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Elastic stability of β-Ti under pressure calculated using a first-principles plane-wave pseudopotential method

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The elastic moduli c' and c_{44} of β-Ti with respect to external pressure P (up to about 138 GPa) are calculated with a first-principles plane-wave pseudopotential method. The accuracy of the calculations regarding the plane-wave cut-off energy, k-point mesh, and transferability of the pseudopotentials is carefully tested. It is found that the critical pressure beyond which β-Ti satisfies the elastic stability conditions is about 60 GPa. The Mulliken population analysis shows that both s and p electrons transfer to the d orbitals with increasing pressure, however, the number of s electrons starts to increase when the pressure exceeds about 70 GPa. The number of d electrons at the critical pressure is about 2.96, in perfect agreement with the critical number of d electrons for a stable bcc Ti-V alloy, which demonstrates the correlation between the stability of bcc metals and their d orbital occupation. The bonding charge density calculations show charge accumulation on the $d-t_{2g}$ orbitals under high pressure, which may improve the elastic stability of β-Ti.

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The hexagonal-close-packed (hcp) α phase is stable at ambient conditions for the group IVB metals (Ti, Zr, and Hf). At high temperature, the stable phase becomes body-centered-cubic (bcc) β phase. It was generally believed that pressure may also stabilize the β phase to low temperature. The phase transition of these metals under pressure has been extensively investigated both experimentally and theoretically.[1–13] For Zr and Hf, experiments have identified a phase stability sequence of α to ω (collapsed hexagonal) to β with increasing pressure,[1,2] which is also in qualitative agreement with theoretical calculations.[3–6] However, the pressure induced phase transition in Ti is highly controversial between experiments and theoretical calculations. Room-temperature β-Ti has not been identified experimentally for pressures as high as 220 GPa.[7] On the other hand, various first-principles calculations predicted a critical pressure for a stable β phase from 80 to 136 GPa,[6,8–11] and the absence of the high-pressure β phase in experiments was attributed to the possible nonhydrostatic stress which distorts the β phase.[10,11]

It has been recognized that the instability of β-Ti at ambient conditions is closely related to its elastic instability, i.e., $c'=\frac{1}{2}(c_{11}-c_{12})<0$, with c' being the elastic modulus of the shear of $\{011\}$ plane along $\langle 110\rangle$ direction, and c_{11} and c_{12} the elastic stiffness coefficients. The pressure at which $c'=0$ provides a lower bound for a stable β-Ti under pressure. Therefore, the pressure dependence of c' is of fundamental interest to understanding the stability of β-Ti. The elastic stiffness coefficients of β-Ti under compression have been reported by Ahuja *et al.*[6] but without much detail presented.

It was generally accepted that the pressure induced phase transition in group IVB metals can be ascribed to the electron transfer from s to d orbital.[7] However, recent experiments have shown that the ω' to β phase transition in Ti-Zr alloy under pressure interrupts the s-d electron transfer and triggers the reverse d-s redistribution of the electrons.[14] A theoretical investigation of the correlation between the pressure dependent d orbital occupation and the elastic stability of β-Ti would be very interesting.

The purpose of this work is to give an accurate description of the pressure dependence of elastic stability of β-Ti through first-principles calculations, and to investigate the response of the electronic structure of β-Ti to the pressure and its connection to the elastic stability of β-Ti. The calculations in the present work are performed by the use of a first-principles plane-wave pseudopotential method based on density-functional theory,[15] implemented as CASTEP.[16,17] Since the Ti-$3s3p$ electrons may respond to the high-stress compression, to describe accurately this response, we adopt ultrasoft pseudopotentials[18] with Ti-$3s3p$ electrons treated as valence electrons beside Ti-$3d4s$. The electronic exchange correlation potential is described within generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE).[19] Brillouin-zone sampling was performed using Monkhorst-Pack special points.[20] We compress the bcc cell homogeneously so as to model the external hydrostatic pressure, P.

For a cubic system, the number of the independent elastic constants reduces to three (c_{11}, c_{12}, and c_{44}) due to the symmetry of the crystal. When applying a strain tensor

$$\delta\epsilon = \begin{pmatrix} e & \frac{e}{2} & 0 \\ \frac{e}{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

to a cubic crystal, one gets

$$\sigma_{xx}=c_{11}e,$$
$$\sigma_{yy}=\sigma_{zz}=c_{12}e,$$
$$\sigma_{xy}=c_{44}e,$$
$$\sigma_{zx}=\sigma_{zy}=0, \tag{2}$$

TABLE I. Elastic moduli of β-Ti at low and high pressure from pseudopotential and all-electron full-potential plane-wave calculations with k-point mesh of $45\times45\times45$. (Details of the full-potential calculations: WIEN2K package; muffin-tin radius of 2.0 a.u.; augmented plane-wave basis set; plane-wave cut-off energy of 22.5 Ry; XC functional of GGA-PBE.)

