Interatomic bonding, elastic properties, and ideal strength of transition metal aluminides: A case study for Al₃(V,Ti)

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On the basis of ab initio density-functional calculations we have analyzed the character of the interatomic bonding in the intermetallic compounds Al₃(V,Ti) with the D₀₅₅ and L₁₂ structures. In all structures we found an enhanced charge density along the Al-(V,Ti) bonds, a characteristic feature of covalent bonding. The bonds in Al₃V with the D₀₅₅ structure are more saturated and stronger than the corresponding bonds in Al₃Ti. High symmetry of the transition metal sites in the L₁₂ structure leads to higher metallicity of alloys assuming this structure. The bond strength is quantitatively examined by tensile deformations. The ideal strength of Al₃V and Al₃Ti under uniaxial tensile deformation was found to be significantly higher than that of both fcc Al and bcc V. We investigated also the changes of the interatomic bonding in Al₃V during tensile deformation. We found that the covalent interplanar Al-V bonds disappear before reaching the maximal stress. The weakening of the bonding between the atomic planes during the deformation is accompanied by a strengthening of in-plane bonding and an enhanced covalent character of the intraplanar bonds. Interplanar bonding becomes more metallic under tensile deformation.

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I. INTRODUCTION

The mechanical properties of materials have been for a long time studied extensively by various experimental methods. The progress in the development of ab initio methods during the past decade allows to approach this interesting topic also from the theoretical side. The elastic constants describe the mechanical properties of materials in the region of small deformations where the stress-strain relations are still linear. An important quantity, which describes the mechanical properties of the material beyond the linear region is the ideal (or theoretical) strength. It represents the stress necessary for de-cohesion or fracture of the crystal. The ideal strength represents upper strength limit for a solid under a given load. Morris and Krenn have investigated the conditions of elastic stability that set the upper limits of mechanical strength. The ideal strength is one of few mechanical properties that can be calculated from first principles. It is an inherent property of the crystal lattice and thus offers insight into the correlation between the intrinsic chemical bonding and the symmetry of a crystal and its mechanical properties.

Recently several theoretical studies of the ideal strength of elemental metals have appeared. Černý et al. investigated elastic properties of Fe, Co, Ni, and Cr crystals under isotropic tri-axial deformation. The ideal shear strength of the bcc metals Mo, Nb, and W were studied by Luo, Krenn, and co-workers. Roundy, Krenn, and co-workers calculated ideal shear strength of fcc Al and Cu.

The most straightforward way to calculate the elastic limits from first principles is to stretch or shear the crystal in the desired direction and to calculate the changes of the total energy and of the induced stress. The stress associated with a particular strain is proportional to the derivative of the energy with respect of the strain. One has to calculate the stress as a function of strain, and to look for the maximum of the stress. The elastic limits can be strongly anisotropic. For a calculation of the ideal strength one has to deform the crystal along a path of the weakest deformation. The maximum stress is the ideal strength, and is associated with the inflection point in the curve of energy as a function of strain along the path toward the saddle point. The paths of weakest deformation for common crystals are known. For an fcc crystal it is a shear deformation in a ⟨112⟩ direction in a {111} plane. For a bcc crystal it is a slip of {110} planes along the ⟨111⟩ direction. This procedure yields an upper bound on the theoretical strength. Instabilities along eigenvectors perpendicular to the direction of the stretch may appear at lower values of the stress. For instance, bcc crystals become unstable after a relatively small stretch along ⟨100⟩. This instability is responsible for their tendency to cleave along {100} planes. Very recently Clatterbuck et al. calculated phonon spectra of aluminum as a function of strain and found that phonon instabilities may occur before a material becomes elastically unstable.

The calculations of elastic limits of a solid are computationally expensive, particularly when the distorted solid has a low symmetry. The crystal must be reconfigured at every step to relax the lateral stresses. Such calculations are computationally very difficult even for simple monoatomic cubic systems. Extension of these studies to more complex crystalline structures requires an extreme computational effort close to and often beyond what is now computationally feasible.

Transition metal aluminides are known to be of great technological importance. Al based compounds of transition metals (TM) are among the most promising candidates for high-performance structural materials. The reported tensile strength of, e.g., nanocrystalline Al₉₅V₄Fe₂ is above 1300 MPa, which exceeds the strength of usual technical
steels.\(^{18}\) The enhanced strength of these materials is mostly attributed to their nano-crystalline and nano-quasicrystalline structure. However, in transition metal aluminides interatomic bonding between Al and transition metals may exhibit enhanced covalency, with a significant influence on the mechanical properties. Covalency can increase the strength of interatomic bonding\(^{20,21}\) and consequently increase the mechanical strength and hardness, but on the other hand it leads also to an undesired higher brittleness.

*Ab initio* calculations of the elastic limits of transition metal aluminides are a great challenge. The crystals structures of transition metal aluminides can be quite complex: For instance, \(\text{Al}_10\text{V}\) has 176 atoms per unit cell. A search for the path of easiest deformation can be a difficult task. In the present paper we attempt to achieve a deeper understanding of the relation between interatomic bonding and the mechanical properties of the transition metal aluminides. For this study we have chosen \(\text{Al}_3\text{V}\) and some related compounds as for these systems the enhanced covalency in the bonding is known. The trialuminide intermetallic \(\text{Al}_3\text{Ti}\) has many attractive characteristics such as low density \((=3.3\ \text{g/cm}^3)\), high hardness, good oxidation resistance, and moderately high melting temperature \((=1700\ \text{K})\).\(^{22}\) Therefore, this intermetallic may be useful for elevated temperature applications.\(^{22}\) Both stable \(\text{Al}_3(V,\text{Ti})\) compounds crystallize in the \(0\ 2\ 2\) structure. In Sec. III we present a picture of bonding in the \(0\ 2\ 2\) structure. Nuclear magnetic resonance (NMR) studies suggest a strong directional bonding\(^{23,24}\) in \(\text{Al}_3\text{V}\). This conjecture is further corroborated by the structural analysis: The short Al-V distances\(^{25}\) indicate that the bonding may have a covalent character. Recently, we have performed a detailed study of the electronic structure and bonding in \(\text{Al}_3\text{V}\).\(^{20}\) The electronic density of states of this compound exhibits an unusually deep pseudogap very close to the Fermi level. We have demonstrated that a strong hybridization between the Al\((s,p)\) and V\((d)\) orbitals which is responsible for forming of a deep pseudogap near the Fermi level is also associated with the formation of covalent bonds. We analyzed the charge distribution in the elementary cell and found an enhanced charge density along the Al-V bonds and certain Al-Al bonds that is characteristic for covalent bonding. The character of the bonds was investigated by the analysis of the density of states projected on bonding and antibonding configurations of atomic orbitals. This analysis reveals that the Al-V bonds in the \(0\ 2\ 2\) structure are almost saturated. Because of a lower \(d\)-band filling a similar result is not expected for \(\text{Al}_3\text{Ti}\) with the same crystal structure.

In addition to the stable \(\text{Al}_3\text{V}\) phase in the \(0\ 2\ 2\) structure there exists a metastable \(\text{Al}_3\text{V}\) phase with the \(L_1_2\) (Cu_3Au) structure. It is also known that \(\text{Al}_3\text{Ti}\) can be transformed to the high-symmetry \(L_1_2\) cubic structure by alloying with transition metals with more \(d\)-electrons in the valence band.\(^{22}\) Both the \(0\ 2\ 2\) and the \(L_1_2\) structures can be considered as a special decoration of a face-centered cubic lattice. In the \(L_1_2\) structure the TM site has full octahedral symmetry, while in the \(0\ 2\ 2\) structure the symmetry of this site is lower. It appears that just this high symmetry of the TM site in the \(L_1_2\) structure prevents a saturation of all Al-TM bonds. Higher metallicity of bonding is generally considered to be reason for a better ductility of these materials.

To investigate the relation between interatomic bonding and the mechanical properties we first calculated the elastic properties of \(\text{Al}_3(V,\text{Ti})\) compounds. Then we investigated the stress-strain relation under triaxial (homogeneous) and uniaxial deformations and studied in detail the change of interatomic bonding under these tensile strains.

