Magnetic properties of thin films of a magnetocaloric material FeRh

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Abstract

A FeRh alloy is a well-known efficient magnetocaloric material and some experimental and theoretical studies of bulk FeRh have been reported already by several groups. In this study we report first-principles calculations on magnetic properties of different thickness FeRh thin films in order to investigate the possibility to enhance further the magnetocaloric efficiency. We used two methods of a Vienna Ab-initio Simulation Package (VASP) code and SIESTA package. We found that the FeRh thin films have quite different magnetic properties from the bulk when the thickness is thinner than 6-atomic-layers. While bulk FeRh has a G-type antiferromagnetic(AFM) state, thin films which are thinner than 6-atomic-layers have an A-type AFM state or a ferromagnetic (FM) state. We will discuss possibility of magnetic phase transitions of the FeRh thin films in the view point of a magnetocaloric effect. And we found 4-, 5-, 6-layers films with Fe surface and 7-layers film with Rh surface are FM and they have relatively small magnetocrystalline anisotropy (MCA) energy about less than 70 meV. The small MCA energy leads to reduction of the strength of magnetic field in operating a magnetic refrigerator.

1. introduction

These days, many scientists are focusing on protecting environment and improving energy efficiency. One of the recent subjects is refrigeration technologies. And a magnetic refrigeration is the leading replacement technique instead of a gas refrigeration [14]. And its efficiency reaches about 70% of the Carnot efficiency [1]. In the magnetic refrigeration, magneto caloric materials are the key point for a working body [2]. For magneto caloric materials, FeRh has been studied by many groups both theoretically and experimentally. The reasons of selecting FeRh are described below. First, there are another magneto caloric materials not only FeRh but also Gd based alloys [3]. But Gd as known as rare earth element is too hard to obtain for practical applications. And it has poisonous [4]. So it is hard to use although it has large potential for magneto caloric material. Second, FeRh indicates magnetic transition nearby room temperature about 340 K with no change its CsCl structure [6]. So this property leads that we can obtain large entropy change which is key point in magneto caloric phenomena in FeRh [5]. So those are why we focus on FeRh. In some group, they reported magnetic transition in bulk FeRh when its volumes increase or decrease [6]. And they also found sizes of external magnetic field in each volume by using the common-tangent construction in fixed magnetic moment calculations [7]. In the other group, they studied film FeRh experimentally. They implemented these experiences according to temperature and annealing time. And they found AFM/FM (from antiferro state to ferro state) transition in their samples [8]. At low temperature, experiment shows that FeRh is AFM. But at high temperatures, this material is found FM [9]. So several groups studied about FeRh properties depends on volume, temperature or annealing time. But we found different magnetic properties and magnetic transitions in thin film FeRh according to the films layer. So In this paper, we analyze FeRh films magnetic property trend depends on thickness. And we also report FeRh thin films MCA energy which is an important factor for reduce size of magnetic field in the magnetic refrigerator [11] [12].

2. materials and calculation method

In this study, VASP (Vienna Ab-initio Simulation Package) code and LCAODFTLab program were selected for density functional theory (DFT) calculation. We used LCAODFTlab to find most stable atomic arrangement in materials. And we used VASP to find materials magnetic properties.

In order to understand an effect of thickness, we calculated 3-, 4-, 5-, 6-, 7- and 9-layers films, and also analyzed and calculated bulk FeRh properties which are already reported by some groups. And in order to understand an effect of surface, we changed a unit cells surface from Fe to Rh. FeRh in the ordered CsCl structure [10]. But the tetragonal magnetic unit cell was used in our calculations to capture both observed ferro magnetic state (FM) and A-type, G-type and C-type antiferro magnetic state (AFM) which are shown in figure 1. In AFM calculations, we considered Fe magnetic moment and direction excluding Rh magnetic direction. Here, the lattice constant $\sqrt{2}a^{*}$, where a^{*} is the basic CsCl lattice constant, and c= $\sqrt{2}a$ [6].

In all calculations, we used generalized gradient approximation(GGA) Pseudopotential, and used 12x12x12 K-Points for bulk, 12x12x1 K-Points for films. In bulk calculatins, for finding magnetic transition according to lattice constant, we made unit cell like figeure 1.

In film calculations, the Fe/Rh/Fe, Fe/Rh/Fe/Rh/Fe are called 3-layers and 5-layers each. We calculated from 3 layers film to bulk in this way.

3. Result and discussion

3.1 Bulk

According to the bulk calculation results, type-2 AFM (AFM2) is more stable about 0.218 eV than FM in ground. But if increase its lattice constant about 0.2 Å more than ground state lattice constant, there is magnetic transition from AFM2 to FM. We provide figure 2 which shows the magnetic transition trend curves.

