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RESEARCH ARTICLE

Response of fcc metals and $L1_2$ and $D0_{22}$ type trialuminides to uniaxial loading along [100] and [001]: Ab-initio DFT calculations

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Ab-initio density-functional calculations have been used to investigate the response of the face-centred cubic (fcc) metals Al and Cu, and of the $L1_2$ - and $D0_{22}$ -type trialuminides $Al_3(Sc,Ti,V)$ to uniaxial loading along the [100] and [001] directions. The results obtained under uniaxial strains are compared to the response to biaxial (epitaxial) strains. The ideal tensile and compressive strengths and their limitation by shear instabilities along these deformations paths have been calculated. Although the response of both pure fcc metals could be expected to be very similar, our results show a fundamental difference: whereas for Cu a special invariant state with $C_{22} = C_{23}$, leading to a bifurcation from the tetragonal to an orthorhombic deformation path, is reached at a strain of 10%, for Al this state is reached only at a strain of 33% close to the critical strain defining the ideal tensile strength. The reaction of the $L1_2$ -type trialuminides is comparable to the response of Al, no bifurcation to an orthorhombic deformation path is predicted. The response of the $D0_{22}$ -type trialuminides is different from that of the $L1_2$ -type phases because of the difference in the stacking of the atomic planes along the [001]. For $D0_{22}$ -type trialuminides, the uniaxial compression along this direction or epitaxial tension in the (001) leads to the formation of a stress-free $D0_3$ structure, in complete analogy to the fcc $\rightleftharpoons$ bcc transformations observed for the pure metals. Under uniaxial [100] loading the guiding symmetry along the deformation path is orthorhombic and leads to the formation of special structures under both tension and compression parts, which are related to the $D0_3$ structure in the same way as the parent $D0_{22}$ -lattice to the $L1_2$ structure.

1. Introduction

Trialuminides of early transition-metal (TM) elements (Al_3TM , TM=Sc, Ti, V) are of great technological interest because of their potential applications as light-weight high performance structural materials [1–3]. However, their practical applications are limited because of high brittleness and poor ductility at room temperature. These undesirable properties are immediately related to the structural properties: Al_3Sc crystallises in the cubic $L1_2$ structure, while $Al_3(Ti,V)$ adopt the tetragonal $D0_{22}$ structure [4–6]. The observed poor ductility is attributed to the insufficient number of slip planes in the tetragonal structure to satisfy the von Mises criterion for slip deformation of polycrystalline aggregates [7, 8]. Therefore many attempts have been made to induce a transformation from the tetragonal to the cubic phase by the addition of ternary elements or mechanical alloying.

The technological interest has also stimulated a large number of theoretical investigations based on first-principles electronic structure methods. Based on an

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in-depth analysis of the electron structure, we have developed a bonding picture for the trialuminides in the language of hybrid atomic orbitals [9, 10], and we have established a correlation between this picture and the tensile anisotropy in the elastic limit [10, 11]. We have shown that in contrast to general expectation the anisotropies of the tensile strength and of the Young's modulus Y are only weakly correlated. This lack of correlation has been attributed to different deformation scenarios under loading along the $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 100 \rangle$ directions). Very recently we have presented a detailed study of the response to uniaxial tension along the $\langle 110 \rangle$ direction [12]. Now, we present the results for the next deformation path, i.e. $\langle 100 \rangle$ direction. Deformation under uniaxial $\langle 110 \rangle$ tension is essentially volume conserving, while deformation under uniaxial $\langle 100 \rangle$ loading (for the $L1_2$ phases) or $\langle 001 \rangle$ tension (for the $D0_{22}$ structures) is accompanied by a strong volume expansion [10].

The general theory of the response of cubic metals to uniaxial loading along the $\langle 100 \rangle$ directions has been developed in a series of classical papers by Milstein *et al.* [13, 14]. That a transformation from fcc to bcc occurs on a path of *compressive* $\langle 100 \rangle$ loading (i.e. along the Bain path) [15] had been known for some time, but Milstein and Farber [13] demonstrated that a fcc $\rightarrow$ bcc transition occurs also under strictly uniaxial $\langle 100 \rangle$ *tensile* strain. Starting from an unstressed fcc configuration, under initially uniaxial $\langle 100 \rangle$ tensile load, the crystal follows first a primary path with a tetragonal guiding symmetry. Hill and Milstein [16] had been shown a bifurcation to a secondary deformation path with orthorhombic guiding symmetry can occur under strictly uniaxial loading at a special "invariant eigenstate", where the elastic moduli satisfy $C_{22} = C_{23}$. This special state is directly associated with an shear instability which is required for a departure from tetragonality in the absence of a transverse load¹.

This secondary orthorhombic deformation path may be considered as the primary deformation path for bcc crystals under $\langle 110 \rangle$ loading [14]. This implies that a reverse transformation from bcc to fcc might be initiated by uniaxial compression along $\langle 110 \rangle$. Therefore, there exist three distinct transformation paths for the fcc $\rightarrow$ bcc phase transitions: (i) the Bain path, i.e. uniaxial $[100]$ compression on the primary deformation path, (ii) $[100]$ uniaxial tension induces a transformation to bcc via bifurcation at the "invariant eigenstate" with $C_{22} = C_{23}$, and (iii) uniaxial tension along $[110]$ where the initial deformation follows the secondary orthorhombic deformation path which branches to the primary tetragonal path for $C_{22} = C_{23}$. The analogous bcc $\rightarrow$ fcc transitions may follow just the reverse paths. Crystal symmetry causes the appearance of three stress-free states along the deformation path labelled F(fcc), B(bcc) and T (tetragonal), but the order of appearance of these unstressed states along the stress-strain curve depends on the specific material (or force-field model). The three possible orderings are, taking fcc as the reference state: (I) F, T, B, (II) F, B, T, and (III) T, F, B under tensile loading (the sequence is the reverse under compression). The centrally located stress-free state is always unstable, due a falling load. Either or both other unstressed states may be elastically stable. Case (I) is realised for the alkali's [14]. For these metals it is known that the uniaxial tensile or compressive stresses required to initiate a transformation from bcc to fcc are two orders of magnitude lower than the hydrostatic pressures required to initiate this transition. Case (II) is realised e.g., for the

¹Note that the invariance condition has been formulated for uniaxial strain along $[100]$ where $C_{22} = C_{33}$ and $C_{12} = C_{13}$. Under uniaxial $[001]$ loading where $C_{11} = C_{22}$ and $C_{13} = C_{23}$ the "invariance condition" reads $C_{11} = C_{12}$. In this more conventional notation it is evident that the invariance condition is equivalent to a vanishing tetragonal shear modulus $C' = (C_{11} - C_{12})/2$ (for the tetragonal axis along $[001]$) or $C' = (C_{22} - C_{23})/2$ (for the tetragonal axis along $[100]$), see also Ref. [17].

noble metals [14, 18], here bcc is the unstable phase but in this case the deformation scenario permits the existence of an elastically stable, stress-free tetragonal phase. The stress-free bct state has been analysed also for some binary alloys, e.g. RuNb [19] or TiAl [20].

Milstein and Chantasiriwan [21] have demonstrated that for fcc metals the tensile strength under uniaxial $\langle 100 \rangle$ loading can be limited by the bifurcation to the secondary orthorhombic deformation path. For the noble and transition metals covered by their study the bifurcation occurs at less than 50.0% of the maximum tensile stress along the tetragonal deformation path, but Al was found to be a special case where the bifurcation occurs only close to the stress-maximum along the primary path.

In the present paper we report the results of detailed *ab-initio* density-functional based investigations of the response of the fcc metals Al and Cu and of the inter-metallic compounds $\text{Al}_3(\text{Sc}, \text{Ti}, \text{V})$ in the $L1_2$ and $D0_{22}$ phases to uniaxial loading along the $[100]$ and $[001]$ directions. The results for uniaxial loading are compared with the response to epitaxial (biaxial) deformation in the plane perpendicular to the uniaxial strain. In Sec. 3 we first discuss the relations between the structural changes induced by the application of uniaxial and epitaxial, tensile and compressive strains to fcc structures - the high symmetry of the parent lattice leads to very interesting symmetries. In Secs. 4 and 5 we present our results for the tri-aluminides in two different crystal structures. Similarities and differences compared to the response of the fcc metals are discussed in relation to the crystal structures and to the changes in the chemical bonding under strain.

2. Computational methodology

Our *ab-initio* total-energy and force calculations are based on density-functional theory (DFT) as implemented in the Vienna *ab-initio* simulation package (VASP) [22, 23]. A gradient-corrected functional has been used to describe electronic exchange and correlations [24]. Electron-ion interactions are treated within the projector-augmented-wave (PAW) method [25, 26]. For all elements we used the standard PAW pseudopotentials (PP) distributed with VASP with reference configurations $_{13}\text{Al}$: $[\text{Ne}] 3s^2 3p^1$, $_{29}\text{Cu}$: $[\text{Ar}] 3d^{10} 4s^1$, $_{21}\text{Sc}$: $[\text{Ar}] 3d^2 4s^1$, $_{22}\text{Ti}$: $[\text{Ar}] 3d^3 4s^1$, $_{23}\text{V}$: $[\text{Ar}] 3d^4 4s^1$. The plane-wave basis set contained components with kinetic energies up to 350 eV.