For the study of the uniaxial tensile deformation we have chosen the \([001]\) direction. This choice is determined by the tetragonal symmetry of the crystals and the orientation of the observed covalent bonds. The orientation of the bonds in the \(D_0_{22}\) structure indicates that the \([001]\) direction is the direction of the most difficult deformation. It would be interesting to know also a direction of the weakest deformation. It is known that for fcc-based phases the weak direction for a tensile deformation is \([110]\). Although the \(D_0_{22}\) and \(L_{1_2}\) phases are fcc-like, the weakest direction is not determined by the symmetry of the crystal alone but also by the anisotropy of the bonding which is very pronounced in tetragonal phases, and particularly in the case of \(\text{Al}_3\text{V}\) in \(D_0_{22}\). The determination of the weakest direction would be an interesting but rather extensive study which exceeds the scope of our work.

In the next section computational tools are briefly described. In Sec. III we present a picture of bonding in the \(D_0_{22}\) and \(L_{1_2}\) structures. In Sec. IV we study the elastic properties and the tensile deformation of \(\text{Al}_3(Ti, V)\) compounds and compare them with the properties of the constituent metals: fcc Al, bcc V, and hcp Ti. In Sec. IV D we demonstrate how the interatomic bonding in \(\text{Al}_3\text{V}\) changes during the tensile deformations of the elementary cell.

### II. METHODOLOGY

The electronic structure calculations have been performed using two different techniques: The plane-wave basis Vienna *ab initio* simulation package VASP\(^{26,27}\) has been used for calculations of the electronic ground-state and for the optimization of the atomic volume and unit-cell geometry. The VASP-program has also been used to calculate charge-distributions. In its projector-augmented-wave (PAW) version\(^{27}\) VASP calculates the exact all-electron eigenstates, hence it can produce realistic electron-densities. The plane-wave basis allows to calculate Hellmann-Feynman forces acting on the atoms and stresses on the unit cell. The total energy may by optimized with respect to the volume and the shape of the unit cell and to the positions of the atoms within the cell. We used VASP for highly accurate calculations of the total energy changes necessary for the determination of the elastic constants. VASP was successfully used also for the calculation of stresses during our tensile computer experiments. All our calculation were performed with PAW pseudopotentials in generalized gradient approximation (GGA) according to Perdew and Wang.\(^{28}\)

For Al and Ti we used the standard PAW pseudopotentials (PP) distributed by VASP with reference configurations \(\text{Al}:[\text{Ne}]3s^23p^1\) and \(\text{Ti}:[\text{Ar}]3d^24s^2\). In the case of vanadium we obtained better results with PP which treat the 3-p core electrons as valence electrons, in the reference configuration \(\text{V}:[\text{Ar}]3p^34d^4s^1\). It is well known that the 3-p en-
energy levels of the early transition metals are close to the bottom of the valence band and exhibit non-negligible broadening. This seems to be the reason why the standard vanadium PP does not reproduce the V-V interaction correctly. However, as in the studied Al-V compounds there are not any direct V-V interactions we could use the standard PP for these compounds.

A plane-wave-based approach such as used in VASP produces only the Bloch-states and the total density of states (DOS), a decomposition into local orbitals and local orbital-projected DOS’s requiring additional assumptions. To achieve this decomposition, self-consistent electronic structure calculations have been performed using the tight-binding linear muffin-tin orbital (TB-LMTO) method in an atomic-sphere approximation (ASA). The minimal LMTO basis includes s, p, and d-orbitals for each Al and TM atom. The two-center TB-LMTO Hamiltonian has been constructed and diagonalized using the standard diagonalization techniques. The TB-LMTO basis is used to construct the symmetrized hybrid orbitals from which the DOS projected on bonding and antibonding configurations are calculated. The difference between bonding and antibonding configurations of two orbitals \( \phi_1 \) and \( \phi_2 \), located on two neighboring atoms is proportional to \( \langle \phi_1 | \delta(E-H) | \phi_2 \rangle \). This information is essentially equivalent to the crystal-orbital overlap populations (COOP) introduced by Hoffmann. We note that also a more sophisticated approach to the characterization of the interatomic bonding has been proposed.

III. STRUCTURE AND INTERATOMIC BONDING

A. \( Al_3(V,Ti) \) in the \( D0_{22} \) crystal structure

Both stable \( Al_3V \) and \( Al_3Ti \) phases crystallize in the \( D0_{22} \) (\( Al_3Ti \)) crystal structure. The space group is \( 14/mmm \) (No. 139). The primitive cell contains 4 atoms. The tetragonal elementary cell consists of two primitive cells, see Fig. 1. All atoms are located on the sites of a slightly tetragonally deformed face-centered-cubic (fcc) lattice. The elementary cell consists of two fcc units stacked along the \( z \)-direction. In the \( z=0 \) plane the vertices of the cubic lattice are occupied by transition metal (TM) atoms and the face-centers by aluminum atoms. In the \( z=0.5 \) plane the arrangement is the opposite. The planes \( z=0.25 \) and \( z=0.75 \) are occupied by aluminum atoms only. In the elementary cell there are one TM crystallographic site (Wyckoff notation 2a) and two aluminum sites \( Al_1 \) (2b) and \( Al_2 \) (4d). Each TM atom has 4 \( Al_1 \) neighbors and 8 \( Al_2 \) neighbors. \( Al_1 \) neighbors are located in the \((x,y)\) plane at \( z=0 \) and \( z=0.5 \) on vertices of a square centered by the TM atom. Considering only nearest neighbors the point-group symmetry of the TM-site would be \( O_h \), but nonequivalent neighbors from the second and higher shells reduce the point-group symmetry to \( D_{4h} \). An \( Al_1 \) atom sees 4 TM neighbors on the vertices of a square and 8 \( Al_2 \) neighbors forming a tetragonal prism centered by the \( Al_1 \) atom. \( Al_2 \) has four \( Al_1 \) neighbors in the \((x,y)\) plane forming together a square grid of aluminum atoms. \( Al_2 \) has also 4 \( Al_1 \) and 4 TM neighbors, both with tetrahedral coordination. In summary, the TM atom has 12 aluminum nearest neighbors, both aluminum atoms have 4 TM neighbors and 8 aluminum neighbors in the first coordination shell.

The \( D0_{22} \) structure may be considered as a superstructure of the simple cubic \( L1_2 \) cell, described in the next subsection. The \( D0_{22} \) unit cell consists of two \( L1_2 \) cubes stacked along, say, the \( z \)-direction, with a \([1/2,1/2,0]\) antiphase shift between the cubes. This structure can be also viewed as a stacking of two types of tetragonal planes. The plane \( A \) consists of \( Al_1 \) and TM atoms occupying vertices of a square network, the plane \( B \) consists of \( Al_2 \) atoms only. The stacking of the planes is \( ABA'BA'... \), where \( A' \) is the \( A \) plane shifted horizontally with respect to \( A \) by a half of a square diagonal.

The lattice parameters of the elementary cells are given in Table I. We note that during the tensile deformations discussed later in this paper the distance between planes increases with increasing \( c \) parameter while the \( a \) parameter shrinks.

B. \( Al_3(V,Ti) \) in the \( L1_2 \) crystal structure

The \( L1_2 \) (\( Cu_3Au \)) crystal structure is similar to the \( D0_{22} \) structure, but its symmetry is higher. The space group is \( Pm3m \) (No. 221), all atoms are located on the sites of a
face-centered-cubic lattice, see Fig. 1(b). TM atoms are located on the vertices of the cubic lattice, aluminum atoms occupy the face centers. In contrast to the \( D_{022} \) structure there is only one Al site (3c) and one TM site (1a). An aluminum atom has 12 nearest neighbors, 8 aluminum, and 4 TM atoms. A TM atom has 12 equivalent aluminum nearest neighbors. The total number of nearest neighbors around aluminum and TM atoms is thus the same as in the \( D_{022} \) structure. A notable difference between both structures is that all nearest-neighbor Al-TM and Al—Al distances are the same and that the point-group symmetry of the TM site is exactly \( O_h \). The \( L1_2 \) structure can be viewed as an \( ABAB \ldots \) stacking of the same \( A \) and \( B \) planes as in the \( D_{022} \) structure.