Method	Lattice constants	Pressure	c'	c_{44}
	(Å)	(GPa)	(GPa)	(GPa)
FP-APW	3.2510	0.6	−10.8	41.4
PW-PP		0.3	−10.8	41.2
FP-APW	2.6964	140.1	56.0	46.5
PW-PP		138.0	61.6	44.7

according to Hooke's law.[21] σ is the stress resulting from the applied strain, which can be evaluated by the first-principles method.[22,23] The elastic constants are obtained by a linear fit to the stress-strain relationship as shown above. Four strain steps ($e=-0.003,-0.001,0.001,0.003$) are used in our calculations for the fitting. In the present work, we do not discuss directly the elastic stiffness coefficients c_{11} and c_{12}. Instead, we concentrate ourselves on the elastic moduli, $c'=\frac{1}{2}(c_{11}-c_{12})$ and c_{44}, which described the stability of the cubic crystals with respect to the shear deformations along $\{110\}\langle1\bar{1}0\rangle$ and $\{001\}\langle100\rangle$ directions, respectively. It should be noted that the strain tensor is applied to the compressed crystal for those crystals under external pressure. Therefore, the strain induced by the external pressure is not included in the strain tensor.

The plane-wave cut-off energy (E_{cut}), number of k points, and quality of the pseudopotentials for both ambient and high-pressure cases are carefully tested to make sure that the calculated elastic constants are reliable. We find that, for both 0 and high-pressure cases, the elastic moduli converge very quickly with increasing E_{cut}. Converged elastic moduli are already obtained at E_{cut} of about 330 eV. Although it may not be absolutely necessary, we choose a very high E_{cut} of 400 eV for our plane-wave pseudopotential calculations reported hereafter. The number of k points affects heavily the calculation of the anisotropically distorted system under pressure.[24] Our test calculations demonstrate that, without external pressure, both c' and c_{44} converge very fast with increasing number of k points. Reasonably stable elastic moduli are already obtained with the k-point grid of $25\times25\times25$ corresponding to 455/2197 special k points in the irreducible Brillouin zone (IBZ) for undistorted/distorted bcc primitive cell. However, the elastic moduli under high pressure converge extremely slowly. With the densest k-point mesh ($51\times51\times51$) considered in this work, we get an error bar of about ±3 GPa for both c' and c_{44}. As we will show later on in this Brief Report, such an error bar does not affect significantly the trend of the elastic moduli with respect to external pressure. The transferability of the pseudopotential under high pressure is checked by comparing the pseudopotential and all-electron full-potential augmented plane-wave (FP-APW) calculations[25] (see Table I). It is seen that, at low pressure, the pseudopotential calculations generate essentially the same elastic moduli as those from FP-APW calculations. At high pressure, the elastic moduli from pseudopotential and full-potential calculations differ slightly from each other, but the error is still acceptable.

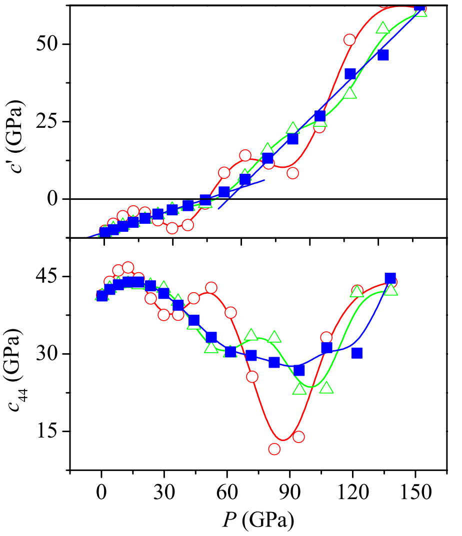


FIG. 1. (Color online) c' and c_{44} of β-Ti with increasing pressure (circles, triangles, and squares for $25\times25\times25$, $35\times35\times35$, and $51\times51\times51$ k-point grids, respectively).