The response of the crystal to uniaxial tensile/compressive deformation was calculated by increasing/decreasing the strain along the chosen directions in small steps. A quasi-reversible deformation process at zero absolute temperature was considered. The crystal structure was fully relaxed at each deformation step until all lateral stresses vanished. It must be noted that in contrast to experiment where a given uniaxial load is applied, the simulation imposes a fixed value of the strain along this direction and calculates the stress along the loading direction and the lateral strains under the condition that all lateral stresses are zero. Similarly, the response to epitaxial tension/compression was determined for a fixed value of the biaxial strain while the biaxial stress and the perpendicular strain was calculated under the condition that the perpendicular stress vanishes. In both cases the strains vary along all three axes and are hence triaxial. In the following, the expression "uniaxial deformation (or uniaxial load)" or "epitaxial (biaxial) deformation" always imply that a fixed uniaxial (epitaxial) strain was imposed and the stress along this direction (in this plane) was calculated under the condition that the lateral (perpendicular) stresses vanish.

For the relaxation of forces and lateral stresses we have used the very effi-

cient external optimiser GADGET developed by Bučko *et al.* [27] performing an energy- and force minimisation using symmetry-adapted generalised coordinates. The forces acting on the atoms were computed via the Hellmann-Feynman theorem [28], the stress tensor acting on the unit cell was computed via the generalised virial theorem [29, 30]. The use of a high cut-off energy allows to achieve a high accuracy of the components of the stress tensor. The Brillouin zone (BZ) was sampled using various types of meshes according to the size and symmetry of the computational cells. For Al (fcc) we were forced to use a very fine mesh of $25 \times 25 \times 25$, since the electronic density of states of Al is strongly structured around the Fermi level. The BZ of the $L1_2$ structure was sampled on an $25 \times 25 \times 25$ mesh, for the $D0_{22}$ structures we used a $15 \times 15 \times 10$ mesh. All integration meshes were constructed according to the Monkhorst-Pack scheme [31]. The integration over the BZ used the tetrahedron method with Blöchl corrections [32]. The total energy was calculated with high precision, converged to 10^{-6} eV/atom. The structural relaxation was stopped when all forces acting on the atoms where converged to within 10^{-3} eV/Å and all components of the stress tensor (except σ_{11}) where converged to within 0.05 GPa.

For the calculation of the elastic constants we used the symmetry-general least-squares extraction method proposed by Le Page and Saxe in connection with VASP [33]. For each set of strains $\pm \varepsilon_i$ three different magnitudes 0.25%, 0.5% and 0.75% were used. For the calculation of the elastic constants the total energy was calculated with even higher accuracy, converged to 10^{-7} eV/atom.

3. Fcc metals under [100] tensile and compressive loading

The high symmetry of the cubic (bcc and fcc) lattices leads to interesting relations between the structures formed under uniaxial (U) and biaxial or epitaxial (E) deformations. These relations are illustrated in Fig. 1. One of the main topics of this paper is a computational study of the bcc $\leftrightarrow$ fcc phase under uniaxial tension (T) or compression (C) along the [100] direction. To this type of load, the initial response of all fcc materials is to follow a tetragonal deformation path, where the $\vec{a}_1 \equiv [100]$ lattice vector is elongated/contracted while both orthogonal lattice vectors $\vec{a}_2 \equiv [010]$ and $\vec{a}_3 \equiv [001]$ are contracted/elongated by equal amounts under tension/compression. This deformation path is called the primary tetragonal path (PTP). A tetragonal distortion of the fcc lattice can also be achieved by epitaxial (E) compression/tension, see Fig. 1. Uniaxial compression (UC) and epitaxial tension (ET), and uniaxial tension (UT) and epitaxial compression (EC) lead to the formation of the same type of structures with the same structural energies. To visualise the congruent behaviour of these types of deformation in the energy-strain and stress-strain diagrams, the strain coordinate used (i) for uniaxial deformation along [100] as $\varepsilon = \varepsilon_1$, (ii) for uniaxial deformation along [001] as $\varepsilon = \varepsilon_3$, and (iii) for epitaxial (biaxial) deformation in the (001) as $\varepsilon = \varepsilon_1 + \varepsilon_2$ with $\varepsilon_1 = \varepsilon_2$.

However, under epitaxial conditions the lattice is forced to remain tetragonal, only one lattice parameter can relax in response to the applied strain. In contrast, under uniaxial strain both orthogonal lattice parameters can relax, in principle independently, to the strain. Under uniaxial deformation the lateral stress components are relaxed to zero, under epitaxial constraints the normal stress vanishes after relaxation. Deformation under uniaxial load does not necessarily follow a tetragonal path. If the tetragonal structure becomes shear-unstable, a bifurcation to the so-called secondary orthorhombic path (SOP) proposed by Milstein *et al.* [13, 14] takes place.

Figure 1. (Colour online) The relationship between uniaxial (U) and epitaxial or biaxial (E) compression (C) and tension (T) applied to the cubic fcc lattice. The congruent behaviour can be observed between uniaxial tension and epitaxial compression (UT↔EC) and between uniaxial compression and epitaxial tension (UC↔ET). The existence of the secondary orthorhombic deformation path (SOP) leads to a correlation between epitaxial (ET) and uniaxial (UT) tension, elucidating the competition between the SOP and the primary tetragonal path (PTP) represented by UT.

3.1. Fcc metals under uniaxial [100] load

We begin with the investigation of the response of two typical fcc metals – Al and Cu. The aim of this exercise is to create a reference for the following investigations of the intermetallic compounds. The starting state (labelled F) is the face-centred cubic lattice (space group $Fm\bar{3}m$, no.225) with the lattice parameter $a_{fcc}^0 = 4.046 \text{ \AA}$ and $a_{fcc}^0 = 3.632 \text{ \AA}$ for Al and Cu, respectively. Under tensile/compressive load along the direction $\langle 100 \rangle$ the cubic symmetry of state F is broken. The metals adopt a face-centred tetragonal (fct) lattice with the tetragonal axis parallel to the direction of the applied tension or compression (space group $P42/ncm$, no.138). This is the "guiding" symmetry for the entire deformation path called the primary tetragonal path (PTP). Fig. 2 shows the variation of energy, stress, and lattice parameters under increasing tensile or compressive deformation for Al (left) and Cu (right).

The energy-strain curve for the PTP shows no special behaviour on the tensile side, the energy increases monotonously as a function of strain. Uniaxial compression along the PTP induces structural transformations to a stress-free body-centred-cubic (B) and further to a face-centred tetragonal (T) phase. The bcc states $B^{(1)}$ are realised at strains of $\varepsilon = -19.9\%$ and $\varepsilon = -20.4\%$, the structural energy differences are 96 meV and 35.1 meV for Al and Cu, respectively. The lattice constants of the bcc phases are $a_{bcc} = 3.240 \text{ \AA}$ and $a_{bcc} = 2.890 \text{ \AA}$ for Al and Cu (corresponding to an expansion of the atomic volume of 2.7% and 0.7%), respectively. The energy of the state $B^{(1)}$ represents a transition barrier to a stress-free face-centred tetragonal state $T^{(1)}$ realised at strains of $\varepsilon = -30.8\%$ and $\varepsilon = -23.3\%$, at energies which are 69 meV and 34.7 meV higher than for the fcc phase for Al and Cu, respectively. Their lattice constants and axial ratios are $a_1 = 2.799 \text{ \AA}$, $a_3/a_1 = a_2/a_1 = 1.7701$ and $a_1 = 2.785 \text{ \AA}$, $a_3/a_1 = a_2/a_1 = 1.493$

Figure 2. (Colour online) Energy-strain (top panels) and stress-strain (middle panels) relationship for fcc Al (left) and Cu (right) under $\langle 100 \rangle$ uniaxial loading, together with the variation of the face-centred cubic lattice parameters a_1 , a_2 , and a_3 as a function of the strain ε applied along the direction of loading (bottom panels). The results for the primary tetragonal path (PTP) are presented by full symbols and black lines. The stress and lattice parameters (note that $a_2 = a_1$) calculated under epitaxial tension (the epitaxial tetragonal path – ETP) as a function of the biaxial strain $\varepsilon = \varepsilon_1 + \varepsilon_2$ are represented by grey (brown) lines with open symbols. The results for the secondary orthorhombic path (SOP), starting by applying tension/compression to the stress-free bcc state $B^{(2)}$ on the ETP are shown by grey (blue) lines and full symbols. The thick dashed black lines represent the transformation from the bcc states $B^{(1,2)}$ to the fcc states $F^{(1,2)}$ under a shear deformation (cf. the discussion at the end of this section). Capital letters and vertical dotted lines mark special states discussed in the text. In the bottom panel showing the variation of the lattice constants the rectangles of thin dotted lines connect the stress-free states $B^{(1)}$, $T^{(1)}$ and $B^{(2)}$, $T^{(2)}$ formed under uniaxial compression and epitaxial tension, respectively. As for the fcc metals the appearance of these states is symmetry-dictated, their structures are exactly identical. The thin black dashed lines represent the variation of the half length of the diagonal in the (a_1, a_2) plane along the PTP (thin brown dashed lines for ETP). The thin black dash-dotted lines represent the variation of the half length of the diagonal in the (a_2, a_3) plane along the PTP. The thin red dash-dash-dotted lines show the variation of the lattice constant a_3 along the PTP calculated under strict volume conservation. Cf. text.

for Al and Cu, respectively. The transformation from F to $B^{(1)}$ and to $T^{(1)}$ is almost exactly volume conserving for Cu.

