Non-magnetic impurities to induce magnetism in α-PbO crystal structure

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Abstract - A new route to $d^0$ magnetism is established with the help of the first-principles methods. Non-magnetic elements in groups 13 and 14 of the periodic table are found to act as the magnetic centers upon embedding in polycrystalline α-PbO structure. Thus, the local magnetic moment is generated on the impurity site ($1.0\mu_B$ and $2.0\mu_B$ for elements in groups 13 and 14, respectively) due to $p$ orbitals partially filled with electrons whose on-site spin ordering is governed by the first Hund’s rule. The magnetic interactions between impurities are controlled by occupation of the $p$ orbitals so that antiferromagnetic (AFM) ordering occurs between impurities of $2.0\mu_B$ while ferromagnetic (FM) ordering occurs between impurities possessing $1.0\mu_B$. With respect to the strength of the magnetic interactions, the atomic radius of impurity is found to be a key element to tune the wave function tails of localized electrons: with the reduction of the atomic radius, the on-site stability of the spin-polarized state grows while losing in the long-range order interactions. However, it has been shown that a suppression of the long-range order interactions can be compensated by higher impurity concentration that is allowed by the shift of the solubility limit to higher magnitude.

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The research on magnetic semiconductors has intensified in recent years due to the requirements imposed by the rapidly developing field of spintronics [1]. Originally, magnetic semiconductors were created by doping of the conventional semiconductors with magnetic ions whose $d$ or $f$ orbitals are partially filled [2,3]. The enormous attention given to the so-called “diluted magnetic semiconductors” has been rewarded with the discovery of a mechanism of the “intrinsic” magnetism in semiconductors—defect-induced magnetism. Initially, in the semiconductors doped with magnetic ions, the intrinsic defects were considered only to mediate the magnetic coupling between localized spins occupying the partially filled $d$ or $f$ orbitals of ions, thus contributing to the collective magnetism effect [4–6]. However, a better understanding of the defect properties has revealed that the defects with their $sp$ localized spins are able to generate the magnetic phenomenon themselves [7–11]. The discovery of defect-induced magnetism dubbed as $d^0$ magnetism, i.e. magnetism which is not due to partially filled $d$ orbitals, brought new impetus into the field of magnetic semiconductors and more importantly in spintronics.

In order to pursue the spintronics applications, the collective magnetic ordering is required to be established between the magnetic centers provided the spin-polarization energy of the localized state is large enough for the local magnetic moment to appear above the room temperature. The stability of the local magnetic moment is defined by the impurity wave function localization that unfortunately results in the suppression of its tails thus precluding the collective ordering. Therefore, the success of $d^0$ magnetism in spintronics is recognized to be defined by the proper combination of defect/host [3] enabling both components. In practice, the weak magnetic interactions between the magnetic centers can be compensated by their high concentration [7,8]. However, raising a defect concentration is not always a straightforward solution [3]. For those defects known to induce magnetism—the vacancy [10–12] and substitutional defects [13–15]—the low limit to the defect concentration even at the most favorable growth
conditions is often applied as defined by their formation energy [12]. Moreover, defects especially in high concentration are not always mechanically tolerated by the crystal lattice, not to mention that the defect-induced lattice perturbation may lead to unwanted changes in the electronic properties [3]. Therefore, an idea of intrinsic magnetism requires some efforts to bring it to a level of practical applications.

Our recent finding of a new route to $d^0$ magnetism offers an elegant solution and, therefore, is promising to obtain a breakthrough in the development of magnetic semiconductor [16]. Instead of crystalline systems, the layered materials are proposed to be applied as the semiconductor host. In crystalline solids, the vacancies only have been considered to establish $d^0$ magnetism [10–15] because the formation energy of other defects is too high to reach the concentrations required for the magnetic percolation to occur. With respect to the layered systems, the interstitial defects become a feasible source of unpaired electrons because they are incorporated between layers which significantly lowers their formation energy. In this work we consider the polycrystalline $\alpha$-PbO to be a semiconductor host for $d^0$ magnetism. We found that the Pb interstitial defect in $\alpha$-PbO induces a local magnetic moment of 2.0$\mu_B$ [16]. The origin of the local magnetic moment upon bonding of the impurity with the host is unique: the Pb interstitial of Pb$_i$: 6$s^2$6$p^2$ valence shell utilizes its only Pb$_i$: 6$s^2$ electrons to be attached to the host (through Pb: 6$s^2$ electrons as well) while leaving two unoccupied 6$p^2$ electrons on the defect site. Hund’s rule dictates the spin alignment of the 6$p^2$ electrons (the triplet ground state) manifesting in on-site magnetic moment of 2.0$\mu_B$ and in the high stability of the spin-polarized state defined by the spin-polarization energy $E_{pol} = 0.235$ eV [16]. As a result, the Pb atom gains magnetization upon embedding as the interstitial defect into the $\alpha$-PbO crystal lattice (an appearance of the magnetic moment is verified experimentally$^1$). In analogy with magnetic ions, magnetism occurs due to partially filled orbitals, but here it is due to the $p$ orbital.