Figure 1 shows the shear moduli, c' and c_{44}, of β-Ti with respect to pressure for three different k-point grids. It was shown that the elastic moduli oscillate significantly for the k-point grid of $25\times25\times25$. With increasing number of k points, the amplitude of the oscillation decreases. One may expect that finally c' increases monotonously with pressure, and c_{44} gets a maximum at a pressure of about 15 GPa and a minimum at a pressure of about 90 GPa. The behavior of c_{44} of β-Ti with respect to external pressure P is quite different from most other crystals where c_{44} increases monotonously with P. However, it is interesting to note that the c_{44}-P curve of β-Ti is very similar to that of bcc vanadium of which c_{44} shows a minimum (<0) at about 20 GPa.[26] The c_{44} instability is believed to be the trigger of the bcc to rhombohedral structure transition in vanadium.[27]

As is seen from Fig. 1, c' is negative at low pressure. It starts to be positive when P increases to about 60 GPa. Figure 1 clearly shows that two linear fits have to be respectively applied to the negative and positive c' parts in order to give a reasonable description of the c'-P relationship, namely,

$$c' = -10.66 + 0.24P, \quad c' \le 0,$$

$$c' = -39.34 + 0.72P, \quad c' > 0. \tag{3}$$

Born[28] has proposed that the elastic constants of a mechanically stable lattice have to satisfy

$$c_{44} \ge 0,$$

$$c' \ge 0,$$

$$c_{11} + 2c_{12} \ge 0. \tag{4}$$

This is the well-known Born stability criteria. It has been noted that Born criteria for the elastic stability are only valid for the crystal under 0 pressure. As derived by Wang *et al.*[29] and Morris and Krenn,[30] the internal stability conditions for a cubic system under hydrostatic compression are

$$C_{44} - P \geq 0,$$

$$C' - P \geq 0,$$

$$C_{11} + 2C_{12} + P \geq 0. \tag{5}$$

It should be noted that the elastic constants C_{ij} in the latter criteria are obtained with respect to Lagrange finite-strain coordinates, i.e., the strains induced by the external pressure are included. The elastic constants obtained in such a way are different substantially from the elastic stiffness c_{ij} in this Brief Report which is evaluated with respect to the infinitesimal strain applied to the compressed crystal. In our case, the conventional Born criteria are still at work.[31] It is seen from Fig. 1 that the elastic constants of β-Ti satisfy Born criteria under the pressure beyond about 60 GPa, i.e., the low-pressure limit for a stable β-Ti is 60 GPa. In comparison, we have also investigated the pressure dependence of c' and c_{44} for bcc Zr and Hf. The critical pressures for elastically stable bcc Zr and Hf are 10.2 and 7.7 GPa, respectively, much lower than that for β-Ti, which is consistent with the experimental finding that bcc Zr and Hf have been identified under pressure but bcc Ti has not.

In order to analyze the electron transfer between different electronic orbitals, the plane-wave states are first projected onto the localized linear combination of atomic orbitals (LCAO) basis sets with s, p, and d components using a technique described by Sanchez-Portal *et al.*[32] Then electronic population analysis on the resulting projected states is performed using Mulliken formalism,[33] which gives the number of electrons on different orbitals. Although it is recognized that the absolute magnitude of the atomic charge generated by the population analysis has little physical meaning due to its sensitivity to the atomic basis set, we expect that the relative electron transfer with respect to pressure may be qualitatively correct as the same atomic basis set was adopted for the systems under different pressures.

Figure 2 shows the variation of the number of electrons on s, p, and d orbitals with increasing pressure. It is seen that the number of d electrons (N_d) increases monotonously with the pressure whereas the number of p electrons (N_p) decreases. It is interesting to note that the number of s electrons (N_s) decreases with pressure up to 70 GPa; however, further increasing the pressure results in an increase in the number of s electrons. The number of d electrons is about 2.74 and 3.28 at $P=0$ and $P=138$ GPa, respectively. In comparison, we have also calculated the Mulliken populations of bcc-V at 0 pressure, which is about 3.78, much larger than that for β-Ti at 138 GPa.

