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Ab initio study of basal slip in Nb₂AlC

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Abstract

Using *ab initio* calculations, we have studied shearing in Nb₂AlC, where NbC and Al layers are interleaved. The stress–strain analysis of this deformation mode reveals Nb–Al bond breaking, while the Nb–C bond length decreases by 4.1%. Furthermore, there is no evidence for phase transformation during deformation. This is consistent with basal slip and may be understood on the basis of the electronic structure: bands below the Fermi level are responsible for the dd bonding between NbC basal planes and only a single band with a weak dd interaction is not resistant to shearing, while all other bands are unaffected. The Al–Nb bonding character can be described as mainly metallic with weak covalent–ionic contributions. Our study demonstrates that Al layers move with relative ease under shear strain. Phase conservation upon shearing is unusual for carbides and may be due to the layered nature of the phase studied. Here, we describe the electronic origin of basal slip in Nb₂AlC, the atomic mechanism which enables reversible plasticity in this class of materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Shearing in solids can theoretically be studied by investigating relevant elastic constants, in particular C_{44} and the shear modulus. In order to design the mechanical properties of solids, an atomic level understanding of the ideal strength of an infinite defect-free crystal is required. Such studies have been performed for strong solids. For instance, Zhang *et al* have investigated the deformation modes in diamond and cubic BN and found that both C–C and B–N bonds break under shear strain [1]. Jhi *et al* have reported that the pd bonding states in binary carbides

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and nitrides are resistant to shearing, while the dd bonding states are not [2, 3]. Understanding the electronic origin of shearing and calculations of C_{44} as a function of valence electron concentration [2, 3] may be used to design new hard materials as well as damage tolerant phases. Recently, it has been shown that $M_{n+1}AX_n$ phases, where M is an early transition metal, A is an A group element and X is C and/or N, are ductile ceramics [4–6]. This is a direct consequence of the layered nature of these phases (MX and A layers are interleaved). In Ti_3SiC_2 , an example of an $M_{n+1}AX_n$ phase, basal slip operates at all temperatures and fully reversible stress–strain relationships at room temperature have been reported [7, 8]. This reversibility has been explained through reversible formation and annihilation of incipient kink bands. However, the electronic origin of basal slip, the atomic mechanism which enables reversible plasticity in these ternary solids, has not yet been explored.

Nb_2AlC is another representative of an $M_{n+1}AX_n$ phase [4, 5] which possesses a combination of properties usually associated with metals and ceramics [5, 6]. They are good thermal and electrical conductors [5, 9] and exhibit high stiffness and strength at elevated temperatures [5, 9]. Furthermore, they are comparatively soft and machinable and possess good thermal shock and oxidation resistance [5, 9]. This unique combination of properties serves as motivation for fundamental as well as applied research. Nb_2AlC can be synthesized by hot isostatic pressing of Nb, Al and C powders [10]. Its bulk properties are comparatively well studied. On the basis of the velocity of sound measurements, the bulk modulus and hardness values of Nb_2AlC were reported to be 209 and 6 GPa, respectively [11, 12]. The bulk modulus value is consistent with our *ab initio* data (205 GPa) [13, 14]. Nb_2AlC was reported to oxidize in air at 650 °C by forming Nb oxides and $NbAlO_4$ [15]. By the formation of a solid solution with Ti_2AlC , the oxidation onset can be shifted to 900 °C [15]. Furthermore, Nb_2AlC is a good thermal and electrical conductor with the corresponding coefficients of $22 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.29 \mu\Omega \text{ m}$ at 300 K, respectively [16]. While many physical properties of Nb_2AlC have been studied, shearing and the electronic origin thereof have not yet been investigated.

In this work, we study shearing in Nb_2AlC using *ab initio* calculations. It is our ambition to contribute towards understanding of the correlation between electronic structure, bonding and shearing. The stress–strain analysis of this deformation mode reveals Nb–Al bond breaking, conservation of Nb–C bonds and no phase transformation during deformation, which is unusual for carbides. These findings are consistent with basal slip. Here, we describe the electronic origin of basal slip in Nb_2AlC , the atomic mechanism which enables reversible plasticity in this family of solids [7, 8].