### C. Electronic structure

The electronic structure of Al-TM systems typically exhibits a narrow TM \( d \)-band superposed on a parabolic-like Al band. The total density of states is more or less modulated by van Hove singularities, bonding-antibonding \( d \)-band splitting and possible hybridization effects. For transition metals the Fermi level is located in a region of high density of states, which results in the characteristic metallic properties of the system.

The electronic structure of both Al\(_3\)V and Al\(_3\)Ti is well known. \(^\text{35,36,20}\) Figure 2 compares the total density of states (DOS) of Al\(_3\)Ti and Al\(_3\)V, both in the \( D_{022} \) structure and Al\(_3\)V in the \( L1_2 \) crystal structure. Around the Fermi level the TM contribution to the DOS is almost entirely formed by the \( d \)-electrons. The most interesting feature is the deep minimum at the Fermi level in the DOS of Al\(_3\)V in the \( D_{022} \) structure. Although the V site in the \( L1_2 \) structure has full \( O_h \) symmetry, the splitting of the vanadium \( d \)-band is not so clearly resolved as in the \( D_{022} \) structure where the point-group symmetry of the vanadium site is only \( D_{4h} \). The splitting of the \( d \)-band in the \( D_{022} \) structure, therefore, cannot be attributed to the \( e_g-t_{2g} \) splitting of \( d \)-orbitals in a local field with \( O_h \) point-group symmetry. Our recent study\(^\text{20}\) revealed that the origin of the deep minimum is in the bonding-antibonding splitting of molecular orbitals formed predominantly by \( sp^3 \) hybrids on the Al\(_3\)Ti sites and \((d_{zx},d_{zy})\) orbitals on the vanadium sites. The bonding of the Al\(_3\)V atoms with V exhibits enhanced covalency as discussed in next Sec. III D.

The similarity of the shape of the DOS of Al\(_3\)Ti with that of Al\(_3\)V is not surprising as both are of the same crystal structure. The minimum of the DOS of Al\(_3\)Ti falls \( \approx \)0.85 eV above the Fermi level. The minimum has apparently the same origin as in Al\(_3\)V, but the position of the Fermi level indicates that the Al\(_2\)-Ti bonds are not fully saturated.

### D. Charge densities and bonding

Using the VASP program we calculated the charge-density distribution in the elementary cells of Al\(_3\)V and Al\(_3\)Ti. Figure 3 compares a contour plot of the valence-charge distribution in the elementary cells of the \( D_{022} \) and \( L1_2 \) structures for the \((x,z)\) plane at \( y=0.5 \). If the character of the bonding is purely metallic, the charge distribution among atoms should be homogenous. A possible covalency is indicated by an enhanced charge distribution along connections between atoms. In Fig. 3 we see regions of enhanced charge-density between the TM atom and neighboring Al atoms. For Al\(_3\)V and Al\(_3\)Ti in the \( D_{022} \) structure we observe an enhanced charge-density approximately halfway between the central TM atom and the neighboring Al\(_3\) atoms. These maxima of charge density correspond to \( sp^3 \) hybrids on the Al\(_3\) atoms are bonded with \( d_{zz} \) orbitals on the TM atoms (see below). A similar bonding is observed also for Al\(_3\)V and Al\(_3\)Ti in the \( L1_2 \) structure. Here the enhanced charge distribution between Al and TM atoms corresponds to the \( sp^2d \) hybrid orbitals on Al atoms bonded with \( d_{xz} \) orbitals on the vanadium atoms. The maximum of the charge density in
halfway between the central V atom and the Al₂ atoms (marked in Fig. 3 by a dot) has in the case of the $D_{022}$ structure the value of 0.24 electrons/Å³. In the case of the $L1_2$ structure this value of 0.23 electrons/Å³ is little lower. In the case of the Al₁Ti compounds for both crystal structures we found the same value of 0.22 electrons/Å³.

A similar analysis was performed for other bonding configurations in the elementary cells. A detailed discussion of the results for Al₁V can be found in our previous work.²⁰ In summary, we identified three types of bonds, as sketched in Fig. 4: Each vanadium atom forms two types of bonds: V-Al₂ bonds are marked as dashed lines, V-Al₁ bonds are displayed as dash-dotted line segments. The Al₂ atoms form also Al₂-Al₂ bonds marked in Fig. 4 by dotted lines. All bonds are characterized by an enhanced degree of covalency. Al₁ and Al₂ atoms are also nearest neighbors, but from the analysis of the charge density distribution it is obvious that

FIG. 2. Comparison of the density of states of Al₃V and Al₃Ti in the $D_{022}$ and $L1_2$ structures. Al₃Ti in $D_{022}$ (a), Al₃V in $D_{022}$ (b), Al₁Ti in $L1_2$ (c), and Al₁V in $L1_2$ (d). Thin lines represent the contribution from d-electrons.

FIG. 3. Comparison of the contour plots of valence electron density in the $(x,z)$ plane of the $D_{022}$ and $L1_2$ structures for $y$ = 0.5. High charge density—black regions corresponds to the TM atoms. Positions of the aluminum atoms are marked by small black (Al₁) and gray (Al₂) circles. The islands of enhanced charge between the central TM atom and neighboring Al atoms marked by black dots. Al₁V in $D_{022}$ (a), Al₁Ti in $D_{022}$ (b), Al₁V in $L1_2$ (c), and Al₁Ti in $L1_2$ (d).

FIG. 4. An elementary cell of Al₃V in the $D_{022}$ structure. Positions of aluminum atoms are represented by smaller black (Al₁) and gray (Al₂) circles, positions of vanadium atoms are represented by larger circles. Three types of covalent bonds are sketched: V-Al₂ bonds are marked as dashed lines, V-Al₁ bonds are displayed as dash-dotted lines, Al₂-Al₂ bonds are marked in by dotted line segments.
The character of bonding in the $D_{0_{22}}$ structure can be described as follows: (i) $V(Ti)\cdot Al_1$ bonds. The $V(Ti)$ atom interacts with four $Al_1$ atoms in the A plane (see dot-dashed line segments in the Fig. 4). The corresponding set of symmetrized hybrid orbitals centered at $Al_1$ is $sp^3d$ with $s$, $p_x$, $p_y$, and $d_{xy}$ orbitals. From the point of view of the $V(Ti)$ atom the $V(Ti)\cdot Al_1$ bonds are oriented from the central $V(Ti)$ atom to four $Al_1$ atoms located at the vertices of a square. The corresponding set of symmetrized orbitals is again $sp^3d$. However, as the contribution of $p$-states to the TM DOS is negligible and the contribution of $s$-states is small, the $d_{xy}$ orbital is dominant. The calculated projected density of states shows that for $Al_1V$ the states below the Fermi level have almost completely bonding character while above the Fermi level the states are antibonding. For $Al_3Ti$ the bonding orbitals are not completely saturated.

(ii) $V(Ti)\cdot Al_2$ bonds. The $V(Ti)$ atom is bonded with four $Al_2$ atoms located in vertices of a tetragonal prism, see dashed lines in the Fig. 4. These bonds mediate inter-planar bonding between atomic planes $A$, $B$ and $A'$, $B$. The $Al_2$ atoms have four $V(Ti)$ neighbors located at the vertices of a tetrahedron. The symmetrized orbitals on the $Al_2$ atoms are thus $sp^3$ hybrids. We found that bonding from $V(Ti)$ side is mediated by $d^4$ hybrid orbitals formed by $d_{xz}$, $d_{yz}$, $d_{zx}$, $d_{xy}$ states (or $sd^3$ hybridization if we consider $s$ orbital instead of $d_z$). Four $d^4$ hybridized orbitals possess inversion symmetry point towards the vertices of a tetragonal prism. A more detailed analysis of the $V(Ti)(d^4)\cdot Al_2(sp^3)$ bonding has shown that the main bonding contribution out of the four $d^4$ hybridized orbitals comes from the components $d_{xz}$ and $d_{yz}$ both belonging to the $E_g$ irreducible representation. Figures 5(a) and 5(b) represent the bonding and antibonding densities corresponding to bonding of the $d_{xy}$ orbital on the $V(Ti)$ atoms with $sp^3$ hybrids on $Al_2$ atoms. While for $V\cdot Al_2$ the bonding-antibonding projected DOS changes sign almost exactly at the Fermi level, for $Ti\cdot Al_2$ this change of the sign is $=0.85$ eV above the Fermi level.

