Substitutional 4d transition metal doping in atomically thin lead

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To study the potential of plumbene as a dilute magnetic semiconductor, we computationally investigate the structural, electronic, and magnetic properties of 4d transition metal (TM) doped plumbene using density functional theory (DFT). These calculations show that Zr, Nb, Mo, Tc-doped plumbene systems are magnetic while no magnetic solution was found for Y, Ru, Rh, and Pd-doped cases. We also calculate the magnetic couplings between two TM impurities in the system with an impurity concentration of less than 2%. Strong exchange couplings and large magnetic anisotropic energies, indicate the potential for spintronics applications.

DMSs in the 2D case can be obtained by the engineering of the electronic and magnetic properties of 2D materials through substitutional doping or adsorption of 3d-TM elements. Magnetic substitutional doping can induce spin and valley polarization due to the spin–orbit and exchange interaction in transition-metal dichalcogenides (TMDs).

None of these species is magnetic in the bulk. However, a spontaneous magnetization should appear for certain elements if their dimensionality is reduced. For example, large magnetic moments were calculated for monoatomic Ru, Rh, and Ir overlayers on Ag 001 ref. 22 and for Mo and Tc wires on Ag(117) vicinal surfaces.

In this work, ab initio DFT calculations, that include SOC are performed to systematically investigate the structural, electronic, and magnetic properties of 4d TM-doped plumbene systems. First, the stability, electronic, and magnetic properties of TM defects in plumbene are studied. A generalized gradient approximation (GGA). These functionals have been shown to provide accurate description of the electronic and magnetic properties of TM nanostructures such as adatoms and nanowires. The convergence with respect to the size of $\mathbf{k}$-sampling, cutoff radius, and vacuum thickness was checked. These

II. Computational details

The vienna ab initio simulation package (VASP) was used to perform the calculations within the framework of spin-polarized DFT including SOC. The electronic properties of plumbene can be highly influenced by SOC. The frozen-core full-potential projector augmented-wave method (PAW) was used with the Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation (GGA). These functionals have been shown to provide accurate description of the electronic and magnetic properties of TM nanostructures such as adatoms and nanowires. The convergence with respect to the size of $\mathbf{k}$-sampling, cutoff radius, and vacuum thickness was checked. These

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III. Results and discussions

A. Structure and energetics

The calculated band gap energy, lattice constant, and buckling height of freestanding plumbene are 0.43 eV, 4.93 Å, and 1.01 Å, respectively.\textsuperscript{36}

To model the single impurity TM-doped systems, we chose a 4 × 2 supercell along the zigzag and armchair directions with lattice constants of \(a = 19.74\) Å and \(b = 17.09\) Å, as shown in Fig. 1. This corresponds to 31 Pb atoms in a TM atom in the supercell. For structural relaxations of the TM-doped system in this supercell, we used only the \(\Gamma\) point sampling of the Brillouin zone. We first test the equilibrium configuration of a pristine plumbene sheet. As obtained by PBE calculations, the equilibrium lattice constant, Pb–Pb bond length, and buckling height were estimated to be 4.93 Å, 3.02 Å, and 1.01 Å, respectively, which are consistent with previous studies.\textsuperscript{5,36–38}

Table 1 lists the geometric, electronic, and magnetic characters of TM-substituted plumbene. The binding energy in our calculations is defined as follows:

\[
E_b = E_{Pb-Vac} + E_{TM} - E_{Pb-TM},
\]

where, \(E_b\), \(E_{Pb-Vac}\), \(E_{TM}\), and \(E_{Pb-TM}\) represent the binding energy, the total energy of plumbene with a single vacancy, the energy of an isolated TM impurity, and the total energy of the substitutional system, respectively. After full geometry relaxation, all TM impurities form strong bonding to plumbene with a single vacancy because the values of \(E_b\) are in the range of 3.08 eV and higher.

Generally, the \(E_b\) values are significantly higher than those form 3d TM-doped in plumbene\textsuperscript{36} and phosphorene,\textsuperscript{11} but still lower than those from 4d TM-doped doped in graphene.\textsuperscript{39} The binding energy values suggest that the bonding strength of the 4d TM impurities to plumbene is rather strong (see Fig. 3).

