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DFT calculations of structural, magnetic and thermal properties of C15, C14 and C36 Laves phases in Fe-Nb-Zr

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ABSTRACT

The Pseudo-Potential Density Functional Theory (PP-DFT) method is applied to investigate the C15, C14 and C36 Laves phases within the Fe-Nb-Zr system. The lattice parameters, bulk moduli, heats of formation and magnetic moments are predicted considering various spin configurations. $ZrFe_2$ and $Zr_{0.5}Nb_{0.5}Fe_2$ are found to be ferromagnetic in the C15 and C36 structures, respectively. $NbFe_2$ is predicted to be ferrimagnetic in C36. The magnetic states dependency of these compounds on the volume compression shows interesting magnetic transition from the low to high spin state. This transition is more pronounced for $NbFe_2$ and $Zr_{0.5}Nb_{0.5}Fe_2$. The thermal properties of $NbFe_2$ and $Zr_{0.5}Nb_{0.5}Fe_2$ are well predicted by using the quasi-harmonic Debye model. The obtained linear volume expansion for $ZrFe_2$ is in excellent agreement with the experimental value at 800 K. The vibrational entropies of the studied alloys confirm the coexistence of the three Laves phases at high temperature.

1. Introduction

The materials with the cubic-C15, hexagonal-C14 and dihexagonal-C36 structures Laves phases form a large family of binary and ternary intermetallic compounds. These materials are particularly attractive because of their unusual physical and chemical properties as well as their potential and effective applications [1–3]. More recently, Laves phases have attracted more attention as they are proposed as permanent magnets materials based on 3*d*-4*d* or 3*d*-5*d* alloys. These constituents possess a strong spin-orbit coupling and therefore support high Magneto-Crystalline Anisotropy (MCA) [4].

The $ZrFe_2$ compound has a cubic-C15 structure which was observed at the stoichiometric composition up to the congruent melting point [5]. However, while the composition range of this phase extends down to about 27 *at*-% Zr on the Fe-rich side, the C14 and C36 hexagonal polymorphs of this Laves phase can occur [6,7]. Additionally, $ZrFe_2$ is quite ferromagnetic with magnetic moment value and Curie temperature that are very sensitive to the concentration ratio in Fe and Zr [8–12]. The $NbFe_2$ compound has variable structural and magnetic properties and its proposed lattice structure is hexagonal C14 [13]. Experimental investigations have shown that the C14-$NbFe_2$ compound is nonmagnetic with a pronounced Pauli paramagnetic character [14,15]. Mossbauer measurements and nuclear magnetic resonance (NMR) studies have revealed that the stoichiometric $NbFe_2$ is a weak ferromagnetic compound below 10 K [16–18]. Another contradictory experimental study has revealed that $NbFe_2$ is a weak antiferromagnetic phase with a Neel temperature around 10 K leading to the coexistence of ferro- and antiferromagnetic spin fluctuations [17]. These states were suggested to be responsible for the anomalous magnetic susceptibility observed above 200 K. Despite the controversy about the magnetic states of the stoichiometric $NbFe_2$, weak ferromagnetism has been observed for both Fe-excess and Nb-excess alloys [19–23]. Recently, Vélez et al. have found that $NbFe_2$ is paramagnetic at room temperature and exhibits spin glass and antiferromagnetic behaviour at low temperatures [24]. The pseudo binary $(Zr_{1-x}Nb_x)Fe_2$ alloys are known to show co-existence of C14, C15 and C36 Laves phases and various magnetic behaviours depending on the Nb concentration [17,19,25,26]. However, Tang et al. have concluded that the ternary Fe-Nb-Zr phase diagram is incomplete and still under debate [27].

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Basing on theoretical analysis, several investigations have revealed that $ZrFe_2$ is ferromagnetic in the C15 structure and $NbFe_2$ is paramagnetic in the C14 structure [8,10,11]. However, the C36 structure was not considered in these studies. Another study has reported that $NbFe_2$ is more stable in the ferromagnetic state with the C36 structure [28]. Considering only the C14 structure, Liu et al. have found that $NbFe_2$ is more stable in the antiferromagnetic state [29]. Subedi et al. [30] have reported that the magnetism of this material is highly itinerant, with magnetic moment values depending on the magnetic ordering. They have also predicted a ferrimagnetic ordering as the most stable but almost degenerate with the antiferromagnetic one. Tompsett et al. [31] have found an antiferromagnetic state which was not previously considered. The ferrimagnetic state was also evidenced by Haynes et al. [32] and more recently a more exhaustive study of Ladines et al. [33] have included both the C15 and C36 structures. They have found that the ferrimagnetic state with the C36 structure was the most favourable ground state. They have suggested that this state could be easily altered to C14 under low pressure (~few hundreds of Mpa). Therefore, there is an evident controversy, between experimental and theoretical studies. The theoretical ones that are most recent, suggest a new magnetic state that has not been already observed experimentally. In this framework, the magnetism of the $NbFe_2$ and has to be deeply reinvestigated, which is the main aim of this work.