The unique mechanism of bonding which utilizes only $s^2$ valence electrons allows to extend a choice of the host and the impurity to several candidates. Because the family of the $\alpha$-PbO lattice shows the lone pair $s^2$ valence shell electrons as a common feature, in principle any of those systems can be used as a host. In fact, the $\alpha$-PbO crystal structure is well recognized in superconductivity [17]: Fe-pnictides (the basics are FeSe, FeAs), cuprate (the basics are CuO, CuS), and lanthanum compounds (the basics are LaF, LaO). However, among others, the $\alpha$-PbO compound seems to be the best candidate due to its wide band gap. For the wide band systems, impurity induces the localized defect states inside the band gap whose location may vary with the impurity choice. Any chemical elements

$^1$Preliminary results: EPR spectroscopy performed on undoped PbO samples has revealed the paramagnetic centers in the triplet state at room temperature.

possessing a partially filled $p$ valence shell can gain magnetic properties upon embedding into the $\alpha$-PbO crystal lattice. Thus, elements of the same valence shell as the Pb atom, i.e. belonging to group 14 of the periodic table (see fig. 1(b)), are expected to induce the local magnetic moment 2.0$\mu_B$. Following the same principle, the chemical elements of the $s^2p^1$ valence shell from group 13 of the periodic table would work as magnetic centers characterized by the local magnetic moment 1.0$\mu_B$. Since we can expect both a difference in the atomic radius of impurity and the occupation of the $p$ orbital to control the magnetic behavior, we focus on the possibility to tune magnetism with different impurities looking for a proper combination impurity/host allowing to reach $d^0$ ferromagnetism. If our hypothesis is proven true, this approach can open a wide perspective to design the desired magnetic behavior in the $\alpha$-PbO semiconductor by generating a network of the interstitial defects acting as the magnetic centers. The feasibility to generate such network is considered through the thermodynamics of the defect formation.

In our study we applied the generalized gradient approximation (GGA) with the PBE parametrization [18] provided by the WIEN2k package for the density functional

Fig. 1: (Colour on-line) (a) The $\alpha$-PbO crystal structure which contains the impurity interstitial atom. (b) The list of impurities from group 13 and 14 in the periodic table used by us to create the local magnetic moments $\mu = 1.0\mu_B$ and $\mu = 2.0\mu_B$, respectively (the atomic number on the top and the standard atomic weight at the bottom). (c) The Pb self-interstitial: the spin density map is plotted with isovalues of $\pm 0.003$ e/Å$^3$ in XCrySDen for the energy range $(E_D+E_V)\pm 0.15$ eV. It demonstrates the alignment of electrons at the impurity site for which defect tails can be traced up to the last oxygen atom shown.
calculations [19] (augmented plane wave + local orbitals approach). The Pb : 5p, 5d, 6s, 6p and O : 2s, 2p electrons have been treated as the valence electrons (the energy cutoff was −8 Ry). The supercell approach (RKmax = 7) with sufficiently large supercell of 108-atom size (3 × 3 × 3 array of the primitive unit cells) has been used for a single-impurity calculation while the 190-atom size (4 × 4 × 3) supercell for the interacting defects. For the integration of the Brillouin zone, the Monkhorst-Pack scheme of the 5 × 5 × 4 (or 4 × 4 × 2) k-mesh was applied. In application to the unpaired electrons, the GGA often fails to perform the localization of the defect wave function due to an electron self-interaction error [20] that has been examined here with the Hartree-Fock (HF) approach applied directly to the unpaired electrons. Moreover, it is known that when the band gap size is underestimated by the GGA, the hole-carrying impurity orbital may appear above the bottom of the conduction band thus inducing the spurious long-range order interactions [3]. For the lattice parameters optimized with the GGA, the band gap is 1.8 eV (very close to the experimental value [21]) while it found to shrink by 0.22 eV when the experimental lattice parameters are considered [22]. Such gap deviation originates as a result of the interlayer distance mismatch to occur upon lattice optimization performed with GGA [22]. Since in the α-PbO crystal structure the band gap size is controlled by the interlayer interactions of the Pb : 6s2 electrons, the application of the GGA to the optimization of the lattice parameters through the overestimation of the interlayer distance causes the band gap to increase. In order to prevent the “spurious” effect, calculations of the electronic property are performed for the lattice parameters optimized with the GGA as it gives a better agreement of the band gap size with the experimental data. On other hand, to prevent the defect formation energies from being underestimated, the experimentally determined interlayer distance has been used for those calculations. The formation energies of the interstitials have been evaluated for the vacuum conditions (details on the formation energy simulations are presented in ref. [23]).

