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PAPER

Prediction of first-order martensitic transitions in strained epitaxial films

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S Schönecker^{1,2}, M Richter¹, K Koepernik¹ and H Eschrig^{1,3}¹ IFW Dresden, PO Box 270116, D-01171 Dresden, Germany² KTH Royal Institute of Technology, Brinellvägen 23, SE-10044 Stockholm, Sweden³ deceasedE-mail: stesch@kth.se and m.richter@ifw-dresden.de**Keywords:** structural transitions, crystallography, superconducting films, nanoscale materials**Abstract**

Coherent epitaxial growth allows us to produce strained crystalline films with structures that are unstable in the bulk. Thereby, the overlayer lattice parameters in the interface plane, (a , b), determine the minimum-energy out-of-plane lattice parameter, c_{\min} (a , b). We show by means of density-functional total energy calculations that this dependence can be discontinuous and predict related first-order phase transitions in strained tetragonal films of the elements V, Nb, Ru, La, Os, and Ir. The abrupt change of c_{\min} can be exploited to switch properties specific to the overlayer material. This is demonstrated for the example of the superconducting critical temperature of a vanadium film which we predict to jump by 20% at a discontinuity of c_{\min} .

1. Introduction

Epitaxy is an important concept for the fabrication of films with good crystalline quality such as overlayers, multilayers, compound materials, and ordered alloys. Such films are technologically important materials with adjustable electronic, magnetic, and optical properties [1]. Epitaxial growth also allows us to study fundamental aspects of low-dimensional structures and interfacial effects, and it allows us to produce structures that are unstable in the bulk [2]. For example, body-centered cubic (BCC) Co does not exist as a bulk phase but was stabilized by epitaxial growth on a GaAs substrate [3].

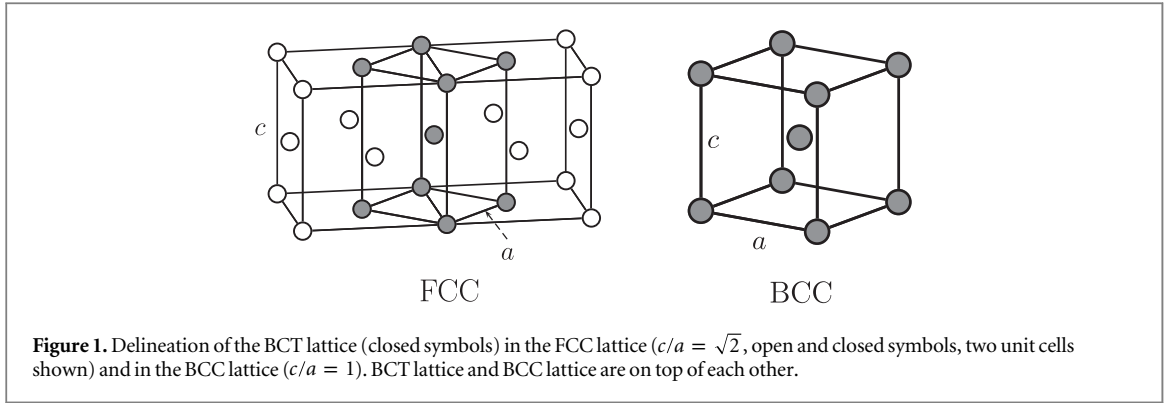
In coherent or pseudomorphic film growth, the in-plane film lattice parameters are determined by the substrate-in-plane lattice parameters. This allows us to expose a material to static, non-isotropic but homogeneous strain, which is a valuable means to influence its intrinsic properties [4]. Experiments on ferromagnetic bulk-like films showed that the magnetic moments, the Curie temperature, and the magnetic anisotropy can be tuned in a quasi-continuous manner by varying the substrate [5, 6]. Using piezoelectric substrates, even a continuous variation of the lattice parameters and of the related film properties was achieved [7, 8].