Moreover, the \(E_b\) trend is not monotonic as the atomic number increases and it decreases when 4d shells are fully filled or almost empty. For instance, \(E_b\) is minimized for Y and Pd. Additionally, \(E_b\) is maximized twice at Mo and Rh, while Mo forms the strongest interaction among this series. This trend is shown in Fig. 2. The \(E_b\) shows a different trend in the case of 3d TM-doped plumbene so that it has a minimum value at the

| Dopant | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Pristine |
|--------|---|----|----|----|----|----|----|----|---------|
| \(E_b\) (eV) | 3.47 | 3.77 | 3.45 | 4.82 | 3.28 | 4.01 | 4.57 | 3.08 | 1.97 |
| TM-Pb (Å) | 3.06 | 2.89 | 2.83 | 2.80 | 2.68 | 2.63 | 2.61 | 2.64 | 3.02 |
| \(\Delta E\) (meV) | 13.98 | 16.25 | −19.96 | 13.59 | 2.69 | 1.77 | 0.04 | 0.11 | 0.12 | 0.04 |
| \(m_s\) (\(\mu_b\)) | 0.46 | 1.59 | 2.69 | 1.77 | 0.04 | 0.12 | 0.04 | 0.11 | 0.12 | 0.04 |
| TM charge transfer (e) | −1.16 | −0.84 | −0.42 | −0.08 | +0.14 | +0.42 | +0.51 | +0.49 |
| Pb charge transfer (e) | +0.37 | +0.31 | +0.17 | +0.04 | −0.04 | −0.13 | −0.17 | −0.14 |
| \(\Delta E\) (meV) | −19 | 33 | 29 |
| \(\Delta E\) (meV) | −3 | −24 | 13 |

Fig. 1 Schematic representation of the system under study. The unit cell is highlighted by the red rectangle.
middle of the 3d series indicating that the binding is weakest when the d shell is half-filled.

TM–Pb bond length decreases from Y to Pd as the atomic radius decreases, except for Pd, for which the binding energy is the weakest among this series. The TM–Pb bond length is smaller than Pb–Pb bond length in plumbene because the atomic radii of 4d series TM are smaller than that of Pb, except for Y, for which the atomic radius is the same as Pb.\(^{40}\) The presence of Jahn–Teller distortion was explored for the 4d series by placing them at asymmetric sites, but all the 4d TM atoms relaxed back to the symmetric sites in order to maintain \(\text{C}_{3v}\) symmetry.

Charge transfer is an important feature for the substitutional systems. The charge transfer is mainly from TM to the neighboring Pb atoms for the early 4d TM elements up to Mo, then from Pb atoms to the TM. TM atoms bond with three Pb atoms, retaining some unpaired electrons, which eventually leads to magnetic quality, however, for the electrons of 4d orbitals more than five, it is more complicated.

Since Pd-doped plumbene exhibited the \(E_{\text{b}}\), we explored its thermal stability via \textit{ab initio} molecular dynamics (MD) simulations at room temperature. These simulations showed that the Pd-doped system is structurally stable throughout the entire MD simulation. Since Pd-doped plumbene was structurally stable, TM-doped systems with higher binding energies are expected to be even more stable.

The DOS and projected DOS (PDOS) of TM-doped systems (Fig. 4) show that the energy splitting between the TM-4d peaks is large, signifying that magnetism mainly originates from TM impurities. Several resonance peaks can be found in the DOS, which is caused by the strong hybridization between the 4d orbitals of TM and 3p orbitals of Pb.

### B. Magnetic properties

DFT calculations suggest doping with Y, Ru, Rh, and Pd results in nonmagnetic states, whileagnetism is observed for Zr, Nb, Mo, and Tc-doped plumbene systems. Particularly, the impurities from Mo to Tc have magnetic states due to more valence electrons than Pb and an open shell structure. Isolated TM atoms have large spin and orbital magnetic moments according to Hund’s rules. However, electron delocalization and crystal field effects compete with intra-atomic Coulomb interactions leading to an overall reduction of spin moments as well as a quenching of orbital moments in TM impurities dissolved in nonmagnetic hosts. As shown in Table 1, the absolute values of spin magnetic moments are \(0.46 \mu_\text{B}, 1.59 \mu_\text{B}, 2.69 \mu_\text{B}, 1.77 \mu_\text{B}\) for Zr, Nb, Mo, and Tc, respectively. Plumbene doped with TM impurities has a fractional magnetic moment due to a partially occupied 4s orbital, which is unoccupied for TM-substituted graphene. The orbital magnetic moments of the TM-doped systems are \(0.21 \mu_\text{B}\) for Zr, \(0.20 \mu_\text{B}\) for Nb, \(0.11 \mu_\text{B}\) for Mo, \(0.12 \mu_\text{B}\) for Tc, and \(0.04 \mu_\text{B}\) for Rh.

