

# Structural transformations in metals at high compression ratios

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**Abstract.** An analysis of crystal structure stability against homogeneous deformation is carried out for simple and transition metals with body-centered cubic (bcc) and face-centered cubic (fcc) lattices under pressure. It is shown that at high compression ratios a crystal lattice can turn unstable against shear deformations, leading to new lower-symmetry structures. To analyze these structures, the Landau theory of phase transitions with finite deformation tensor components as order parameters is applied. A comparison is made with experimental data on high-pressure phases. Prospects are discussed for using the suggested approach to explain structural transformations in solids at high pressures.

## 1. Introduction

In recent years, a number of review papers [1–4] have been published on experimental and theoretical work on the high-pressure phases of simple elements (which typically possess a cubic structure under normal conditions). Experimental crystal structure studies of elementary substances at high pressures using diamond anvil cells, high-power synchrotron radiation sources, and advanced methods of processing X-ray diffraction patterns showed that at high compression ratios ( $V/V_0 < 0.5$ , where  $V$  and  $V_0$  are the atomic volumes at pressure  $P$  and at atmospheric pressure, respectively) these substances undergo a number of structural transformations, often leading to less symmetrical and less compact high-pressure phases compared to those realized under normal conditions. Some of the high-pressure phases may be classified as composite crystalline structures comprised of two interpenetrating substructures with incommensurate translation periods along one of the crystallographic directions—which is also uncharacteristic of the structures the elements form at atmospheric pressure. Moreover, commen-

surate and incommensurate structures containing two or more sublattices are more the rule than the exception for the high-pressure phases of elementary substances [5]. These results are at odds with the existing crystallographic conception that the higher the pressure, the more tightly packed the structure, and the larger the coordination number, even though such a model explains well the polymorphism of elements and simple compounds at relatively low compression ratios.

Modern *ab initio* calculations using density functional theory [2] provide a means to calculate the energy of any crystal structure for any unit cell volume. By comparing the energies of a number of lattices at a given pressure, it is possible to determine what type of lattice is more favorable energetically for this pressure. What complicates predicting high-pressure phases is that finding a stable phase requires sorting through and comparing the total energies of all possible crystal structures—which is quite a job because, as experimental evidence suggests, even the high-pressure structures of simple elements are often too complex to presuppose, thus greatly increasing the number of crystal lattices whose total energies should be calculated. To add to the problem, the energy difference between different structures is often comparable to the error of calculations.

## 2. Crystal lattice stability and elastic phase transitions

Experimental data suggest that the structural transformations under study occur at pressures comparable to the elastic constants of the materials and, hence, by implication, are due to the fact that a crystal lattice under pressure loses its stability, especially against homogeneous deformations. As a result, in parallel with very commonly occurring structural transitions caused by chemical potential equality between different structures and normally observed at low compression ratios, the phase transitions triggered by crystal lattice instability can also take place. And if the former always proceed as first-order transitions, those driven by instability can be first-order and second-order alike. Therefore, electrophysical property changes in relation to Brillouin-zone–Fermi-surface interplay [2, 3] are not the only thing to consider when discussing pressure-driven structural transformations; importantly, crystal lattice stability against homo-

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geneous deformations and stability loss-induced phase transitions should also be analyzed.

For a cubic crystal at pressure  $P$ , the conditions for the lattice to be stable against homogeneous deformation are obtained by requiring that the quadratic part of the thermodynamic potential be positive definite and the frequencies of the long-wave vibrations be real, to give [6]

$$C_{11} + 2C_{12} + P > 0, \quad (1)$$

$$C_{11} - C_{12} - 2P > 0, \quad (2)$$

$$C_{44} - P > 0, \quad (3)$$

where  $C_{\alpha\beta}$  are Brugger's second-order elastic constants at a given pressure (in Voigt notation). Violation of one of these conditions, whether caused by a change in temperature or pressure, gives rise to what is known as the elastic phase transition, a transition to a spontaneously deformed state which depends on the anharmonic terms in the potential expansion for its stability [7]. An analysis of a number of stability loss situations [7, 8] reveals the strong suppression of fluctuations in these cases, resulting in these structural transformations being able to be treated in terms of the Landau theory of phase transitions [9] using deformation tensor components as order parameters.

