Effect Of Interstitial Atom X On Structural, Elastic And Electronic Properties of NbRu$_3$, NbXRu$_3$ WITH (X= B or C).

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Abstract— **We report results obtained from first principle calculations of NbRu$_3$, NbBRu$_3$ and NbCRu$_3$ compounds with antiperovskite structure. The estimated equilibrium lattice parameters are in agreement with the experimental ones. Elastic constants C_{ij} for single crystal are calculated, then polycrystalline elastic moduli (bulk, shear and Young moduli, Poisson ration, anisotropy factor) are presented. Based on Debye model, Debye temperature Θ_D is calculated from the sound velocities V_l, V_t and V_m. Band structure results show that the compounds under study are electrical conductors and the conduction mechanism is assured by Ru-d electrons. Bonding nature and bonds strength are discussed based on the partial densities of states, population analysis and the electronic charge distribution.**

Keywords— **Intermetallic compounds, Ab initio calculations, Elastic properties**

Introduction

Inverse-perovskites borides, carbides or nitrides have shown interesting and exceptional properties, like superconductivity [1, 2], negative thermal expansion [3, 4], giant magnetoresistance [5, 6] and high temperature resistant [7] . These compounds have the general formula M$_3$AX [1] where X is either B, C or N. While both of M and A are metal atoms. The unit cell is cubic with M elements at *3c* (1/2,1/2,0), A elements at *1a* (0,0,0) and X elements at *1b* (1/2,1/2,1/2). The interest to the antiperovskite AXM$_3$ has been raised by the discovery of superconductivity for Ni$_3$MgC at 8 K [8], nevertheless and then many experimental and theoretical studies were carried to investigate the origin of this behaviour [9]. Several studies were published on the synthesis of possible new borides based antiperovskite. Shaack *et al.* [10] have succeeded to fabricate many intermetallic perovskite borides and carbides in the ternary systems AXM$_3$. The hardness as afunction of the continuous solid solution ScRh$_3$B$_x$C$_{1-x}$ was studied by Shishido *et al.* [11], they found that the microhardness increases with increasing boron content. In addition to the aforementioned experimental studies, theoretical works are carried out to accomplish the investigation of the physical properties of these antiperovskites compounds [12-20]. The study of the chemical bonding in roughly 20 boron-based antiperovskites RM$_3$B shows an alternating covalent-ionic and metallic bonding in these compounds [12]. The substitution effect on electronic structure of MgXNi$_3$ (X=B, C and N) was discussed [13], Electronic structure and lattice parameters of RPd$_3$B$_x$ (with R: rare earth metal) [14] and RRh$_3$B$_x$C$_{1-x}$ (R=Sc, Y) [15] were studied according to the boron content. Mechanical and optical properties of Sc$_3$InX (X=B, C and N) [16]. Kellou *et al.* [17] reported a detailed work on structural and thermal properties of Fe$_3$Al and Fe$_3$AlX (X=H, B, C, N, O) compounds. They showed that C addition on Fe$_3$Al has the highest effect of the strengthening cohesive energy, then the Fe$_3$AlC is the most stable while Fe$_3$AlH and Fe$_3$AlO are relatively meta-stable. Using first principle method, A. Bouhemadou [18] has studied the pressure effect on the structural and elastic properties of RCRh$_3$ (R=Sc, Y, La and Lu) up to 25 GPa therefore numerical estimations of bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Lame's coefficients, average sound velocity and Debye temperature have been obtained for polycrystalline RCRh$_3$. ACRu$_3$ (A=V, Nb and Ta) have shown a good structural stability up to 50 GPa [19], according to the band structure calculations these compounds are electrical conductors and they are bonded by a mixture of covalent, ionic and metallic bonds. Depending on the type of A sublattices (A= Zn, Ca, Al, Ga, In, Ge, Hg, Sn, Cd, Pb, Ag, Sc, Ti, Y, Nb, Mo, and Ta), Pd- and Pt- based ternary carbides have demonstrated a rich variety of mechanical and electronic properties [20].

In this study, we report the effect of boron and carbon addition on the structural, elastic and electronic properties of NbRu$_3$. These compounds have an inverse-perovskite structure, in which Nb atoms occupy primitive cubic sites, Ru atoms fill the fcc positions and B or C located at the bcc [1, 10]. After this introduction, the computational details were presented in section 2. In section 3, various results of NbRu$_3$, NbBRu$_3$ and NbCRu$_3$ such as lattice parameters, single crystal elastic constant C_{ij}, polycrystalline elastic moduli were discussed. In addition the electronic properties and chemical bonding are also investigated. This work was finished by a conclusion in section 4.