Then we compared total energies of FM and AFM2 according to total magnetic moment in ground lattice constant 4.26 Å. And we found two different ground states, one of them has AFM, and the other one has FM. In bulks ground volume 4.26 Å, we implemented fixed magnetic moment calculations for understanding size of the external magnetic field when the systems magnetic state changes from AFM state to FM. We can find sizes of external magnetic field in each volume by using the common-tangent construction in fixed magnetic moment calculations [7]. We provide that total energy trend curves in figure 3, and atoms magnetic moment trend in figure 4. Actually bulk FeRh is already studied by several groups. We compared our bulk calculation results with one of them which is implemented by V. L. Moruzzi and P. M. Marcus [6]. Then the results almost same within 1% error range. Only different thing is we calculate about AFM3 systems in FeRh but their energy is about 1.583 eV more unstable than AFM2 which has ground energy. So we don't consider about that systems.

3.2 Film

Then we discuss about ground magnetic state trend and their magneto crystalline-anisotropy (MCA) energies in thin films. We compare stable magnetic state depends on films thickness. We choose Fe layer for surface. That trend is displayed in figure 5. And if their total magnetic moments show kind of ferrimagnetism state and small MCA energy, they have potential that be controlled easily for MCE material [11] [12]. 'small MCA energy' means its spins have less characteristic that array one side. So if some materials have small MCA energy, we can control their spin with less size of magnetic field. we display each films magnetic moment in figure 7. And discuss about MCA energy in some films which have ferrimagnetism state.

In figure 5, if bar is located in negative side, it means that magnetic state is more stable than AFM2. On the contrary, if bar is located in positive side, it means that state is more unstable than AFM2. In Y-axis, we set up 0 to AFM2 energy which is most stable magnetic structure in bulk to compare energy with FM, AFM1.

Then now, we know stable magnetic states are different each layers. From 7 layers to bulk have AFM2 for ground state. But excluding them, 3-, 4-, 6-layers indicate AFM1 and 5-layers indicates FM on ground .

In each layers, changing magnetic structure trends are displayed in figure 6.

6-layers films trend curve is almost same with 4-layers, and 9-layers films is almost same with 7-layers. so that why we display only this four kind of graph.

According to figure 6, excluding 5-layers they have more stable energy when their magnetic structures are AFM1. But in 5-layers film, FM is most stable magnetic state.

Now we have to consider their magnetic moment. We can see AFM1 in 4 layers, 5 layers and 6 layers film have ferri state. And also AFM2 in 6 layers has ferri state. So we are more concerned with them. Then we calculated magneto crystalline-anisotropy (MCA) energy about these films which have ferromagnetic state. That result display in table 1 and their magnetic moment also display in same table.

4-layers and 6-layers films which in the table 1, have small magneto crystalline-anisotropy (MCA) energy which are below 20 meV while compare their absolute values. That mean their spins don't have big directivity. So they can be ferromagnetism under the weak external magnetic field. And they also have ferrimagnetism. So they have potential to reduce critical current for applications.

In order to understand effect of surface in films, we changed surface atoms from Fe to Rh. And we also compare stable magnetic state according to films thickness. That energy trend is displayed in figure 8, each film magnetic moment is in figure 9. Just like the Fe surface case, in Y-axis, we set up 0 to AFM2 energy which is most stable magnetic structure in bulk to compare energy with FM, AFM1. In Rh surface case, we don't discuss about bulk because it is totally same with the foregoing discussions. Excluding 5-layers film, they indicate different magnetic structure with bulk which has AFM2. We can know if the films thickness is over 7-layer, the films magnetic structure is AFM2. But under 6-layers, excluding 5-layers film, they have FM or AFM1. Then we have to discuss about magnetic moment in Rh surface case like Fe surface case.

In our calculations, only 7-layers film indicates ferrimagnetism state for reducing size of external magnetic field. So we calculated MCA energy in 7-layers film. And that result is presented in table 2.

4. Conclusion

It's time to give serious consideration to environmental problems. One of effort to solve environmental problems is replacing gas refrigeration to magnetic refrigeration. To operate magnetic refrigerator successfully, finding materials which have good properties in room temperature is very important factor. Here, good property means that material has phase transition nearby room temperature and has large entropy difference and so on. And material have to consist of components which are easily available for practical applications.

FeRh has been studied by several groups both theoretically and experimentally for magneto caloric material. Because it doesn't consist of rare earth elements and indicates magnetic phase transition nearby room temperature. In this paper, we considered not only bulk FeRh but also films according to thickness. Then we found if that films which are thicker over 7-layers, their magnetic structures indicate AFM2, but becoming thin, the ground magnetic state change from AFM2 to AFM1 or FM.

