Stability and elastic properties of Nb_xC_y compounds*

Gao Xu-Peng(高旭鹏)[a], Jiang Ye-Hua(蒋业华)[a]†, Liu Yang-Zhen(刘洋赈)[a], Zhou Rong(周 荣)[a], and Feng Jing(冯 晶)[b]

[a] *Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming* 650093, *China*
[b] *School of Engineering and Applied Sciences, Harvard University, Cambridge, MA* 02138, *USA*

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Density functional theory (DFT) is applied to investigate the stability and mechanical properties of Nb_xC_y compounds. The structures of Nb_xC_y compounds are optimized, and the results are in good agreement with previous work. The calculated results of the cohesive energy and the formation enthalpy of Nb_xC_y show that they are thermodynamically stable structures, except for *Pmc*21-Nb_2C. The mechanical properties such as the bulk modulus, Young's modulus, the shear modulus, and Poisson's ratio are obtained by Voigt–Reuss–Hill approximation. The results show that the Young's modulus and shear modulus of NbC are larger than other Nb_xC_y compounds. The mechanical anisotropy is characterized by calculating several different anisotropic indexes and factors, such as universal anisotropic index (A^U), shear anisotropic factors (A_1, A_2, A_3), and percent anisotropy (A_B and A_G). The surface constructions of bulk and Young's moduli are illustrated to indicate the mechanical anisotropy. The hardness of Nb_xC_y compounds is also discussed in this paper. The estimated hardness for all Nb_xC_y compounds is less than 20 GPa.

Keywords: ceramic, carbides, anisotropy, hardness

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1. Introduction

Transition-metal carbides show excellent properties such as high temperature resistance, hardness, chemical, good thermal stability, thermal conductivity, and wear resistance. Nowadays these compounds have attracted people's interests and have been applied to the reinforcement of tools, catalysts, and the chemical and aviation industries.[1–6] Niobium carbides also show excellent properties such as a reinforced phase in the iron matrix, the hard coating on iron base alloys, and thin film for electrical contact applications.[7–10] Landsman *et al.* studied high-resolution neutron diffraction of Nb_6C_5 powders.[11] Zhi *et al.* discussed the effects of niobium on the as-cast microstructure of the hypereutectic and considered that NbC carbides were formed in the hypereutectic high chromium cast irons with the addition of Nb.[8] Recently, Du *et al.* researched biotemplating fabrication, mechanical and electrical characterizations of NbC nanowire arrays from the bamboo substrate high chromium cast iron, and demonstrated that Young's modulus of NbC nanowires was in the range from 281 GPa to 453 GPa.[12] Volodin *et al.* explored the structures and phase compositions of Nb–C deposited films using the methods of ion-plasma sputtering and the co-precipitation of ultradispersed Nb and C particles.[13] Khvan *et al.* described the thermodynamic assessment of Cr–Nb–C and Mn–Nb–C systems.[14] However, the stability and mechanical properties of Nb_xC_y compounds have not been systematically analyzed, and lacked theoretical research. In this paper, we studied the stability and mechanical properties of Nb_xC_y compounds by calculating various modulus, cohesive energy, formation enthalpy, and hardness using first principles calculations.

2. Methods and details

The whole calculations have been obtained using the first principles calculations based on density function theory (DFT) which is implemented in CASTEP code.[15–17] Ultrasoft pseudo potentials were used to optimize crystal structures and charactered the interactions between the ionic core and electrons. The effects of exchange correction energy were treated with the generalized gradient approximation (GGA) function developed by Perdew, Burke, and Ernzerhof (PBE).[18] The k-point mesh of the first irreducible Brillouin-zone was used in the Monkhorst-pack scheme. All calculations were used $8 \times 8 \times 8$, and the maximum energy cutoff was 360 eV for good convergence. The valence electron structures of Nb and C are $4d^35s^2$, and $2s^22p^2$, respectively. Different stoichiometric Nb_xC_y including different space groups: Fm-3m-NbC (cubic); *Pmc*21, P-3m1, and $P1m$1-Nb_2C (orthorhombic, trigonal, monoclinic, respectively); double $C12/m1$-Nb_6C_5 (monoclinic, including α-Nb_6C_5 and β-Nb_6C_5); Pm-3m-Nb_4C_3 (cubic) have been studied in this paper.

In order to investigate the stability of Nb_xC_y compounds, the cohesive energy and formation enthalpy were calculated according to

$$E_{\mathrm{coh}}(\mathrm{Nb}_x\mathrm{C}_y) = \frac{E_{\mathrm{total}}(\mathrm{Nb}_x\mathrm{C}_y) - xE_{\mathrm{iso}}(\mathrm{Nb}) - yE_{\mathrm{iso}}(\mathrm{C})}{x+y}, \quad (1)$$

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†Corresponding author. E-mail: jiangyehua@kmust.edu.cn
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$$\Delta_r H_m(Nb_xC_y) = \frac{E_{total}(Nb_xC_y) - xE_{bulk}(Nb) - yE_{bulk}(C)}{n}. \quad (2)$$

Here, E_{coh} and $\Delta_r H_m$ are the cohesive energy and formation enthalpy, respectively; E_{iso} refers to the total energy of an isolated Nb or C atom; $E_{total}(Nb_xC_y)$ is the total cell energy and E_{bulk} is the chemical potential of Nb or C atom in the bulk state, and n represents the total number of formula per cell. The crystal structures of Nb_xC_y are shown in Fig. 1.