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I. CALCULATIONS METHOD

CASTEP (Cambridge Serial Total Energy Package) code [21] was used to perform this study. The problem of fundamental eigenvalue is resolved using the density functional theory [22] and the Kohn-Sham approach [23]. In the purpose of reducing the very important number of plane waves (PW), that's describe the electron functions, a fictive potential (pseudopotential) is generated to replace the real atomic potential [24]. Pseudo atomic calculations were performed with; B: $2s^22p^1$, C: $2s^22p^2$; Nb: $4s^24p^6\ 4d^45s^1$ and Ru: $4s^24p^6\ 4d^75s^1$. Local density approximation LDA with the CA-PZ functional [25] was used to calculate the exchange correlation energy. The Broyden- Fletcher- Goldfarb- Shanno (BFGS) algorithm [26, 27] was used to find the fundamental energy of the crystal. After careful convergence tests, we have used 10x10x10 irreducible k points to sampling the first Brillouin zone sampling [28]. The ultra-soft pseudopotential was employed [24] with a cut off energy $E_{cut\ off}$ = 380 eV. Calculations were done since the energy tolerance is about to 5.10^{-6} eV/atom, the maximum force is equal 0.01 eV/ Å, the maximum stress is lower than 0.02 GPa and a maximum displacement doesn't exceed 5.10^{-4}Å.

III. RESULTS AND DISCUSSION

A. *Structural and elastic properties*

Equilibrium lattice parameters of the studied compounds are listed in Table 1. We note the good agreement of our calculated lattice parameter *a* with the experimental ones [10], The deviation of calculated *a* from experimental ones varies from 1.3% for $NbCRu_3$ up to 2% for $NbBRu_3$. The addition of B and C atoms in the interstitial site (X) of $NbRu_3$ increases the lattice constant by about 4.6% and 4.1% respectively. When substitute B by C atom the calculations show that the equilibrium volume of $NbBRu_3$ goes from 64.08 $Å^3$ to 63.18 $Å^3$ for $NbCRu_3$, i.e. a reduction of about 1.4%. This decrease might be related to the difference in the atomic radii of B (8.5 Å) and C (7 Å) where B radii is about 17% higher than the C radii.

TABLE I THE CALCULATED LATTICE CONSTANTS AND SINGLE CRYSTAL ELASTIC CONSTANTS.

		NbRu$_3$	NbBRu$_3$	NbCRu$_3$
a (Å)	Our results Exp. [3] Other calc. [19]	3.825 3.880	4.001 3.921	3.982 3.928 4.045
v(Å^3)	Our results	55.98	64.08	63.18
C_{11}(GPa)	Our results Other calc. [19]	477	634	600 546
C_{44}(GPa)	Our results Other calc. [19]	202	160	155 150
C_{12}(GPa)	Our results Other calc. [19]	228	137	187 187

Results of elastic constants C_{ij} are carried out based on the finite elastic strain technique [29, 30]. Elastic stiffness of a cubic symmetry can be described using three independent elastic constants C_{11}, C_{12} and C_{44} [29]. Our results for C_{ij} are summarised in Table 1 with previous calculated data. The requirements for mechanical stability of the cubic system are [31]: $C_{11}-C_{12}>0$; $C_{11}+2C_{12}>0$ and $C_{44}>0$, these requirements are fulfilled by the values reported in Table 1. The highest value is that of C_{11} which reflects the high stiffness along the principal directions in the cubic structure, the value of C_{11} is higher than the shear elastic modulus C_{44} by about 57% for $NbRu_3$, 74% for both $NbBRu_3$ and $NbCRu_3$. By inserting B and C atoms in the interstitial sites X of $NbRu_3$, C_{11} (C_{44}) increases (decreases) by about 32% (20%) and 25% (23%) respectively. However the passage from $NbBRu_3$ to $NbCRu_3$ doesn't affect considerably the values of C_{11} and C_{44}. The observed overestimation between our results and those of Haddadi *et al.*[19] could be explained by the use of LDA, which well known to overestimate the elastic moduli of crystal as compared to the GGA [22].

Polycrystalline elastic constants are presented using only the Hill's assumption, which is defined as the arithmetic average of the Voigt and Reuss approximations [29]. The bulk modulus *B* gives information about resistance to volume changes. However, shear modulus *G* provides information on shape change resistance [29]. Our results for the bulk modulus *B*, shear modulus *G*, tetragonal shear modulus $G'= (C_{11} - C_{12})/2$, Young's modulus *Y*, Poisson's ratio *P*, anisotropy factor *A* and Pugh's criterion *B/G* for the ductility or brittleness are summarized in Table 2.