The first extrema on both sides of the stress-strain curve (tensile/compressive loading) determine the ideal strength (IS) [34], provided no other instabilities occur before reaching it. Under tension, for Al, our calculations yield an ideal tensile strength (ITS) of $\sigma_{max}[100] = 11.4$ GPa at 34.3% strain. This result is in good agreement with the results of other authors [21, 35–38]. For example, the embedded atom result of Milstein and Chantasiriwan [21] for Al is $\sigma_{max}[100] = 12.6$ GPa at a strain of 38.6%. For Cu we calculated an ITS of $\sigma_{max}[100] = 23.8$ GPa at 36.0% strain, again in good agreement with the em-

bedded atom results ($\sigma_{max}[100] = 23.7$ GPa at a strain of 38.1%) [21]. We also find good agreement with the DFT calculations of Černý *et al.* [17] performed using the same code and exchange-correlation functional. Černý *et al.* also compared the VASP results with those obtained using a full-potential linearised augmented plane-wave (FLAPW) and tested the influence of the exchange-correlation functional. The GGA results derived using VASP and FLAPW are found to be in excellent agreement, the use of the local density approximation (LDA) instead of the GGA led to a much higher ITS ($\sigma_{max}[100] = 32.4$ GPa). This illustrates the over-binding characteristic for the LDA which is largely cured by the GGA. A compilation of earlier results for both metals, based on different computational approaches can be found in the work of Pokluda *et al.* [38]. This compilation shows that large differences exist even between ab-initio calculations (caused by the choice of different exchange correlation functionals, basis set, level of convergence, ...). In practise, the theoretical tensile strength of fcc metals under [100] is limited by elastic instabilities on the PTP at lower strains – this will be discussed in detail below.

The compressive region of the PTP represents the (fcc→bcc) transformation along the so-called inverse Bain path. The first negative stress maximum determines the ideal compressive strength (ICS) provided no other instabilities occur before reaching it. These negative stress maxima determining the ICS are found at strains of $\varepsilon = -11.4\%$ and $\varepsilon = -9.0\%$ with values $\sigma_{min}[100] = -8.6$ GPa and $\sigma_{min}[100] = -3.4$ GPa for Al and Cu, respectively. Our results for Al are in a reasonable agreement with previous studies [35], if we take the difference of computational methods into account. For Cu, our results agree with the data of Černý *et al.* [17].

3.2. Epitaxial deformation of the fcc metals

As discussed above (see Fig. 1) under uniaxial compression (UC) along [100] and under epitaxial (or isotropic biaxial) tension (ET) applied to the (001) plane ($\varepsilon_1 = \varepsilon_2$, $\varepsilon = \varepsilon_1 + \varepsilon_2$) a fcc crystal undergoes the same sequence of tetragonal deformations. In both cases the unit cell is compressed along the tetragonal axis and stretched along both orthogonal directions in the basis plane. The difference between the UC and ET deformations paths is the different number of degrees of freedom for structural relaxation. Along the UC path, only a uniaxial compressive strain is applied along the direction of loading and the stress must vanish in the perpendicular plane. The system is free to relax independently along both directions perpendicular to the direction of loading, the resulting deformation may be tetragonal or orthorhombic. Under ET, an isotropic strain is applied in a plane, and the stress must vanish along the perpendicular direction. Only the perpendicular lattice vector is allowed to relax – the deformation is tetragonal by construction. Both the UC and the ET deformation paths connect the fcc and bcc structures, they are usually called the uniaxial Bain path (UBP) and the epitaxial Bain path (EBP) [15]. Both are physically realisable – the UBP by uniaxial loading, the EBP by epitaxy to tetragonal substrates. The relation between the UBP and EBP has been discussed by Alippi *et al.* [39].

The congruent behaviour under uniaxial compression (UC) and epitaxial tension (ET) is clearly seen in Fig. 2 for both Al (left) and Cu (right). The energy and strain curves have very similar shape (scaled and mirrored), the energies of the stress-free structures are identical, but we find considerable differences in the extremal values of the stresses. The bcc B⁽²⁾ and fct T⁽²⁾ lattices are found on the ET path at strains (13.2%; 22.6%) and (12.5%; 15.0%) for Al and Cu, respectively. The

lattice constants of the bcc and fct structures along the ET and UC paths are also identical within computational accuracy. As shown in our earlier study [12], for Al this face-centred tetragonal state is the saddle point on the deformation path under uniaxial [110] loading leading to the restoration of the initial fcc structure by the "flip-strain" mechanism (see state C in Fig. 2 of our earlier work). The state $T^{(2)}$ is elastically stable only under epitaxial conditions, but unstable without this constraint. Under uniaxial [110] loading a slight further increase of the strain leads to the formation of the "special invariant" state with $C_{22} = C_{23}$ at which the orthorhombic deformation path under [110] loading collapses to tetragonal symmetry.

3.3. Orthorhombic deformation of fcc metals

Along the secondary orthorhombic deformation path [13, 14] for uniaxial [100] loading the guiding symmetry is described by space group *Immm* (no.71). This path can be considered as the primary deformation path of a bcc structure under uniaxial [110] loading [13]. This allows to explore the orthorhombic deformation path even in those cases where no bifurcation from the PTP takes place. The results of the uniaxial [110] strain applied to the state $B^{(2)}$ along the ET path are included in Fig. 2.

Under a slight compression the tetragonal state $T^{(2)}$ [with $a_1 = a_2 = 4.960 \text{ \AA}$, $a_3 = 2.780 \text{ \AA}$ (Al) and $a_1 = a_2 = 4.180 \text{ \AA}$, $a_3 = 2.760 \text{ \AA}$ (Cu) at a strain of $\varepsilon = 22.6\%$ (Al) or $\varepsilon = 15.0\%$ (Cu)] transforms immediately to the body-centred cubic state $B^{(2)}$. For Cu, the tetragonal symmetry is conserved, only the axial ratio changes upon transformation from $T^{(2)}$ to $B^{(2)}$. Upon further compression an orthorhombic deformation takes place (a_2 decreases, a_3 increases strongly until at state D with $\varepsilon = 10.0\%$ the tetragonal symmetry (with $a_1 = 3.995 \text{ \AA}$, $a_2 = a_3 = 3.516 \text{ \AA}$) is restored. Hence state D is really the bifurcation point from the PTP to the SOP. We have verified that the invariance condition $C_{22} = C_{23}$ is indeed satisfied along the PTP. Fig. 3 shows the variation of C_{22} and C_{23} under uniaxial strain along [100]. For Cu the curves cross at a modest strain of 10.0%, state D is indeed the bifurcation point from the PTP to the SOP.

For Al, however, under uniaxial [110] deformation of the $T^{(2)}$ state tetragonal symmetry is not conserved (in contrast to the epitaxial deformation: at strains between 22.6% ($T^{(2)}$) and 13.2% ($B^{(2)}$) an orthorhombic structure is adopted. Hence the ETP and the "SOP" pass through the same stress-free $T^{(2)}$ and $B^{(2)}$ states, but connect both configurations along different paths in configuration space. State $B^{(2)}$ is shear-unstable, upon further compression the SOP collapses to the PTP. The energy of state $B^{(2)}$ lies above the corresponding state on the PTP, the crossing between the PTP and the "SOP" occurs at a strain of 17.0%, but the structures realised at this point are different: State D on the PTP has tetragonal symmetry with $a_1 = 4.733 \text{ \AA}$, $a_2 = a_3 = 3.897 \text{ \AA}$, state D on the "SOP" is orthorhombic with $a_1 = 4.733 \text{ \AA}$, $a_2 = 4.962 \text{ \AA}$, $a_3 = 2.864 \text{ \AA}$. The two states differ also considerably in the atomic volume. On the "SOP" the volume is nearly conserved (the volume expansion of 1.3% is even slightly smaller than for the $B^{(2)}$ and $T^{(2)}$ states), while along the PTP the volume is expanded by about 8.0% at this strain. Hence in this case the crossing of the two deformation paths does not lead to a bifurcation from the PTP to an SOP. This is also confirmed by the strain-dependence of the elastic constants, see Fig. 3. For Al the condition $C_{22} = C_{23}$ is fulfilled only at a very large strain of 33.0%. This is almost exactly equal to the strain at the stress maximum at 34.3%. At strains of about 13% the difference between C_{22} and C_{23} becomes rather small, but we have verified that it never vanishes.

Figure 3. Variation of the elastic constants C_{22} and C_{23} of Al (top) and Cu (bottom) under uniaxial [100] loading. The crossing point with $C_{22} = C_{23}$ defines the special invariant state at which a bifurcation from a tetragonal to an orthorhombic deformation path occurs. Cf. text.