There have been a number of studies using the molecular dynamics, functional density, and pseudopotential methods to calculate elastic constants for various materials under pressure. An important point when analyzing these results is that a stressed crystal has the following three types of elastic constants [6] (which are all equal at  $P = 0$ ): the coefficients in the free energy expansion in terms of the components of the Lagrange finite deformation tensor (Brugger type elastic constants), proportionality coefficients in Hook's law (Birch moduli), and sound propagation coefficients. Ignoring this fact leads to confusion given that the numerical values of some moduli are often ascribed to others (specifically, the Birch moduli are sometimes called Brugger moduli).

### 3. Elastic constants and phase transitions under pressure: analysis of calculated results

Elastic constant calculations for gold [10], aluminium [11], and the alkali metals Na, K, Rb, and Cs [12] showed that stability condition (1) is violated for negative pressures  $V/V_0 > 1$ , so our analysis below concerns conditions (2) and (3). Reference [13] employed the functional density method to calculate the elastic constants of the body-centered cubic (bcc) lattices of sodium and potassium at high compression ratios. It is demonstrated that in either case the first to be violated (at  $V/V_0 \approx 0.25$ ,  $\approx 150$  GPa and  $V/V_0 \approx 0.40$ ,  $P \approx 20$  GPa, respectively) is condition (2), with condition (3) following at  $V/V_0 \approx 0.20$ ,  $P \approx 200$  GPa and  $V/V_0 \approx 0.20$ ,  $P \approx 60$  GPa, respectively. Similar results for Na were reported in Ref. [14]. Figures 1 and 2 show  $(C_{11} - C_{12})/2 - P$  and  $C_{44} - P$  as functions of the compression ratio  $V/V_0$  as obtained by the pseudopotential method for the bcc and face-centered cubic (fcc) structures of Na [14]. It is seen that the fcc lattice of sodium, while stable with respect to shear deformation related to the elastic constant  $(C_{11} - C_{12})/2$  at any compression, loses its stability against the deformation associated with  $C_{44}$ .

Reference [15] used the density functional method to determine the elastic constants of the fcc and bcc lattices of

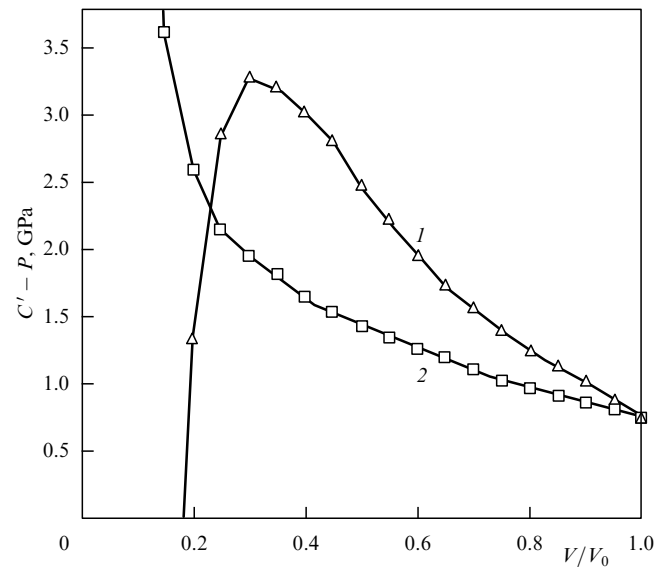


Figure 1.  $C' - P$  vs.  $V/V_0$  for sodium [ $C' = (C_{11} - C_{12})/2$ ]: 1, bcc, and 2, fcc.