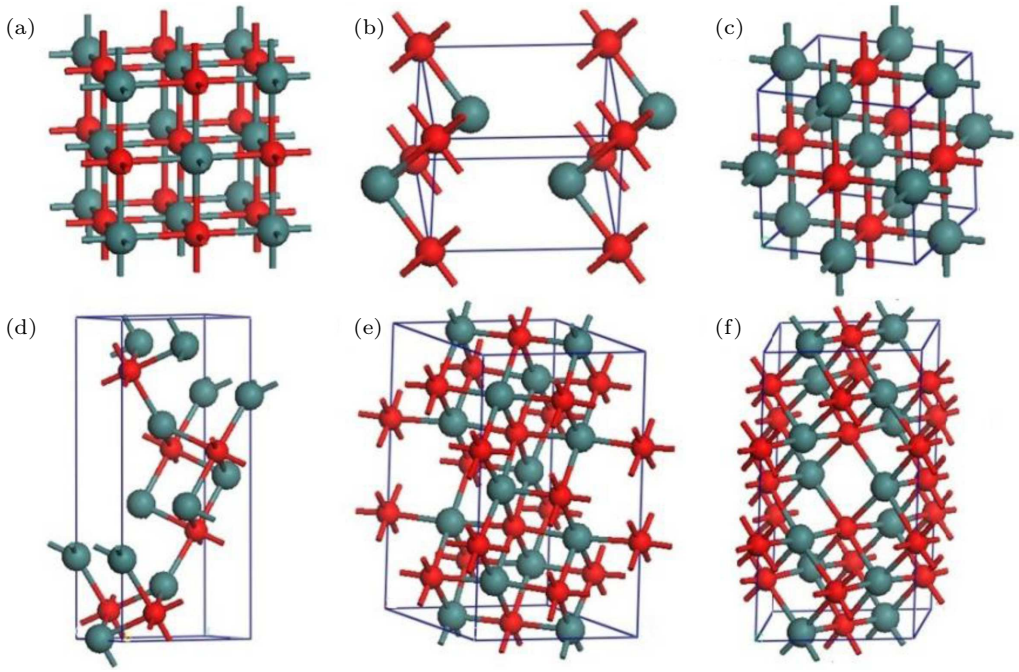


Fig. 1. (color online) The crystal structures of (a) NbC, (b) *P*-3*m*1-Nb_2C, (c) *Pm*-3*m*-Nb_4C_3, (d) *P*1*m*1-Nb_2C, (e) α-Nb_6C_5, (f) β-Nb_6C_5 compounds, respectively (red balls represent C atoms, gray balls represent Nb atoms).

3. Results and discussion

3.1. Cohesive energy and formation enthalpy

It is commonly believed that cohesive energy refers to the released energy of the crystals with a combination of free atoms. The structural stability of crystals is related to the cohesive energy and formation enthalpy. To compare the calculated results about the stability of phase, we have discussed them firstly.

Table 1 shows optimized lattice parameters, calculated cohesive energy, and formation enthalpy of Nb_xC_y compounds. Since the geometry optimizations were used by the GGA approach, the result of lattice constants may be overestimated. Nevertheless, it is notable that the theoretical values are all preferred to be obtained at 0 K rather than at room temperature in experimental results. As indicated in Table 1, we find the values of both cohesive energy and the formation enthalpy of *Pmc*21-Nb_2C compound are positive (48.4 and 57.66 eV/atom, respectively). It can be considered that *Pmc*21-Nb_2C cannot exist energetically at ambient pressure. Moreover, we can conclude that the calculated cohesive energy values are −9.83 eV/atom, −9.81 eV/atom, −9.79 eV/atom, −9.89 eV/atom, −9.93 eV/atom, and −9.74 eV/atom of NbC, *P*-3*m*1-Nb_2C, *P*1*m*1-Nb_2C, α-Nb_6C_5, β-Nb_6C_5, and Nb_4C_3, respectively. Therefore, the β-Nb_6C_5 is more stable than other compounds. In Ref. [19], Zhou *et al.* proposed that the stability of the compound is determined by formation enthalpy rather than cohesive energy.

Table 1. Calculated lattice parameters, cohesive energy, and formation enthalpy of Nb_xC_y compounds.

Compounds	Space group	Lattice parameters/Å						E_{coh}/(eV/atom)	$\Delta_r H_m$/(eV/atom)
		Theoretical parameter			Optimization parameter				
		a	*b*	*c*	*a*	*b*	*c*		
Nb_2C	*Pmc*21	10.920[a]	4.974	3.090	16.508	5.346	2.574	48.40	57.66
NbC	*Fm*-3*m*	4.4691[b]	4.4691	4.4691	4.4845	4.4845	4.4845	−9.83	−0.56
Nb_2C	*P*-3*m*1	3.125[c]	3.125	4.965	3.131	3.131	4.990	−9.81	−0.55
Nb_2C	*P*1*m*1	10.9391[d]	3.0989	4.9819	10.868	3.127	5.007	−9.79	−0.54
α-Nb_6C_5	*C*12/*m*1	5.460[e]	9.457	5.460	5.494	9.569	5.455	−9.89	−0.66, −0.639[h]
β-Nb_6C_5	*C*12/*m*1	5.447[f]	9.435	5.447	5.493	9.566	5.457	−9.93	−0.70, −0.639[h]
Nb_4C_3	*Pm*-3*m*	4.445[g]	4.445	4.445	4.4489	4.4489	4.4489	−9.74	−0.50, −0.445[h]

[a] Ref. [20], [b] Ref. [21], [c] Ref. [22], [d] Ref. [23], [e] Ref. [24], [f] Ref. [25], [g] Ref. [26], [h] Ref. [27].

