

STRUCTURAL AND THERMAL PROPERTIES OF $Fe_2(Zr, Nb)$ SYSTEM IN C15, C14 AND C36 LAVES PHASES: FIRST-PRINCIPLES STUDY

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Abstract

The pseudopotential method (PP), based on Density Functional Theory (DFT) using the Generalized Gradient Approximation (GGA) was applied to investigate the $Fe_2(Zr, Nb)$ system within the three Laves phases structures: Cubic C15, Hexagonal C14 and C36. The effects of Nb concentration on structural, thermal and stability of the system were studied. The lattice parameters and bulk modulus of the three phases were predicted and showed a good agreement with the available experimental data. The rigidity of the Fe_2Nb was higher than the Fe_2Zr one for C15, C14 and C36. The energetic phase diagram of the systems was also established by determining the heat formation of the different phases. The obtained results showed that the Laves phases have close formation energies which suggests that the C15, C14 and C36 phases can co-exist at low-temperature. Finally, the temperature effect on the structural parameters, thermal expansions, heat capacities and Debye temperatures are determined from the non-equilibrium Gibbs functions and discussed accordingly.

Keywords : *Debye's Quasi Harmonic Model, First-principles calculations, Laves phases, PP method.*

Résumé

La méthode du pseudopotentiel (PP), sur la base de théorie fonctionnelle de densité (DFT) en utilisant le Generalized Gradient Approximation (GGA) a été utilisée pour étudier le système $Fe_2(Zr, Nb)$ dans les trois Laves phases structures: Cubic C15, Hexagonal C14 et C36. Les effets de la concentration sur la structure de Nb, thermique et la stabilité du système ont été étudiés. Les paramètres de maille et module de masse des trois phases ont été prévues et ont montré un bon accord avec les données expérimentales disponibles. La rigidité de la Fe_2Nb est plus élevée que celle de Fe_2Zr pour C15, C14 et C36. Le diagramme de phase dynamique des systèmes a également été établi en déterminant la formation thermique des différentes phases. Les résultats obtenus ont montré que les phases de Laves ont près énergies de formation qui suggère que les phases C15, C14 et C36 peuvent coexister à basse température. Enfin, l'effet de la température sur les paramètres structurels, des dilatations thermiques, les capacités de chaleur et des températures de Debye sont déterminées à partir des fonctions de Gibbs non-équilibre et discuté en conséquence.

Mots clés: *Modèle quasi harmonique de Debye, premiers principes calculs, Laves phases, méthode PP.*

ملخص

الكلمات المفتاحية:

وقد تم تطبيق الطريقة (PP) pseudopotential ، على أساس الكثافة النظرية الوظيفية (تجهيز الدوائر) باستخدام المعجم التدرج التقريب (GGA) للتحقيق في نظام لل Fe_2 (عنصر الزركون، ملحوظة) ضمن ثلاثة Laves مراحل الهياكل: مكعب C15، سداسي C14 و C36. تم دراسة تأثير تركيز ملحوظة على الهيكلية، والحرارية واستقرار النظام. وتوقع المعلمات شعيرية ومعامل الحجم من المراحل الثلاث وأظهر اتفاق جيد مع البيانات التجريبية المتاحة. وكانت صلابة من Fe_2Nb أعلى من واحد Fe_2Zr لـ C15، C14 و C36. تأسست الرسم البياني مرحلة حيوية من الأنظمة أيضا تحديد تشكيل الحرارة للمراحل المختلفة. أظهرت النتائج المتحصل عليها أن مراحل Laves لها الطاقات تشكيل وثيقة مما يوحي بأن مراحل C15، C14 و C36 يمكن بالتواجد في درجات الحرارة المنخفضة. وأخيرا، يتم تحديد تأثير درجة الحرارة على المعلمات الهيكلية، التوسعات الحرارية، والقدرات الحرارة ودرجات حرارة ديباي من وظائف جيبس عدم التوازن ومناقشتها وفقا لذلك.

كلمات البحث: ديباي في شبه متناسق النموذجي، أول مبادئ الحسابات، Laves مراحل، طريقة PP.

I. INTRODUCTION

Laves phases have been considered for many important and attractive applications, such as superconducting materials, giant magneto-strictive materials and hydrogen storage materials, because they have excellent physical and chemical properties [1-4]. Recently, Laves phases have also been investigated for high-temperature structural applications due to their high melting point, high strength and reasonably good oxidation resistance at elevated temperatures [4]. Although several calculation methods have been successively applied to predict the stable ground state structure of various Laves phases, these calculations are always limited to only one structure type at the stoichiometric composition, and very often restricted to 0 K [1]. However in real systems the stability of Laves phase type is a function of temperature and composition and also different Laves phases types may coexist in a single system [1]. In order to avoid these limitations, the Pseudo-Potential (PP) method is applied in the present work to investigate the stability and structural properties of $\text{Fe}_2(\text{Zr},\text{Nb})$ system within the three Laves phases structures. In addition, the quasi-harmonic Debye model [5], which is added within the framework of the PP method, is used to reproduce the temperature effects. Thus, the aim of this work is threefold: (i) testing the validity of the quasi-harmonic Debye model using the total energy and molar volume set obtained with the (PP) method and making it suitable for a large number of solids, (ii) highlighting the stability of $\text{Fe}_2(\text{Zr},\text{Nb})$ Laves system, and (iii) giving structural and vibrational properties of this phases since there is a lack in experimental data .