(iii) $Al_2\cdot Al_2$ bonds. Each $Al_2$ atom has four $Al_2$ neighbors located at the vertices of a square located in plane $B$. The symmetrized orbitals correspond to an $sp^3d$ hybridization. Although the bond exhibits enhanced covalency, it is only partially populated by electrons. The calculated bonding-antibonding projected DOS does not change its sign at the Fermi level, these bonds are not fully saturated.

The picture of bonding in $Al_2(V,Ti)$ in the $L_{12}$ structure is more simple as here only one type of bonding exists, namely $V(Ti)\cdot Al$ bond. Each TM atom has twelve $Al$ neighbors located in three orthogonal planes. The bonding in each plane is the same. From the TM side the bonding is mediated predominantly by $d$-orbitals with $e_y$ symmetry, from the $Al$ side we have $sp^3d$ hybrids. Figure 5(c) shows the bonding and antibonding densities of states in $Al_2V$. The symmetry of the local neighborhood of the $Al$ site favors participation of $Al$ $d$-states in the bonding. The bond is not saturated as the bonding-antibonding projected DOS changes sign $=1$ eV above the Fermi level. In $Al_3Ti$ [Fig. 5(d)] the saturation of the $Ti\cdot Al_1$ bonds is even smaller.

FIG. 5. The density of states projected on bonding (B) and antibonding (A) combinations of symmetrized hybrid orbitals located on atoms (dotted lines). In addition the difference (B-A) between bonding and antibonding DOS is presented by a thick line. This figure compares TM($d_{yz}$)$- Al_1(sp^3)$ bonding for $Al_3Ti$ in $D_{0_{22}}$ (a), $Al_3V$ in $D_{0_{22}}$ (b), and TM($d_{yz}$)$- Al_1(sp^3d)$ bonding for $Al_3Ti$ in $L_{12}$ (c), and $Al_3V$ in $L_{12}$ (d).

there is no significant bonding between them. The picture of bonding in $Al_3Ti$ is very similar to that in $Al_3V$. The main difference are less saturated and hence weaker $Ti\cdot Al$ bonds. A comprehensive analysis of the stability of $Al_3Ti$ interpreted in a chemical language of interatomic bonding was performed recently by Bester and Fähnle and leads to the same conclusion.

To gain a deeper understanding of the bonding, we constructed sets of symmetrized hybrid orbitals oriented along the bonds and calculated the density of states projected onto bonding and antibonding combinations of these symmetrized orbitals. The difference of these projected DOS's is essentially equivalent to the differential crystal orbital overlap population (COOP) defined by Hoffmann. Figure 5 compares the projected DOS's for $Al_3V$ and $Al_3Ti$ in the $D_{0_{22}}$ and in the $L_{12}$ structures. In addition to the bonding and antibonding DOS the difference between bonding and antibonding densities is presented.
TABLE II. Computed and experimental values of elastic constants and related material properties of Al, V, Ti, and their compounds. The line under each set correspond to experimental value for that element or structure, \( B \) represents bulk modulus in GPa, \( C_{ij} \) is set of elastic constants typical for each crystal, all in GPa, \( C' \)—shear modulus in GPa, relevant only for cubic structures, \( G/B \)—ratio between shear modulus \( G \) and bulk modulus, \( Y \)—Young’s modulus in GPa and \( \nu \) is Poisson’s ratio (two values correspond to tension along the \( x \) and \( z \) axis).

<table>
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<th>System</th>
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<th>( C_{11} )</th>
<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>( C_{66} )</th>
<th>( C' )</th>
<th>( G/B )</th>
<th>( Y )</th>
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<td>55</td>
<td>0.31</td>
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<td>Ti(hcp)</td>
<td>118</td>
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<td>40</td>
<td>40</td>
<td>0.43</td>
<td>148/133</td>
<td>0.27/0.32</td>
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<td>Exp. (Ref. 47)</td>
<td>107</td>
<td>162</td>
<td>92</td>
<td>69</td>
<td>181</td>
<td>47</td>
<td>47</td>
<td>0.46</td>
<td>103/147</td>
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<td>Al(<em>1)V (D0(</em>{22}))</td>
<td>118</td>
<td>233</td>
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<td>258</td>
<td>104</td>
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<tr>
<td>Al(_1)V (L1(_2))</td>
<td>118</td>
<td>178</td>
<td>88</td>
<td>87</td>
<td>45</td>
<td>59</td>
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<td>0.65</td>
<td>120</td>
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<tr>
<td>Al(<em>1)Ti (D0(</em>{22}))</td>
<td>107</td>
<td>192</td>
<td>84</td>
<td>49</td>
<td>216</td>
<td>94</td>
<td>94</td>
<td>0.84</td>
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<td>other calc.</td>
<td>118(^{a,b,c,d})</td>
<td>120(^b)</td>
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<td>Al(_1)Ti (L1(_2))</td>
<td>107</td>
<td>192</td>
<td>65</td>
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<tr>
<td>Al(_{10})V (cF176)</td>
<td>85</td>
<td>116</td>
<td>69</td>
<td>62</td>
<td>24</td>
<td>55</td>
<td>55</td>
<td>0.55</td>
<td>65</td>
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</table>

\(^a\)FLAPW results of Ref. 50.
\(^b\)LMTO-ASA results of Ref. 51 (LDA).
\(^c\)FLAPW results of Ref. 52 (LDA).
\(^d\)FP-LMTO results of Ref. 53 (LDA).

Comparing the total DOS’s (Fig. 2) and the projected DOS’s (Fig. 5) of both Al\(_1\)V crystal structures we see that while the high vanadium \( d \)-peak at \( \approx 0.8 \) eV above the Fermi level in the DOS of \( D0_{22} \) has antibonding character, the similar high vanadium \( d \)-peak just above the Fermi level in case of \( L1_2 \) structure has still bonding character. This will be confirmed also in Sec. IV C by examination of the variation of the strength of bonding under tensile deformation.

IV. INTERATOMIC BONDING AND MECHANICAL PROPERTIES

A. Elastic properties

For the calculation of the elastic constants we used the symmetry-general least-squares extraction method proposed by Le Page and Saxe.\(^{37}\) This novel method allows automated approach to the calculation of a set of elastic constants for a crystal of arbitrary crystalline symmetry. The input consists of a set of values of the total energy for special strained states of the crystal. We implemented the method in connection to VASP. The combination of this two programs creates a very powerful tool for calculation of elastic constants.

All elastic constants and related quantities are in Table II. In this work we are dealing with crystals of three different symmetry classes: cubic (bcc, fcc, \( L1_2 \), and cF176 in Pearson notation), hexagonal (hcp) and tetragonal (\( D0_{22} \)). For each symmetry there exists a set of independent elastic constants. For cubic symmetry there are three independent elastic constants, \( C_{11} \), \( C_{12} \), and \( C_{44} \) for a tetragonal crystal with \( 4/mmm \) symmetry there are six constants, \( C_{11}=C_{22}, C_{33}, C_{44}=C_{55}, C_{66}, C_{12} \) and \( C_{13}=C_{23} \). Hexagonal crystals have five independent elastic constants, the same set of elastic constants as for the tetragonal crystals except \( C_{66} \): \( C_{66} = \frac{1}{2}(C_{11} − C_{12}) \), see Ref. 38. To obtain the set of elastic constants from the changes of the total energy one has to apply a set of distortions (strains) on the crystal. For tetragonal symmetry we applied the strains: \( \pm \epsilon_1, \epsilon_1 \pm \epsilon_3, \epsilon_1 \pm \epsilon_5, \pm \epsilon_6, \pm \epsilon_4, \) and \( \pm \epsilon_6 \), for hexagonal symmetry the same set without \( \pm \epsilon_6 \) and for crystals with the cubic symmetry: \( \pm \epsilon_1, \epsilon_1 \pm \epsilon_3, \) and \( \pm \epsilon_4 \). For each set of strain \( \pm \epsilon_i \) three different magnitudes 0.25\%, 0.5\%, and 0.75\% were used.