The lower the negative values of formation enthalpy, the more stable the compound. Compared with the formation enthalpy of these compounds, we have found that the formation enthalpy value of β-Nb_6C_5 (-0.70 eV/atom) is the lowest, and the value of Nb_4C_3 (-0.50 eV/atom) is the largest, which are in good agreement with Ref. [27]. Therefore, one can believe that the compound of β-Nb_6C_5 is the most stable.

3.2. Elastic constants and modulus

As we all know, the elastic properties define the properties of materials undergoing stress, deforms, and recovers and returns to its originals shape after stress ceases. The mechanical property of a compound is characterized by the full set of elastic constants. The elastic constants were calculated, and the results were listed in Table 2.

Table 2. Calculated elastic constants (the unit is GPa) of Nb_xC_y compounds.

Compounds	Space system	Elastic constants												
		C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
Nb_2C	orthorhombic	79.0	78.1	465.2	12.9	−28.7	−20.4	9.4	38.2		36.1			
NbC	cubic	557.2			146.5			162.5						
Nb_2C	trigonal	425.7		526.3	78.5			129.3	108.2					
Nb_2C	monoclinic	358.5	338.5	326.4	39.0	89.6	116.0	130.1	125.6	−3.1	144.6	−0.9	−3.6	−1.4
α-Nb_6C_5	monoclinic	422.7	493.5	487.0	170.3	198.1	182.2	121.5	136.7	12.2	109.0	18.4	−11.7	25.4
β-Nb_6C_5	monoclinic	413.5	416.5	437.5	157.8	183.1	172.9	138.2	127.0	18.7	128.7	25.5	−21.7	27.2
Nb_4C_3	cubic	495.3			110.3			146.5						

From Table 2, we can easily find that the calculated C_{11} and C_{33} are very large among elastic constants, which indicates that they are very incompressible under uniaxial stress along the $x(\varepsilon_{11})$ or $z(\varepsilon_{33})$ axis. According to Born–Huang lattice dynamical theory, the mechanical stability criterions can be depicted as follows.[28,29]

The criteria for mechanical stability are given by (orthorhombic phase)

$$\begin{aligned}&C_{11}>0,\ C_{22}>0,\ C_{33}>0,\ C_{44}>0,\ C_{55}>0,\ C_{66}>0,\\&[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,\\&C_{11}+C_{22}-2C_{12}>0,\ C_{11}+C_{33}-2C_{13}>0,\\&C_{22}+C_{33}-2C_{23}>0.\end{aligned}$$

The criteria for mechanical stability are given by (trigonal phase)

$$\begin{aligned}&C_{11}>|C_{12}|,\ (C_{11}+C_{12})C_{33}>2C_{13}^2,\\&(C_{11}-C_{12})C_{44}-2C_{14}^2>0.\end{aligned}$$

The criteria for mechanical stability are given by (monoclinic phase)

$$\begin{aligned}&C_{11}>0,\ C_{22}>0,\ C_{33}>0,\ C_{44}>0,\ C_{55}>0,\ C_{66}>0,\\&(C_{22}+C_{33}-2C_{23})>0,\\&[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,\\&(C_{33}C_{55}-C_{35}^2)>0,(C_{44}C_{66}-C_{46}^2)>0,\\&[C_{22}(C_{33}C_{55}-C_{35}^2)+2C_{23}C_{25}C_{35}-C_{23}^2C_{55}-C_{25}^2C_{33}]>0,\\&g=C_{11}C_{22}C_{33}-C_{11}C_{23}^2-C_{22}C_{13}^2-C_{33}C_{12}^2+2C_{12}C_{13}C_{23},\\&\{2[C_{15}C_{25}(C_{33}C_{12}-C_{13}C_{23})+C_{15}C_{35}(C_{22}C_{13}-C_{12}C_{23})\\&\quad+C_{25}C_{35}(C_{11}C_{23}-C_{12}C_{13})]-[C_{15}^2(C_{22}C_{33}-C_{23}^2)\\&\quad+C_{25}^2(C_{11}C_{33}-C_{13}^2)+C_{35}^2(C_{11}C_{22}-C_{12}^2)]+C_{55}g\}>0.\end{aligned}$$

The criteria for mechanical stability are given by (cubic phase)

$$C_{11}>0,\ C_{44}>0,\ C_{11}>C_{12},\ C_{11}+2C_{12}>0.$$

One can observe that all elastic constants of Nb_xC_y compounds satisfy the above conditions except for Nb_2C of the orthorhombic phase, implying that they are mechanically stable without orthorhombic Nb_2C. It is the same conclusion for the stability of Nb_xC_y carbides by judging formation enthalpy. Hence, we can predict that *Pmc*21-Nb_2C with an orthorhombic phase is not a stable structure. Hence, other Nb_xC_y compounds are mechanically stable.

The mechanical properties are mainly determined by the modulus including the bulk modulus (B), Young's modulus (E), and the shear modulus (G) which can be obtained by Voigt–Reuss–Hill (VRH) approximation.[30] The VRH approximation is the average of the two bounds, namely the lower bound of Voigt and upper bound of Reuss, which is a method to estimate the mechanical properties of crystalline materials with elastic constants for single crystals[31]

$$B=\frac{1}{2}(B_{\rm V}+B_{\rm R}),\tag{3}$$

$$G=\frac{1}{2}(G_{\rm V}+G_{\rm R}),\tag{4}$$

$$E=\frac{9BG}{3B+G},\tag{5}$$

$$\sigma=\frac{3B-2G}{2(3B+G)},\tag{6}$$

where $B_{\rm V}$, $B_{\rm R}$, $G_{\rm V}$, and $G_{\rm R}$ are the bulk modulus and shear modulus, σ represents Poisson's ratio. The calculated formulas in the VRH method are dependent on the crystal symmetry, and the results of all moduli of Nb_xC_y binary compounds are shown in Table 3 (only list the stable structures).