With respect to the origin of the local magnetic moment in the α-PbO compound on the site of the Pb interstitial [16], our study has revealed that the Pb interstitial combines the advantages of the vacancies [7–11] and magnetic ions [2,3]. The high spin-polarization energy is observed for the Pb interstitial due to the spin ordering of 6p2x+y to be governed by Hund’s rule as for magnetic ions. At the same time a hybridization of the impurity state with the host lattice results in the extended defect tails which are promising to induce the long-range order interactions. As shown in fig. 1(c), the defect tails appear in the upper and lower layers, they are extended up to seven nearest neighbors and show the higher spin localization at the oxygen atoms. Although the impurity interacts with the top layer through bonding while it does with the bottom layer only through the hybridization interactions, the defect tails are observed to be more pronounced at the bottom layer. This occurs because the Pb interstitial is tightly sandwiched between layers which results in its strong hybridization with the bottom layer.

The redistribution of the spin density from Pb interstitial site to the host lattice explains the on-site stability of the triplet state \(E_{\text{pol}} = 0.235 \text{ eV}\) to be lowered in comparison to the magnetic impurities of d or f types [24] known to exhibit the localized nature of the unpaired electrons. We expect a hybridization with the host to be a key element to tune the magnetic behavior when the atomic radius of the impurity is reduced. In this work we track an alteration in the electronic properties of the host upon the replacement of the Pb interstitial with different impurities through a behavior of the impurity associated bands depicted in fig. 2 as 1s, 1d, 2s and 2d. The 1s and 1d bands are those induced by p-localized electrons (the spin-up band 1s is occupied by p electrons from the impurity valence shell, while the spin-down band 1d is empty), the 2s and 2d bands are antibonding orbitals of the Imp-Pb bond (Im-Pb). The appearance of all four bands inside the band gap upon changing the impurity type is shown in fig. 3 (the absence of 2s and 2d bands is due to the antibonding orbitals outside of the band gap). Other important parameters such as impurity atomic radius \(R_{Im}\), length of the impurity-host bond Im-Pb, spin-polarization energy \(E_{\text{pol}}\), and splitting of the 1s and 1d bands \((E_1 - E_2)\) are given in table 1.

The common trends on the formation of the local magnetic moment as a function of the impurity atomic radius are investigated based on elements from group 14 with the \(s^2p^2\) valence shell generating the local magnetic moment 2.0μ\textsubscript{B}. It was found that the reduction in the atomic
Fig. 3: The energetic location of the $1^u$, $1^d$, $2^u$, and $2^d$ bands relative to the top of the valence band $E_V$ and splitting of the $1^u$ and $1^d$ bands.

Table 1: The stability of the spin-polarized state determined within the GGA calculation as a function of the impurity atomic radius $R_{Im}$ [25]: the spin-polarization energy $E_{pol}$ and the energy splitting of the $1^u$ and $1^d$ bands ($E_1 - E_2$). $Im$-$Pb$ is the length of the bond to be formed between the impurity and the host.