The small total energy differences between the strained states must be calculated with a very high precision. It is also important that the internal atomic positions not fixed by symmetry are fully relaxed. All total energy calculation were done with VASP with the accuracy parameter set to HIGH, which results in a cutoff of the plane-wave basis increased by 25\%. For all cubic crystalline elements we used a very fine \( k \)-point mesh (\( 25 \times 25 \times 25 \)). This gives almost 1000 \( k \)-points in the irreducible part of the Brillouin zone (IBZ) for the unstrained state and about 2000 for strained states. For the tetragonal binary compounds, because of the higher number of atoms in the elementary cell we could use a somewhat smaller number of \( k \)-points (\( 20 \times 20 \times 10 \)). The total energy was calculated using the tetrahedron method with Blöchl corrections,\(^{39}\) converged to \( 10^{-7} \) eV/atom.

A good check for the calculated elastic constants is a consistency test. The bulk modulus can be computed from the elastic constants and independently also from the energy vs volume curve. A similar consistency test is possible for the Young modulus. It can be calculated from the elastic constants or extracted from the stress-strain curve as the slope of this curve at the origin.
In Table II available experimental values are also presented. The overall agreement of theory and experiment is satisfactory. One notable exception is the value of the $C_{44}$ parameter of bcc vanadium. The experimental value of 47 GPa here differs substantially from the calculated one of 20 GPa. Vanadium exhibits the highest value of the bulk modulus, $B=185$ GPa. This value is somewhat overestimated by the calculations. The reason for the discrepancy noted for V (too high bulk modulus, too small resistance to tetragonal shear) are not clear at the moment. Calculations with full-potential linearized augmented plane wave methods (FP-LAPW) have led to similar conclusions. On the other hand the bulk modulus of Al is the lowest, $B=75$ GPa. The bulk moduli of transition metal aluminides lie between these extremal values. The calculated values of $B$ approximately follow the relation $B \approx \eta^2$, where $\eta$ is the electron density.\(^{40}\)

The comparison of the values of bulk moduli shows that the bulk modulus does not depend significantly on the structure, but depends dominantly on the chemical composition. This is clearly seen from the results for Al$_3$V and Al$_3$Ti in both crystal structures. Both calculated values of $B$ are the same, $B=118$ GPa and $B=107$ GPa, respectively.

For engineering applications the most important quantity is the Young modulus. The Young modulus is highest for Al$_3$V in the $DO_{22}$ structure. Its value is particularly high in the $Y$ direction, $Y=244$ GPa. This high value can be attributed to enhanced covalency of the Al-V bonds. Relative values of $Y$ for other systems well agree with the picture of bonding resulting from the analysis of the charge distribution. In the case of vanadium the calculated Young modulus $Y_{(100)}=175$ GPa is somewhat higher than the value of $Y_{(100)}=155$ GPa calculated from the experimental values of the elastic constants. This discrepancy is obviously related to the problem with the $C_{44}$ constant mentioned above.

**B. Triaxial deformations**

The ideal strength represents the upper strength limit for a solid under a given load. Triaxial (hydrostatic) tension is considered to lead to the highest value of the ideal strength. There exist some strong arguments suggesting that for cubic structures no other types of instability (phase transformation, phonon resonance, shear collapse) occur before reaching the strength limit during deformation under hydrostatic tension.\(^3\) The ideal strength is relatively easy to calculate. However, from the experimental point of view a verification of these values is extremely difficult. Triaxial tension occurs in the solid in the vicinity of some type of defects in the microstructure of crystalline solids, e.g., cracks, voids, or grain boundaries.\(^5\) The ideal strength of solids under triaxial isotropic deformation was studied by several authors.\(^{4,6,17}\)

Figure 6 shows the stress-strain relation of elemental metals and intermetallic compounds under triaxial deformation. In addition to the systems considered so far the figure includes also the curve for Al$_{10}$V. All significant results from the triaxial deformations are collected in the Table III. The ideal strength corresponds to the maximum of the induced stress.

The stress-strain curves of the elements demonstrate higher strength of bonding in TM elements in comparison with Al. It is remarkable that for large strains the stress-strain curves of all transition metal aluminides converge to the approximately same value as for pure fcc Al. This behavior is apparently the consequence of a shorter range of the Al-TM bond exhibiting enhanced covalency in comparison with the predominantly metallic Al—Al bonding. In this sense the study of triaxial strength can be considered as a probe of the interatomic bonding.

The comparison of the values in Table III reveals some interesting relations. It seems that all fcc-like structures (Al, Al$_3$V and Al$_3$Ti in $L1_2$, Al$_{10}$V) have the same value of the triaxial tensile strain, $\varepsilon_{tiss} \approx 14.4\%$ at which the stress reaches its maximum. Similarly, all $DO_{22}$ structures reach their stress maximum at about $\varepsilon_{tiss} \approx 15.2\%$. Although the difference of these values is small, it apparently reflects a difference in the bonding.

**C. Uniaxial tensile deformations**

A better probe for the characterization of interatomic bonding in crystals than the isotropic triaxial deformation is...
an uniaxial tensile deformation. We imposed a tensile strain on the Al$_3$V and Al$_3$Ti crystals in both the D0$_{22}$ and L1$_2$ structures. The strain was imposed in the high-symmetry direction (001) common for both crystal structures. We consider a quasireversible deformation process at zero absolute temperature. The total energy and induced stresses of the strained crystals are calculated. For a higher accuracy of the stress tensor we increased the plane wave cutoff by 30% or even more, which results in 350 eV for the binary compounds and 320, 245, 250 eV for Al, Ti, and V, respectively. The k-point sampling was the same as used at the calculation of the elastic constant. The calculation proceeds by evaluating the energy and stress as a function of the tetragonal lattice constants $a$, and $c$. As the parameter $c$ increases, the crystal is reconfigured at every step to relax the lateral stresses. For comparison we have performed the same study also for all constituent elements: fcc Al, bcc V, and hcp Ti. As both D0$_{22}$ and L1$_2$ structures are certain variants of an fcc structure it is possible to compare the results directly with fcc Al. The comparison with bcc V, and hcp Ti crystals is less straightforward.

Figure 7 collects the results of the tensile deformation calculations. In the upper panel [Fig. 7(a)] the strain-stress curves of constituent elements Al, V, and Ti are presented, in the lower panel [Fig. 7(b)] the results for Al$_3$V and Al$_3$Ti crystals are shown. Full curves represent stresses induced by tensile strain applied on the elementary cells. Near the origin one observes a short region of a linear behavior. The slope of the linear part of the stress-strain curve near the origin is related to the Young modulus that can be calculated also from the elastic constants—dotted straight lines, cf. text.

no other instabilities occur before reaching it.

The stress-strain curve for an fcc Al crystal deformed along the [100] direction increases monotonously and reaches its maximum of $\sigma_{uis}$=11.4 GPa at the strain $\varepsilon_{uis}$=34.3%. These values can be compared with the results of other authors. Clatterbuck et al. 17 report a value of $\sigma_{uis}$=12.92 GPa at $\varepsilon_{uis}$=34.0%. In addition to the [100] direction we have calculated for fcc Al the stress-strain curve for tensile strain along the [111] direction. For this case a maximal stress of $\sigma_{uis}[111]$=9.8 GPa is obtained for the strain of $\varepsilon_{uis}[111]$=34.7%. These values can again be compared with those of Clatterbuck et al. For [111] tension they report values of $\sigma_{uis}[111]$=11.30 GPa at $\varepsilon_{uis}[111]$=33.0%. Our values of the maximal stresses are by about 10% lower, but it is necessary to emphasize that Clatterbuck et al. performed their calculations within the LDA while our values were obtained using the GGA exchange-correlation functional. It is known that the LDA consistently gives
smaller lattice constants and a stress that is 10%–20% higher than that obtained in the GGA. The ideal strength in a tensile deformation is significantly higher than the value of the ideal shear strength. Roundy et al. report an ideal shear strength for fcc Al of 1.85 GPa. We did not calculate the ideal shear strengths as it would go beyond the scope of this work.