II. COMPUTATIONAL METHODS

Ab initio calculations

All calculations in this study were done using the density functional theory (DFT) using pseudopotential method as implemented in the pseudo-potential plane wave self-consistent field package Quantum Espresso [6]. The many-body problem of interacting electrons and nuclei was mapped to a series of one-electron equations, the so-called Kohn-Sham (KS) equations [7-8]. The generalized gradient approximation (GGA) of Perdew et al. (PBE) to the local density approximation was taken to include the exchange-correlation energy [9] and ultrasoft pseudopotentials of Vanderbilt were used [10]. A well converged value of the cut-off energy and the k -point mesh over the Brillouin zone were considered. All structures were allowed to fully relax using Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme [11] 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.

Thermal properties within the Quasi-harmonic Debye model

In order to take into account the temperature effects, the quasi-harmonic Debye model has been applied [5]. Accordingly, the non-equilibrium Gibbs function $G^*(V, T, P)$ takes the following formulation:

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

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

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

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. The non-equilibrium Gibbs function $G^*(V, P, T)$ as a function of V , P and T can be minimized with respect to volume V :

$$\left(\frac{\partial G^*(V; p, T)}{\partial V} \right)_{p, T} = 0 \quad (3)$$

By solving Eq.(3), we get the associated thermal properties for different temperatures and pressures.

III. RESULTS AND DISCUSSION

In order to determine the static structural parameters at 0 K, a set of total energy versus total volume calculations was carried out for the Fe_2Nb and Fe_2Zr compounds in C15, C14 and C36. The corresponding values were fitted with the universal Birch-Murnaghan equation of state [12]. The lattice parameters, (c/a) ratios, Bulk Moduli, as well as the heats of formation of the studied compounds are presented in Tables 1, and when available, some experimental and theoretical data are given.

TABLE I: STRUCTURAL PROPERTIES of Fe_2Nb AND Fe_2Zr COMPOUNDS

Phases	Structure	a (Bohr)	c/a	B (Gpa)	ΔH_f
Fe_2Nb	C14	9.14	1.627	153	-0.11(7)
		Exp 9.11 ^{13,14}	1.633	/	/
	C15	12.90	/	166.1	-0.11(1)
	C36	9.13	3.262	159.2	-0.11(2)
Fe_2Zr	C14	9.45	1.629	143.6	-0.27(0)
		13.34			
	C15	Theo 13.25 ¹⁵	/	139.5	-0.28(8)
		Exp 13.31 ^{13,14}			
	C36	9.44	3.262	141.3	-0.276(7)
		Exp 9.36 ^{13,14}	3.256		

From this TABLE I, the predicted lattice parameters of the C14- Fe_2Nb , C15- Fe_2Zr and the C36- Fe_2Zr are very consistent with those measured experimentally by X-ray diffraction [13,14] as well as with those calculated from theoretical methods [15] (FP-LAPW). However, according to our knowledge, there have been no available experimental values of the bulk moduli of the named compounds. But considering our results, we remark that Fe_2Zr is less compressible than Fe_2Nb on the same kind of structure.

The groundstate of each compound, was determined from the evaluation of the formation energies. The formation energy is calculated as the difference between the Laves phase total energy and the sum of the total energy of the constituents in their corresponding ground state structure (bcc-Fe, hcp-Zr and bcc-Nb). For each structure

(C14, C15 and C36), the last column in Table I, lists the formation energies of the two studied compounds. As a first remark, the obtained values are always negatives, showing that the formation of the C14, C15 or C36 phases is favored compared to the phase separation. Moreover, the C15 structure is the most stable for the Fe_2Zr compound, while it is difficult to predict from our results (At 0 K), which of the three Laves structures is the most stable for the Fe_2Nb one, because the heats of formation values are very closes. This small variation is related to the close relation between the structures of the three Laves phase polytypes, which results in very similar nearest neighbor geometries [4]. This is in good agreement with former calculations of the structural energies, by various pseudo potential or model potential calculations and e.m.f measurements [4]. Therefore, the stability of a particular crystal structure type depends sensitively on temperature, composition (deviation from stoichiometry or presence of impurities) and also different Laves phase types may coexist in a single system.