The equilibrium diagram of the Fe-Nb-Zr system and the stability of the observed Laves phases (C15, C14 and C36) with their favourable magnetic states are not clearly established up tp now. These compounds have a close correlation between their atomic arrangements owing to their particularly comparable nearest-neighbour geometries and lattice types. The first aim of the present work is to establish a correlation between the magnetic properties and the structural stability of the $NbFe_2$, $Zr_{0.5}Nb_{0.5}Fe_2$ and $ZrFe_2$ compounds. As $NbFe_2$ presents still complex and questionable magnetic properties, a particular investigation is then considered. The second aim of this study is (*i*) to assess the formation energies and the vibrational entropies of C15, C14 and C36 which are helpful in discussing their problematic coexistence at high temperature and (*ii*) to predict the volume expansion, bulk modulus and Debye temperature evolution with temperature for each compound. These thermal properties are difficult and/or costly to obtain from experiments for complex structures such Laves phases at high temperature. For these purposes, the density functional density (DFT) calculations taking into account several magnetic configurations as well as the quasi-harmonic Debye model are used.

The present paper is organized as follows. The technical details of the DFT calculations and the quasi-harmonic Debye model are presented in Sec. 2. The main results are presented in Sec. 3. The obtained results are discussed in Sec. 4 while concluding remarks are given in Sec. 5.

2. Computational details

2.1. DFT calculations

The present study calculations were performed basing on the density functional theory (DFT) using pseudopotential method as implemented in the pseudo-potential plane wave self-consistent field package Quantum-Espresso [34]. The many-body problem of interacting electrons and nuclei was treated by using a series of one-electron equations, the so-called Kohn-Sham (KS) equations [35,36]. The generalized gradient approximation (GGA) of Perdew et *al.* (PBE) to the local density approximation was taken to include the exchange-correlation energy [37] and ultrasoft pseudopotentials of Vanderbilt were used [38]. These pseudopotentials explicitly treat $[3s^2 3p^6 3d^6 4s^2]$ state of Fe, $[4s^2 4p^6 4d^4 5s^1]$ state of Nb and $[4s^2 4p^6 4d^2 5s^2]$ state of Zr as valence states. A kinetic energy cut-off of 544 *eV* and a well converged value of the *k*-point mesh over the Brillouin zone were considered. Namely, $8 \times 8 \times 8$, $6 \times 6 \times 4$, $6 \times 6 \times 2$ for the C15, C14 and C36 structures, respectively. All structures were allowed to fully relax using Broyden-Fletcher-Goldforb-Shanno (BFGS) scheme [39] until the total energy has converged to less than 10^{-5} eV/atom. The maximum force has converged to lower than 0.004 *eV*/Å.

The Laves phases crystallize into one of the three topologically close-packed structures: cubic-C15 ($CuMg_2$), hexagonal-C14 ($MgZr_2$) and dihexagonal-C36 (MgNi2). For C14 and C36, we have considered a set of initial magnetic configurations. All the possible combinations were initially considered, by degenerating Wyckoff positions or/and by restraining the Fe magnetic moment value to zero as proposed in the literature [30–33]. Some representative results are reported in Table 1. However, the C4 and C5 configurations are only considered for NbFe2 as it exhibits a quite complex magnetic structure [30–32]. For C15, only the ferromagnetic configuration (*C1*) is taken into account. All the magnetic moments are along the *z*-axis.

2.2. Thermal properties within the quasi-harmonic Debye model

In order to take into account the temperature effect, the quasi-harmonic Debye model was applied [40]. Accordingly, the non-equilibrium Gibbs function $G^*(V,T,P)$ takes the following formulation:

$$G^*(V;T,P) = E(V) + pV + A_{vib}(T,\theta(V)), \tag{1}$$

where $\theta(V)$ is the Debye temperature, and the vibrational term A_{vib} can be expressed as:

$$A_{vib}(T,\theta(V)) = nkT\left[\frac{9}{8}\frac{\theta}{T} + 3\ln\left(1-e^{-\theta T}\right) - D(\theta/T)\right], \tag{2}$$

where $D(\theta/T)$ represents the Debye integral, n is the number of atoms per formula unit, k is the Boltzmann constant and T is absolute temperature. For an isotropic solid, the Debye temperature $\theta(V)$ is expressed as:

$$\theta = \hbar\left(6\pi^2 V^{1/2} n\right)^{\frac{1}{3}} f(\sigma)\sqrt{\frac{B_S}{k_B^2 M}}, \tag{3}$$

Where M is the molecular mass per formula unit, V the molar

Table 1
The magnetic configurations of C14 and C36 Laves structures. The up and down arrows represent the direction of the Fe local magnetic moment on each Wyckoff position along the *z* axis. The *C4* and *C5* configurations are only considered for $NbFe_2$.

Laves phases	Wyckoff position	*Z* coordinate	Magnetic configurations				
			C1	C2	C3	C4	C5
C14	Fe1 *2(a)*	*0*	↑	↑	↑	↑	0
		1/2	↑	↑	↑	↓	0
	Fe2 *6(h)*	*1/4*	↑	↓	↑	↑	↑
		3/4	↑	↓	↓	↓	↓
C36	Fe1 *6(h)*	*1/4*	↑	↓	↓	↑	↓
		3/4	↑	↓	↓	↑	↓
	Fe2 *6(g)*	*0*	↑	↓	↑	↑	↑
		1/2	↑	↓	↑	↑	↑
	Fe3 *4(f)*	*Z*	↑	↑	↑	↑	↑
		z + 1/2	↑	↑	↑	↑	↓
		z−1/2	↑	↑	↑	↓	↑
		−z	↑	↑	↑	↓	↓