Table 3. Bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio σ of Nb_xC_y compounds.

Compounds	Crystal system	Space group	Moduli/GPa				σ
			B	E	G	B/G	
NbC	cubic	Fm-3m	294.1	484.0	193.4	1.52	0.23
			300[a)]	488	198		0.22
Nb_2C	trigonal	P-3m1	229.3	310.0	121.6	1.89	0.27
Nb_2C	monoclinic	$P1m1$	202. 6	220.8	83.8	2.42	0.31
α-Nb_6C_5	monoclinic	$C12/m1$	237.1	426.0	177.4	1.34	0.20
β-Nb_6C_5	monoclinic	$C12/m1$	228.2	386.4	158.7	1.44	0.22
			234[b)]	395	162		0.218
Nb_4C_3	cubic	Pm-3m	262.7	340.5	132.6	1.98	0.28

[a)]Ref. [32], [b)]Ref. [27].

The obtained moduli values of Nb_xC_y compounds in Table 3 are in good agreement with Refs. [27]–[32], and we can identify that these compounds are mechanically stable.[33–36] From Table 3, we conclude that the largest bulk modulus is attributed to NbC and the value is 294.1 GPa, which is larger than other Nb_xC_y compounds. At the same time, we can see that the bulk modulus of $P1m1$-Nb_2C (202.6 GPa) is the smallest. To our knowledge, there is an enhancement of bulk modulus as compared with pure Nb metal (170 GPa). Comparing Young's modulus and the shear modulus with the carbon content, we find that Young's modulus E and shear modulus G increase monotonically with the carbon content, and reach the maximum values of 193.4 GPa and 484 GPa, respectively. What is more, C_{44} has the same changed trend with Young's modulus G and shear modulus E, shown in Fig. 2. The E value of NbC is the largest, but the corresponding B/G ratio is smaller. Referring to other literature, the chemical bonds in this compound with more ionic features may be the main reason.

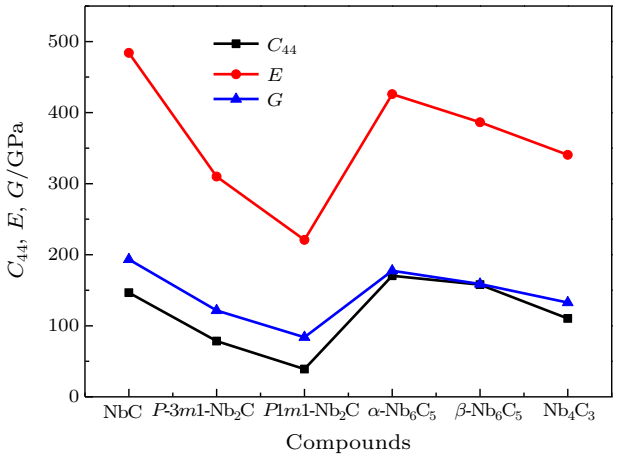


Fig. 2. (color online) The variations of shear modulus, Young's modulus, and C_{44} of the Nb_xC_y compounds.

According to Pugh's work,[37] the ratio of the bulk modulus to shear modulus (B/G) is used to indicate the brittle and ductile behavior of materials. A high (low) B/G value is consistent with ductility (brittleness). The critical value (B/G) which separates ductility from brittleness is about 1.75. From Table 3, B/G values vary from 1.34 to 2.42. The B/G values are 1.52, 1.89, 2.42, 1.34, 1.44, 1.98 of NbC, P-3m1-Nb_2C, $P1m1$-Nb_2C, α-Nb_6C_5, β-Nb_6C_5, and Nb_4C_3, respectively. On the basis of the criterion, we believe that P-3m1-Nb_2C, $P1m1$-Nb_2C, and Nb_4C_3 compounds have good ductility, while two kinds of Nb_6C_5 and NbC compounds show the brittleness functions. There are similar trends and predicted results of hardness and brittleness by B/G and G individually. Therefore, we may conclude that G is more closely related to hardness than the B.

Furthermore, the values of Poisson's ratio σ are applied to predict the ductility and brittleness of materials. The critical value which separates ductility from brittleness is about 0.26. More than (less than) 0.26 of σ is consistent with ductility (brittleness). From Table 3, Poisson's ratio σ numerical ranges from 0.20 to 0.31. We know that the σ values of P-3m1-Nb_2C, $P1m1$-Nb_2C, and Nb_4C_3 are all over 0.26, which illustrate their good ductility by our calculations. Meanwhile the other two kinds Nb_6C_5 and NbC compounds are in brittleness, which is inconsistent with the above analysis. To the best of our knowledge, the experimental values of Nb_xC_y crystal structure are rarely observed, and those results can be a fine reference for further investigation.

3.3. Elastic anisotropy

The elastic anisotropy of a crystal can be characterized by many different ways. In this paper, we calculate several anisotropic indices, such as the universal anisotropic index (A^U) and percentage of anisotropy (A_B and A_G). The equations used are shown in the following:

$$A^U = 5\frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0, \tag{7}$$

$$\begin{cases} A_B = \dfrac{B_V - B_R}{B_V + B_R}, \\ A_G = \dfrac{G_V - G_R}{G_V + G_R}. \end{cases} \tag{8}$$

It is clear that for an isotropic structure, all indices in Eqs. (7) and (8) are zero. The large deviations from zero indicate the high anisotropic mechanical properties. At the same time, the

Table 4. The calculated universal anisotropic index (A^{U}), percent anisotropy (A_G and A_B), and shear anisotropic factors (A_1, A_2, and A_3) of Nb_xC_y compounds.