TABLE II POLYCRYSTALLINE ELASTIC MODULI; BULK MODULUS *B*; SHEAR MODULUS *G*; TETRAGONAL SHEAR MODULUS; YOUNG'S MODULUS *E*; POISSON'S RATIO *P*; ANISOTROPY COEFFICIENT *A*; PUGH'S CRITERION *B/G*; DENSITY *P*; SOUND VELOCITIES V_L, V_T, V_M AND DEBYE TEMPERATURE Θ_D.

	NbRu$_3$	NbBRu$_3$	NbCRu$_3$
B(GPa)	311	303	325; 307[19]
G(GPa)	166	191	173; 161[19]
G'(GPa)	124	248	206
E(GPa)	422	473	440; 412[19]
P	0.2734	0.2395	0.2739; 0.2762[19]
A	1.62	0.64	0.75; 0.839[19]
B/G	1.87	1.58	1.87; 1.9[17]
$\rho(gcm^{-3})$	11.7499	10.5447	10.7258; 10.4758[17]
$V_l(ms^{-1})$	6730	7272	7197; 7085[19]
$V_t(ms^{-1})$	3758	4255	4471; 3958[19]
$V_m(ms^{-1})$	4184	4719	4471; 4407[19]
$\theta_D(K)$	445	480	457; 559[19]

The bulk modulus of $NbRu_3$ is 311GPa. When adding B atom to this compound, the bulk modulus decreases by about 2.5%, however, it increases by about 4.5% when inserting C atom. According to our results, we observe an increase of the bulk modulus when going from $NbBRu_3$ to $NbCRu_3$, these results agree with the relation between the lattice parameter and the bulk modulus (*B* α *1/V*) [32]. The resistance to shape change *G* is about 46% lower than the resistance to volume change *B* for $NbRu_3$ and $NbBRu_3$ and about

34% for NbCRu$_3$. The highest resistance to shear deformation (G or G') is that of NbBRu$_3$. Moreover, the sequence $B>G>G'$ clearly demonstrates that the mechanical stability of the binary NbRu$_3$ is limited by the tetragonal shear modulus G'. However, in the ternary NbBRu$_3$ and NbCRu$_3$ the mechanical stability is limited by the shear modulus G (i.e. $B>G'>G$). Our results for NbCRu$_3$ are in good agreement with those reported in [19].

Young's modulus E describes the behavior of a material versus one directional stress and gives a measure of the stiffness. NbBRu$_3$ presents the higher stiffness, however NbRu$_3$ presents the lower one. As reported by Haines *et al*. [33], a Poisson's ratio of around 0.25 corresponds to predominate ionic bonding, while values around 0.33 reflect the presence of metallic bonding. The obtained values of $0.2395 < P < 0.2739$ confirm the existence of ionic bonds in these compounds.

For isotropic materials $A = 1$, and any deviation of A from unity suggests the elastic anisotropy [29]. The obtained results show that the anisotropy factor deviates from the unity, then our compounds are all elastically anisotropic. The Pugh's factor B/G expresses the malleability of a material. The B/G values higher than 1.75 indicate a ductile behavior, while the values lower 1.75 indicate brittleness [34]. Our calculated values of B/G for NbRu$_3$ and NbCRu$_3$ are slightly higher than the critical value separating brittleness from ductility, which is in good agreement with the low resistance to shear deformation. In opposite, NbBRu$_3$ can be classified as brittleness compound with Pugh's criterion of about 1.58. Note that there is a good agreement of our results with those reported in [19] for NbCRu$_3$.

Based on Debye's model [35], we have calculated the Debye's temperature Θ_D from the longitudinal V_l and the transversal V_t velocities of the elastic waves as shown in Table 2. Longitudinal wave velocity V_l is approximately 40% higher than V_t, and the average sound velocity V_m is inversely proportional to the density ρ. As compared to NbRu$_3$, the density ρ of NbBRu$_3$ (NbCRu$_3$) increases by 10% (8.7%), while the Debye's temperature decreases by 7.8% (2.6%). Therefore, and according to the relation between the melting temperature (T_m) and the Debye's one ($T_m \ \alpha \ \theta_D$) [35], we can suggest that NbBRu$_3$ has the higher melting temperature.

