Surface-termination dependent magnetism and strong perpendicular magnetocrystalline anisotropy of a FeRh (001) thin film: A density-functional study

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Magnetism of FeRh (001) films strongly depends on film thickness and surface terminations. While magnetic ground state of bulk FeRh is G-type antiferromagnetism, the Rh-terminated films exhibit ferromagnetism with strong perpendicular MCA whose energy +2.1 meV/□ is two orders of magnitude greater than 3d magnetic metals, where □ is area of two-dimensional unit cell. While Goodenough-Kanamori-Anderson rule on the superexchange interaction is crucial in determining the magnetic ground phases of FeRh bulk and thin films, the magnetic phases are results of interplay and competition between three mechanisms - the superexchange interaction, the Zener direct-interaction, and magnetic energy gain.

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FeRh alloys have attracted significantly because of their various intriguing physics phenomena including magnetic caloric effect and huge magnetoresistance [1-4]. Transition between antiferromagnetism (AFM) and ferromagnetism (FM) occurs above room-temperature about 350 K and ultrafast phase transition of magnetic phases in the FeRh alloys is induced by femto-second laser, which have drawn more attention due to possibility of applications for heat-assisted magnetic recording (HAMR) [5-7].

Magnetic properties of FeRh are even more interesting. The first-order phase transition from AFM to FM [8,9], in chemically ordered CsCl-structure, was first observed as early as in 1938. The ground state of the bulk FeRh is G-type antiferromagnetic (G-AFM). However, FM state has been predicted to be so close in energy that can be assessed by thermtiferromagnetic (G-AFM). However, FM state has been predicted to be so close in energy that can be assessed by thermtiferromagnetic (G-AFM). However, FM state has been predicted to be so close in energy that can be assessed by thermal excitation or by external magnetic field [10]. A collinear magnetic structure of the FeRh was observed using Mss-bauer spectroscopy [11] and neutron diffraction [12]: Fe and Rh have magnetic moments of 3.3 (3.2) and 0.0 (0.9) μB in AFM (FM) state, respectively. Very recently, feasibility of room-temperature memories based on the AFM spintronics has been successfully demonstrated in the FeRh alloys utilizing anisotropic magento-resistance (AMR) of the bistable AFM states [13]. This AFM spintronics has some advantages over that based on FM states [13-20] owing to the absence of stray magnetic field from the zero net magnetization and the insensitivity to the external magnetic fields.

Regarding FeRh thin films, several experiments have been reported [21-23]. Instead of the G-AFM in bulk, some thin films exhibit FM states stabilized at the interface with metal, while the FM states are unstable at interface with oxide [21]. Interestingly, it is reported that an electric field of only a few volts is necessary to drive the AFM-FM transition for the epitaxially grown FeRh films on the ferroelectric BaTiO$_3$ substrate [22]. Also, it is revealed that the spin orientation of the FeRh film on the MgO (001) depends on the strength of lattice strain and magnetic state [23]. Nevertheless, no model exists so far to explain the origin of the magnetic phase transition. Summing up all these features, FeRh deserves continuous attention in both academia and industry.

In this letter, magnetism and magneto-crystalline anisotropy (MCA) of FeRh films are investigated using first-principles calculations. It is found that magnetism and MCA are significantly affected not only by film thickness but also by the surface-terminations. The Rh-terminated films are more stable in FM state by quite big energy differences relative to the magnetic ground G-AFM state in bulk. Furthermore, the Rh-termination exhibits strong perpendicular MCA of +2.1 meV/□, where □ is two-dimensional unit cell area. The Fe-terminations, on the other hand, are in G-AFM states as in bulk. The strikingly different behavior of these two terminations is explained mainly in the framework of Goodenough-Kanamori-Anderson (GKA) rule on the superexchange interaction [24,25] with the Zener-type direct exchange interaction [26] also taken into account.

Density functional calculations are performed using Vienna *ab initio* Simulation Pseudopotential package (VASP) [27]. Results by VASP, particularly MCA, have been double-checked with the highly precise full-potential linearized augmented plane wave (FLAPW) method [28]. Generalized gradient approximation (GGA) within projector augmented-wave (PAW) scheme [29] is employed for the exchange-correlation interaction. $k$ meshes of 24×24×24 and 24×24×1 in Monkhorst-Pack scheme are used for bulk and films, respectively. For wave function expansions, 500 eV is used for cutoff energy. Convergence with respect to cutoff energy and number of $k$ points are seriously checked.