2. Theoretical methods

Density functional theory was used for the present calculations [17], as implemented in the Vienna *ab initio* simulation program (VASP). Projector augmented wave potentials and the generalized-gradient approximation were applied in all calculations [18], with the so-called Blöchl corrections for the total energy [19]. The integration in the Brillouin zone is done on special k -points determined following the Monkhorst–Pack approach [20]. A unit cell containing eight atoms was studied on a mesh of $7 \times 7 \times 7$ irreducible k -points. The convergence criterion for the total energy (E) was 0.01 meV within a 500 eV cut-off. Spin polarization was not considered due to there being only minute differences in E , as obtained previously for Cr_2AlC [21] and V_2AlC [22]. Nb_2AlC was relaxed with respect to the atomic positions and lattice parameter a , i.e. the Wigner–Seitz primitive cell volume and its hexagonal c/a ratio. Shearing was studied in terms of the elastic constant C_{44} , as obtained according to the method developed by Fast and co-workers, where the C_{44} deformation results in triclinic symmetry [23]. The shear stress–shear strain curve was obtained with full structural relaxations at each strain

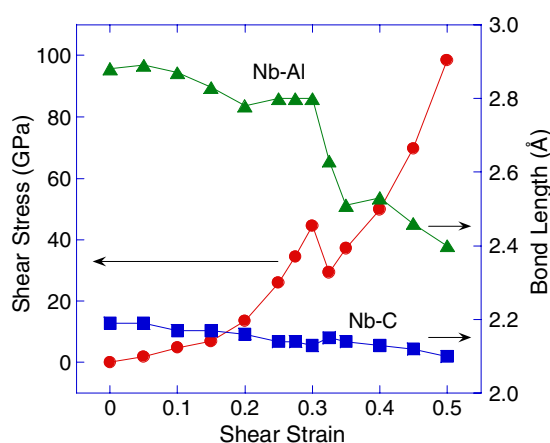


Figure 1. Shear stress–shear strain curve for the shear deformation in Nb₂AlC together with the bond length data for Nb–C and Nb–Al. It is evident that the Nb–Al bonds break at the yield point.

applied and Hellmann–Feynman stress tensors were evaluated. Furthermore, the band structure and decomposed electron density distribution were assessed so as to contribute towards the understanding of the bonding evolution upon shearing.

3. Results and discussion

Figure 1 shows the shear stress–shear strain dependence for Nb₂AlC and the bond length as a function of the applied shear strain. It is evident that there is a peak in the shear stress–shear strain curve at the shear strain of 0.30. The calculated ideal shear strength of Nb₂AlC is 44.5 GPa, which accounts for 47.9% of the ideal shear strength of diamond [1]. This value is also comparable to those for transition metal carbides and nitrides [3]. Furthermore, there are two striking features in the shear stress–shear strain dependence of Nb₂AlC. Firstly, there are curvature changes before the yield point. Secondly, after the bonds were broken, the shear stress–shear strain curve was continued with a slope similar to that before bond breaking. This is consistent with basal slip. In terms of bond length evolution upon shearing, the Nb–C bond length decreases by 4.1% (see figure 1). This may be consistent with the notion of phase stability. On the other hand, the Nb–Al bond length exhibits a 16.7% decrease over the range probed and a rather drastic decrease of 6.1% in the shear strain range from 0.30 to 0.33 (see figure 1). These phenomena may be understood on the basis of the electronic structure.

In figure 2, the band structure of Nb₂AlC for the shear strains of 0 (equilibrium), 0.30 (before bond breaking) and 0.33 (after bond breaking) is shown. The equilibrium structure (figure 2(a)) can be characterized by degenerate bands and at the Γ point, the Fermi level is located at a local minimum. It is known from the electronic structure analysis of M₂AlC phases (M = VB transition metal), that the states in the vicinity of the Fermi level are related to M d orbitals [24]. In the region from approximately -3.5 to -1.0 eV the weak M d–Al 2p hybridization dominates and the deep core levels are assigned to M d–C 2p hybrids [24]. Therefore, it is reasonable to assume that the M d orbitals are relevant for shearing in Nb₂AlC. Some general remarks can be made when comparing the unstrained (figure 2(a)) and strained (figures 2(b) and (c)) band structures. Firstly, originally degenerate bands are split under strain because of symmetry breaking (hexagonal to triclinic transition). Secondly, there are significant changes along the M– Γ –K line near the Fermi level. To make the discussion more transparent,