Hence the relation between the PTP and the SOP (which we have constructed via uniaxial [110] loading of the stress-free state $B^{(2)}$) is very different for Al and Cu. As shown in the inset of Fig. 2 for Cu a bifurcation from the PTP to the SOP takes place at state D, following the classical scenario advocated by Milstein *et al.* [21]: Under increasing uniaxial [100] tension the metal follows first the PTP until state D where a bifurcation to the SOP takes place. Deformation along the SOP leads to the formation of a bcc state which can also be realised by ET. Upon further increasing strain, the SOP and ET deformation paths almost coincide up to the face-centred tetragonal state $T^{(2)}$, but they diverge again upon further deformation.

For Al the PTP and the ETP and "SOP" paths connecting the $B^{(2)}$ and $T^{(2)}$ states intersect at a strain of $\varepsilon \approx 17.0\%$, but the states adopted at this strain on both deformation paths are different. To elucidate the different behaviour of the two metals we calculated the complete set of elastic constants of Cu and Al at the state D on the PTP. For Cu we find $C_{11} = 149$ GPa, $C_{22} = C_{33} = 157$ GPa, $C_{12} = C_{13} = 86$ GPa, $C_{23} = 153$ GPa, $C_{44} = 116$ GPa, and $C_{66} = 38$ GPa. The closeness of the C_{23} and C_{22} elastic constants confirms that the condition for the "special invariant eigenstate" ($C_{22} = C_{23}$) described by Milstein and Huang [40] and hence for Cu the condition for the bifurcation from the PTP to the SOP is fulfilled. For Al the computed set of elastic constants for state D on the PTP is $C_{11} = 52$ GPa, $C_{22} = C_{33} = 134$ GPa, $C_{13} = 24$ GPa, $C_{23} = 74$ GPa, $C_{44} = 46$ GPa, and $C_{66} = 6$ GPa. Evidently, for Al state D is not a special invariant eigenstate ($C_{22} - C_{23} = 60$ GPa) and at this point no bifurcation from the PTP to the SOP is possible. The "SOP" we have constructed by [110] loading of the bcc state does not connect to the PTP. On the other hand, the smallness of the shear constant C_{66} at a stress of $\sigma \sim 8$ GPa indicates that for this state Al is close to another type of instability.

3.4. Instabilities limiting the ideal strength

In the preceding section we have derived the value of ITS of Al and Cu from the maximal gradient of the energy-strain or, equivalently, from the location of the maximum of the stress-strain curve. However, the theoretical strength may also be limited by the occurrence of a shear-related instability [38] or by the softening of a phonon mode. For Cu we have found that the ITS is limited by the occurrence of a special invariant state with $C_{22} - C_{23}$ at $\varepsilon = 10.0\%$, leading to a bifurcation to

Figure 4. (Colour online) (a) Restoration of the fcc structure (state $F^{(2)}$) by applying a $[010](100)$ shear deformation to the bcc state $B^{(2)}$. (b) Special state with hexagonal lattice planes, derived by uniaxial compression from state $T^{(1)}$. Cf. text.

the SOP with decreasing energies and limiting the ITS under uniaxial $[100]$ tension to 9.5 GPa. Černý *et al.* [17] have reported a shear instability with $C' = 0$ at the same strain and stress. As discussed above, the invariance condition is equivalent to a shear instability. Černý *et al.* have also investigated the variation of the elastic constants under uniaxial compression along $[001]$ and found that a shear instability with $C_{66} = 0$ occurs at a strain of $\varepsilon = -19.0\%$, exceeding the maximum strain along the UC path. This means that for Cu the ICS is really determined by the negative stress maximum at $\varepsilon = -9.0\%$.

For Al, Li and Wang [35] have shown that C_{66} is negative at compressive strains between -40.0% and -12.8% , and that $C_{44} + \frac{1}{2}\sigma$ and $C' = C_{11} - C_{12}$ become negative for tensile strains beyond the 27.2% . This means that under compression the elastic criteria for shear stability are violated only at strains exceeding the ICS, while under tension two shear instabilities at strains limiting the ITS which are lower than those calculated by Milstein and Chantasiriwan [21] ($C' = 0$ at $\varepsilon = 23.3\%$) and in our present work ($C' = 0$ at $\varepsilon = 33.0\%$). The discrepancies are due to different computational methodologies: Milstein and Chantasiriwan used an embedded atom approach, Li and Wang norm-conserving pseudopotentials with a very low cut-off energy. However, for Al the ideal tensile strength is limited by phonon instabilities occurring at even lower strains. Clatterbuck *et al.* [37] have shown that under $[100]$ uniaxial tension phonon instabilities occur at strains of 17.0% and 18.0% for Al, reducing the ITS to 9.2 GPa compared to the peak value in the stress strain curve (their value of $\sigma_{max}[100] = 12.9$ GPa is in good agreement with our results). The first phonon instability occurs at the Brillouin zone boundary at $[11\bar{1}]/2$, the displacement pattern of the atoms corresponds to a periodic shear $[1\bar{1}0](11\bar{2})$, the second instability occurs at a wave-vector of $\sim 2\langle 100\rangle/3$ and the displacement pattern shows a $[100](001)$ shear.

We have probed the shear unstable regions by applying a $[010](100)$ shear deformation to the bcc state ($B^{(1)}$ or $B^{(2)}$), see Fig. 4(a). Here, the reaction of the bcc lattice to the compressive loading leads to an extension by different amounts, corresponding to a shear deformation in this plane. The resulting energy-strain relations are presented in Fig. 2 by dashed curves. As can be seen, this deformation leads directly to a transformation into stable, stress-free fcc states $F^{(1)}$ and $F^{(2)}$ located at strains of -29.3% and 22.6% , respectively, for both Al and Cu (see Fig. 2). This demonstrates that the source of the shear instability and the reason for the existence of a metastable fct state in this region is the possibility to restore the fcc lattice.

Parrinello and Rahman [41], using force-field iso-stress molecular dynamics (MD)

simulations modelling fcc Ni have demonstrated that under compressive uniaxial loading a fcc→hcp transition may be initiated, while the material fails under tensile load. Under compression starting from a state close to $T^{(1)}$, the suggested transformation mechanism is based on the occurrence of the special state, where the square lattice of the $\{001\}$ lattice planes is transformed to a triangular lattice. Hence a $[010](001)$ shear deformation in the plane perpendicular to the direction of the uniaxial compression can lead to a hcp-like configuration, see Fig. 4(b). In our case, we identified a such possible points of transformation at strains of -29.8% and -30.7% for Al and Cu, respectively. More recently iso-stress force-field MD simulations of Ni and Cu under tensile and compressive $[100]$ loading have been performed by Milstein *et al.* [42]. For fcc Ni failure under tensile loading was confirmed, while for Cu an inhomogeneous transformation from fcc to hcp under uniaxial tension was reported. The transformation starts immediately after reaching the bifurcation point with $C_{22} = c_{23}$, by creating rotating domains approaching a local hcp structure.

4. Response of the $L1_2$ phases to uniaxial $[100]$ loading

In the $L1_2$ structure (Cu_3Au -type, space group $Pm\bar{3}m$, no. 221) the atoms occupy the sites of an fcc lattice. TM atoms are located at the corners of the unit cell, Al atoms occupy the face centres. The lattice constants are $a^0 = 3.897 \text{ \AA}$, $3.977 \text{ \AA}$, and $4.104 \text{ \AA}$ for Al_3V , Al_3Ti , and Al_3Sc , respectively. The response of $\text{Al}_3(\text{Sc,Ti,V})$ trialuminides with the $L1_2$ crystal structure to uniaxial tensile or compressive loading along the $[100]$ direction is illustrated in Fig. 5. As expected, the deformation scenario shows some similarity with the fcc metals, in particular we find that the reaction to uniaxial compression and epitaxial tension ($\text{UC} \Leftrightarrow \text{ET}$) and to uniaxial tension and epitaxial compression ($\text{UT} \Leftrightarrow \text{EC}$) follows the same pattern. The similarity with the fcc metals is most pronounced for Al_3V where we identify again three stress-free F, B and T states under UC or ET. For Al_3Ti the B and T states are located on plateaus of the UC and ET, while for Al_3Sc no stress-free minima under uniaxial loading exist. An important point which must be noted is that while for the fcc metals the existence of three stress-free states under uniaxial loading is a result of symmetry alone, not such argument applies to the $L1_2$ structure under uniaxial loading. While a Bain deformation applied to the fcc metals induces a transformation to a bcc structure, the same deformation applied to the $L1_2$ structure does not produce a bcc structure - the atoms occupy the sites of a bcc lattice, the symmetry is broken by the chemical decoration of the lattice sites. The stress-free state (if they exist at all) have lower symmetry. States B and T can have tetragonal or orthorhombic symmetry (details are discussed below).

4.1. Uniaxial tensile and compressive loading

The response of $L1_2$ -type trialuminides to tensile strain along the PTP already been discussed rather briefly in our previous work [11, 12]. The guiding symmetry is tetragonal (space group $P4/mmm$, no.123), the energy increases monotonously upon tensile loading. The ideal tensile strength derived from the maximum of the stress-strain curve is $\sigma_{max}[100] = 23.0 \text{ GPa} / 20.0 \text{ GPa} / 16.8 \text{ GPa}$ and strains of $\varepsilon = 38.4\% / 38.0\% / 28.8\%$ for Al_3V , Al_3Ti , and Al_3Sc , respectively.