Compounds	Crystal system	Space group	A^{U}	A_B	A_G	A_1	A_2	A_3
NbC	cubic	Fm-3m	0.108	0	0.011	1.052	0	0
Nb_2C	trigonal	P-3m1	0.733	0.003	0.068	0.427	0	0
Nb_2C	monoclinic	$P1m1$	0.871	0	0.080	0.360	0.954	1.062
α-Nb_6C_5	monoclinic	$C12/m1$	0.104	0.002	0.010	1.071	1.039	1.083
β-Nb_6C_5	monoclinic	$C12/m1$	0.152	0.001	0.015	1.057	1.228	1.249
Nb_4C_3	cubic	Pm-3m	0.256	0	0.025	0.891	0	0

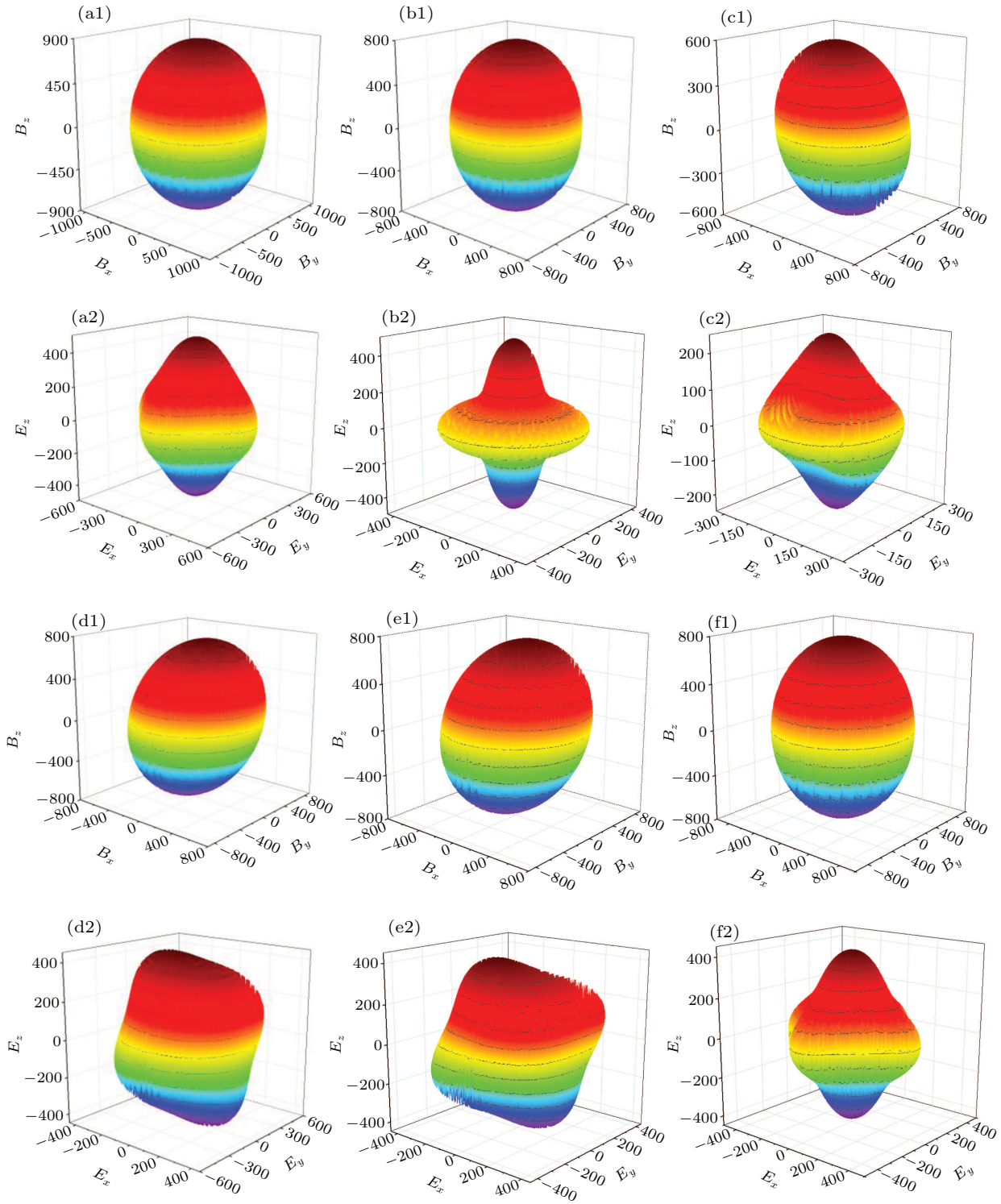


Fig. 3. (color online) The surface constructions of bulk modulus (B) and Young's modulus (E) for NbC ((a1) and (a2)); P-3m1-Nb_2C ((b1) and (b2)); $P1m1$-Nb_2C ((c1) and (c2)); α-Nb_6C_5 ((d1) and (d2)); β-Nb_6C_5 ((e1) and (e2)); Nb4C3 ((f1) and (f2)). The magnitude of bulk and Young's modulus at different directions is represented by the contour. For all graphs, the units are GPa.

