because interaction of Pb\textsubscript{i} with V\textsubscript{O} do not vanish completely, the magnitude of the spin polarization energy is

![Figure 2: Schematic band diagrams demonstrate a formation of FM (Pb\textsubscript{i}) and AFM (Pb\textsubscript{i}-V\textsubscript{O} pair) states. The energy values are appearance of the defect levels relative to \(E_V\). The electron density map is plotted for isovales of ±0.005 e/Å\textsuperscript{3} with help of Xcrysden. (a) FM state at the Pb\textsubscript{i} site. The density map demonstrates the spin density calculated for the energy range (1.0 eV+\(E_V\))±0.15 eV. (b) An interaction of Pb\textsubscript{i} with V\textsubscript{O} destroys the FM state at the Pb\textsubscript{i} site. The electron density is plotted for the energy range (0.9 eV+\(E_V\))±0.4 eV.](Image 323x332 to 556x697)
found to be considerably low $E_M = E_{AFM} - E_{FM} = 0.06$ eV. Therefore, the electronic interactions between Pb$_i$ and V$_O$ demonstrate the long-range order due to the long tails of the Pb$_i$ interstitial.

For two interacting interstitial defects, as both defects contribute with their tails into the long-range order interactions, the magnetic coupling between them is expected to sustain over the larger distance. The $6p_x^2 + y^2$ state is exactly half filled and, therefore, for two interacting impurities the virtual hopping is allowed only in the AFM state making it the ground state. For two Pb interstitials placed on distance 4.1 Å we found that $E_M = -0.96$ eV while for distance 12.5 Å it drops down to -0.0056 eV. For the C interstitial the interactions are lower as $E_M = -0.38$ eV for distance 4.1 Å and $E_M = -0.0023$ eV for 12.5 Å. An application of HF for the localized electrons suppresses $E_M$ almost twice. The AFM interaction between impurities can be switched to FM for the impurity of $p^1$ occupation of outer shell (for example, In or Ga work for FM state) or for $p^2$ occupation by choosing the charged state (1+).

In terms of the formation energies of the interstitials, it drastically drops down as the atomic radius decreases. Thus, if the formation energy of the Pb interstitial is 1.23 eV for the Pb-rich/vacuum conditions, it is reduced almost to zero for Ge, Si impurities and already turns to be negative for the C and O impurity (the formation energy of the O interstitial is -0.26 eV) thus implying the higher negative for the C and O impurity-host hybridization results in the extended defect tails. The manifesting long-range order interactions between defects in combination with their high solubility create conditions for magnetic percolation to occur.

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