Here, we predict by density-functional calculations scanning 30 non-magnetic metallic elements, that bulk-like epitaxial films of at least six metals show first-order martensitic transitions upon variation of the epitaxial strain. For example, we find jumps in the lattice parameter of La by 0.83 Å and in the superconducting critical temperature of V by 20%.

The examples considered in the present work include only the simplest case of tetragonal non-magnetic mono-atomic films. We, however, emphasize that our main result, the possibility of isostructural phase transitions [9, 10] under epitaxial strain and a related discontinuous dependence of intrinsic film properties on the interface lattice parameters, is not restricted to certain structures, compositions, or ground states.

2. Method

We model the structures of the considered films by the epitaxial Bain path (EBP) [11]. The EBP model applies to the bulk part (i.e., the interior) of a coherently grown thick film [12]. It assumes that the film can be described by



a bulk structure with periodicity in all three dimensions. Due to epitaxial coherency, the in-plane film lattice parameters are rigidly tied to the substrate lattice parameters in the substrate-film interface via the underlying epitaxial relationship. On the other hand, the film is free to relax its geometry perpendicular to the interface due to the absence of forces. Summarizing, the model neglects all surface and interface effects except the determination of the in-plane film lattice parameters by the substrate.

In the past, the EBP model was used to predict metastable states in transition metals [11, 13–16], to investigate the magnetic order in strained overlayers [17–20], and to identify the mother phases of strained bulk-like films [11, 21–23]. In the same context, we recently suggested Ru, Os, and U films to be ferromagnetic in certain ranges of epitaxial strain [24].

Focusing on the important case of substrates with four-fold surface symmetry and body-centered tetragonal (BCT) films with (001) orientation, we denote the in-plane film lattice parameter by a and the out-of-plane lattice parameter by c ; see figure 1. The mentioned absence of forces perpendicular to the substrate-film interface allows for a relaxation of c minimizing the total film energy $E(a, c)$ at any fixed value of a [11, 12]. Hence, the EBP of a certain BCT material is the set of points $\{(a, c_{\min})\} \subset \{(a, c)\}$, for which

$$\text{EBP} \stackrel{\text{def}}{=} \left\{ (a, c_{\min}) \mid E(a, c_{\min}) = \min_c E(a, c) \right\}. \quad (1)$$

The side condition determines the relaxation of c for a given a and defines the relation $c_{\min}(a)$. Quantities traced along the EBP only depend on a , e.g., the total energy $E_{\text{EBP}}(a) \stackrel{\text{def}}{=} E(a, c_{\min}(a))$. The difference between $E_{\text{EBP}}(a)$ and the ground state energy of the film material, E_0 , corresponds to the general definition of an epitaxial strain energy [12].

A strict implementation of the notion ‘relaxation of c minimizing $E(a, c)$ ’ leads to relevant, until now disregarded consequences for all materials to which strained coherent epitaxy applies. As we show, the function $E(a, c)|_a$ can have two equal-valued global minima at $c_{\min}^1 \neq c_{\min}^2$ for certain values of $a = a_{\text{crit}}$. Thus, $c_{\min}(a)$ can be discontinuous at a_{crit} in a first-order transition. This includes, by epitaxial coherency, also the dependence of c_{\min} on the substrate lattice parameters in the interface plane. In this way, the possibility to tune overlayer-material-specific properties can be restricted to a discontinuous manner. However, one can switch these properties on purpose, if one succeeds to control the lattice parameter a in a narrow interval around a_{crit} , e.g., by a piezoelectric substrate.