B. *Electronic properties and chemical bonding*

The calculated energy band structure at equilibrium lattice parameters for NbRu$_3$, NbBRu$_3$ and NbCRu$_3$ along the high symmetry directions in the Brillouin zone is shown in Fig.1. It can be assessed that there is no gap at the Fermi level E_F, at the vicinity of E_F it exists an overlapping of bonding and antibonding states. As results NbRu$_3$, NbBRu$_3$ and NbCRu$_3$ will exhibit metallic properties. At the Fermi level E_F, the total density of state (TDOS) for NbRu$_3$, NbBRu$_3$ and NbCRu$_3$, are 3.96, 1.43 and 3.36 (states / unit cell. eV) respectively. Thus there is an important decrease in the TDOS at E_F from NbRu$_3$ to NbBRu$_3$. At lower energy level, the band structure of NbRu$_3$ is formed from d electrons of Nb and Ru atoms. Boron and Carbon didn't contribute to the TDOS at the Fermi level and therefore are not included in the conduction properties. Ru-d electrons are mainly contributing to the TDOS at the Fermi level, and should be involved in the conduction properties. Valence band curves of NbBRu$_3$ and NbCRu$_3$ are moved to lowest energy level owing to more electronegativity of Boron and Carbon atoms. The valence band structure of NbBRu$_3$ and NbCRu$_3$ is formed from two parts. The lower part is derived from B-s, and Ru-d electrons. The upper section is derived from d electrons of Nb and Ru atoms. The conduction band is built from d states of Nb and Ru atoms, with a minor contribution from p states of Nb, Ru, B and C atoms.

To provide a deeper study on the bonding properties, we have studied the partial density of states. Fig.2 shows a strong hybridization of Ru-d and Nb-d states from -5 eV till Fermi level. We observed a forte hybridization Ru-d and B-p at -10 eV for NbBRu$_3$, and Ru-d and C-p at -13 eV for NbCRu$_3$, the later hybridization locates at deeper energy level, and then these bands are the stiffest in these compounds.
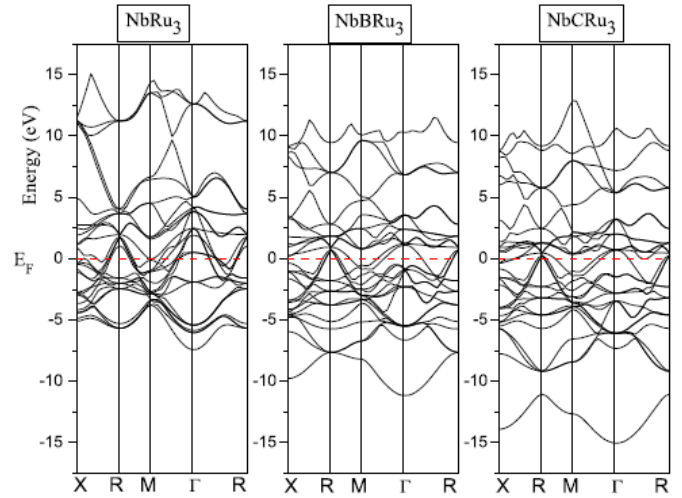

Fig. 1 Calculated band structure for NbRu$_3$, NbBRu$_3$ and NbCRu$_3$.

To give a good comprehension of the bonding in these compounds, we have calculated the overlap population for nearest neighbors in the crystal (Table 3). Positive values express bonding states between atoms, while negative values show antibonding states [36, 37]. The present calculations reveal a positive overlapping population between Ru—Ru, B—Ru and C—Ru bonds of NbRu$_3$, NbBRu$_3$ and NbCRu$_3$ respectively, then the present bonds are in bonding state. Moreover, the high overlap value, the high degree of covalency in the bond [38]. According to the values reported in Table 3, these bonds are strong and of covalent type. On the other side, the difference in electronegativity between Ru, Nb , B and C atoms gives rise to a charge transfer and an ionic bonds will be occurred. Important charge transfer between Ru and Nb atoms causes a strong ionic bonding in NbRu$_3$. For NbBRu$_3$ and NbCRu$_3$ the charge transfer from Nb atoms toward Ru is lessening, and then the ionic bonding is weakened. An important charge transfer from Nb towards both B and C atoms leads to a strong ionic bonding Ru—B and Ru—C. Strengthen Ru—B and Ru—C bonds and weaken Ru—Nb bonds give us a good explanation of the calculated bulk moduli for the under study compounds.
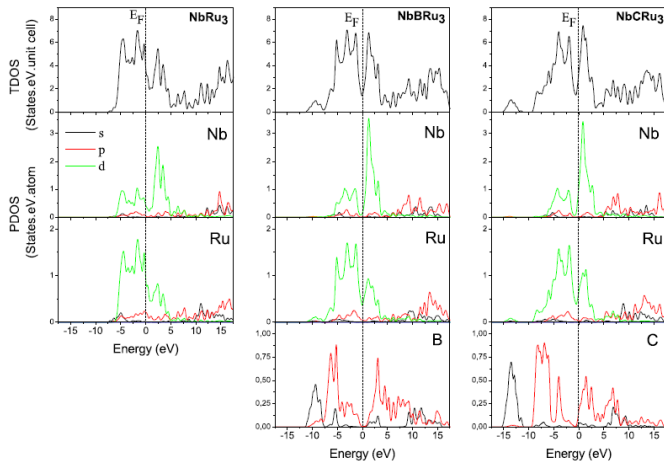
Fig. 2 Calculated total and partial density of states
(respectively TDOS and PDOS) for $NbRu_3$, $NbBRu_3$ and $NbCRu_3$.