| $Im$ | $R_{Im}$ (Å) | Im-Pb (Å) | $E_{pol}$ (eV) | $(E_1 - E_2)$ (eV) |
|------|--------------|-----------|---------------|-------------------|
| Pb   | 1.81         | 2.90      | 0.235         | 0.523             |
| Sn   | 1.72         | 2.86      | 0.258         | 0.585             |
| Ge   | 1.52         | 2.70      | 0.306         | 0.680             |
| Si   | 1.46         | 2.65      | 0.338         | 0.734             |
| C    | 0.90         | 2.30      | 0.538         | 1.058             |
| In   | 2.00         | 3.06      | 0.000         | 0.000             |
| Ga   | 1.81         | 2.92      | 0.051         | 0.173             |
| Al   | 1.82         | 2.71      | 0.003         | 0.131             |
| Al   | 1.17         | 2.71      | 0.000         | 0.000             |

The effect of the spin-orbit coupling (+so) on the defect bands splitting has been investigated with GGA + so for the heavier elements (see fig. 3). It is found that for the Pb impurity the spin-orbit coupling breaks the degeneracy of the $1^u$ and $1^d$ levels resulting in their splitting by 0.52 eV. Although, such large splitting is responsible for the reduction of $(E_1 - E_2)$, the triplet state remains stable that is confirmed by the exhibition of the local magnetic moment in the experiment at room temperature (see footnote 1). The spin-orbit effect is less pronounced for the Sn impurity for which the spin-orbit splitting is reduced to 0.19 eV. For elements with smaller atomic radius, the spin-orbit coupling can be neglected: it is 0.07 eV for the Ge atom and decreases further down for impurities of smaller radius.

We also have examined an effect of the electron self-interaction error [20] on the magnetic behavior of the Pb impurity through the application of the HF approach directly to the unpaired electrons. The spin-polarization energy is found to increase more than twice to $E_{pol} = 0.490$ eV as a result of the enhancement of the splitting of the $1^u$ and $1^d$ bands to 1.12 eV: the $1^u$ orbital is shifted towards the valence band, while $1^d$ towards the conduction band by $\sim 0.4$ eV each. However, the opposite effect is observed when the experimental lattice parameters are taken into account because a reduction in the interlayer distance results in the enhancement of the impurity hybridization with the opposite host layer. When both are applied, the compensation effect is developed causing a reduction of the band splitting to $(E_1 - E_2) = 0.68$ eV. This value is very close to that found with the GGA (see table 1), which indicates the reliability of GGA for this task.

The chemical elements from group 13 in the periodic table are also found to be able to act as the magnetic impurity forming the local magnetic moment $1.0\mu_B$ induced by the $p$ electron occupying the $s^2p^1$ valence shell. Since the $2^u$ and $2^d$ bands appear in the conduction band, they are not presented in fig. 3. In contrast to $s^2p^2$ impurities, the $1^u$ orbital occupied by a single unpaired electron is
found to appear very close to the conduction band. This causes the significant defect wave function delocalization and, therefore, much weaker splitting of the 1\textsuperscript{u} and 1\textsuperscript{d} bands. Thus, the In atom possesses almost zero splitting. The expected growth of $(E_1 - E_2)$ is observed for the Ga impurity for which splitting reaches 0.17 eV. Because of small splitting, the electron density is redistributed from 1\textsuperscript{u} to 1\textsuperscript{d} inducing the reduction of the local magnetic moment to 0.96\textmu_B. The spin-orbit coupling effect is weakly pronounced for the Ga impurity causing a negligible reduction of $(E_1 - E_2)$ by 0.015 eV. Although further increase in the splitting of the 1\textsuperscript{u} and 1\textsuperscript{d} bands has been expected for the Al impurity, the modification of the bonding mechanism has discontinued such trend. The Al atom is attached to the Pb atom from the bottom layer instead of the top layer shown in fig. 1(a). This results in the shift of the Im-Pb bonding orbital from the valence band into the band gap. The splitting of the 1\textsuperscript{u} and 1\textsuperscript{d} bands is found to decrease to 0.13 eV, which induces a further reduction of the local magnetic moment to 0.78\textmu_B. For the B atom as the magnetic impurity, a suppression of the $(E_1 - E_2)$ is even stronger leading to the disappearance of the local magnetic moment. Therefore, for the new bonding mechanism, the opposite trend is observed: the spin-polarization energy $E_{\text{pol}}$ defining the stability of the local magnetic moment decreases with the reduction of the atomic radius. The general conclusion is that among the chemical elements the In atom possesses almost zero splitting.

