Polyhedron 66 (2013) 157–161

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Significant charge transfer between a single-molecule magnet Mn_{12} and a Bi substrate

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ARTICLE INFO

Article history:
Available online 21 March 2013

Keywords:
Single-molecule magnet
Density-functional theory
Bismuth
Spin–orbit coupling

ABSTRACT

We investigate electronic and magnetic properties of a single-molecule magnet Mn_{12} adsorbed on Bi(111) without any linker molecules, using a first-principles method. This study is motivated by a scanning tunneling microscopy experiment on individual Mn_{12} molecules on a Bi substrate. We apply density-functional theory including spin–orbit coupling, on-site Coulomb repulsion U, and dipole corrections. With geometry relaxation, the Mn_{12} molecule remains slightly tilted relative to the surface such that its magnetic easy axis is 6° away from the axis normal to the surface. Upon adsorption, a gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Mn_{12}, is reduced to 0.43 eV, compared to the corresponding gap of 1.07 eV for an isolated Mn_{12}. The total magnetic moment of the adsorbed Mn_{12} increases to 21 μ_B. This is due to charge transfer from the Bi slab to the Mn_{12}. The tilted geometry of the Mn_{12} allows to favor one of the outer Mn sites for charge transfer and magnetic moment change. Although bulk Bi is semimetal, there are surface states near the Fermi level, which facilitates significant charge transfer and a change in the magnetic moment.

1. Introduction

Bulk forms of single-molecule magnets (SMMs) have shown quantum effects such as quantum tunneling of magnetization [1,2] and quantum phase interference [3], despite their large magnetic moments. To investigate such quantum effects at lower dimensions or even at the single-molecule level, in the past decade, SMMs have been deposited onto various substrates [4–10] or bridged between electrodes [11–13]. In this case, two important questions can be addressed: (i) Do magnetic cores of SMMs remain intact upon adsorption? (ii) How do interactions between a substrate and SMMs affect electronic and magnetic properties of SMMs? The previous experimental effort suggested that prototype SMMs Mn_{12} may not be stable on Au, in that SMMs may be broken into smaller clusters or that the oxidation states of some Mn ions change [7]. To stabilize SMMs on a metallic substrate, long alkane chains were used to first functionalize a Au surface [5] or an insulating layer was placed between SMMs Mn_{12} and a metallic substrate [10]. A recent scanning tunneling microscopy (STM) experiment shows a possibility of deposition of individual SMMs Mn_{12}, $[Mn_{12}O_{12}(COOCH_3)_{16}(H_2O)_4]$, (not aggregates) onto a Bi(111) substrate without any linker molecules [14]. Recently, Bi-based alloys were shown to belong to a new class of matter referred to as topological insulators [15,16]. Although bulk Bi is semimetal, a Bi slab has surface states with large spin–orbit coupling (SOC) near the Fermi level E_F. Interactions between SMMs Mn_{12} and a Bi substrate via strongly spin–orbit-coupled surface states, are interesting but they have not been explored yet.

We examine properties of a SMM Mn_{12}, $[Mn_{12}O_{12}(COOH)_{16}(H_2O)_4]$, adsorbed on Bi(111) without any linker molecules, using density-functional theory (DFT) including on-site Coulomb repulsion U and SOC. Motivated by the STM experiment [14], we consider a Mn_{12} molecule slightly tilted relative to the surface such that its magnetic easy axis is several degrees tilted from the axis normal to the surface (z axis). The tilting of the magnetic easy axis remains with geometry relaxation. We find that a gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the Mn_{12} is reduced to 40% of the HOMO–LUMO gap of an isolated Mn_{12}, and that the total magnetic moment increases by 1 μ_B. This change is due to significant charge transfer from the Bi slab to the Mn_{12}. Our results suggest mechanisms of changes of oxidation states of Mn sites in an asymmetric fashion. We discuss our computational method and model in Section 2 and present our results and discussion in Section 3. A brief conclusion is followed in Section 4.