Using a given set of total energy versus molar volume values, $E(V)$, and a numerical EOS, the thermal properties of Fe_2Nb and Fe_2Zr within the three laves phases structures were obtained. As a first remark, the lattice parameters and bulk moduli obtained with a numerical EOS, at $T=0 K$ (static case), for the three Laves Structures are in fairly good agreement with the murnaghan EOS and the available experimental and theoretical results (see Table.1). The effects of temperature on the volume and Bulk moduli of each compound are shown in fig.1 (a) and (b) respectively

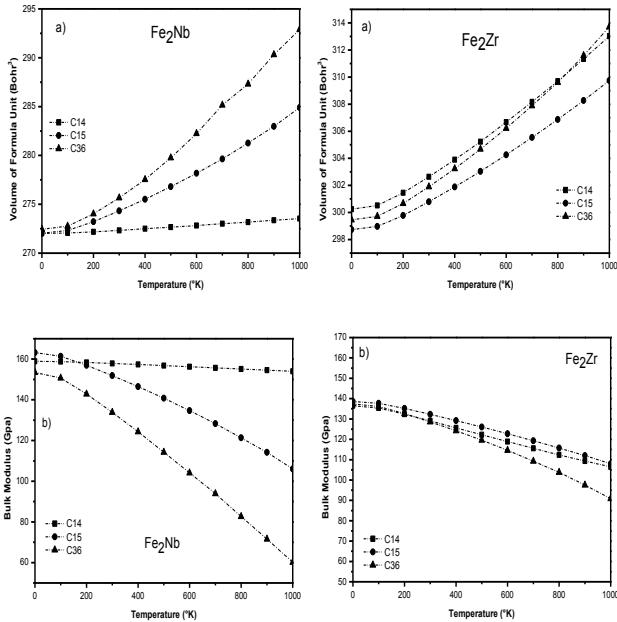


Fig. 1. Temperature effects on the a) Volume and b) Bulk moduli of Fe_2Zr and Fe_2Nb Laves Phases

As shown in the Figure I, The volume of Fe_2Nb and Fe_2Zr within the different structures increases with increasing temperature but the rate of increase is more important in the case of C36 structure of the First compound, whereas, the effect of temperature on the C14- Fe_2Nb

compound volume are very moderate. In terms of bulk modulus, the unique remark is that the C14- Fe_2Nb compound is insensitive to the temperature variations, as its value at 1000 K is still about 154 Gpa.

Another vibrational property is the heat capacity. The Figure 2, shows the evolution of this parameter with temperature of the two compounds Fe_2Nb and Fe_2Zr , within the three Laves phases structures.

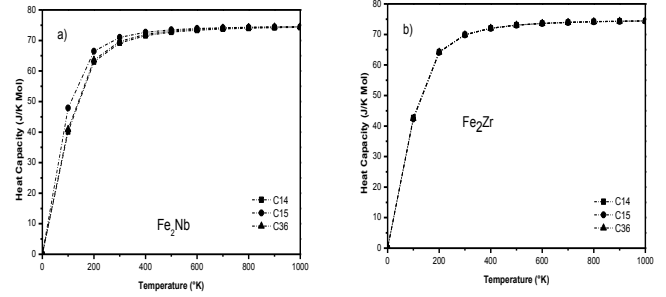


Fig.2 Heat capacity variation with temperature of Fe_2Nb and Fe_2Zr Laves phases.

We remark that, the evolution is similar for the different alloys. It follows the Debye model at low temperature (0-300 K) ($CV(T) \sim T^3$) and the classical behavior ($CV(T) \sim 3R$ For mono-atomic solids) is found at sufficient high temperatures; obeying Dulong and petit's Rule. The specific heat capacity of the different materials at sufficient high temperature does not depend much on temperature and tends to approach 75 J mol⁻¹ K⁻¹.

IV. CONCLUSION

The pseudopotential DFT method as well as the Debye model is used to give new insights on structural and thermal properties of three Laves phases of Fe-Nb-Zr system. The main results can be summarized as follows:

- The calculated lattice parameters and bulk modulus of Fe_2Zr and Fe_2Nb are in good agreement with available experimental data.
- Fe_2Zr is less compressible than Fe_2Nb on the same kind of structure.
- The calculated heats of formations show that the Fe-Zr-Nb system favors binary Fe_2Zr and Fe_2Nb compounds formation over phase separation. In addition, it is difficult (At 0 K) to predict, which of the three Laves structures is the most stable for a given compound, because the heats of formation values are very closes.
- The use of the quasi-harmonic Debye model was successfully applied to determine the thermal properties of the Fe_2Nb and Fe_2Zr Laves phases in the 0-1000 K temperature range. Significant differences in properties are obtained Above 300 K.
- The C14- Fe_2Nb compound is insensitive to the temperature variations.

Finally, the approach presented here is a promising alternative for the determination of several properties in complex structures that are difficult and/or costly to obtain from experiments.

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