On the UC path stress-free states $B^{(1)}$ are found at strains of -18.7% and -25.0% strains, they form local maxima on the energy-strain curves. States $T^{(1)}$ located in energy minima occur at strains of -28.3% and -27.5% , for Al_3V and Al_3Ti ,

respectively. These states are closely related to the stress-free states formed under epitaxial tension. No stress-free states are formed under uniaxial compression of Al_3Sc . The ideal compressive strength is determined by the first stress-minimum, $\sigma_{\min}[100] = -13.0 \text{ GPa} / -17.0 \text{ GPa} / -17.0 \text{ GPa}$, at strains of $\varepsilon = -12.5\% / -12.0\% / -10.0\%$ for Al_3V , Al_3Ti , and Al_3Sc , respectively.

4.2. Epitaxial tensile loading

Under epitaxial tension stress-free states with structures very similar (but not necessarily identical) to those formed under uniaxial compression are found for $\text{Al}_3(\text{V}, \text{Ti})$, but not for Al_3Sc . The formation of states $\text{B}^{(2)}$ and $\text{T}^{(2)}$ under epitaxial tension has already been investigated in our previous study [12], here we recapitulate only very briefly the main results. The $\text{B}^{(2)}$ states correspond to local maxima on the energy-strain curve with $\Delta E \sim 152 \text{ meV}$ and 218 meV relative to the undeformed $L1_2$ structures, they are located at strains of 12.4% and 16.8% for Al_3V and Al_3Ti , respectively. For Al_3V the $\text{B}^{(2)}$ state has a special tetragonal lattice with space group $P4/nmm$ (no.129). As explained in our earlier work two tetragonal cells stacked along the $[001]$ direction complete a cubic cell. An $[\frac{1}{2}, 0, 0]$ or $[0, \frac{1}{2}, 0]$ anti-phase shift between these cells would lead to the formation of a cubic $D0_3$ structure where the atoms decorate a bcc lattice, in analogy to state $\text{B}^{(2)}$ of Al [see Fig.6(a,b)]. Alternatively, the crystal structure of the $\text{B}^{(2)}$ state can be regarded as a tetragonal lattice with lower symmetry (space group $P4/mmm$, no. 123) corresponding an unstable $L6_0$ crystal structure. Under increased epitaxial tension the structure transforms to the metastable and stress-free tetragonal $L6_0$ structure labelled $\text{T}^{(2)}$ which is the analogue of the stress-free tetragonal structure of Al (for detailed information on crystal structure and lattice constants we refer to our earlier work [12], but the different choice of the basis vectors should be considered). For Al_3Ti the energy maximum along the ET path does not correspond to the special tetragonal lattice which is reached already at lower epitaxial strain, the stress-free state $\text{B}^{(2)}$ has already the lower $P4/mmm$ symmetry. States $\text{T}^{(2)}$ have $\Delta E \sim 111 \text{ meV}$ and 216 meV , they are located at strains of 20.2% and 19.5% strains for Al_3V and Al_3Ti , respectively. The B states are elastically unstable, state $\text{T}^{(2)}$ is elastically stable only for Al_3V . For Al_3Sc no metastable states are found along the ET path. It is worthwhile to note that the formation of the stress-free $\text{B}^{(2)}$ states is associated for Al_3V with a small volume expansion of 1.13% , for Al_3Ti with an expansion of 3.9% .

The structures of the stress-free states under epitaxial tension are not completely identical to those reached under uniaxial compressive loading, as illustrated in the bottom panel of Fig. 5. The exact correspondence to state $\text{B}^{(2)}$ on the ETP on the compressive PTP ($\text{B}^{(1)}$ brown) is defined by the intersection of the dot-dashed line representing the variation of the length of the half-diagonal of the unit cell in the (a_2, a_3) plane with the straight line representing the variation of a_1 . This criterion can be used to define corresponding structures on the deformation paths for Al_3Sc where no stress-free states exist.

4.3. Orthorhombic deformation

As for the fcc metals, we have constructed an orthorhombic deformation path by applying a uniaxial $[110]$ strain to the state $\text{B}^{(2)}$ located on the ET path. However, as under an orthorhombic guiding symmetry fewer constraints are imposed than under epitaxial tension, for Al_3V the shear-unstable $\text{B}^{(2)}$ state immediately relaxes to orthorhombic symmetry. For Al_3Ti the tetragonal symmetry of state $\text{B}^{(2)}$ is

Figure 5. (Colour online) Energy-strain (top panel) and stress-strain (middle panel) relationship for $\text{Al}_3(\text{V,Ti,Sc})$ (L_{12}) [from left to right] under $\langle 100 \rangle$ uniaxial loading, together with the variation of the cell lattice parameters a_1 , a_2 , and a_3 as a function of the applied strain ϵ (bottom panel) (cf. Fig. 2 and text).

Figure 6. (Colour online) The $B^{(2)}$ states of trialuminides obtained by epitaxial tension in (001) plane (biaxial strain $\varepsilon = \varepsilon_1 + \varepsilon_2$): (a) The state $B^{(2)}$ for the L_{12} phases. (c) The $B^{(2)}$ state of the D_{022} phases forming a bcc D_{03} structure. Panel (b) shows that the structure of state $B^{(2)}$ of the L_{12} phases can be considered as a D_{03} structure with stacking faults. Two tetragonal cells (marked by grey shading) stacked along the [001] direction complete a cubic cell (as marked by bold lines) - however, the cubic symmetry is broken by the chemical decoration. A $[1/2, 0, 0]$ or $[0, 1/2, 0]$ anti-phase shift between these cells restores the full symmetry of the bcc D_{03} structure (some atoms are hidden for better view).

conserved. In both cases under even minimal compression the "SOP" collapses to the PTP. Upon tensile loading the "SOP" passes through the $T^{(2)}$ state on the ETP, but connects the stress-free states through different regions in configuration space. The results are included in Fig. 5. For Al_3V and Al_3Ti we find, as for Al, that the "SOP" crosses the PTP between states $T^{(2)}$ and $B^{(2)}$. The crossing occurs at strains of 18.1% (Al_3V) and 22.2% (Al_3Ti), respectively, and defines a special state D. At these strains, states D on the PTP are tetragonal, their volumes are strongly expanded by 7.7% (Al_3V) and 12.5% (Al_3Ti). The corresponding states on the orthorhombic path have lower symmetry and show only a much lower volume expansion by 2.0% and 6.0% respectively. After passing through the $T^{(2)}$, state the ETP and the "SOP" diverge again, with the orthorhombic deformation leading to lower energies.

However, the crossing between the PTP and the "SOP" does not necessarily mark a bifurcation to a deformation path with lower energy. This would be the case only if a shear instability exists on the PTP. Again we have analysed the stability of the tetragonal states along the PTP by calculating the elastic constants as a function of strain. The result for Al_3V is shown in Fig. 7. We find that the invariance condition $C_{22} = C_{23}$ is satisfied only at a very large strain of about 31.0%. This corresponds to about 80% of the strain at the stress-maximum along the PTP - only at this point the tetragonal structure becomes shear-unstable against an orthorhombic deformation. The shear instability also limits the ITS of Al_3V to about 20.0 GPa compared to 23 GPa derived from the position of the stress maximum.

Hence for Al_3V and Al_3Ti we find a situation similar to that discussed for Al. The ECP and PTP cross at a strain intermediate between the stress-free $B^{(2)}$ and $T^{(2)}$ states (but remember that in contrast to Al, the structure of $B^{(2)}$ is only tetragonal). An orthorhombic deformation path connecting to the stress-free configurations along the ETP can be constructed, it is close, but not coincident with the ETP at strains around the crossing with the PTP. The uniaxially strained tetragonal structures are stable at the crossing point, a branching to the "SOP" with lower energies requires to overcome a potential energy barrier.

Like under uniaxial [110] loading the response of Al_3Sc is very different. The energy increases monotonously along both the PTP and the ETP. We have con-

Figure 7. Variation of the elastic constants C_{22} and C_{23} of Al_3V (top) and Al_3Sc (bottom) under uniaxial [100] loading. The crossing point with $C_{22} = C_{23}$ defines the special invariant state at which a bifurcation from a tetragonal to an orthorhombic deformation path occurs. Cf. text.

constructed an orthorhombic deformation path starting from a point on the ETP where the $B^{(2)}$ phase according to the criterion defined above [crossing of the dashed lines representing the half-diagonal of the (a_1, a_2) face of the unit cell with the lattice parameter a_3], see Fig. 5. Under orthorhombic guiding symmetry without epitaxial constraints the structure collapses to the PTP, the volume of this tetragonal phase at a strain of 16.0% is expanded by 10.3% compared to the initial $L1_2$ structure. Under increased loading the system follows the PTP under further volume expansion. At a strain of $\varepsilon = 24.0\%$ a transformation to an orthorhombic structure takes place, accompanied by a slight volume contraction. At a further increased strain a second transition leads to an enhanced orthorhombic distortion. The analysis of the elastic constants under varying strain (see Fig. 7) shows that these transitions are associated with a shear instability, the "invariant state" with $C_{22} = C_{23}$ is reached at $\varepsilon \sim 27.0\%$, i.e. just between the two transformations on the SOP – in this case the condition for a bifurcation from the PTP to the SOP is satisfied. The critical strain of 27.0% is only slightly lower than the strain of 28.6% at the stress maximum.