In the following, we verify the existence of degenerate global minima in $E(a, c)|_a$ by high-precision density-functional theory (DFT) calculations, carried out with the full-potential local-orbital scheme FPLO-7.00–28 [25]. Using the local-density approximation according to [26] (PW92) and a scalar-relativistic mode for elements with atomic number < 49 , a full-relativistic mode otherwise, we scanned the EBP of 30 elements with the atomic numbers 20–23, 29, 30, 38–48, 56, 57, 71–80, and 92 in a wide range of parameters a [16]. The convergence of numerical parameters and the basis set were carefully checked [16]. In order to converge the total energy per atom at a level smaller than 0.3 meV, linear-tetrahedron integrations with Blöchl corrections were performed on a $24 \times 24 \times 24$ mesh in the full Brillouin zone, apart from the elements Cu, Ru, Ir, and Pt, for which a denser $48 \times 48 \times 48$ mesh was required. All detected degenerate minima in $E(a, c)|_a$ were cross-checked by additional calculations employing the Perdew–Burke–Ernzerhof (PBE96) parameterization of the exchange-correlation functional [27] (results listed in table 1).

3. Results and discussion

Vanadium is one of the elements for which EBP was studied in several investigations [11, 15, 28, 29]. This provides us with the following, and as we will argue incomplete, picture. The EBP of vanadium includes two

Table 1. List of elements with discontinuous EBPs in PW92, which were cross-checked in PBE96. The exchange-correlation functional (XC), the position of the discontinuity, a_{crit} , the related out-of-plane lattice parameters $c_{\text{min}}^{1/2}$, the change of c_{min} across the discontinuity, Δc_{min} , the relative volume change $\Delta V/V = 2\Delta c_{\text{min}}/(c_{\text{min}}^1 + c_{\text{min}}^2)$, and the strain energy at a_{crit} with respect to the energy of the ground state are tabulated.

Element	XC	a_{crit} [Å]	c_{min}^1 [Å]	c_{min}^2 [Å]	Δc_{min} [Å]	$\Delta V/V$ %	$E_{\text{EBP}}(a_{\text{crit}}) - E_0$ [meV/atom]
V	PW92	2.637(3)	3.97	3.39	0.58	16	313
	PBE96	2.698(2)	3.96	3.51	0.44	12	280
V	PW92	3.345(5)	2.54	2.37	0.17	7	323
	PBE96	3.447(2)	2.59	2.46	0.13	5	330
Nb	PW92	2.933(2)	4.38	3.76	0.62	15	390
	PBE96	2.988(2)	4.41	3.87	0.54	13	354
Ru	PW92	3.010(1)	3.26	3.03	0.23	7	685
	PBE96	3.062(2)	3.31	3.05	0.26	8	627
La	PW92	4.043(1)	4.50	3.67	0.83	20	178
	PBE96	4.232(2)	4.65	3.91	0.74	17	103
Os	PW92	3.063(1)	3.28	3.02	0.26	8	907
	PBE96	3.104(1)	3.39	3.03	0.36	11	900
Ir	PW92	3.077(2)	3.23	2.89	0.24	11	630
	PBE96	3.118(1)	3.31	2.93	0.38	12	818