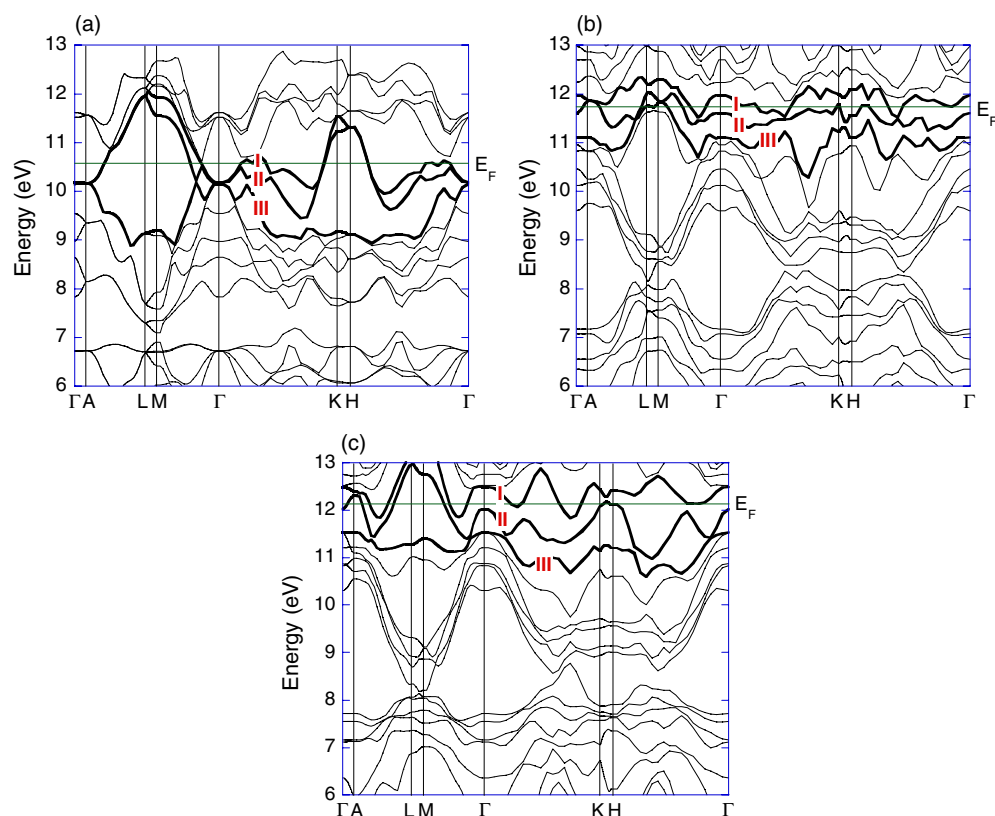


Figure 2. Band structure of Nb₂AlC for the shear strains of (a) 0.00 (equilibrium), (b) 0.30 (before breaking) and (c) 0.33 (after breaking) along the major symmetry lines of the hexagonal Brillouin zone. E_F designates the Fermi level and four bands in its vicinity are highlighted and marked with Roman numerals.

Roman numerals I, II and III are used to mark three bands just below the Fermi level. As the shear strain is increased from 0 to 0.30 (before bond breaking), band I moves above the Fermi level, while bands II and III are still below the Fermi level. This suggests that band I is not resistant to shearing, while bands II and III are resistant to shearing. As the shear strain is further increased from 0.30 to 0.33 (after bond breaking), band I is still above the Fermi level, while bands II and III remain below. Besides the notion that band I is not resistant to shearing, this also suggests that the chemical bonding before and after the peak in the shear stress–shear strain curve may be conserved.

In figure 3, decomposed electron density distributions in the $(11\bar{2}0)$ plane of the bands highlighted in figure 2 are given. We can thus discuss both atomic and electronic mechanisms related to shearing in Nb₂AlC. It is evident that Al moves from left to right in the unit cell, while Nb moves in the opposite direction, i.e. it partially reappears in the $(11\bar{2}0)$ plane due to the periodic boundary conditions. This is consistent with basal slip. These atomic mechanisms are also compatible with the phonon modes found in Ti₂AlC, V₂AlC, Cr₂AlC, Nb₂AlC, Ti₃SiC₂ and Ti₄AlN₃ [25]. Phonon modes related to Al were found to be active at the lowest peak energies [25] in the range of 150 cm⁻¹, which is consistent with the results obtained here. The Nb–C bond length decreases monotonically by 4.1% in the shear strain range studied and