TABLE III BOND LENGTH AND OVERLAP POPULATION FOR
NEAREST NEIGHBORS IN $NbRb_3$, $NbBRu_3$ AND $NbCRu_3$.

Compounds	Bonds	Bond length (Å)	Bond population (|e|)	Anion and cation charge (|e|)
$NbRu_3$	Ru—Nb	2.70498	-0.26	Ru: -0.18
	Ru— Ru	2.70498	0.42	Nb:0.57
$NbBRu_3$	Ru— Nb	2.82962	0.48	Ru: -0.05
	Ru— Ru	2.82962	-0.41	Nb: 0.69
	Ru—B	2.00084	0.50	B:-0.54
$NbCRu_3$	Ru—Nb	2.81637	0.40	Ru: -0.04
	Ru— Ru	2.81637	-0.49	Nb: 0.70
	Ru— C	1.99147	0.55	C:-0.58

We have extended our investigation of the chemical bonding to the charge density distribution in these compounds. We have illustrated the valence charge density in the upper panel for the (110) plane, and for (002) plane in the lower panel, as presented in Fig.3. For $NbRu_3$ the electrons are shared between Ru and Nb atoms. For $NbBRu_3$ and $NbCRu_3$, we can observe a forte directional charge distribution along Ru—B and Ru—C directions, the electrons are shared between Ru—B and Ru—C atoms, which is a characteristic of the covalent bonds. It can be observed that Ru—B and Ru—C bonds are stronger than Ru—Ru bonds in $NbRu_3$. Nb—Ru are less strong and of ionic nature, these results are in agreement with the observed hybridized states in Fig.2.
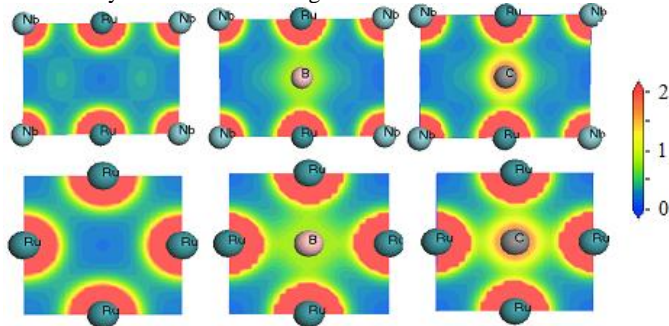

Fig. 3 Calculated charge density for $NbRu_3$, $NbBRu_3$ and $NbCRu_3$.

IV. CONCLUSION

Based on first principle calculations, we have presented a study on the effect of interstitial atom X on structural, elastic, electronic properties of $NbRu_3$, $NbXRu_3$ (X=B and C). The calculated lattice parameters are in agreement with previous experimental and theoretical data. Elastic constant of single crystal C_{ij} are in satisfactory agreement with the available theoretical data. Adding B and C atoms to $NbRu_3$ increases the elastic stiffness. It was found that $NbCRu_3$ has the higher bulk modulus, while $NbBRu_3$ has the higher Young modulus, $NbRu_3$ has the lower shear modulus. From the calculated band structure, total and partial densities of states, we have concluded that these compounds are good electrical conductors, where the electrical conductivity is assured by the Ru-d electrons. The results show different hybridizations between Ru-d—(B/C)-p, Ru-d—Nb-d and Ru-d—Ru-d. From Mulliken analysis of the overlap population and the valence charge density, the bonds in these compounds are mixture of covalent, ionic and metallic.

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