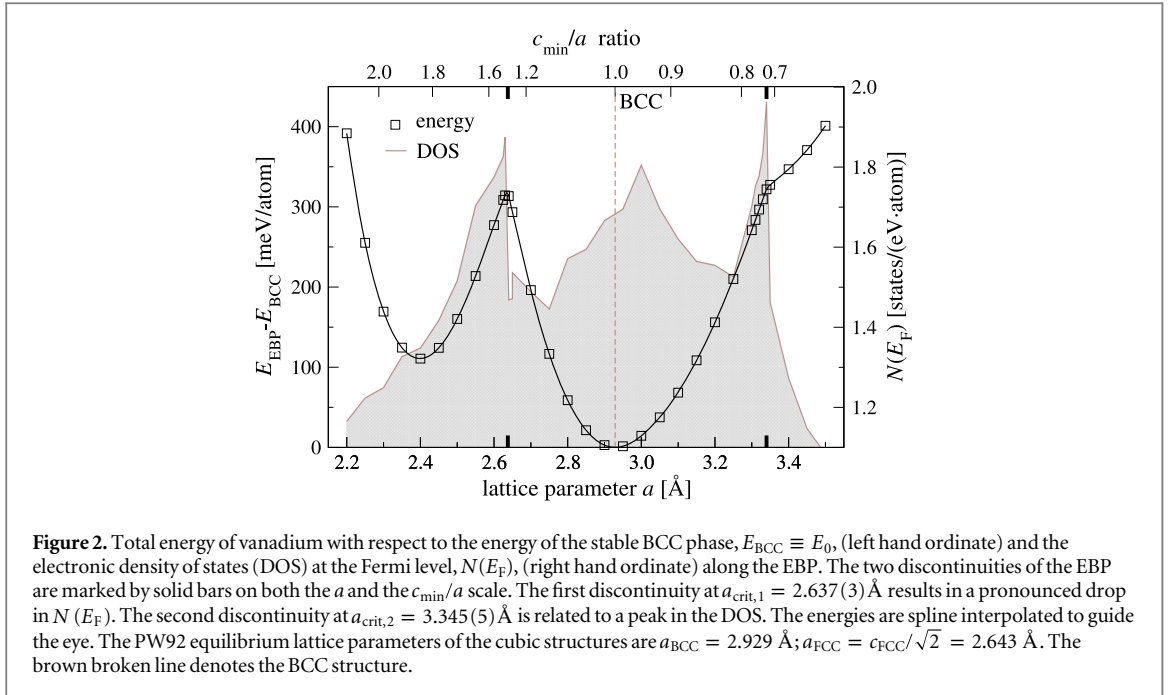
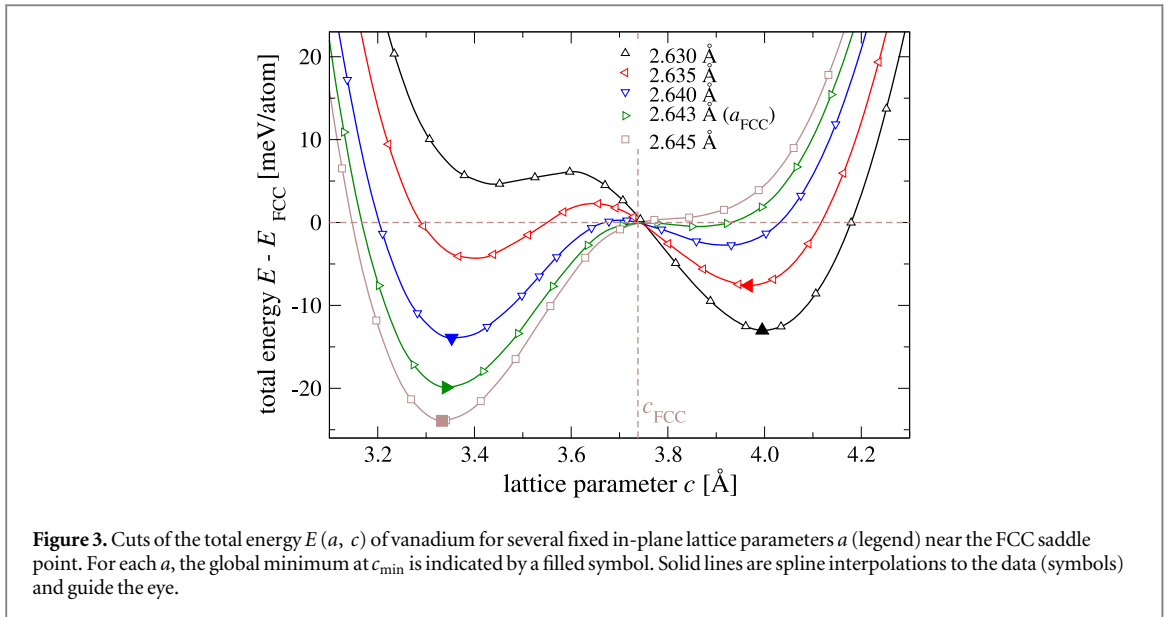