shear anisotropic factors A_1, A_2, A_3 defined in the following were calculated and discussed:[38]

$$A_1 = \frac{4C_{44}}{C_{11}+C_{33}-2C_{13}}, \tag{9}$$

$$A_2 = \frac{4C_{55}}{C_{22}+C_{33}-2C_{23}}, \tag{10}$$

$$A_3 = \frac{4C_{66}}{C_{11}+C_{22}-2C_{12}}. \tag{11}$$

For anisotropic crystals, all three factors should be one. The results are shown in Table 4. The A^{U} values are 0.108, 0.733, 0.871, 0.104, 0.152, 0.256 for NbC, P-3m1-Nb_2C, $P1m1$-Nb_2C, α-Nb_6C_5, β-Nb_6C_5, Nb_4C_3, respectively. Hence, we can consider that the sizes of the order of elastic anisotropy for calculated Nb_xC_y are $P1m1$-Nb_2C, P-3m1-Nb_2C, Nb_4C_3, β-Nb_6C_5, NbC, α-Nb_6C_5. From all calculated anisotropic indices, it is easily concluded that the Nb_xC_y compounds show anisotropic mechanical properties. At the same time, one can easily find that A_{B} values for NbC, $P1m1$-Nb_2C, Nb_4C_3 are zero. It is because that B_{V} and B_{R} are equal.

The simplest way to illustrate the anisotropy of mechanical moduli is to plot them in three-dimensional space as a function of direction. Here, we plot the modulus and Young's modulus at different directions using spherical coordinates (Fig. 3).

In Fig. 3, we can clearly see that the Young modulus shows a strong anisotropic property for different orientations. On the other hand, the anisotropic property of the bulk modulus of Nb_xC_y compounds is less prominent than Young's modulus. The calculated anisotropic indices or factors are in agreement with these graphs.

In Fig. 4, we plot the projections of bulk and Young's moduli at different (001) and (110) crystal planes. It is very apparent that the anisotropy of the bulk modulus for different Nb_xC_y compounds has little change. However, the differences among the anisotropy of Young's modulus are very clear. On the (110) plane, the Young's modulus of $P1m1$-Nb_2C is more anisotropic than that of others, which are in good agreement with the calculated anisotropic factors or indices in Table 4.

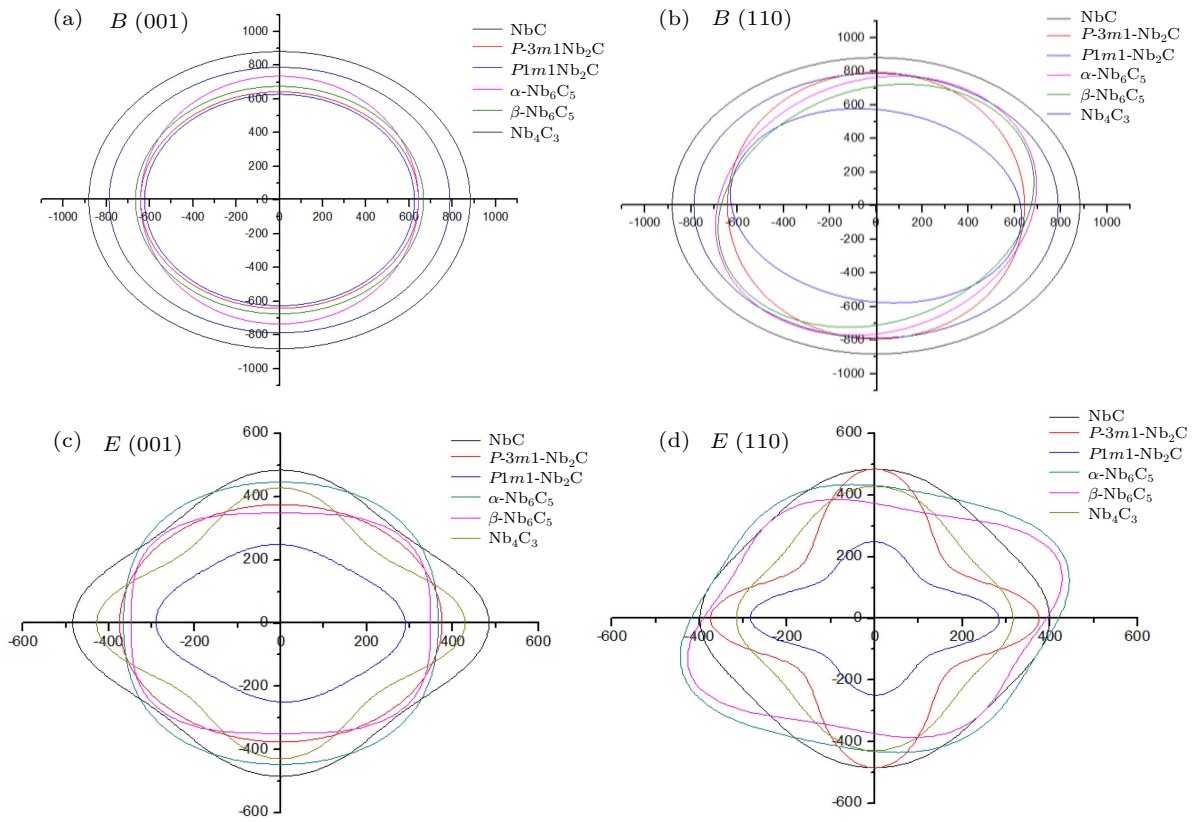


Fig. 4. (color online) The projections of bulk modulus (B) and Young's modulus (E) for the Nb_xC_y compounds at (001) and (110) planes. (a) B(001), (b) B(110), (c) E(001), (d) E(110),