5. Response of the $D0_{22}$ phases to uniaxial and epitaxial loading

The $D0_{22}$ crystal structure (space group $I4/mmm$, no. 139) has a tetragonal elementary cell which can be considered as a consisting of two slightly distorted $L1_2$ cubes stacked along the [001] direction, with a $[\frac{1}{2}, \frac{1}{2}, 0]$ anti-phase shift between these cubes. A $D0_{22}$ structure with an axial ratio of $\sqrt{2}$ is identical with a bcc $D0_3$ structure. This shows that for the $D0_{22}$ phase under compressive uniaxial [001] loading and under epitaxial deformation in the (001) the occurrence of stress-free B and T states is symmetry-imposed as for the fcc metals. However, this is not the case under uniaxial [100] loading

The lattice parameters of the trialuminides are $a^0 = 3.766 \text{ \AA}$, $3.851 \text{ \AA}$, and $4.021 \text{ \AA}$, the axial ratio is 2.207, 2.227, and 2.194 for Al_3V , Al_3Ti , and Al_3Sc , respectively. This represents the starting state F. Because of the tetragonal symmetry, the response to uniaxial loading along [100] and [001] is no longer equivalent. We shall investigate the response to both modes of deformation. The analysis of the response to uniaxial loading along the [001] direction where the tetragonal symmetry is conserved allows to explore the analogy with the fcc metals and the $L1_2$

Figure 8. (Colour online) The relationship between uniaxial tension (UT) and compression (UC) along the [001] and [100] directions and epitaxial or biaxial compression (EC) and tension (ET) in the (001) plane applied to the tetragonal $D0_{22}$ structure. In the central picture showing the unstrained $D0_{22}$ lattice the slightly distorted cubo-octahedron surrounding the TM atom in the centre of the cell has been inscribed. The cubo-octahedron can be decomposed into three inter-penetrating, slightly distorted cubes. Under different modes of tension or compression, these objects transform to body-centred cubic cells. The unit cell of the structure formed under epitaxial tension or uniaxial [001] compression can be considered as a stacking of two such cubes, one centred by a TM atom and one by an Al atom such that a $D0_3$ structure is formed (state B⁽²⁾). The $R^{(1,2)}$ structures formed under uniaxial [100] tension or compression can also be considered by a stacking of these cubic cells along the $[\frac{1}{2}, 0, \frac{1}{2}]$ or $[0, \frac{1}{2}, \frac{1}{2}]$ directions. In these cases, however, the chemical decoration is such that a $D0_3$ structure could be formed only by an anti-phase shift by half a face-diagonal between these cubes. Cf. text.

phases. In particular uniaxial tension/compression along [001] and epitaxial compression/tension in the (001) plane lead to the formation of the same sequence of structures (see Fig. 8). In particular under UC along [001] and ET a bcc $D0_3$ -type structure will be adopted [see Fig. 6(c)].

Uniaxial loading along [100] necessarily destroys the tetragonal symmetry. Due to the orthorhombic symmetry along the primary deformation path (POP) the close correlation between uniaxial tension and epitaxial compression in the perpendicular plane ($UT \rightleftharpoons EC$) and between uniaxial compression and epitaxial tension ($UC \rightleftharpoons ET$), which is characteristic for the response of the $L1_2$ -type compounds and the fcc metals, is lost. However, there is a correlation $UT \rightleftharpoons UC$, since the orthorhombic structures on the primary path (where the a_2 lattice parameter is compressed due to relaxation) can be realised also by compression of the starting state along the $\vec{a}_1 \equiv [100]$ lattice vector (where the a_2 lattice parameter is expanded due to relaxation), see Fig. 8. Under both uniaxial tension and compression structures based on bcc cells, closely related to the $D0_3$ structure will be formed.

The response of the $D0_{22}$ -type trialuminides to uniaxial loading along the [100] and [001] directions and under epitaxial loading in the (001) plane is shown in

Fig. 9. Although the $D0_{22}$ structure does not have cubic symmetry, the response to tensile and compressive loading displays some similarity to that of the $L1_2$ -type compounds. As we shall show below this is due to the similarity of the driving forces whose chemical origin is the same.

5.1. Uniaxial tension and compression along [001]

Results for the response to uniaxial tension along [001] have partially been published before [10, 11]. Here these investigations are extended to the compressive mode and a much more detailed analysis of the structures is provided. If a tensile strain is applied along the tetragonal axis, the symmetry of the crystal structure remains unchanged. Under [001] tensile loading the energy increases monotonously with increasing strain (see Fig. 9), the stress maximum is reached at $\varepsilon = 24.7\% / 29.4\% / 29.4\%$, the ITS is $\sigma_{max}[001] = 28.2 \text{ GPa} / 29.4 \text{ GPa} / 20.2 \text{ GPa}$ for $\text{Al}_3(\text{V}, \text{Ti}, \text{Sc})$, respectively. It is remarkable that up to strains where the ITS is reached, the lattice constants in the tetragonal basal plane decrease only by about 2.0%. As a consequence the volume per atom increases linearly with the imposed strain, at the ITS the volume expansion reaches 21.0%. The small change of the lattice parameters in the plane perpendicular to the applied strain indicates an increasing stiffness of the interatomic bonding, arising from an increasingly covalent character of the in-plane TM-Al bonds and the formation of direct TM-TM bonds between next-nearest neighbours (as already discussed in detail elsewhere) [11].

Under uniaxial compression along [001] two stress-free states are formed, in close analogy to those found under epitaxial tension. The energy maximum at $\varepsilon \sim -25.0\% / -25.4\% / -24.7\%$ for $\text{Al}_3(\text{V}, \text{Ti}, \text{Sc})$ corresponds to a state $B^{(1)}$ with the body-centred cubic $D0_3$ structure (space group $Fm\bar{3}m$, no. 225) with $\Delta E \sim 476 \text{ meV}$, $\sim 433 \text{ meV}$, and $\sim 271 \text{ meV}$ relative to the undeformed structure. The formation of the $D0_3$ structure under uniaxial compression of the $D0_{22}$ lattice is in complete analogy to the transition from an fcc to a bcc structure along the uniaxial Bain path. The same $D0_3$ structure is also formed upon epitaxial tension in the (001) plane applied either along the $\langle 100 \rangle$ (see Fig. 8 and below) or along the $\langle 110 \rangle$ directions as in our earlier work [12]. At further increased compression of $\varepsilon = -35.4\% / -35.7\% / -33.0\%$ for $\text{Al}_3(\text{V}, \text{Ti}, \text{Sc})$ a local energy minimum is found for the tetragonal state $T^{(1)}$ states with space group $I4/mmm$ (no. 139) and $\Delta E \sim 390 \text{ meV}$, 347 meV , and 249 meV relative to the $D0_{22}$ structure, with a corresponding stress-free state $T^{(2)}$ along the epitaxial deformation path. The unit cell of the $T^{(1,2)}$ structures consists of two $L6_0$ cells stacked along the z direction, with a $[\frac{1}{2}, \frac{1}{2}, 0]$ anti-phase shift between them. Hence the relation between the $T^{(1,2)}$ states formed by uniaxial [001] compression or epitaxial tension in the (001) of the $D0_{22}$ and $L1_2$ structures shows the same relation as the parent structures. This state is elastically unstable with a negative value of C_{66} [10]. The same states are also formed upon epitaxial tension.

The ideal compressive strength is determined by the first negative stress maximum at increasing negative strain. We find $\sigma_{min}[001] = -30.0 \text{ GPa} / -24.5 \text{ GPa} / -14.0 \text{ GPa}$ at $\varepsilon = -12.5\% / -12.9\% / -15.0\%$ for $\text{Al}_3(\text{V}, \text{Ti}, \text{Sc})$. As under tensile strain, the variation of the lattice constants is nonlinear under compressive strain. Under compression of a_3 , $a_1 = a_2$ expands initially only very slowly. As a consequence, up to the limit set by the ICS the volume per atom is contracted by -6.1% for Al_3V and Al_3Ti , while a slightly smaller contraction is found for Al_3Sc . This reflects the stiffness of the in-plane bonding characteristic for the response to [001] tensile loading. Under increasing compression, however, the in-plane lattice

Figure 9. (Colour online) Variation of energy (top), stress (middle), and lattice parameters (bottom) as function of the applied strain ϵ for $D0_{22}$ -type $Al_3(V,Ti,Sc)$ [from left to right]. The black lines and full symbols show the results under uniaxial [100] tension and compression [the primary orthorhombic path (POP)], the grey (blue-green) lines and full symbols the results for uniaxial tension and compression along [001] [the primary tetragonal path (PTP)]. Cf. Fig. 2; Special states discussed in the text are labelled by capital letters.

constants are strongly expanded, causing a volume expansion reaching about 3.0% at state B⁽¹⁾ and 6.0% for state T⁽¹⁾ for the V and Ti compound, it is slightly lower for Al₃Sc in accordance with a reduced covalent character and therefore reduced stiffness of the bonding.