Figure 2. Total energy of vanadium with respect to the energy of the stable BCC phase, $E_{\text{BCC}} \equiv E_0$, (left hand ordinate) and the electronic density of states (DOS) at the Fermi level, $N(E_F)$, (right hand ordinate) along the EBP. The two discontinuities of the EBP are marked by solid bars on both the a and the c_{min}/a scale. The first discontinuity at $a_{\text{crit},1} = 2.637(3) \text{ \AA}$ results in a pronounced drop in $N(E_F)$. The second discontinuity at $a_{\text{crit},2} = 3.345(5) \text{ \AA}$ is related to a peak in the DOS. The energies are spline interpolated to guide the eye. The PW92 equilibrium lattice parameters of the cubic structures are $a_{\text{BCC}} = 2.929 \text{ \AA}$; $a_{\text{FCC}} = c_{\text{FCC}}/\sqrt{2} = 2.643 \text{ \AA}$. The brown broken line denotes the BCC structure.

energy minima: one corresponds to the stable BCC phase; the other one at $a = 2.400 \text{ \AA}$, $c_{\text{min}}/a = 1.84$, is a local minimum; see figure 2. This local minimum corresponds to an unstable BCT bulk state [15, 16], since its energy is lowered by a shear deformation. Tian *et al* [22, 29], however, succeeded in stabilizing coherently grown vanadium films on Cu{001} and Ni{001}, the structures of which were determined to be strained derivatives of this BCT state. The face-centered cubic (FCC) structure was found at a saddle point of $E(a, c)$ and assigned to a maximum of E_{EBP} [11, 15, 28, 29].

By symmetry, the BCC structure ($c/a = 1$) and the FCC structure ($c/a = \sqrt{2}$) are stationary points of $E(a, c)$ [15, 28], but the side condition in definition 1 determines whether they are located at the EBP or not. In contrast to previous reports [11, 15, 28, 29], we find that the FCC structure does not belong to the EBP of vanadium, because it is unstable against a tetragonal distortion at fixed $a = a_{\text{FCC}}$. We note that in terms of linear elasticity theory this instability of FCC vanadium with respect to a relaxation of c corresponds to a negative elastic constant $c_{zzzz} < 0$, since $c_{zzzz} \propto d^2 E/dc^2$. This is obvious from the plot of $E(a_{\text{FCC}}, c)$ in figure 3. There, $E(a_{\text{FCC}}, c)$ has a local maximum at $c_{\text{FCC}} = \sqrt{2} a_{\text{FCC}}$ and the global minimum is situated at $c_{\text{min}} = 3.35 \text{ \AA}$, $c_{\text{min}}/a = 1.27$.

The characteristic feature of this instability is the occurrence of a double well in $E(a_{\text{FCC}}, c)$ versus c with the global minimum at c_{min} and a local minimum. According to figure 3, double wells also occur for other values of a



in the vicinity of a_{FCC} . The energies of both minima vary with a such that the two minima are degenerate at a critical value $a = a_{\text{crit}}$. All in all, the behavior shown in figure 3 is typical for a first-order phase transition. One can readily read off the energy barrier of somewhat less than 10 meV per atom, an upper limit for the hysteresis of $\Delta a_{\text{hyst}} \approx 0.015 \text{ \AA}$, and the discontinuity of c_{\min} , $\Delta c_{\min} = |c_{\min}^1(a_{\text{crit}}) - c_{\min}^2(a_{\text{crit}})| \approx 0.58 \text{ \AA}$.

