First-principles calculations on elastic and entropy properties in FeRh alloys

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First-principles calculations were employed to investigate elastic and entropy properties of *B2* ferromagnetic and antiferromagnetic FeRh phases. We calculated lattice parameters, elastic constants, isotropic moduli like bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio of two phases and compared these with other calculations and experiments. At finite temperatures, the values of vibrational (from both Debye model and phonon dispersion) and thermal electronic contributions to the total entropy change between the two phases are calculated about -50 J/kg/K and 7.8 J/kg/K comparable to the experimental results (-33±9 J/kg/K and 8±1 J/kg/K).

Keywords: Elastic constants, Isotropic moduli, Pugh ratio, Entropy change, First-principles calculations

1. Introduction

Recently, magnetocaloric effect (MCE) in LaFeSi [1], FeRh [2-4], and NiCoMnIn Heusler [5, 6] alloys has received much attention because it's potential application in magnetic refrigeration technology an alternative technology to the current gas-compression method. The MCE is characterized by two parameters: the adiabatic temperature change ΔT and the isothermal entropy change ΔS . The total entropy change ΔS_{tot} usually can be written as the sum of i.e.: $\Delta S_{\text{tot}} = \Delta S_{\text{ele}} + \Delta S_{\text{lat}} + \Delta S_{\text{mag}}$ the entropy change of the lattice ΔS_{lat} , of the magnetic ΔS_{mag} and of the thermal electronic system ΔS_{ele} . The study on the separation of these contributions to the MCE is of great importance to understand this giant MCE [6]. By direct experimental measurement of the MCE in NiCoMnIn alloys, Kihara *et al.* [6] showed that ΔS_{ele} is negligibly small whereas ΔS_{lat} plays the dominant role in the MCE. Gruner *et al.* [1] demonstrated that ΔS_{lat} contributes cooperatively with the magnetic and thermal electronic entropy changes in LaFeSi by nuclear resonant inelastic X-ray scattering and first-principles calculations. Cooke *et al.* [7] reported $\Delta S_{\text{lat}} = -33$ J/kg/K and $\Delta S_{\text{ele}} = 8$ J/kg/K by low-temperature specific heat and photoemission measurements in FeRh alloys, which is promising material for the magnetic refrigeration because of the highest $\Delta T = 12.9$ K of all known materials [8].

However, recent first-principles calculations underestimated the difference in entropy of lattice and thermal electronic which was 11.7 J/kg/K [9] (experimental value -25 J/kg/K [7]). Besides, the first-principles determination of isotropic moduli which is important for application and thermodynamical parameters like Debye temperatures are lacking in the literature. In this paper, we firstly determined the lattice parameters, elastic constants, and isotropic moduli of the two phases. Then we obtained the values of lattice vibrational (from both Debye model and phonon dispersion) and thermal electronic contributions to the total entropy change.

2. Computational details

First-principles calculations were carried out with the Vienna *ab-initio* simulation package (VASP) code [10, 11] and the projector augmented wave (PAW) as well as the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [12]. The kinetic energy cut-off of 650 eV was used for plane-wave set, and the Brillouin zone (BZ) was sampled with special k-points of an

11×11×11 grid for total energy calculations, as proposed by Monkhorst and Pack [13]. The Fe (4s, 3d, 3p) and Rh (5s, 4d, 4p) were treated as valence electrons. The influence of correlations was studied using the DFT+*U* method by applying a rotationally invariant $U = 1$ eV by Dudarev *et al.* [14]. The calculations parameters were from Aschauer *et al.* [15]. Phonon calculations were performed using the finite displacement approaches and 2×2×2 supercell of the conventional unit cell (128 atoms) with the PHONOPY [16, 17] code.