AFM1 in 4-, 5- and 6-layers indicate ferrimagnetism, then we calculated magneto crystalline-anisotropy (MCA) energy about these three kinds of films. Because if some systems have ferrimagnetism state they have possibility to have smaller MCA energy than FM or AFM [13]. And materials which have small MCA energy can reduce external magnetic field in magnetic refrigerators working body. Because 'small MCA energy' means its spins have less characteristic that array one side. According to our MCA energy calculation, 4-, 6-layers film have small MCA energy about less than 20 meV. Moreover, AFM1 magnetic structure has most stable energy in 4-, 6-layers film.

And we also calculated the films which have Rh surface, and only 7-layers film has ferrimagnetism. So we consider the 7-layers films MCA energy which has Rh surface. It has small MCA energy about 3.4 meV. But it doesn't have most stable energy in AFM1 system.

Finally, we expect AFM1 in 4- and 6-layers which have ferrimagnetism can perform a role for magneto caloric materials in the magnetic refrigerator.

5. Reference

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Table 1 MCA energies and each atoms magnetic moment in films which have ferrimagnetism.

	MCA energy	magnetic moment (Fe(s))	magnetic moment2 (Fe(s-1))	magnetic moment3 (Fe(s-2))	magnetic moment4 (Rh(s))	magnetic moment5 (Rh(s-1))	magnetic moment6 (Rh(s-2))
4layers (AFM1)	**-18.6 meV**	**3.180 μB**	**-3.111 μB**		**0.601 μB**	**0.045 μB**	
5layers (AFM1)	**-68.8 meV**	**3.169 μB**		**-3.157 μB**		**-0.156 μB**	
6layers (AFM1)	**19.8 meV**	**3.185 μB**	**3.130 μB**	**-3.136 μB**	**0.601 μB**	**0.104 μB**	**0.067 μB**

Table 2 MCA energies and each atoms magnetic moment in 7-layers film which has ferrimagnetism.

	MCA energy	magnetic moment (Fe(s-1))	magnetic moment3 (Fe(c))	magnetic moment4 (Rh(s))	magnetic moment6 (Rh(s-2))
7layers (AFM1)	3.4 meV	3.155 μ_B	-3.148 μ_B	0.944 μ_B	-0.015 μ_B

(a)A-type AFM. (b) G-type AFM. (c) C-type AFM.

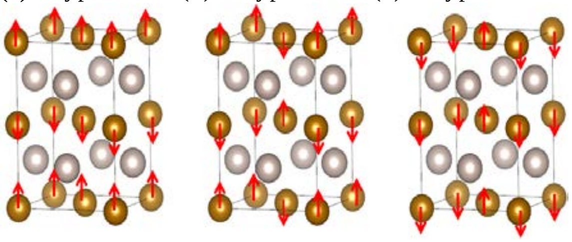

Figure 1. Magnetic units cells of bulk FeRh. Arrows represent spin direction.

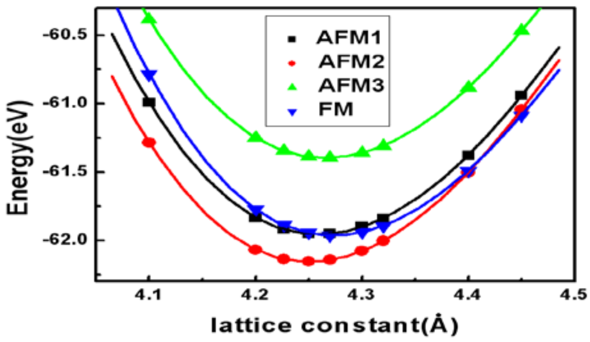

Figure 2 Total energies of different magnetic states as functions of lattice constant.

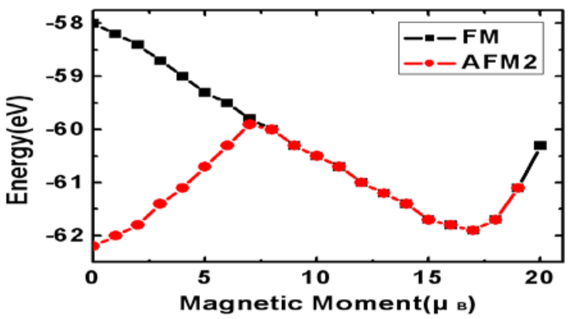

Figure 3. Total energies of FM and AFM2 calculated from the fixed moment approach.

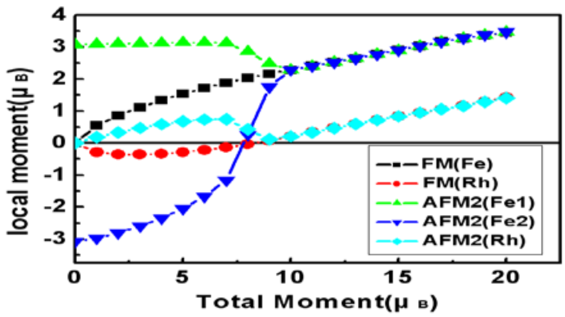

Figure 4. Atom-projected magnetic moment with respect to fixed total magnetic moment.