The value of the Young modulus of Y = 73 GPa extracted from the linear (elastic) region agrees well with the experimental value, see Table II. Aluminum is known to have rather isotropic Young moduli calculated for different crystal directions. A similar isotropy is observed also under tensile deformations. The triaxial strength of Al is \( \sigma_\text{uis} = 11.1 \) GPa, a value comparable with maximum stresses of 11.4 and 9.8 GPa under uniaxial deformation along the [100] and [111] directions, respectively.

Figure 7(a) shows also the stress-strain curve of bcc vanadium. The shape of this curve differs substantially from the other materials. A bcc crystal deformed tetragonally in the (001) direction transforms to a stress-free fcc crystal. The stress-strain curve intersects here the zero value. This transformation path is known as the Bain path. Along this path the crystal undergoes a bcc \( \rightarrow \) fcc phase transition. The strain at which the bcc cell assumes the fcc structure (Bain strain) at constant volume is \( e = (\sqrt{3} - 1) \times 100 = 25.99\% \). At this strain the c/a ratio of the tetragonally deformed bcc lattice is just equal to 1/\( \sqrt{3} \) and the lattice becomes fcc. For tetragonally deformed bcc vanadium we got a value of Bain strain \( e_p = 27.4\% \) at an excess volume of 4.9%. The maximum value of the stress is \( \sigma_\text{uis} = 18.9 \) GPa at a strain of \( e_\text{uis} = 18.2\% \). The ideal strength of the related bcc metals Nb and Mo was studied recently by Luo et al. For tetragonally deformed bcc Nb homologous to V they report a similar value of the peak stress of \( \sigma_\text{uis} = 18.8 \) GPa. However, they also found that between the bcc and the stress-free fcc structure the body-centered tetragonal (bct) structure is not stable against orthorhombic deformations. The ideal strength along a path allowing for orthorhombic deformations (the orthorhombic path) is \( \sigma_\text{uiot} = 13.1 \) GPa, i.e., it is significantly lower than that for the tetragonal path. A similar instability along the tetragonal Bain path is expected also for vanadium.

It is obvious that the existence of a stress-free structure on the deformation path significantly reduces the peak value of the stress. This is to be the reason why the maximal stress of hcp Ti is higher than that of bcc V. (We note that if one continues with the tensile deformations beyond 50%, vanadium undergoes another structural phase transitions at a strain of 51.5% from fcc to bct and then at a strain of 98.0% the stress reaches a maximum of 36.6 GPa.) For hcp Ti we found a maximal stress of \( \sigma_\text{uis} = 23.6 \) GPa at a relatively high value of the strain of \( e_\text{uis} = 44.3\% \). A small inflection on the stress-strain curve between strains of 10%–15% requires a comment. The hcp structure can be viewed as a \( AA'AA' \) ... packing of hexagonal planes. We assume that the inflection is related to the disappearance of the covalent bonding component between the hexagonal planes. A detailed analysis of bonding shows that three neighboring atoms from the A plane together with two other atoms from the opposite A' planes form a strongly bonded cluster. The cluster has the shape of a trigonal bipyramid with two atoms from the A' plane in the tips. We observed a strong bond charge inside the bipyramid. This charge represents a covalent contribution to the inter-planar bonding. When the distance between the planes increases the inter-planar bond with enhanced covalency breaks and the bond charge is distributed homogeneously in the planes.

Figure 7(b) presents the stress-strain curves for Al\( _3 \)V and Al\( _3 \)Ti in the \( D_{022} \) and \( L1_2 \) crystal structures. The curves for both \( D_{022} \) compounds have a simple bow shape. The peak value of the stress is \( \sigma_\text{uis} = 28.2 \) GPa at a strain \( e_\text{uis} = 24.7\% \) for Al\( _3 \)V, and \( \sigma_\text{uis} = 25.2 \) GPa at \( e_\text{uis} = 29.4\% \) for Al\( _3 \)Ti. The ideal strengths of the same systems in the \( L1_2 \) structure are lower: \( \sigma_\text{uis} = 23.0 \) GPa at \( e_\text{uis} = 38.4\% \) for Al\( _3 \)V and \( \sigma_\text{uis} = 20.0 \) GPa at \( e_\text{uis} = 38.0\% \) for Al\( _3 \)Ti. All these results are consistent with the picture of bonding that we have deduced from the charge distribution analysis. Al–V bonds are more saturated and hence stronger than Al–Ti bonds, and this is reflected in higher values of the ideal strength of Al\( _3 \)V in comparison with those of Al\( _3 \)Ti in both structures. The higher symmetry of the \( L1_2 \) structure leads to a higher metallicity manifest in higher values of the strains corresponding to the peak values of stresses.

Although at first sight this picture seems to be satisfactory, there is one unanswered question. All the values of the maximal stresses in the transition metal aluminides are surprisingly high. The maximal value of the induced stress of Al\( _3 \)V in the \( D_{022} \) structure is 2.5 times higher than that of fcc Al and 1.5 times higher than that of V. There is no doubt that other deformation paths can lead to lower values of the maximal stresses, but this point is not so important. Both \( D_{022} \) and \( L1_2 \) structures are fcc-like structures and, therefore, so significant an increase of their strength along the same deformation path asks for an explanation.

It is tempting to attribute this increased strength to the enhanced covalency of the interplanar bonding. However, a detailed analysis shows that it is not the case. The covalent contribution to the interatomic bonding disappears at strains between 10% and 15%, but the maximal stress is observed at 24% or even at 38.4% in case of the \( L1_2 \) structure. What keeps the crystal together at such high strains? A possible answer to this question is suggested by the results presented in Fig. 8. Figure 8(a) shows the development of the lattice parameter \( a \) in the plane normal to the direction of the tensile strain during deformations. It is striking that for both Al\( _3 \)V and Al\( _3 \)Ti in the \( D_{022} \) structure the change of this parameter is minimal, at 50% strain the lattice parameter \( a \) is reduced only by \( \approx 3\% \). The change of the \( c \) parameter for both systems in the \( L1_2 \) structure is similar to that of fcc Al. A small change of the lattice parameter indicates stiffness of bonding in the atomic planes perpendicular to the direction of the tensile deformation. Below we shall demonstrate that this stiffness comes from an increased covalency of the in-plane bonding. Figure 8(b) shows development of the cell volume during tensile deformation. The almost linear variation observed for Al\( _3 \)V and Al\( _3 \)Ti confirms this argument. The change of the volume is the highest for both systems in the \( D_{022} \) structure. Interesting variations of volume are observed under tensile strain for V. The volume change increases up to a strain of 20%, at the stress-free fcc structure at \( e_\text{uis} = 27.4\% \) the excess volume is about 5%, but between \( e_\text{uis} \)
FIG. 8. The development of the lattice parameter $a$ (a) and excess volume (b) during the tensile deformation. It is striking that for both Al$_{3}$V and Al$_{3}$Ti in the $D_{022}$ structure the change of this parameter is minimal, at 50% strain the lattice parameter $a$ is reduced only by $\approx$3%. Small change of the lattice parameter indicate the stiffness of bonding in the atomic planes perpendicular to the direction of tensile deformation. The increase of the excess volume is the highest for both systems in the $D_{022}$ structures. Interesting variations of volume are observed in case of V. The excess volume between 32% and 48% is negative, i.e., the volume of the cell shrinks, cf. text.

FIG. 9. The changes of the total energy during tensile deformation of the monoatomic crystals Al, V, and Ti and their compounds Al$_{3}$V and Al$_{3}$Ti. The increase of the total energy per atom in the case of Al$_{3}$V in the $D_{022}$ structure is the highest.

$\approx$32% and 48% the excess volume is negative, i.e., the volume of the cell even shrinks. While for vanadium one could consider the volume of the elementary cell as being approximately constant (within 5% accuracy), other systems and particularly the $D_{022}$ structures are more close to the model where volume increases linearly with the strain.