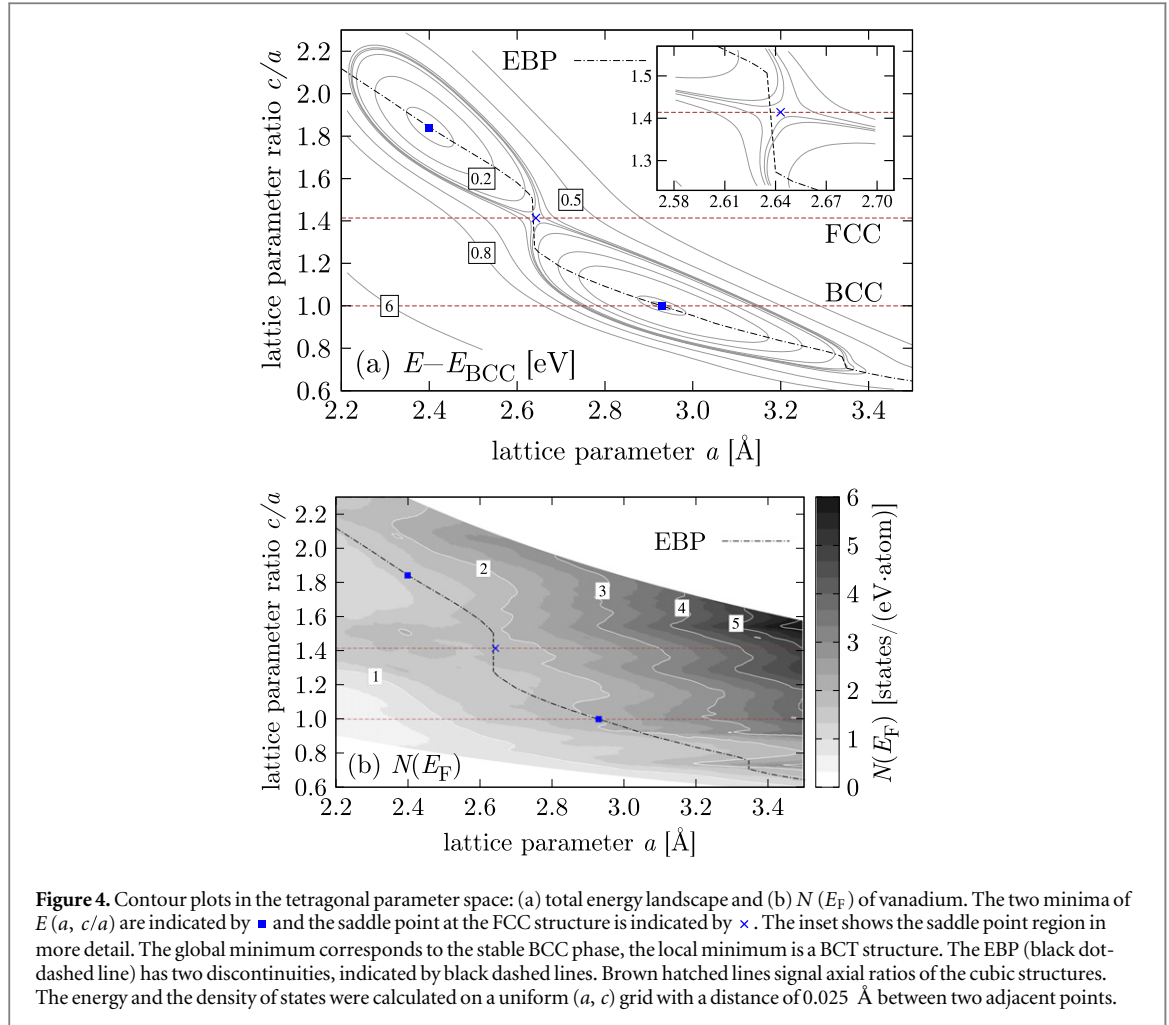
In general, a saddle point in $E(a, c)$ (here, at $(a_{\text{FCC}}, \sqrt{2}a_{\text{FCC}})$) and a discontinuity in the EBP do not have the same a -coordinates. In the case of vanadium, the already-described (first) discontinuity occurs at $2.635 \text{ \AA} < a_{\text{crit},1} < 2.640 \text{ \AA} < a_{\text{FCC}}$. The associated change of c_{\min}/a amounts to $\Delta c_{\min,1}/a_{\text{crit},1} \approx 0.2$. Surprisingly, the EBP of vanadium shows yet another discontinuity at $3.34 \text{ \AA} < a_{\text{crit},2} < 3.35 \text{ \AA}$ with $\Delta c_{\min,2}/a_{\text{crit},2} \approx 0.05$.