Magnetic structures of the bulk FeRh are illustrated schematically in Fig. 1(a)-(c) for A-, C- and G-type AFM, respectively, where arrows represent the direction of magnetic...
FIG. 1: Schematic diagrams of magnetic structures of (a) A-, (b) C- and (c) G-AFM states of bulk FeRh, and (d) exchange interaction between Fe atoms in the G-AFM state. Small balls at the corners of cubic present Fe atoms and large balls at the center Rh atoms, and thick solid, thin solid, and dotted line represent the 180° superexchange, the 90° superexchange, and the direct exchange interaction, respectively, in (d).

**TABLE I: Magnetic moments ($\mu_B$) of Fe and Rh atoms of the Fe-terminated FeRh(001) films in the G-AFM states**

|                | 3-ML  | 5-ML  | 7-ML  | 9-ML  | 11-ML |
|----------------|-------|-------|-------|-------|-------|
| Fe(S)          | 3.065 | 3.122 | 3.140 | 3.145 | 3.141 |
| Rh(S-1)        | 0.000 | 0.036 | 0.036 | 0.035 | 0.025 |
| Fe(S-2)        | -     | 3.008 | 3.044 | 3.075 | 3.123 |
| Rh(S-3)        | -     | 0.001 | 0.005 | 0.017 |       |
| Fe(S-4)        | -     | -     | 3.102 | 3.101 |       |
| Rh(S-5)        | -     | -     | -     | 0.001 |       |

In FeRh (001) films, the interlayer spacing exhibits oscillatory feature: the topmost surface moves downward whereas the subsurface layers do upward, and so on, where the innermost layer converge to bulk behavior [See Supplementary Information for fully relaxed interlayer spacings of the Fe- and the Rh-terminated film in Fig. S1(a) and (b), respectively]. 7- or 9-ML films are thick enough due to short metallic screening length.

**TABLE II: Magnetic moments ($\mu_B$) of Fe and Rh atoms of the Rh-terminated FeRh(001) films in the FM states**

|                | 3-ML  | 5-ML  | 7-ML  | 9-ML  | 11-ML |
|----------------|-------|-------|-------|-------|-------|
| Rh(S)          | 1.026 | 1.082 | 1.105 | 1.117 | 1.092 |
| Fe(S-1)        | 3.116 | 3.173 | 3.174 | 3.179 | 3.184 |
| Rh(S-2)        | -     | 1.043 | 1.052 | 1.054 | 1.054 |
| Fe(S-3)        | -     | -     | 3.193 | 3.189 | 3.196 |
| Rh(S-4)        | -     | -     | -     | 1.036 | 1.038 |
| Fe(S-5)        | -     | -     | -     | -     | 3.176 |

Before we discuss magnetism the FeRh films, we provide here a detailed analysis of bulk magnetism. Density of states (DOS) of G-AFM, FM, A-AFM, and C-AFM states are presented in Fig. 3 from top to bottom, where left and right panels of the G-AFM (FM) are 3.158 (3.144) $\mu_B$ and 0.00 (1.041) $\mu_B$, respectively. Lattice constants and magnetic moments in this work are reasonably consistent with experiments [11,12] and previous calculation [10].
are for Fe and Rh atoms, respectively. $e_g$ and $t_{2g}$ are degenerate in G-AFM and FM due to the cubic symmetry, whereas those in A- and C-AFM are no longer degenerate owing to the tetragonal magnetic structure. Strong hybridization between Fe and Rh $d$ states brings in almost fully occupied (unoccupied) majority (minority) spin states of Fe $d$ orbital, particularly $e_g$ states for all magnetic phases, which results in enhanced moments of Fe atoms. The nearly half-filled band favors AFM as in bulk Mn and Cr. It is noteworthy that the majority spin bands of Rh are almost fully occupied in the FM similarly to Fe, but featureless in AFM states.