2. Computational method and model

We use Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) [17] for exchange–correlation potential and

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http://dx.doi.org/10.1016/j.poly.2013.03.021

projector-augmented-wave (PAW) pseudopotentials [18], implemented in VASP [19]. For Bi, 6*s* and 6*p* orbitals are treated as valence states, while for Mn, 3*d* and 4*s* orbitals as valence states. We include $U = 4$ eV only for the Mn *d* orbitals following the scheme in Ref.[20] to take into account additional electron correlation in localized *d* electrons. The value of U is chosen to coincide with the experimental HOMO–LUMO gap for bulk forms of Mn_{12} molecules [21]. We consider SOC self-consistently within DFT and include dipole corrections along the z axis. In the current study, van der Waals interactions are not included.

Bulk Bi forms a rhombohedral unit cell with two inequivalent atoms and the following lattice vectors: $\vec{a}_1 = (-a/2, -\sqrt{3}a/6, c/3), \vec{a}_2 = (a/2, -\sqrt{3}a/6, c/3)$, and $\vec{a}_3 = (0, \sqrt{3}a/3, c/3)$, where experimental lattice constants $a = 4.5332$ Å and $c = 11.7969$ Å [22]. For bulk band structure, the kinetic energy cutoff of 105 eV is used, and k points of $11 \times 11 \times 11$ are sampled. Along the (1 1 1) direction, Bi atoms form covalently bonded bilayers with intra-bilayer distance of 1.590 Å, and inter-bilayer distance of 2.343 Å [22]. We construct a Bi(1 1 1) slab of $4 \times 4 \times 6$ atoms to fully cover one Mn_{12} and to separate it from neighboring Mn_{12} molecules in the unit cell. For slab band structure, the kinetic energy cut off of 400 eV is used with k points sampling of $3 \times 2 \times 1$. Regarding the Mn_{12}, to save computational cost, we consider a simplified form of Mn_{12} (of 100 atoms) where CH_3 molecules in terminating ligands are replaced by H atoms [23]. It was confirmed that this simplification did not alter electronic and magnetic properties of an isolated Mn_{12} molecule [23].

We build a unit cell of the whole structure consisting of the simplified form of Mn_{12} physisorbed on the Bi(1 1 1) slab with a vacuum layer of 11 Å [Fig. 1(a)]. Topographic images of the STM experiment [14] indicate that 50% of identified individual Mn_{12} molecules have a flat-lying orientation with slight tilting relative to the surface (tilting angle of about 6°), as shown in Fig. 1(a). Thus, we start with this orientation and small tilting for geometry relaxation. All atoms in the whole structure is then relaxed except for the bottommost Bi atomic layer such that the magnitude of the forces exerted on all the atoms is less than 0.05 eV/Å. In the geometry relaxation, the U term and self-consistent SOC are included. We find a significant effect of surface reconstruction upon Mn_{12} adsorption. The intra-bilayer - distance increases in the range of 1.628-1.646 Å and the inter-bilayer distance increases to 2.487-2.515 Å. To examine properties of the whole structure, self-consistent calculations are performed, using the optimized geometry, until the total energy converges up to 9×10^{-6} eV. The kinetic energy cutoff of 400 eV is used, and k points of $3 \times 2 \times 1$ are sampled. Corrections caused by the induced dipole moment along the z axis are included. We set an initial vertical position of the Mn_{12} molecule such that there is no chemical bonding between the Mn_{12} and the Bi. We consider three initial vertical positions of the Mn_{12}. (In the three cases, the initial shortest vertical distances between the Mn_{12} and Bi are 1.57, 2.07, and 2.57 Å, and after geometry optimization, the distances become 1.80, 2.03, 2.33 Å.) The energy difference among them is less than 50 meV, and all the three cases give the same physical properties including the same tilting angle of 6° and the same total magnetic moment of the Mn_{12}. Here we show the result with the initial vertical distance of 1.57 Å.