It is also remarkable that changes of the lattice parameter $a$ and volume changes for both systems Al$_{3}$V and Al$_{3}$Ti in the $D_{022}$ crystal structure are almost identical. For the $L1_{2}$ structures a larger difference is seen. Such behavior can be deduced also from the elastic constants, see Table II. The elastic constant that relates the changes of the crystal in the $x$ and $z$ direction is Poisson’s ratio $\nu$. The calculated values of this constant for Al$_{3}$V and Al$_{3}$Ti in $D_{022}$ are $\nu$=0.15, and 0.18, respectively, i.e., they are almost identical and rather small. On the other hand, for the cubic $L1_{2}$ structure the values of this constant for Al$_{3}$V and Al$_{3}$Ti are $\nu$=0.33 and 0.25, respectively. These values are larger and do not coincide so well as in case of $D_{022}$. The elastic constants describe the behavior of the crystal only for small deformations, but the trends of this behavior in this linear region are continued also for larger deformations.

The $D_{022}$ and $L1_{2}$ structures can be considered as two different decorations of the fcc lattice. While the equilibrium lattice parameter $a$ in fcc Al is 4.05 Å in the $D_{022}$ structure the lattice parameter $a$ is 3.77 Å, i.e., 7% smaller. This means that already in the un-strained system the distances between the aluminum atoms in the $B$-plane are shrinked. The $D_{022}$ and $L1_{2}$ structures can be considered as two different decorations of the fcc lattice. While the equilibrium lattice parameter $a$ in fcc Al is 4.05 Å in the $D_{022}$ structure the lattice parameter $a$ is 3.77 Å, i.e., 7% smaller. This means that already in the un-strained system the distances between the aluminum atoms in the $B$-plane are shrinked.

Figure 9 presents changes of the total energy per atom during the tensile deformations. The increase of the total energy is largest for Al$_{3}$V in the $D_{022}$ structure. This strong increase reflects again the highest strength of bonding of Al$_{3}$V in the $D_{022}$ structure. The figure also confirms that the observed Al-TM bonding in Al$_{3}$V and Al$_{3}$Ti is stronger than TM-TM bonding in bcc V and hcp Ti.

D. Changes of bonding in Al$_{3}$V during tensile deformation

An uniaxial stretch of the crystal along the direction perpendicular to the planes can provide an insight to the character of bonding between the atomic planes. The structure of Al$_{3}$V can be considered as a $ABA'BA'$... stacking of the atomic planes, see Sec. III. With increasing strain the distance between $A$ and $B$ or $A'$ and $B$ increases equally.

Figures 10 and 11 display the difference electron-density, i.e., a superposition of the atomic charge-densities is subtracted from the total charge density. The contour plots represent the regions of positive difference electron-density in selected planes; in the blank space the difference density is negative. We remind the reader that vanadium forms two types of bonds: V-Al$_{2}$ bonds are marked in Fig. 4 as dashed lines, V-Al$_{1}$ bonds as dash-dotted lines. The Al$_{2}$ atoms have in addition to the bonds with the V atom Al$_{2}$-Al$_{2}$ bonds marked in Fig. 4 by dotted lines. Figures 10 and 11 show the
FIG. 10. The development of the bonding in Al$_2$V in the D0$_{22}$ structure. The contours represent the difference charge density in (x,0.5,z) plane in dependence on the tensile deformation, cf. text. The tension is imposed along z axis (horizontal). In undeformed states one can identify the bond-charges between the V (big black circle) and Al$_2$ atoms (gray circles). The bonds are directed from the central vanadium atom to the vertices of a tetragonal prism formed by the Al$_2$ atoms. These bonds mediate inter-planar bonding between atomic planes A, B, and A'. When the tensile strain is imposed the the inter-planar bonds are tilting to in-plane position and gradually transform to nonbonding states. This covalent component of this bonding disappears at the strains between 10% and 15%. On the other hand one observes development of bond charge between the neighboring vanadium atoms. The right hand panels show the the development of the density of states structure during tensile deformation. The deep pseudogap close to the Fermi level disappears with increasing strain simultaneously with the disappearance of the covalent interplanar bonding.

development of the difference electron-density for the three types of covalent bonds sketched in Fig. 4.

Figure 10 shows the difference charge density in the (x,0.5,z) plane. The tension is imposed along the z axis (horizontal). In the undeformed state one can clearly identify the “bond-charges” between the V and Al$_2$ atoms (gray circles). The bonds are directed from the central vanadium atom to the eight vertices of a tetragonal prism formed by the Al$_2$ atoms. The bond charges correspond to the tetrahedrally oriented $sp^3$ hybrids on the Al$_2$ atoms. The overlap of the $sp^3$ hybrids with the vanadium $d_z$ orbitals promotes the interplanar bonding between the planes A and B or A' and B.

In Fig. 11(a) bonding between the V and Al$_1$ atoms (small black circles) is presented. The figure shows the difference electron density in the (x,y) plane at $z=0.5$ (A' plane) and at $z=0.25$ (B plane). The bonds are directed from the central vanadium atom to the four vertices of a square formed by the Al$_1$ atoms. The picture of bonding in the A plane is the same as in the A' plane. An enhanced charge density can be observed also between Al$_2$ atoms in the B planes, Fig. 11(b).

When the tensile strain is imposed, the tetrahedrally oriented $sp^3$ hybrids on the Al$_2$ atoms tilt to a in-plane position and gradually transform to nonbonding states. The covalent component of the interplanar bonding disappears at strains between 10% and 15%. Although the distance between vanadium atoms in the A plane changes only little (less than 3%) one observes the development of bond charges between neighboring V atoms. This is the consequence of a charge flow from the interplanar region towards the atomic planes. This charge transfer has a significant effect on the in-plane bonding. The covalent bonds in the atomic planes become stronger. The increased strengths of the V-Al$_1$ bonds in the atomic plane A’ and of Al$_2$-Al$_2$ bonds in the plane B are distinctly observable in Figs. 11(a) and 11(b).

The right hand panels of Fig. 10 presents the development of the density of states in Al$_2$V in the D0$_{22}$ structure. The contours represent the difference charge density in $A'=(x,y,0.5)$ and $B=(x,y,0.25)$ planes in dependence on the tensile deformation. In the plane $A'$ the bonds of enhanced are directed from the central vanadium atom to the four vertices of a square formed by the Al$_1$ atoms (small circles). An enhanced charge density was found also in the planes at the B planes where Al$_2$ atoms (small gray circles) are located. In the strained states the covalency of bonds in both atomic planes becomes stronger. 

FIG. 11. The development of the bonding in Al$_2$V in the D0$_{22}$ structure. The contours represent the difference charge density in $A'=(x,y,0.5)$ and $B=(x,y,0.25)$ planes in dependence on the tensile deformation. In the plane $A'$ the bonds of enhanced are directed from the central vanadium atom to the four vertices of a square formed by the Al$_1$ atoms (small circles). An enhanced charge density was found also in the planes at the B planes where Al$_2$ atoms (small gray circles) are located. In the strained states the covalency of bonds in both atomic planes becomes stronger.
The increased covalency of the intraplanar bonding explains its higher stiffness preventing the shrinking of the lateral parameter $a$ under uniaxial deformation, cf. Fig. 8. On the other hand, as the covalent component of inter-planar bonding parallel to the direction of the strain disappears at a strain of $\approx 15\%$, the question what keeps the crystal together at larger strains still arises. We assume that the origin of the inter-planar bonding forces under large tensile strains comes from an increased kinetic energy of electrons associated with an increased spatial variation of the charge density in the strained crystal. When charge flows from the inter-planar space into atomic planes, the variation of the spatial charge density distribution increases.

A flow of charge from the inter-planar region to the atomic planes can be expected to occur in all systems loaded by tensile strains. We quantitatively analyzed these flows. A prerequisite for such an analysis is to characterize the charge distribution in the unstrained state. Figure 12 shows the distribution of the charge in the elementary cells across the direction of the tensile deformation. The figure shows the variation of the charge distribution in unstrained state, cf. text.

FIG. 12. Normalized distribution of the charge in the elementary cells across the direction of the tensile deformation. The figure shows the variation of the charge distribution in unstrained state, cf. text.