5.2. Uniaxial tension and compression along [100]

Under [100] uniaxial tensile or compressive loading the tetragonal symmetry is broken, the guiding symmetry is orthorhombic (space group I/mmm , no. 71). The orthorhombic response of $D0_{22}$ -type trialuminides is expected because of the high anisotropy of the Poisson ratio ν [10]. Fig. 9 shows the response to tensile and compressive loading along [100]. The correlation $UT \Leftrightarrow UC$ is clearly recognisable for Al₃V, it is weaker for Al₃Ti, but has almost disappeared to Al₃Sc because no stress-free states are formed upon deformation. As will be discussed in detail below, this trend is correlated with the progressive un-saturation of the covalent contributions to the chemical bonding with decreasing number of d -electrons.

Under both uniaxial tensile and compressive [100] loading of Al₃V stress-free states labelled R⁽¹⁾ and R⁽²⁾ are formed at strains of -20.2% and +18.3%, both are by $\Delta E = 169.6$ meV higher in energy than the unstrained $D0_{22}$ structure. The volume expansion is 1.7% and 2.1 %. The lattice constants of the stress-free R⁽¹⁾/R⁽²⁾ states of Al₃V calculated are $a_1 = 3.006/4.456$ Å, $a_2 = 4.456/3.026$ Å, and $a_3 = 8.944/8.923$ Å. This shows that under both UC and UT the unit cell is slightly expanded along the [001] direction and that under compression a_2 expands by exactly the same amount than a_1 expands under tension. The structures of the R⁽¹⁾ and R⁽²⁾ states are related through a rotation by 90°, as illustrated in Fig. 8. These structures are related to the $D0_3$ structure formed under uniaxial [001] compression or epitaxial tension by an anti-phase shift between the two bcc parts of their unit cell. However, because the chemical decoration breaks the exact cubic symmetry of these cells, the total energy is not necessarily stationary by symmetry for the R^(1,2) structures. An idealised R^(1,2) structure could be defined by $a_2 = a_1/\sqrt{2}$ and $a_3 = 2 \times a_1$. These relations are slightly violated for the states corresponding to the extrema on the stress-strain curves. The symmetry of the UC and UT paths is lost for Al₃Ti and Al₃Sc.

Fig. 9 demonstrates that the variation of the lattice constants under strain is not linear. Along the UT path a_2 changes only slowly at small strains, but the changes are much more dramatic on approaching the stress-free state R⁽²⁾, a_3 changes only in a very small interval preceding the critical strain. Under UC both lattice parameters change continuously with applied strain. For Al₃Ti the states corresponding to the extrema in the stress-strain curves at $\pm 19.7\%$ differ in energy by about 7 meV, there are also differences in lattice constants and volume which are more pronounced for Al₃Sc.

The value of the ideal tensile strength (ITS) determined by the first stress maximum on the primary path is $\sigma_{max}[100] = 18.1$ GPa, 16.6 GPa, and 13.7 GPa at $\varepsilon = 13.7\%$, 13.1%, and 13.6% strains for Al₃(V,Ti,Sc), respectively. The ideal compressive strength (ICS) defined by the first negative stress maximum is $\sigma_{min}[100] = -16.1$ GPa, -9.1 GPa, and -7.2 GPa at $\varepsilon = -11.4\%$, -11.7%, and 6.1% strains for Al₃(V,Ti,Sc), respectively.

5.3. Epitaxial strain applied to the tetragonal basis plane

The response of the trialuminides to epitaxial tension ($\varepsilon = \varepsilon_1 + \varepsilon_2$) has been already investigated in our previous work [12] (note that due to the tetragonal symmetry

epitaxial strains applied to the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions lead to identical results). Here we extend the investigations to include epitaxial compression. Epitaxial strain is applied to the basal plane of the $D0_{22}$ -structure, and the compound responds by varying the a_3 lattice parameter. The epitaxial deformation path is related to both uniaxial deformation paths discussed above. Epitaxial tension in the basal plane corresponds to uniaxial compression along $[001]$ under the constraint of conserving the tetragonal symmetry ($ET \rightleftharpoons UC[001]$), epitaxial compression corresponds to uniaxial tension ($EC \rightleftharpoons UT[001]$). These correlations are illustrated in Fig. 8. This means that for the respective energy-strain curves we will observe the same similarity as for the fcc metals and the $L1_2$ -type compounds. The stress-strain curves, however, will be more different because under epitaxial strain the normal stress perpendicular to the plane is relaxed, while under an uniaxial deformation the stress in the plane perpendicular to the load has to vanish. But the epitaxial deformation of the basis can also be related of uniaxial tension and compression along $[100]$ – under the additional constraint that both in-plane lattice parameters undergo the same variation and only a_3 is allowed to relax.

Under epitaxial tension, energy maxima are found at strains of 17.1%, 17.6%, and 16.1% for $Al_3(V,Ti,Sc)$, see Fig. 9. These unstable states labelled $B^{(2)}$ form a body-centred cubic $D0_3$ structure – the same structure is also formed under uniaxial $[001]$ compression as state $B^{(1)}$ (see also Fig. 8). The $D0_3$ structure can also be described as a tetragonal $D0_{22}$ lattice with the axial ratio $a_3/a_1 = \sqrt{2}$. The bcc symmetry of state $B^{(2)}$ is in evident analogy to the deformation scenario of the fcc metals. Under further increased tensile strain, a metastable fct state $T^{(2)}$ is formed at strains of 28.0%, 28.4% and 23.6% for $Al_3(V,Ti,Sc)$. These structures correspond to the $T^{(1)}$ states formed under uniaxial $[001]$ compression. The formation of the stress-free state with the $D0_3$ structure under epitaxial tension is the counterpart of the same structure formed under uniaxial $[001]$ compression – this is again an analogue of the $fcc \rightleftharpoons bcc$ transformations of the pure metals along the epitaxial and uniaxial Bain paths.

The comparison of the ETP and $UT[100]$ paths illustrates the energetic cost of conserving tetragonal symmetry. The appearance of the $B^{(2)}$ states on the ETP and the $R^{(2)}$ states on the orthorhombic deformation path under uniaxial $[100]$ loading at almost identical strain is not a coincidence. As illustrated in Fig.8 the cubic subunits of their unit cells are related by a rotation, but differ in their chemical decorations. The stress-maxima defining the ITS on the ETP and POP coincide for Al_3Ti , while the ITS on the ETP is higher for Al_3V (19.4 GPa at 12.6%) and lower for Al_3Sc (10.4 GPa at 10.8%). This correlation can be further explored by relaxing the tetragonal constraint imposed along the ETP.

Under epitaxial compression the energy increases very steeply. The strong increase of the energy is a consequence of the imposed constraints: the compression of a_1 and a_2 is counterbalanced only by a modest expansion of a_3 , leading to a volume change of about -30% for all three compounds.

5.4. Secondary orthorhombic deformation path

As for the fcc metals and $L1_2$ -type compounds an alternative orthorhombic deformation path can be constructed by applying a uniaxial $[110]$ load to the stress-free $B^{(2)}$ state on the ETP. As shown in Fig. 9, this $D0_3$ -type state relaxes immediately to the $UT[100]$ path if the epitaxial constraint is released and no strain is imposed. The bcc structure deforms to orthorhombic symmetry, the main changes are a contraction of a_2 and an expansion of a_3 at conserved volume. However, even if only a very small $[110]$ tensile strain is imposed, a new orthorhombic defor-

mation path is stabilised. This secondary orthorhombic deformation path (SOP) passes through both stress-free states on the ETP, but connects these states along a different path in configuration space. For larger values of strain, ETP and SOP diverge, at sufficiently large strains the SOP and the POP intersect. Along the SOP a_3 remains almost constant, while a_2 decreases, along the POP the variation is just the inverse (see Fig. 9). The crossing of the energy-strain curves is preceded by a crossing of the lattice parameter curves where $a_2(\text{POP})=a_3/2(\text{SOP})$ and $a_3/2(\text{SOP})=a_2(\text{POP})$. This means that the $L1_2$ -type parts of the $D0_{22}$ cell are related by a rotation. The crossing of the energy-strain curves does not indicate a bifurcation to a new deformation path. The lower energy along the SOP is the consequence of the formation of TM-TM bonds along the $[110]$.