3.4. Hardness

In this section, based on the previous work of Gao *et al.*,[39] the hardness of Nb–C bonds in each compound is evaluated and compared with each other. The following expressions are used for the bond hardness calculations:[40]

$$H_v^u\,(\mathrm{GPa}) = 740P^u\,(v_b^u)^{-(5/3)}, \tag{12}$$

$$v_b^u = \frac{(d^u)^3}{\sum_v\left[(d^v)^3 N_b^v\right]} = \frac{(d^u)^3}{\sum_v\left[(d^v)^3 \dfrac{N^v}{\Omega}\right]} = \frac{(d^u)^3\,\Omega}{\sum_v\left[(d^v)^3 N^v\right]}, \tag{13}$$

where H_v^u is the hardness of the u-type bond, d^u is the bond length, N_b^v refers to the v-type bond density per cubic angstroms, and N^v is the total number of v-type bonds in the

cell; Ω and P^u are the cell volume and overlap population of the v-type bond, respectively. Moreover, the hardness of Nb–Nb bonds and C–C bonds is not considered in this paper because the metallic bond hardness is hardly defined in the present method. While neglecting the hardness of Nb–Nb bonds and C–C bonds in the crystal, we can calculate the hardness of Nb_xC_y compounds using the expression

$$H = \left(\left(H^{\text{Nb–C}}\right)^N\right)^{1/N}. \tag{14}$$

Here, $H^{\text{Nb–C}}$ is the hardness of Nb–C bond, and N is the total number of v-type bonds in the cell. The calculations of the compound hardness are shown in Table 5.

Table 5. The predicted hardness of Nb_xC_y compounds and other parameters used in the calculation.

Compounds	Space group	Bond	d^u/Å	P^u	N^u	Ω/Å^3	v_b^u	H_u/GPa	H/GPa
NbC	Fm-3m (NO. 225)	Nb–C	2.24	0.76	12	90.19	7.52	19.48	19.48
Nb_2C	P-3m1 (NO. 164)	Nb–C	2.20	0.93	2	42.36	21.18	4.24	4.24
Nb_2C	$P1m1$ (NO. 6)	Nb–C	2.17	0.71	4	170.16	10.29	10.79	5.54
		Nb–C	2.18	0.75	4		10.43	11.14	
		Nb–C	2.19	0.25	4		10.58	3.63	
		Nb–C	2.23	0.17	2		11.17	2.25	
		Nb–C	2.24	0.16	2		11.32	2.08	
α-Nb_6C_5	$C12/m1$ (NO. 12)	Nb–C	2.10	0.49	4	269.67	3.81	39.01	19.52
		Nb–C	2.16	0.44	8		4.15	30.38	
		Nb–C	2.20	0.35	8		4.38	22.09	
		Nb–C	2.21	0.37	8		4.44	22.83	
		Nb–C	2.22	0.36	8		4.50	21.72	
		Nb–C	2.25	0.30	8		4.69	16.90	
		Nb–C	2.26	0.26	8		4.75	14.33	
		Nb–C	2.28	0.18	8		4.88	9.49	
β-Nb_6C_5	$C12/m1$ (NO. 12)	Nb–C	2.10	0.49	4	269.65	3.81	39.01	19.62
		Nb–C	2.16	0.44	8		4.15	30.38	
		Nb–C	2.20	0.35	8		4.38	22.09	
		Nb–C	2.21	0.37	8		4.44	22.83	
		Nb–C	2.22	0.36	8		4.50	21.72	
		Nb–C	2.25	0.30	8		4.69	16.90	
		Nb–C	2.26	0.27	8		4.75	14.88	
		Nb–C	2.28	0.18	8		4.88	9.49	
Nb_4C_3	Pm-3m (NO. 221)	Nb–C	2.22	0.65	6	88.06	9.78	10.75	11.71
		Nb–C	2.22	0.84	3		9.78	13.89	

From Table 5, we can easily find that the hardness of Nb_xC_y compounds is 19.48 GPa (NbC), 4.24 GPa (P-3m1-Nb_2C), 5.54 GPa ($P1m1$-Nb_2C), 19.52 GPa (α-Nb_6C_5), 19.62 GPa (β-Nb_6C_5), and 11.71 GPa (Nb_4C_3), respectively. The hardness of Nb–C bonds of Nb_6C_5 and NbC is significantly larger than that of other Nb_xC_y compounds. In Refs. [39]– [41], it is shown that the bond length and the cell volume were the main factors influencing the bond hardness. Comparing their results with our calculations, we find that the difference of Nb–C bond lengths of Nb_xC_y compounds is not obvious. On the contrary, the cell volume is very different among all Nb_xC_y compounds. The volumes of Nb_xC_y compounds with different crystal systems significantly affect the hardness rather than the bond length. Moreover, the estimated hardness for all Nb_xC_y compounds is less than 20 GPa, so we conclude that the calculated hardness of the niobium carbides is reliable. As a general rule, the compound with a high hardness also has a large bulk modulus.[41] As can be seen from Tables 3 and 5, the bulk modulus, shear modulus, hardness values of Nb_6C_5 (1) are 237.1 GPa, 177.4 GPa, and 19.52 GPa, respectively. We find that two kinds of Nb_6C_5 compounds have larger hardness at the same time with much larger shear modulus. However, there is no obvious trend for bulk modulus. Hence, the large bulk modulus is not a good indicator for the high hardness.