3. Results and discussion

As previous theoretical publication showed [15], the B2 FeRh exhibits two magnetic structures, ferromagnetic (FM) and G-type antiferromagnetic (AFM) ordering. The structural properties are investigated by the 4-th order Murnaghan Equation of State (EOS) equation (1).

$$E(V) = \frac{B_0}{B'(B'-1)} \left[\left(\frac{V_0}{V} \right) + B' \left(1 - \frac{V_0}{V} \right) - 1 \right] + E_0 \quad (1)$$

The predicted equilibrium properties are given in Table I, including lattice parameter a_0 , bulk modulus B , and local magnetic moment. We find the predicted lattice parameter of FM phase is 3.017 Å larger than that of AFM phase 3.000 Å and the volume change is about 1.7%. The local Fe magnetic moment remains large and essentially constant around 3.14 μ_B in two phases (smaller than experimental value 3.30 μ_B [18]). Meanwhile Rh atom possesses 1.0 μ_B in FM phase and loss of its moment in AFM phase. As shown in Table I, the elastic constants of the two phases are obtained with strains (± 0.007) by strain-stress method [19] and fulfill the mechanical stability criteria for cubic structures:

$$C_{11} - C_{12} > 0, C_{11} > 0, C_{33} > 0, C_{11} + 2C_{12} > 0 \quad (2)$$

Table I also lists the isotropic moduli for two phases like bulk modulus B , shear modulus G , Young's modulus E , and Poisson's ratio ν and experimental values are collected for comparison. The bulk and shear modulus are estimated by the Voigt-Reuss-Hill approach. The Young modulus and Poisson's ratio are predicted by Hill approach. It should be noted that the calculated B of two phases from elastic constants (EC) agree well with those directly from the fitting of (EOS) listed in Table I, which further demonstrates the good accuracy of our elastic constants calculations. Also our calculated B is consistent

with the recent work [15] and 1.4 times larger than the experiment [7]. The large difference can be explained by following two reasons: (1) Present calculations did not consider the effect of thermal expansion effect (2) the amorphous and off-stoichiometric nature of the experimental material. In Table I E decrease by as much as 20% from FM to AFM phase as well as an increment of 15% in ν and both agree well with the experiment [7]. The AFM phase has a slightly higher B than FM phase while the FM phase has a higher G and E than AFM phase. According to Pugh criteria [20], B/G ratio of 1.75 separates ductile and brittle materials. The two phases show ductile property especially AFM phase since their Pugh ratio $B/G > 1.75$.

Then we discuss entropy change during AFM-FM transition. Figure 1 shows the phonon dispersion and vibrational density of states (VDOS) for two phases. It is observed that FM phase is dynamical stable since all phonon modes have real values in the whole Brillouin zone. However, the AFM phase shows imaginary frequency at X and K points which means AFM is dynamically unstable [15]. This lattice instability in the AFM phase leads to the discovery of a stable monoclinic or metastable face-centered-cubic-like structure [9, 15]. By the harmonic approximation $\Delta S_{lat} = -10.8$ J/kg/K (-11.7 J/kg/K [9]) is much smaller than the experimental results -39 J/kg/K. This discrepancy is on account that AFM phase is stable below the transition temperature in the experiment. Here we applied the Hubbard- U correction ($U = 1$ eV) to the Fe d orbitals to stabilize AFM phase [15]. In Figure 1(a) the phonon dispersion of FM phase with DFT+ U is similar with PBE calculations. However, that of AFM phase shows no imaginary frequency at X or K points with DFT+ U calculations and it gives Fe magnetic moment equal to $3.35 \mu_B$ close to experimental value $3.30 \mu_B$. Figure 2 shows $\Delta S_{lat} = -50$ J/kg/K with the stable AFM phase. Besides, ΔS_{lat} is estimated about -50 J/kg/K by Debye theory [21] just the same as lattice dynamics predicted in Figure 2.

Next, we investigate the thermal electronic entropy S_{el} with the form [22, 23]

$$S^{el} = -k_B \int n(\varepsilon) [f \ln f + (1-f) \ln(1-f)] d\varepsilon \quad (4)$$

Where $n(\varepsilon)$ is the total electronic density of states (DOS) with f being the Fermi distribution.