6. Conclusions

We find significant differences between the behaviour of Al and Cu under uniaxial $\langle 100 \rangle$ loading. These differences are not unexpected, given the difference in the elastic properties of both metals (Al: isotropic Young's moduli and Poisson ratio, Cu: anisotropic Young's moduli, negative Poisson ratio in a $\langle 110 \rangle$ under perpendicular $[110]$ load). Under small strain both metals adopt a tetragonal deformation path. For Cu, a "special invariant state" with $C_{22} = C_{23}$ (or, equivalently, a shear instability with $C_{11} = C_{12}$) is reached at a strain of 10.0% where a bifurcation to a secondary orthorhombic deformation path takes place. The shear instability also limits the ideal theoretical tensile strength to $\sigma_{max}[100] = 9.5$ GPa, compared to a much larger value of 23.8 GPa at a strain of 36.0% reached along the tetragonal deformation path. The secondary orthorhombic deformation path passes through stress-free bcc and fct states which can also be reached along the epitaxial Bain path. For Al, a shear instability with $C_{11} = C_{12}$ occurs on the primary tetragonal path only at a very large strain approaching the maximum on the stress-strain curve. In this case a bifurcation at dead load to the orthorhombic deformation path is excluded, a transformation to the metastable bcc structure is possible only by overcoming a potential energy barrier. The analysis of the variation of the lattice parameters under epitaxial strain helps to understand this different behaviour. The variation of the lattice parameter a_3 (up to state B) is strictly linear with a high negative slope (-16.6×10^{-3}), whereas for Al, a linear dependence is observed only for the first half of deformation path with a lower slope value (-8.4×10^{-3}). This shows that in Al bonding perpendicular to the $\{100\}$ planes is rather stiff, it is much softer for Cu and leads to a shear instability at much lower strains. For Al the ITS is limited by phonon instabilities at strain of about 17.0% related to a shear instability under tension.

For the cubic $L1_2$ trialuminides we find a response to uniaxial $[100]$ and epitaxial loading which is similar to that of pure Al. This similarity is most pronounced for Al_3V and decreases in the sequence $\text{Al}_3\text{V} \rightarrow \text{Al}_3\text{Ti} \rightarrow \text{Al}_3\text{Sc}$ with decreasing number of d -electrons and hence decreasing covalent character of the bonding. Under uniaxial tensile loading the compounds respond by deformation along a tetragonal path, while under uniaxial compression and epitaxial tension the systems pass through stress-free tetragonal states with a $L6_0$ and a distorted $L6_0$ structure, respectively. A secondary orthorhombic deformation path can be derived from the epitaxial deformation path by applying a uniaxial $[110]$ load. The energy-strain curve for uniaxial tensile loading intersects the epitaxial and the secondary orthorhombic energy-strain curves of $\text{Al}_3(\text{V,Ti})$ between the two stress-free states, but no bifurcation to an orthorhombic deformation can take place, because the invariance condition $C_{22} = C_{23}$ is satisfied only at much larger strain, in analogy to

Al. Only for Al_3Sc a bifurcation occurs just before the stress maximum is reached.

Because of the tetragonal symmetry of the $D0_{22}$ structure, the response to uniaxial loading along $[001]$ (the tetragonal axis) and $[100]$ is no longer the same. In the first case the compounds follow a tetragonal deformation path whereas in the second case the symmetry is immediately reduced to orthorhombic. However, due to tetragonal symmetry we also find interesting symmetries between uniaxial compression and tension along $[100]$ and between uniaxial compression/tension along $[001]$ and epitaxial tension/compression in the (001) plane which have been explored in detail. Under both UC along the tetragonal axis and epitaxial tension in the perpendicular plane, the $D0_{22}$ -type compounds undergo transformations first to an unstable bcc $D0_3$ -phase and further to a metastable fct phase – in complete analogy to the fcc $\rightleftharpoons$ bcc transformations along the uniaxial and epitaxial Bain paths of the fcc metals. If the $[100]$ uniaxial tension/compression is applied (perpendicular to the tetragonal axis), the deformation path passes through structures closely related to the $D0_3$ lattice, but differing by an anti-phase shift between the constituting cubic sub-units. Only for Al_3V , these structures are almost stress-free, but the existence of these low-stress states limits the ideal tensile and compressive strengths under $[100]$ loading. Likewise, the stress-low $D0_3$ -phase necessarily limits the ideal compressive strength under uniaxial $[001]$ loading and the ideal tensile strength under epitaxial tension.

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References

- [1] Y.V. Milman, D.B. Miracle, S.I. Chugunova, I.V. Voskoboinik, N.P. Korzhova, T.N. Legkaya and Y.N. Podrezov, *Intermetallics* 9 (2001) pp.839–845.
- [2] H.A. Calderon, V. Garibay-Febles, M. Umemoto and M. Yamaguchi, *Mat. Sci. Eng. A* 329-331 (2002) pp.196–205.
- [3] K. Venkateswarlu, L.C. Pathak, A.K. Ray, G. Das, P.K. Verma, M. Kumar and R.N. Ghosh, *Mat. Sci. Eng. A* 383 (2004) pp.374–380.
- [4] A.E. Carlsson and P. Meschter, *J. Mater. Res.* 4 (1989) pp.1060–1063.
- [5] P. Villars *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, Materials Park, OH, 1997 Desk Edition.
- [6] Y. Harada, M. Morinaga, J. Saito and Y. Takagi, *J. Phys.: Condens. Matter* 9 (1997) pp.8011–9030.
- [7] R. Misesvon, *Z. Angew. Math. Mech.* 8 (1928) pp.161–185.
- [8] R.B. Schwarz, P.B. Desch, S. Srinivasan and P. Nash, *Nanostruct. Mater.* 1 (1992) pp.37–42.
- [9] M. Krajčí and J. Hafner, *J. Phys.: Condens. Matter* 14 (2002) pp.1865–1879.
- [10] M. Jahnátek, M. Krajčí and J. Hafner, *Phil. Mag.* 87 (2007) pp.1769–1794.
- [11] M. Jahnátek, M. Krajčí and J. Hafner, *Phys. Rev. B* 71 (2005) p.024101.
- [12] M. Jahnátek, M. Krajčí and J. Hafner, *Phys. Rev. B* 76 (2007) p.014110.
- [13] F. Milstein and B. Farber, *Phys. Rev. Lett.* 44 (1980) pp.277–280.
- [14] F. Milstein, J. Marschall and H.E. Fang, *Phys. Rev. Lett.* 74 (1995) pp.2977–2980.
- [15] E.C. Bain, *Trans. Am. Inst. Min. Metall. Pet. Eng.* 70 (1924) pp.25–33.
- [16] R. Hill and F. Milstein, *Phys. Rev. B* 15 (1977) pp.3087–3096.
- [17] M. Černý, M. Šob, J. Pokluda and P. Šandera, *J. Phys.: Condens. Matter* 16 (2004) pp.1045–1052.
- [18] J. Wang, S. Yip, S.R. Phillpot and D. Wolf, *Phys. Rev. Lett.* 71 (1993) pp.4182–4185.
- [19] P.J. Craievich, M. Weinert, J.M. Sanchez and R.E. Watson, *Phys. Rev. Lett.* 72 (1994) pp.3076–3079.
- [20] M. Šob, L.G. Wang and V. Vitek, *Comput. Mater. Sci.* 8 (1997) pp.100–106.
- [21] F. Milstein and S. Chantasiriwan, *Phys. Rev. B* 58 (1998) pp.6006–6018.
- [22] G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* 6 (1996) pp.15–50.
- [23] G. Kresse and J. Furthmüller, *Phys. Rev. B* 54 (1996) pp.11169–11186.
- [24] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhais, *Phys. Rev. B* 46 (1992) pp.6671–6687.
- [25] P.E. Blöchl, *Phys. Rev. B* 50 (1994) pp.17953–17979.

[26] G. Kresse and D. Joubert, Phys. Rev. B 59 (1999) pp.1758–1775.
[27] T. Bučko, J. Hafner and J.G. Ángyán, J. Chem. Phys. 122 (2005) p.124508.
[28] R.P. Feynman, Phys. Rev. 56 (1939) pp.340–343.
[29] O.H. Nielsen and R.M. Martin, Phys. Rev. Lett. 50 (1983) pp.697–700.
[30] O.H. Nielsen and R.M. Martin, Phys. Rev. B 32 (1985) pp.3780–3791.
[31] H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13 (1976) pp.5188–5192.
[32] P.E. Blöchl, O. Jepsen and O.K. Andersen, Phys. Rev. B 49 (1994) pp.16223–16233.
[33] Y. Le Page and P. Saxe, Phys. Rev. B 63 (2001) p.174103.
[34] F. Milstein, Phys. Rev. B 3 (1971) pp.1130–1141.
[35] W. Li and T. Wang, J. Phys.: Condens. Matter 10 (1998) pp.9889–9904.
[36] T. Kitamura and Y. Umeno, Model. Simul. Mater. Sc. 11 (2003) pp.127–136.
[37] D.M. Clatterbuck, C.R. Krenn, M.L. Cohen and J.W. Morris, Jr., Phys. Rev. Lett. 91 (2003) p.135501.
[38] J. Pokluda, M. Černý, P. Šandera and M. Šob, J. Com. Aid. Mat. Des. 11 (2004) pp.1–28.
[39] P. Alippi, P.M. Marcus and M. Scheffler, Phys. Rev. Lett. 78 (1997) pp.3892–3895.
[40] F. Milstein and K. Huang, Phys. Rev. B 18 (1978) pp.2529–2541.
[41] M. Parrinello and A. Rahman, J. Appl. Phys. 52 (1981) pp.7182–7190.
[42] F. Milstein, J. Zhao and D. Maroudas, Phys. Rev. B 70 (2004) p.184102.