Figure 4(a) depicts a contour plot of $E(a, c/a)$ of vanadium together with the EBP. The two minima of $E(a, c/a)$ correspond to the two minima of E_{EBP} from figure 2 and the FCC structure is the saddle point as demanded by symmetry. The contour diagram (see inset) reveals the following: there are pairs of lines of constant energy, $E < E_{\text{FCC}}$, where each line of the pair encloses one of the two minima and the two lines overlap in their a -coordinates in the vicinity of the saddle point. The double wells in figure 3 arise from this overlap. A similar peculiarity of the energy landscape at $a \sim 3.35 \text{ \AA}$ causes the second discontinuity and the related kink of E_{EBP} visible in figure 2.

While the specific energy landscape in the vicinity of the saddle point leads to a discontinuous EBP, the mere presence of a saddle point—be it symmetry dictated or not—does not automatically lead to a discontinuous EBP. For example, if the abscissa and ordinate axes in figure 4(a) were interchanged, determining the EBP would require searching for minima along horizontals, which would result in a continuous EBP, including the FCC structure.

In order to analyze the origin of the discontinuities, we consider the electronic DOS at the Fermi level, $N(E_{\text{F}})$; see figures 2 and 4(b). The transition at $a_{\text{crit},1}$ is accompanied by a pronounced change in $N(E_{\text{F}})$ due to a significant change of the unit cell volume. This change depends monotonously on c ; see figure 4(b). Further analysis of the total energy shows that the discontinuity at $a_{\text{crit},1}$ is mainly driven by the kinetic energy contribution. Since there is no obvious peculiarity in $N(E_{\text{F}})$, the double well has to be assigned to an integral effect of the whole DOS. At the position of the second transition $a_{\text{crit},2}$, however, there is a distinct peak of 1.96 states/(eV · atom) in $N(E_{\text{F}})$ along the EBP (figure 2). The same characteristic peak appears as a tooth-like feature in the large- a region at approximately $c/a = 0.73$ in figure 4(b). The EBP of vanadium, which crosses this area, becomes discontinuous in order to avoid the large $N(E_{\text{F}})$ (Jahn–Teller behavior). At the local maximum of the related double well of $E(a_{\text{crit},2}, c)$ (not shown), $N(E_{\text{F}}) = 2.4$ states/(eV · atom).

We searched the EBPs of the 30 elements listed above for the occurrence of first-order transitions in the same way as described for the case of vanadium [16]. The search space was restricted to $0.7 < c/a < 2.1$ and had a resolution $\Delta a = 0.05 \text{ \AA}$ (Δa was subsequently reduced to pinpoint a_{crit}). Seven transitions were found in this way; see table 1. Apart from vanadium, the group-5 element niobium (but not tantalum) and the elements ruthenium, lanthanum, osmium, and iridium exhibit discontinuous EBPs. For La and Ir, we identified a negative c_{zzzz} of the BCC structure as the driving force of the instability, while in Nb the FCC structure has $c_{\text{zzzz}} < 0$. BCC Ru and Os possess small positive c_{zzzz} but the discontinuities of the EBP occur in the vicinity of the



BCC structure at a lattice parameter being slightly smaller and larger than a_{BCC} , respectively. No second instability was found for any element except vanadium. All seven first-order transitions were also found in additional calculations relying on PBE96; see table 1. Compared to the PW92 results, a_{crit} is shifted to larger values in PBE96.

The present work focuses on non-magnetic elements, where we found first-order martensitic transitions under epitaxial strain due to either a large peak in $N(E_F)$ or a more subtle interplay of all contributions to the total energy in the vicinity of a saddle point. In order to find out whether the epitaxial relation of a particular substance is continuous or not, one usually has to calculate this relation in detail. An FCC or BCC structure with negative c_{zzzz} always results in a discontinuous EBP, but a (small) positive c_{zzzz} does not exclude a discontinuity.