4. Conclusions

We calculated and discussed the stability and mechanical properties of Nb_xC_y compounds by using first principles based on the density functional theory method in this paper. The calculated cohesive energy and formation enthalpy indicate that the Nb_xC_y binary compounds are thermodynamically stable except for the $Pmc21$-Nb_2C compound. The mechanical properties such as the elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio σ of Nb_xC_y were calculated, and the calculated values are consistent with those in other references. It was found that

Young's modulus G and shear modulus E increase monotonically with the carbon content. Meanwhile, the mechanical stability of the Nb_xC_y compounds is very sensitive to shear stress. We also calculated several anisotropic indices and factors to characterize the mechanical anisotropy, such as the universal anisotropic index (A^U), shear anisotropic factors (A_1, A_2, A_3), and percent anisotropy (A_B and A_G). The results show that the shear modulus has strong anisotropic properties, and the bulk modulus is weakly directional dependent. The calculated surface constructions of bulk modulus and Young's modulus verified the results. In addition, the relationship among elastic constants, modulus, and hardness were discussed. The estimated hardness for all Nb_xC_y compounds is less than 20 GPa, which is in good agreement with the experimental data. Two kinds of Nb_6C_5 compounds have the larger hardness.

References

[1] Bazhanov D I, Mutigullin I V, Knizhnik A A, Potapkin B V, Bagaturyants A A, Fonseca L R C and Stoker M W 2010 *J. Appl. Phys.* **107** 083521
[2] Clayton J D 2010 *J. Appl. Phys.* **107** 013520
[3] Wittkowski T, Jung K, Hillebrands B and Comins J D 2006 *J. Appl. Phys.* **100** 073513
[4] Chen X R, Wang Y J and Chang J 2007 *Chin. Phys. Lett.* **24** 2642
[5] Zhang T, Liu B and Song Z T 2004 *Chin. Phys. Lett.* **21** 741
[6] Duo X Z, Men C L and Zhang M 2001 *Chin. Phys. Lett.* **18** 1282
[7] Farah A F, Crnkovic O R and Canale LC F 2001 *J. Mater. Eng. Perf.* **10** 42
[8] Zhi X H, Xing J D, Fu H G and Xiao B 2008 *Mater. Lett.* **62** 857
[9] Sen U 2004 *Mater. Chem. Phys.* **86** 189
[10] Sen U 2005 *Thin Solid Films* **483** 152
[11] Landesmant J P, Chtistensen A N, Denovion C H, Lorenzelli N and Convert P 1985 *J. Phys. C* **18** 809
[12] Du J, Yang Y C, Fan Z, Yang X, Cheng X J, Gan Y P, Hui H, Li X D, Xiao D L, Wen K Z and Xin Y T 2013 *J. Alloy. Compd.* **560** 142
[13] Volodin V N, Teleushev Y Z and Zhakanbaev E A 2013 *Physics of Metals and Metallography* **114** 395
[14] Khvan A V, Hallstedt B and Chang K 2012 *Calphad* **39** 54
[15] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** 864
[16] Segall M D, Lindan P J D and Probert M J 2002 *J. Phys.: Condens. Matter* **14** 2717
[17] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
[18] Perdew J P, Burke K and Emzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[19] Zhou C T, Xiao B, Feng J, Chen J C, Zhou R, Xing J D and Li Y F 2009 *Physica B* **404** 1701
[20] Yvon K, Nowotny H and Kieffer R 1976 *Monatshefte fuer Chemie und verwandte Teile anderer Wissenschaften* **98** 34
[21] Elliott R O and Kempter C P 1958 *J. Chem. Phys.* **62** 630
[22] Stroms E K and Krikorian N H 1960 *J. Phys. Chem.* **64** 1471
[23] Khaenko B V and Gnitetskii O A 1993 *Crystallography Rep.* **38** 55
[24] Remple A A and Gusev A I 1985 *Kristallografiya* **30** 1112
[25] Khaenko B V and Sivak O P 1990 *Kristallografiya* **35** 1110
[26] Zubkov V G, Dubrovskaya L B, Gel'd P V, Tskhai V A and Dorofeev 1969 *Doklady Akademii Nauk SSSR* **184** 874
[27] Wu L L, Wang Y C, Yan Z G, Zhang J W, Xiao F R and Liao B 2013 *J. Alloy. Compd.* **561** 220
[28] Wu Z J, Zhao E J, Xiang H P, Hao X F, Liu X J and Meng J 2007 *Phys. Rev. B* **76** 054115
[29] Haddou A, Khachai H, Khenata R, Litimein F, Bouhemadou A, Murtaza G, Alahmed Z A, Bin-Omran S and Abbar B 2013 *J. Mater. Sci.* **48** 8235
[30] Liu Y Z, Jiang Y H, Feng J and Zhou R 2013 *Physica B* **419** 45
[31] Feng J, Xiao B, Chen J, Du Y, Yu J and Zhou R 2011 *Materials Design* **32** 3231
[32] Brown H L, Armstrong P E and Kempter C P 1966 *J. Chem. Phys.* **45** 547
[33] Letsoalo T and Lowther J E 2008 *Physica B* **403** 2760
[34] Ahmed R, Aleem F E, Hashemifar S J and Akbarzadeh H 2007 *Physica B* **400** 297
[35] Gilman J J, Cumberland R W and Kaner R B 2006 *Int. J. Refract. Met. Hard Mater.* **24** 1
[36] Feng J, Xiao B, Zhou R, Pan W and Clarke D R 2012 *Acta Mater.* **60** 3380
[37] Pugh S F 1954 *Philos. Mag.* **45** 823
[38] Ravindran P, Fast L, Korzhavyi P A and Johansson B 1998 *J. Appl. Phys.* **84** 4891
[39] Gao F, He J, Wu E, Liu S, Yu D, Li D, Zhang S and Tian Y 2003 *Phys. Rev. Lett.* **91** 015502
[40] Zhang X, Luo X, Han J, Li J and Han W 2008 *Comput. Mater. Sci.* **44** 411
[41] Yu R, Jiang Y H, Feng J, Zhou R F, Zhang Y Q and Zhou R 2013 *J. Mater. Sci.* **48** 3443