Of course the increase in N_d of Ti can also be achieved by alloying with transition metals of more d electrons, such as V, etc. It is therefore interesting to compare the effects of the variations of N_d induced by pressure and alloying on the elastic moduli. As is seen from Fig. 1, the pressure corresponding to $c'=0$ is about 60 GPa. At this pressure, the number of d electrons of β-Ti is about 2.96 (see Fig. 2). Ikehata *et al.*[34] have calculated the elastic constants of β-Ti alloyed with V, Nb, Ta, etc. by the use of plane-wave pseudopotential method. It was shown that when the composition of V reaches about 21%, c' of the system raises to 0 GPa. Considering the N_d of the pure Ti (2.74) and V (3.78) calculated in this work, N_d of Ti-21%V is approximately 2.96, in perfect agreement with the N_d corresponding to $c'=0$ for β-Ti under pressure. Namely, either by pressure or by alloying, the critical N_d for an elastically stable β phase is 2.96,

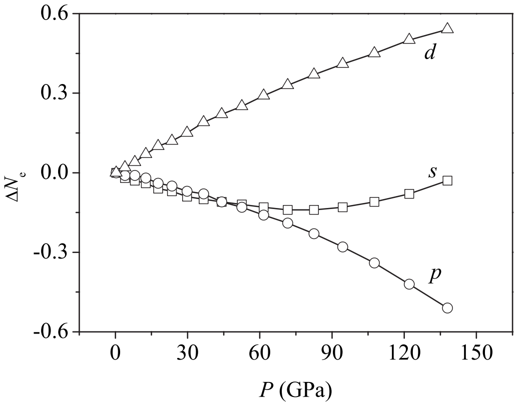
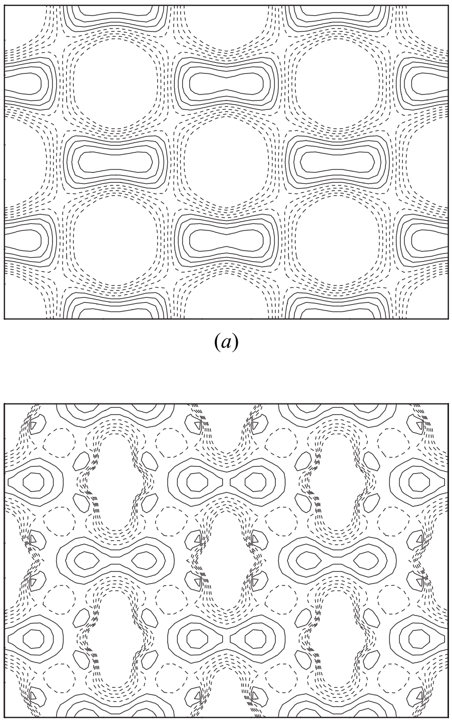


FIG. 2. Number of electrons on s, p, and d orbitals with increasing pressure, relative to those for 0 pressure (2.23, 6.81, and 2.74 for s, p, and d, respectively).



(*a*)

(*b*)

FIG. 3. Bonding charge density on the (011) plane of (a) β-Ti at 0 pressure; (b) β-Ti under pressure of about 138 GPa. Scaling from -20 to 20 me/Å^3. The dashed lines denote a depletion of the charge whereas the solid ones represent a charge accumulation.

which demonstrates the intrinsic connection between the number of d electrons and elastic stability of the transition metals with bcc structure.

Figures 3(a) and 3(b) show the bonding charge density of β-Ti at 0 and high pressure, respectively. The feature of the bonding charge density of β-Ti at 0 pressure is very similar to that of the bcc-Y reported by Grad *et al.*:[35] The bonding charge is concentrated in the octahedral interstices along [001] direction. There is no bonding charge in between two nearest-neighboring Ti atoms along [111] direction, which is responsible for the instability of the β phase at 0 pressure.[35] For β-Ti at a pressure of about 138 GPa, the charge density in the octahedral interstices decreases, and charge accumulation occurs on the $d-t_{2g}$ orbitals such that bonds may build between Ti atoms along [111] direction. Therefore, it is plausible to conclude that pressure induced increase in d population (especially $d-t_{2g}$) strengthens the atomic bond between Ti atoms along [111] direction, which improves the elastic stability of β-Ti.

In summary, we have calculated the elastic moduli c' and c_{44} with respect to external pressure P with an accurate first-principles plane-wave pseudopotential method. The parameters of calculations such as plane-wave cut-off energy, k-point mesh, and transferability of the pseudopotentials are carefully tested in order to obtain reliable c' and c_{44} for different P. The pressure considered in this work is up to 138 GPa. It is found that the critical pressure beyond which the β-Ti is elastically stable is about 60 GPa. The Mulliken population analysis shows that both s and p electrons transfer to the d orbitals with increasing pressure, however, the number of s electrons start to increase when the pressure exceeds about 70 GPa. The number of d electrons for the critical pressure is about 2.96. The bonding charge density calculations show charge accumulation on the $d-t_{2g}$ orbitals under pressure, which may improve the elastic stability of β-Ti.

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