In order to determine the magnetic exchange coupling between two impurities in magnetic systems, two TM (Nb, Mo, and Tc) atoms are doped in a \(7 \times 4\) supercell with a TM concentration of 1.79%. The lattice constants of this supercell are \(a = 34.54\ \text{Å}\) and \(b = 34.18\ \text{Å}\), respectively, which correspond to...
110 Pb atoms and two TM atoms in the supercell. Zr-doped system was not considered in this study due to the small exchange coupling constants, even though it is slightly magnetic.

Energy difference between ferromagnetic (FM) and antiparallel spins (AF) is exchange coupling. The spins are oriented along the corresponding preferential orientation (easy axis) in each case. The FM and AF spin configurations are considered to check the magnetic ground state. We consider two different distances between the two impurities; short (4.89 Å) and far (10.30 Å).

According to the exchange coupling constants between FM and AF states in Table 1, the AF ground state is energetically favorable in the Nb doped cases with either short or far distance. On the contrary, the Tc-doped case is FM ordered and independent of the distance between two Tc impurities. Interestingly, the Mo-doped case shows FM ordering for the short distance and AF ordering for the far distance. It is worth noting that these exchange couplings decay as the inter-impurity separation increases.

Fig. 4  DOS and projected DOS of the TM-substituted systems. The Fermi level has been set to zero and indicated by a vertical gray dashed line.
C. Magnetic anisotropy energy

The total energy of the orientation dependent magnetization $M(\phi, \theta)$ of TM impurity (see Fig. 5) in the lowest non-vanishing terms can be written as

$$E_i = E_0 + \sin^2 \theta (E_1 - E_2 \cos^2 \phi),$$

where $\theta$ is the polar angle of the magnetization $M$ from the $z$-axis and $\phi$ is the azimuthal angle in the $x$-$y$ plane, measured from the $x$ axis. For the TM-doped system, the azimuthal anisotropy energy constant $E_2$ theoretically is zero, due to rotational invariance. Our calculations also showed $E_2$ is significantly smaller than the axial anisotropy energy, $E_1$ and therefore ignored in the present study. The $E_1$, is calculated as the total energy difference between magnetization along the $x(y)$ and $z$ axes, i.e., $E_1 = E^x - E^z$ ($E^x = E^y$). If $E_1$ is positive, the easy magnetization axis is along the $z$ axis.

As shown in Table 1, Nb, Mo, and Tc-doped systems have large magnetic anisotropy energies (MAE) of 13.98 meV, 16.25 meV, and −19.96 meV, respectively. We have attempted to relate these MAEs to the electronic structure, using the PDOS (Fig. 4). We noticed that MAE is related to a hybridization of the s and d states of TM and Pb atoms. The dominant contributions to the MAE arise from a change in the occupation of states below the Fermi level. The contributions from these states are overall increased from Nb to Tc.

IV. Conclusions

Our DFT calculations suggest that the proper choice of 4d TM doped in the ultrathin lead can control its electronic and magnetic properties. The spin polarization is found in Zr, Nb, Mo, Tc, and Rh-doped systems. The long-range and anisotropic interactions between two TM impurities in plumbene with an impurity concentration of 1.79% were calculated. Nb has an AF ordering, but Tc has an FM ordering for both short and long distances. However, Mo has an FM ordering for the short length and changes to an AF order as the interatomic distance increases. Non-collinear spin-polarized DFT is employed to calculate the MAEs. Nb, Mo, and Tc-doped plumbene exhibit large MAE, which is a strong indication of spintronics applications’ potential.

Conflicts of interest

There are no conflicts to declare.

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