The collective magnetic ordering may only occur when two impurities are close to each other to establish the magnetic coupling of their localized spins. In this respect, the long-range order interactions play an essential role. The magnetic coupling between impurities has been simulated for the system containing two interstitials of the $s^2p^2$ valence shell. The $p_{x+y}^2$ electrons localized on impurities have been aligned on-site, while their inter-site ordering has been switched from antiferromagnetic to ferromagnetic in order to evaluate $E_M = E_{AFM} - E_{FM}$. The $p_{x+y}^2$ state is exactly half-filled and, therefore, if the localized electrons of two interacting impurities are ferromagnetically coupled (the total magnetic moments is 4\textmu_B), the inter-site virtual hopping is not allowed [3,10]. The virtual hopping is supported only for AFM coupling (the total magnetic moment for two interacting impurities is zero) and because it lowers the total energy, AFM becomes the ground state. For two Pb interstitials placed at a distance 4.0 Å we found that $E_M(\text{Pb, Pb}) = -0.96$ eV (the negative sign indicates the AFM ground state) while for two interacting C interstitials it is reduced to $E_M(\text{C, C}) = -0.38$ eV. The electronic interactions and the magnetic coupling between defects exponentially decrease with the defect separation. Thus, for two defects placed at a distance 12.5 Å (for this calculation the size of the supercell was $4 \times 4 \times 3$), the energy difference between AFM and FM states is drastically lowered to $E_M(\text{Pb, Pb}) = -0.0056$ eV and $E_M(\text{C, C}) = -0.0023$ eV for the Pb and C interstitials, respectively. These data prove that the larger the atomic radius of impurity, the stronger the hybridization of the impurity state with the host lattice being responsible for the extension of the defect tails. To establish the magnetic percolation, a reduction in the inter-impurity coupling occurring for the impurities of smaller atomic radius can be compensated by the impurity concentration which can be increased due to a shift of the thermodynamic limit of the defect formation to the higher magnitudes. For example, since the C interstitial possesses a negative formation energy, potentially it can be induced on the nearest-neighbouring sites. For this case, the theoretical limit of the exchange interaction strength defined by $E_M(\text{C, C}) = -0.38$ eV can be achieved.

Although the impurities of the $s^2p^2$ valence shell show an interesting physics, their inter-site AFM ordering and appearance of the defect states deep inside the band gap (the coupling of the impurity state to the band-like state is essential to support the spin-polarized carrier transport) make them inappropriate for spintronics applications. The impurities from group 13 have a better fit to the requirements imposed by spintronics: the 1\textsuperscript{u} and 1\textsuperscript{d} bands both couple to the conduction band and the FM ground state should be granted for interacting impurities. Since the Ga impurity has shown the highest potential due to its high spin-polarization energy, here we focus on the development of the magnetic interactions between two Ga impurities. We found that for two defects placed at a distance 4.0 Å, the strength of the magnetic coupling is defined by $E_M(\text{Ga, Ga}) = 1.08$ eV (a positive sign indicates the FM ground state). The distance between impurities has been
increased twice, which corresponds to the realistic defect concentration $x = 2.5\%$. To simulate the worst-case scenario, the impurities have been attached to the opposite layers. In this case, the overlap of the defects tails is weakest as the defect tails for a small atomic radius impurity are more strongly pronounced in the layer the impurity is attached to. Secondly, instead of a straight-line location, the impurities have been placed obliquely that also involves the lead atoms while the defect tails are stronger on the oxygen atoms as shown in fig. 1(c)).

In order to roughly estimate the Curie temperature $T_C$ of the simplified mean-field approximation for the Heisenberg model can be applied as $T_C = 2/3k_B E_M$ [26] ($k_B$ is the Boltzmann constant). The Curie temperature is found to be just above 300 K for 2.5% of impurities in 13 or 14 of the periodic table. In analogy with magnetic ions, the magnetic moment origin is due to partially filled orbitals, but instead of $d$ or $f$ types it is of $p$-type. The partial occupation of the $p$ orbital appears as a result of the unique bonding of impurities with the host lattice: the original partial occupation of the $p$ orbital of the impurity is preserved after its bonding to the host.

In summary, we propose to generate the local magnetic moment in compounds with $\alpha$-PbO crystal structure by its doping with non-magnetic impurities belonging to group 13 or 14 of the periodic table. The magnetic behavior of the dopants depends on their atomic radius: dopants with the smaller radius are found to establish the higher on-site stability of the localized spins. For the Si and C impurities, the on-site stability reaches such a high magnitude that it becomes comparable with that for the magnetic ions of $d$ or $f$ types [24].

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