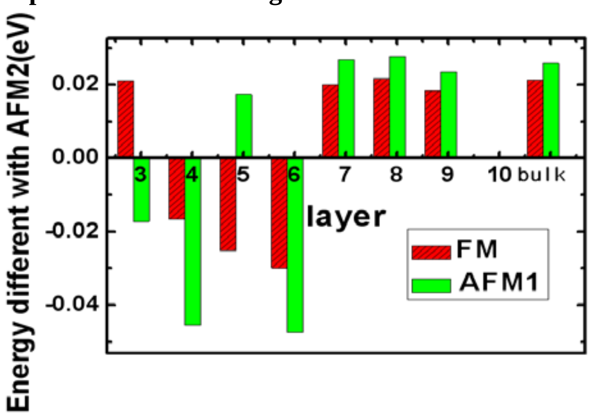

Figure 5. Energy differences of the FM and AFM1 with the Fe-terminated surfaces FeRh thin films from AFM2 which is most stable in bulk.

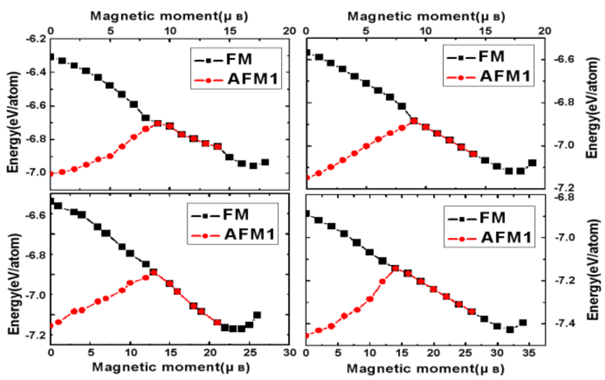

Figure 6. Total energies of FM and AFM1 of (a) 3-layers, (b) 4-layers, (c) 5-layers, (d) 7-layers the Fe-terminated FeRh thin films calculated from the fixed moment approach

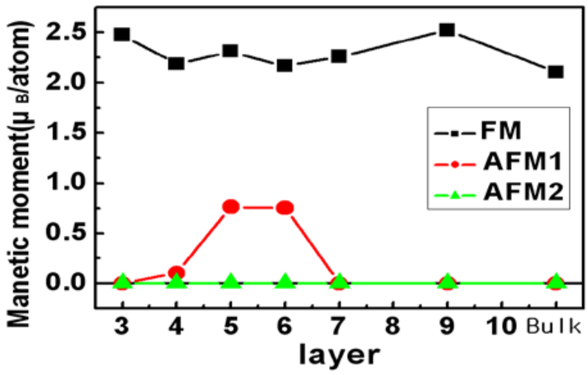

Figure 7. Magnetic moments of the Fe-terminated FeRh thin films as functions of film thickness.

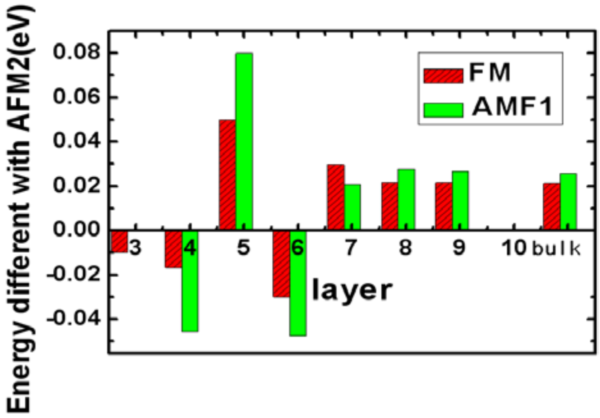

Figure 8. Energy differences of the FM and AFM1 with the Rh-terminated surfaces FeRh thin films from AFM2 which is most stable in bulk.

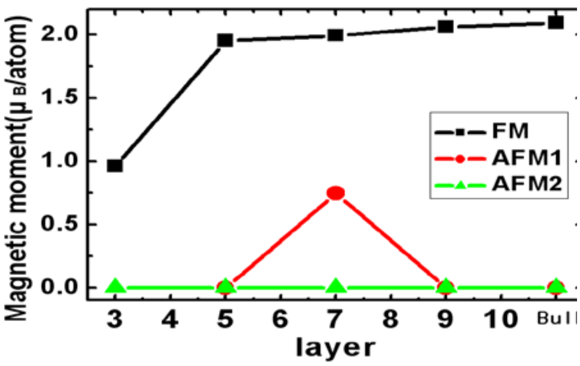

Figure 9. Magnetic moments of the Rh-terminated FeRh thin films as functions of film thickness.