$\Delta S_{ele} = S_{FM} - S_{AFM}$ by equation (4) is estimated about 7.8 J/kg/K (8 J/kg/K expt.[7]) at 370K in

Figure 2. Thus ΔS_{ele} cannot be negligible and is opposite to the ΔS_{lat} . This is very different from LaFeSi[1] and NiCoMnIn[6] alloys where both ΔS_{lat} and ΔS_{ele} contribute cooperatively to the MCE. We point out that the DFT+ U calculations do not change the ΔS_{ele} as in Figure 2.

The Sommerfeld coefficients $\gamma_{FM} = 32.6 \text{ mJ/kg/K}^2$ and $\gamma_{AFM} = 9.6 \text{ mJ/kg/K}^2$ are obtained with the relation $\partial S / \partial T = C^{el} / T = \gamma + \beta T^2$ [9]. According to the theory proposed by Tu *et al.* [24], $\Delta S = (\gamma_{FM} - \gamma_{AFM})T$ by our calculated γ at 310 K is 7.1 J/kg/K much smaller than both Tu's calculations (13.6 J/kg/K) and experimental value 12.5–19.7 J/kg/K [25], therefore ΔS_{ele} from DFT calculations is insufficient to drive the AFM-FM transition in FeRh alloys. We note that γ_{FM} is much smaller than the experiment 53–62.5 mJ/kg/K² and γ_{AFM} is comparable to the experiment 10.5–16 mJ/kg/K² [25]. Following reasons can explain it: (1) the experimental value for γ_{FM} has been measured in slightly more iron-rich alloys and coefficients show the strong sensitivity on small departures from stoichiometry [25] (2) Gu and Antropov *et al.* [26] proposed the driving force of the transition is associated with magnon excitations that have higher entropy in FM phase compared to AFM phase.

4. Conclusions

In summary, the DFT calculations are used to investigate the elastic and entropy properties of $B2$ FeRh in FM and AFM phases. The calculated lattice parameters, elastic constants, bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of the two phases agree with experimental results. The Pugh ratio indicates the two phases especially AFM exhibits ductile property. We obtain $\Delta S_{lat} = -50 \text{ J/kg/K}$ using first-principles phonon calculations as well as Debye model and $\Delta S_{ele} = 7.8 \text{ J/kg/K}$ by the DFT calculated DOS which is insufficient to drive AFM-FM transition in FeRh alloys. The discrepancy between the calculated $\gamma_{FM} = 32.6 \text{ mJ/kg/K}^2$ and experimental value 53–62.5 mJ/kg/K² may be due to the entropy contribution of the magnon excitations in FM phase.

Acknowledgements

This work was supported by National Science Foundation of China under Grant No. 11504020 and No. 1174030.

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Figure captions

Figure 1. Phonon band structure and vibrational density of states (VDOS) for (a) FM (b) AFM FeRh alloys computed with PBE and DFT+ U .

Figure 2. Lattice and thermal electric contribution to entropy change between FM and AFM phase vs temperature. Total entropy change is the sum of the lattice and thermal electronic contribution.

Figure

Figure

Table I. The calculated equilibrium lattice constant a_0 in Å, local magnetic moment m in μ_B , bulk modulus B in GPa, Debye temperature Θ_D in K, elastic constants and isotropic modulus in GPa, Poisson's ratio ν and Pugh ratio of FeRh alloys. * calculated from DFT+ U .

Phase		a_0	m		B	Θ_D	C_{11}	C_{12}	C_{44}	B	G	E	ν	B/G
			Fe	Rh	EOS					EC				
FM	This work	3.017	3.18 3.33*	1.04	195.3	396	278.3	179.4	110.2	194.9	78.1	206.5	0.32	2.49
	Ref.[7]					393				133		197	0.25	
	Ref.[15]	3.018	3.21	1.05			251.5	164.2	109.8	193.3				
AFM	This work	3.000	3.14 3.35*	0	198.2	335	218.7	188.5	119.8	198.5	54.8	150.6	0.37	3.62
	Ref.[7]					340				142		153	0.32	
	Ref.[15]	3.002	3.15	0			225.4	181.2	119.9	195.9				