In the case of magnetic systems, high-spin to low-spin transitions [9] or a change of the ground state magnetic order [17] are usually accompanied by discontinuities of the lattice geometry. An example might be the a -dependence of the magnetic ground state of BCT Fe found by Qiu *et al* [17]. These authors did not, however, discuss the consequence of a transition into a different magnetic state for the lattice parameter c of coherent films.

We now return to the case of vanadium to demonstrate how strongly the structural discontinuity may alter another particular intrinsic property, namely, the superconducting critical temperature T_c . Vanadium is a well-known superconductor and possesses one of the highest T_c -values among all elements, $T_c = 5.4 \text{ K}$, at normal pressure [30]. A significant change of T_c may be expected at $a_{\text{crit},1}$, since $N(E_F)$ jumps by $0.2 \text{ states}/(\text{eV} \cdot \text{atom})$; see figure 2.

The calculations for T_c of BCT vanadium were carried out with the ABINIT-DFT package in the version 6.12 [31, 32] employing a pseudopotential (PP) generated with the FHI98PP code [33] for PW92. With this PP, we found slightly shifted values of $a_{\text{BCC}} = 2.963 \text{ \AA}$ and of $a_{\text{crit},1} = 2.623 \text{ \AA}$ compared with the FPLO results. The phonon properties were obtained through density-functional perturbation theory [34] as implemented in ABINIT [35, 36]. To compute the superconducting properties of V, we used a plane-wave-kinetic-energy cutoff of 650 eV and a $52 \times 52 \times 52$ mesh in the full Brillouin zone for linear tetrahedron integrations. The phonon quantities are sampled by eight wave vectors in the full Brillouin zone.

We verified the accuracy of our approach for BCC vanadium for which we obtained an electron–phonon coupling constant $\lambda = 0.95$ and a logarithmic-averaged phonon frequency $\omega_{\log} = 288$ K. For comparison, tunneling experiments found $\lambda = 0.82$ [37]. We derived a reasonable value of $T_c = 3.2$ K for BCC vanadium according to the Allen–Dynes modified McMillan formula [38]. This equation contains one parameter, the effective Coulomb repulsion μ^* , which we set to a value $\mu^* = 0.13$ commonly used for transition metals [39].

T_c across the discontinuity $a_{\text{crit},1}$ was computed for the points ((a, c_{min}) coordinates) (2.595 Å, 4.128 Å) and (2.646 Å, 3.545 Å). λ changes by $\Delta\lambda = 0.20$ and T_c by $\Delta T_c = 0.6$ K or 20% across $a_{\text{crit},1}$ (from 3.5 K at $a = 2.595$ Å to 4.1 K at $a = 2.646$ Å). The actual value of T_c may depend on the film thickness, as this was found in experiments for BCC vanadium films [40, 41], but we expect that the relative change will not be substantially affected by this dependence.

4. Conclusions

We have shown that coherently grown epitaxial films can exhibit a discontinuous relation between in-plane and out-of-plane lattice parameters in a strain-driven, first-order phase transition. In particular, we predict that BCT bulk-like films of the elements V, Nb, Ru, La, Os, and Ir undergo martensitic lattice transformations induced by epitaxial strain with related volume changes up to 20%. As a consequence, the intrinsic film properties can be switched, if one succeeds in controlling the substrate lattice parameter appropriately. We demonstrated this possibility with the example of vanadium, where the superconducting critical temperature changes by about 20% at a critical strain value.

Since the mechanisms of the discussed instabilities may be present in arbitrary metallic systems, our results are not limited to mono-atomic overlayers, BCT films or specific ground states. Verification of the predicted transitions should be possible by advanced diffraction methods applied to coherently grown overlayers on a series of substrates with quasi-continuous lattice spacings. An indirect verification could be achieved by measuring any other structure-dependent physical property of the film material.

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