The magnetic phase of FeRh alloy is a result of interplay between three mechanisms - superexchange interaction [24,25], Zener-type direct-exchange interaction [26], and magnetic energy gain. In the framework of GKA rule, whether FM or AFM is preferred by superexchange interaction is explained by magnetic ion-ligand-magnetic ion angle. Here we view Fe atoms as magnetic ions and delocalized $s$ and $p$ orbitals of Rh as ligand orbitals in GKA rule. Fig. 1(d) schematically illustrates magnetic interactions between Fe atoms to be involved in determining magnetic structure. The GKA superexchange interactions are shown as solid lines and Zener direct interaction as a dotted line. In accord with GKA rule on magnetic coupling, Fe$_1$ prefers AFM coupling to Fe$_2$ and FM coupling to Fe$_3$ because angles of Fe$_1$-Rh-Fe$_2$ and Fe$_1$-Rh-Fe$_3$ are $180^\circ$ and $109.5^\circ$ (which is close to $90^\circ$), respectively.

On the other hand, the interaction between Fe$_1$ and Fe$_4$ is more or less direct since Rh atom is not much involved in this coupling. The half-filled $e_g$ states directing along the principal axes are more involved in the Zener direct interaction between Fe$_1$ and Fe$_4$ compared to the $t_{2g}$ states, which results in AFM coupling. Since the $d$ states are highly localized giving little wave function overlap, the direct interaction between Fe$_1$ and Fe$_4$ must be weak. As a result of combination of the superexchange and the direct interactions discussed above, G-AFM is most stable among other AFM states. In the FM states, on the other hand, there is magnetic energy gain due to the considerable magnetic moment of Rh atom ($1.041 \mu_B$), which reduces total energy to a certain degree, hence a FM state is more stable than A-AFM and C-AFM states even though it is less stable compared to the ground G-AFM state.

In the Rh-termination, the $180^\circ$ superexchange interaction disappears because of the absence of Fe layer above the Rh-terminated surface. The $90^\circ$ superexchange interaction makes the A-AFM more stable than G-AFM. Instead, the magnetic energy gain of the surface Rh atom plays a key role in stabilizing FM. Hence, FM is the magnetic ground state in the Rh-terminated FeRh thin films. In the Fe-termination, on the other hand, G-AFM is most stable as in bulk since the $180^\circ$ superexchange interaction still works.

In Fig. 4, calculated MCA energies, $E_{\text{MCA}} = E(\rightarrow) - E(\uparrow)$, are presented as function of thickness for the Fe- and the Rh-terminated films in their respective magnetic ground states (denoted in solid lines), G-AFM and FM states. $E_{\text{MCA}}$'s for other magnetic states are also shown for comparison. From the definition of $E_{\text{MCA}}$, positive (negative) value implied...
perpendicular (in-plane) magnetization to the surface normal. Interestingly, the Rh-termination in FM state show quite strong persistent perpendicular MCA regardless of thickness, whereas the Fe-termination exhibit in-plane MCA for all magnetic states. In particular, with $E_{MCA} = +2.1 \text{ meV/\square}$ of the Rh-termination is at least two orders of magnitude greater than conventional 3d magnetic metals, Fe, Co, and Ni. Moreover, the saturated feature of $E_{MCA} = +2.1 \text{ meV/\square}$ with respect to thickness implies that magnetism of the Rh surface plays a key role in determining MCA. From the fact that both the Fe-terminated FM states and the Rh-terminated G-AFM state show in-plane MCA, the magnetic states are not a key factor in determining MCA, but the surface termination is. The Rh-termination is crucial to achieve perpendicular MCA.

To discuss the role of thickness and the surface termination on magnetism as well as MCA, we present DOS of the Fe- and the Rh-terminated 9-ML film in G-AFM and FM states from top and bottom row. Right panel is for Fe and left panel is for Rh as in Fig. 2.

FIG. 5: $d$-projected density of states of the Fe-terminated 9-ML film in G-AFM and FM states, and the Rh-terminated 9-ML film in FM and G-AFM states from top and bottom row. Right panel is for Fe and left panel is for Rh as in Fig. 2.

In summary, magnetism of the Fe- and the Rh-terminated FeRh (001) films are under an applied magnetic field or heat, we present total energy of the Fe-terminated FeRh(001) thin film as a function of angle between magnetic orientations of the closest Fe atoms. [See SI Fig. S2]. The energy barrier of the AFM-to-FM transition under an applied magnetic field is reduced with decreasing of thickness. This information might be useful in designing spintronics devices such as an AFM memory [13] and HAMR [5-7].

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