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FIG. 13. The relative change of the charge distribution in the elementary cells across the direction of the tensile deformation. The figure shows relative changes of the the charge distribution in strained state for $\varepsilon=50\%$, cf. with the previous figure.

$z=1$, the plane $B$ to $z=0.5$. There is no difference in the averaged charge density between the $A$ and $A'$ planes in the $D_{022}$ structure. For fcc and bcc crystals there is also no difference between $A$ and $A'$ planes. Figure 12 shows that the charge is most uniformly distributed in fcc Al. Going through the crystal along the $z$ axis the planar average varies between 0.9 and 1.06. A larger variation is seen in bcc vanadium, the averaged charge density varies between 0.87 and 1.19. The variation of the charge density in hcp Ti is even higher. The higher variation of the charge density in hcp Ti in comparison with that in bcc V has apparently origin in the higher separation of the atomic planes. The distance between the hexagonal planes in hcp Ti is 2.31 Å while in bcc V the distance between the considered atomic planes is 1.50 Å. For the $D_{022}$ and $L_{12}$ structures the variation of charge density is distinctly higher for the $D_{022}$ structures. The Al$_3$V compounds also exhibit a stronger variation than the Al$_3$Ti alloys. The variation of the charge density for Al$_3$V in the $D_{022}$ structure is thus the highest; the charge varies between 0.78 and 1.38, and for Al$_3$Ti in the $L_{12}$ structure the lowest; the charge varies between 0.85 and 1.14.

Figure 13 shows the relative differences of the averaged charge densities in atomic planes between the strained and
unstrained state. The difference increases with increasing strain. In the figure the differences of the charge density for the maximal imposed strain of 50% are presented. The figure provides insight how the charge flows from the inter-planar region into the atomic planes. In the A planes of both $DO_{22}$ and $L1_2$ structures the charge surplus is ≈60%. In the $B$ plane the charge increase differs; for both $DO_{22}$ structures it is ≈50% while for the both $L1_2$ structures it reaches ≈42%. A similar difference between the $DO_{22}$ and $L1_2$ structures is seen for the charge deficit between the atomic planes. The development of the charge deficit on the imposed strain is presented in Fig. 14. Again we observe distinctly different behavior for the $DO_{22}$ and $L1_2$ structures, but on the other hand differences between the Al$_3$V and Al$_3$Ti alloys are minimal.

V. DISCUSSION AND CONCLUSION

We have presented *ab initio* calculations of the tensile strengths of the intermetallic compounds Al$_3$V and Al$_3$Ti, both in their stable $DO_{22}$ and in their metastable $L1_2$ structures, and of the constituent elements: Face-centered cubic Al, body-centered cubic V, and hexagonal closepacked Ti. Our computer simulations of triaxial and uniaxial tensile deformations (with complete relaxation of lateral stresses) have been supplemented by the calculations of the elastic constants and by a detailed analysis of the changing character of the interatomic bonding during deformation.

For the cubic metals Al and V our results are in good agreement with earlier theoretical estimates of the stress-strain relation and the ideal tensile strength.\(^{17,41}\) The investigation of the hexagonal close-packed metal Ti and of the intermetallic trialuminide compounds leads to interesting and novel conclusions. The stress-strain relation of hcp Ti under uniaxial strain shows an inflection at strains in the range between 10% and 15%, related to a change in the bonding properties. The axial ratio of Ti is with $c/a = 1.583$ distinctly smaller than the value $c/a = 1.633$ for optimal dense packing, reflecting a certain degree of covalency of the inter-planar bonding. Under sufficiently strong uniaxial deformation the covalent character of the bonding disappears and the bonding assumes a more metallic character. Mixed metallic and covalent bonding also determines the physical properties of the intermetallic compounds Al$_3$V and Al$_3$Ti. In a previous study we had shown that the unique electronic and mechanical properties of Al$_3$V with the tetragonal $DO_{22}$ structure (deep pseudogap at the Fermi level, high hardness) are related to a substantial covalent contribution to both the V-Al and to some of the Al-Al bonds. The covalent V-Al bonding arises from the overlap of $sp^2d$-type hybrid orbitals on both the V and Al sites, the covalent contribution to the V-Al$_2$ bonds from the overlap of $sp^3$ hybrids on the Al sites with $d^4$ hybrid orbitals on the V sites. The bonding Al-Al orbitals have $sp^2$ character. In Al$_3$V all occupied states have predominantly bonding character, all empty states are antibonding. Due to a lower valence-electron concentration, the saturation of the covalent bonds is lower in tetragonal Al$_3$Ti than in Al$_3$V. In the metastable compounds with the cubic $L1_2$ structure, the higher site-symmetry at the TM sites leads to a $e_g^2t_{2g}^4$ splitting, the bonding is mediated mainly by linear combinations of $e_g$ states and $sp^2d$ hybrids, but the saturation of these bonds is lower than in the tetragonal phase. The increased covalency of Al$_3$V compared to Al$_3$Ti is reflected in higher values of the bulk modulus, the shear modulus and of Young’s modulus. The tetragonal and to the cubic phases of a given compound have approximately the same bulk modulus, but the more covalent cubic phase has higher shear and Young’s moduli.

Under triaxial (homogeneous) deformation we calculate a somewhat higher tensile strength for Al$_3$V than Al$_3$Ti, but there is no significant difference between the cubic and tetragonal phases. This demonstrates that under homogeneous deformation the relative mechanical properties deduced from the elastic limit may be extrapolated up to the maximum induced stress. Under uniaxial tensile deformation things are quite different: (i) The $DO_{22}$ phases have a significantly higher tensile strength at a smaller strain than the $L1_2$ phases. (ii) Al$_3$V has a higher maximum stress than Al$_3$Ti in both structures. (iii) The $DO_{22}$ phases show a very small reduction of the lateral lattice parameter in a plane perpendicular to the direction of the strain, reflecting the strength of the covalent intraplanar bonding. The $L1_2$ phases shrink in the lateral directions in an extent comparable to that observed for fcc Al. As a result we find a volume reduction which is almost equal to the linear strain for the tetragonal intermetallic compounds and a much smaller volume contraction at the same strain in the cubic compounds at in fcc Al. These differences in the stress-strain relations reflect the changing character of the interatomic bonding forces under uniaxial tensile strain. A detailed analysis of the charge-redistributions for tetragonal Al$_3$V shows that with increasing tensile deformations the strong covalent V-Al bonds are gradually destroyed while intraplanar V-V and Al-Al bonds build up. The interplanar bonding acquires a much more metallic character. We note that this is expected to lead to a lower resistance to shearing along a \{001\} plane, but this has not been explored in the present study.

The $DO_{22}$ and $L1_2$ structures are certain occupation variants of the fcc structure. It would be interesting to know how
the anisotropy of bonding observed in the $D_{0_{22}}$ and $L_1_2$ structures affects the anisotropy of the mechanical properties. Already in the fcc metals with a pure metallic and, therefore, isotropic interatomic bonding the mechanical properties exhibit strong anisotropy. For example, a tensile strength of Al of 4.9 GPa for a pull along [110] is significantly lower than the values for [001] (12.92 GPa) or [111] (11.30 GPa) directions. In fcc metals there is also an interesting relation between the tensile and shear deformations. The tension in (110) direction is closely related to a shear on ⟨112⟩{111}. This leads to an important result that an fcc metal does not cleave. It would be interesting to investigate whether this behavior pertains to the $D_{0_{22}}$ and $L_1_2$ structures where the strong anisotropy of bonding competes with the anisotropy originating from the geometry. We believe that in near future we shall be able to extend our calculations to investigate these competing anisotropies and to study their influence on the mechanical properties of the transition metal aluminides.

In summary: Our work represents one of the first attempts to extend atomistic studies of the ideal strength of metallic systems beyond the elemental metals. At the example of the trialuminides Al,V and Al,Ti we have explored the influence of a partially covalent bonding on the mechanical properties. In the elastic limit, covalent intra- and inter-planar bonding forces lead to a significant enhancement of the bulk, shear, and Young’s modulus, as well as to an increased ideal strength under triaxial loading. Under uniaxial stress the covalent bonding between planes perpendicular to the applied strain is gradually reduced, while the covalent intraplanar bonding is even enhanced.

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