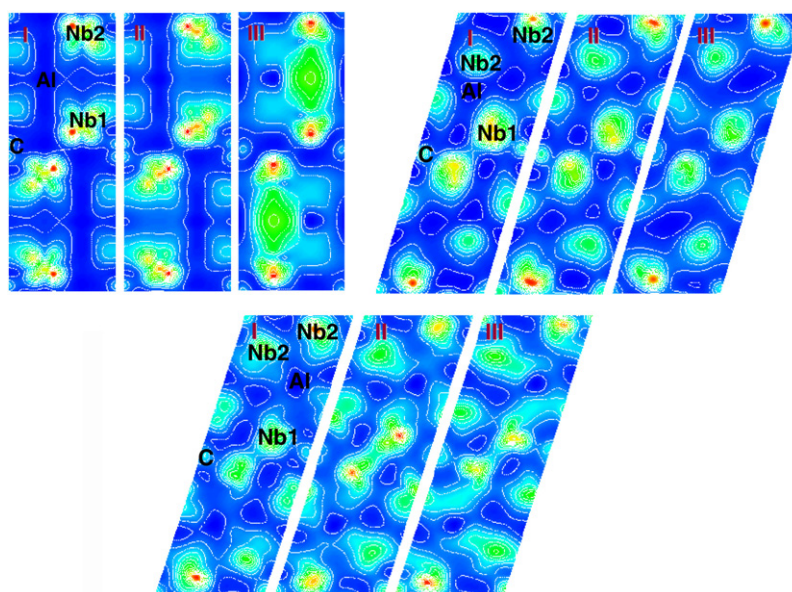


Figure 3. Decomposed electron density distribution of Nb₂AlC in the (11 $\bar{2}$ 0) plane for the shear strains of (a) 0.00 (equilibrium), (b) 0.30 (before breaking) and (c) 0.33 (shortly after breaking). The electron density increases from 0.0 (blue/grey) to 0.1 electrons \AA^{-3} (red/black), with the step of 0.007 electrons \AA^{-3} . Roman numerals designate bands in the vicinity of the Fermi level (see figure 2). Note that Al is not contained in the (11 $\bar{2}$ 0) plane for the shear strains of 0.30.

hence there is no bond breaking. However, the Nb–Al bond length data clearly illustrate that bond breaking occurs (see figure 1). Furthermore, Al is mainly metallically bonded to Nb (non-localized electron density) and can therefore be more easily rearranged than Nb or C. Thus, the Nb–Al bond breaking gives rise to discontinuity in the stress–strain curves (see figure 1). After bond breaking, Al is reattached to the adjacent Nb, which is consistent with the bonding nature of M₂AlC phases (M = VB transition metal) [24]. Mainly metallic Nb–Al bonds are related to bands below the Fermi level and are always occupied during deformation (see figure 2). Furthermore, no evidence of phase transformation can be seen since the bonding nature is conserved during shearing (see figure 3). Nb–C and Nb–Al are still covalent–ionic and metallic in nature, respectively, and there is no coordination change in the course of deformation. This is also consistent with the similarity in the slope of the shear stress–shear strain curve: in the strain region from 0 to 0.30 and from 0.33 to 0.50, shortly after bond breaking. This is rather unique behaviour for carbides and it may be a direct consequence of the layered nature of the compound studied. For instance, in strong solids such as diamond or cubic BN, a phase transformation occurs after the bond breaking [1]. Barsoum and co-workers reported reversible stress–strain behaviour for Ti₃SiC₂ at room temperature [7, 8]. This reversibility was argued to be a direct consequence of formation and annihilation of incipient kink bands. Kinking, however, requires the existence of dislocation pairs on many parallel slip planes. In this work, we describe the electronic origin of basal slip in Nb₂AlC, the atomic mechanism which enables reversible plasticity in this family of solids [7, 8].

Basal slip in Nb₂AlC may be understood on the basis of the electronic structure. It can be deduced that all bands highlighted in figure 2 are responsible for dd bonding or NbC–NbC coupling (marked in figure 3 as Nb1 and Nb2). However, the strength of this interaction

increases from band I (low electron density between Nb1 and Nb2) to band III (high electron density between Nb1 and Nb2), where the latter two have a dominant $t_{2g} + e_g$ symmetry (figure 3(a)). When Nb₂AlC is exposed to shearing (figures 3(b) and (c)), the bonding character is conserved. For both shear strains of 0.30 (before bond breaking) and 0.33 (after bond breaking), the dd interaction for band I is weak and this band is unoccupied at the Γ point, while the dd interaction for bands II and III is strong. All other bands in Nb₂AlC are unaffected upon shearing, which is in agreement with the suggestion that there is no phase transformation after the yield point. These results on the correlation between the decomposed band structure and shearing in M_{n+1}AX_n phases are consistent with our previous work [26].

These findings may be important for the development of low friction ceramic based materials, which are capable of broad temperature range operations. Identification of low shear strength orientations along Al layers in Nb₂AlC can provide such a unique opportunity. The material can be then incorporated into advanced nanostructures for broad temperature lubrication in ambient and space environments, which are currently being developed for aerospace engineering [27]. Furthermore, since such materials contain intrinsically nanolayered arrangements of metal/covalent–ionic bond interfaces, their friction response can be influenced through substitution of M and A elements [5, 6, 14] to tune tribo-chemical activated reactions and processes.

4. Conclusions

We have studied shearing in Nb₂AlC using *ab initio* calculations and found by analysing the stress–strain dependence that Nb–Al bonds break during deformation, while the Nb–C bond length decreases by 4.1%. Furthermore, there is no evidence for phase transformation. This is consistent with basal slip and may be understood on the basis of the electronic structure: bands below the Fermi level are responsible for the dd bonding between NbC basal planes and only a single band with a weak dd interaction is not resistant to shearing, while all other bands are unaffected. The Al–Nb bonding character can be described as mainly metallic with weak covalent–ionic contributions. Thus, Nb–Al bonds break and Al layers move upon deformation, resulting in basal slip, the atomic mechanism which enables reversible plasticity in M_{n+1}AX_n phases.

Acknowledgments

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