3. Results and discussion

3.1. Bulk Bi and bare Bi slab

We calculate band structure of bulk Bi without SOC (not shown) and with SOC at several symmetry points, using the experimental lattice constants [22] [Fig. 2(a)]. Due to time-reversal symmetry and inversion symmetry, each band has double degeneracy: $\mathcal{E}(\mathbf{k},\uparrow) = \mathcal{E}(-\mathbf{k},\downarrow) = \mathcal{E}(\mathbf{k},\downarrow)$, where $\mathcal{E}$ is an energy as a function of momentum $\mathbf{k}$ and electron spin ↑ (↓). The band structure without SOC qualitatively differs from that with SOC. Only with SOC, a shallow electron pocket is shown at the L point, and a small hole pocket appears at the T point. This result agrees with experiments [22] and other DFT calculations [24].

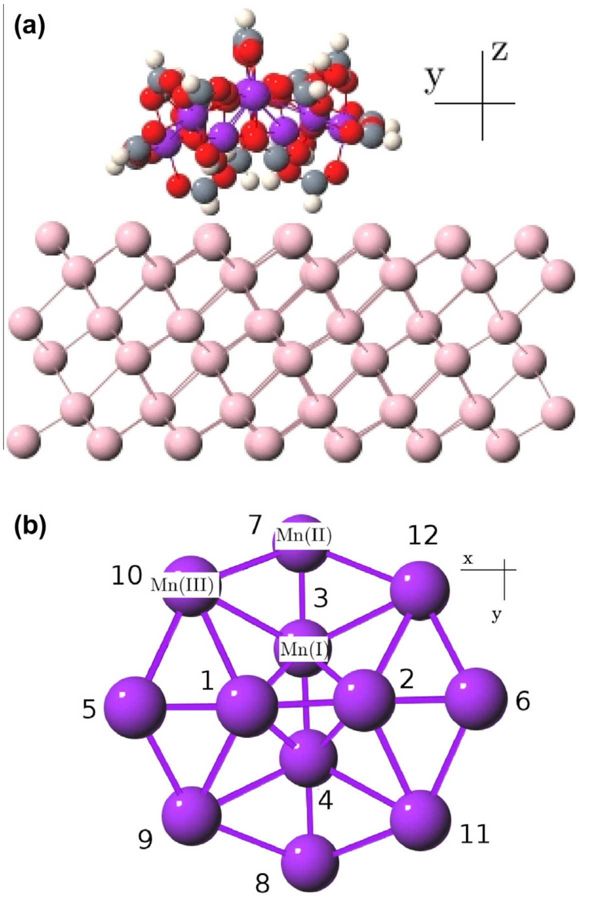

Fig. 1. (a) Side view (in the *yz* plane) of SMM Mn_{12} on a Bi slab of six atomic layers. (b) Geometry of the twelve Mn atoms in the Mn_{12} in the *xy* plane. For a S_4 symmetric Mn_{12}, the inner Mn ions, Mn(I), are Mn^{4+} ($S = 3/2$) and the outer Mn ions, Mn(II) and Mn(III), are Mn^{3+} ($S = 2$).

Now we compute band structure of bare Bi slabs of $1 \times 1 \times 6$ (not shown) and $4 \times 4 \times 6$ with SOC using the experimental lattice constants [22] in the two-dimensional (2D) Brillouin zone (BZ) [Fig. 2(b)]. The Bi slabs are not passivated with H. Time-reversal symmetry and inversion symmetry also allow double degeneracy in each band of the slabs. States near E_F shown in Fig. 2(b) are surface states localized at the surface atoms.

3.2. Isolated Mn_{12} molecule

We discuss electronic and magnetic properties of an isolated Mn_{12} molecule with S_4 symmetry. Note that the geometry of Mn_{12} considered in this subsection, is not exactly the same as that of the Mn_{12} in the whole structure due to geometry relaxation upon adsorption. Based on S_4 symmetry, the twelve Mn ions can be classified into three inequivalent types referred to as Mn(I), Mn(II), and Mn(III) [Fig. 1(b)]. In the ground state, each inner Mn site, Mn(I), has Mn^{4+} ($S = 3/2$), while each outer Mn site [Mn(II) and Mn(III)] has Mn^{3+} ($S = 2$). Antiferromagnetic superexchange coupling between the Mn sites results in the total ground-state spin of $S = 10$. The previous DFT calculation showed that without