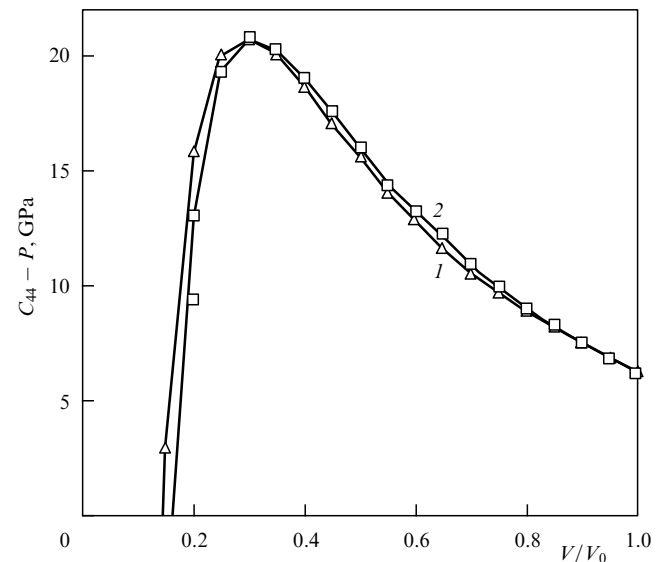


Figure 2.  $C_{44} - P$  vs.  $V/V_0$  for sodium: 1, bcc, and 2, fcc.

aluminium in the  $V/V_0$  range between 1 and 0.3. The results imply that for the aluminium fcc, whereas the lattice loses stability at  $V/V_0 \approx 0.39$ ,  $P \approx 400$  GPa according to criterion (2), criterion (3) is satisfied over the entire  $V/V_0$  range considered. The bcc lattice, according to inequality (2), becomes unstable in the range  $V/V_0 = 1 - 0.63$ , explaining why aluminium possesses the fcc lattice at low compressions. However, for  $V/V_0 < 0.6$  the quantity  $C_{11} - C_{12} - 2P$  becomes positive and monotonically increases with a further decrease in  $V/V_0$ . Condition (3) is satisfied for all values of  $V/V_0$  for the bcc lattice of aluminium.

For the tantalum bcc lattice, the calculated elastic constants at  $V/V_0 = 1 - 0.5$  [16] indicate that relation (2) becomes zero for  $V/V_0 \approx 0.6$ ,  $P \approx 250$  GPa, and, further, that for the intervals  $V/V_0 = 0.68 - 0.60$ ,  $P \approx 150 - 250$  GPa the quantity  $C_{44} - P$  becomes less than zero, but for  $V/V_0 < 0.60$  it is again positive—a behavior of the elastic

constant  $C_{44}$ , which the authors of Ref. [16] relate to a topological electronic transition they previously discovered in a first-principles study of the tantalum equation of state [17]. It was emphasized that the elastic constants are more sensitive to changes in the Fermi surface than the equation of state. Similar results on the elastic constants of tantalum at pressures of up to 400 GPa were reported in Ref. [18].

Density functional calculations in Refs [18, 19] of the elastic constants of the bcc lattices of V, Nb, Mo, and W as functions of pressure show that for Nb, Mo, and W the stability conditions (2) and (3) are satisfied for pressures of up to  $P \approx 400$  GPa—that is, the bcc lattice of these metals remains stable against shear deformations over the entire pressure range investigated. The situation is different for vanadium, where the bcc lattice becomes unstable to the  $C_{44}$  shear mode. It should be noted here that the  $C_{\alpha\beta}$  values calculated in the two studies agree quite well for Nb, Mo, and W, but disagree considerably for vanadium [18, 19]. Furthermore, the values of  $C_{\alpha\beta}$  for vanadium at atmospheric pressure agree poorly with experimental results. However, based on the data on the pressure dependence of  $C_{44}$  [19], the bcc lattice of vanadium loses stability at pressures of  $P \approx 60$  GPa.

A recent synchrotron X-ray diffraction study [20] of the structure of vanadium under pressure revealed a phase transition at a pressure of  $P \approx 69$  GPa, caused by the rhombohedral deformation of the bcc lattice (rhombohedral deformation corresponding to the elastic constant  $C_{44}$ ). Importantly, there is no jump in atomic volume as we move along the equation of state curve in the vicinity of the transition; the inclination of this dependence only varies. According to the researchers [20], the structural transition they observed constitutes a second-order phase transition. In Ref. [21], density functional calculations of the total energy were performed and showed that the rhombohedral phase can indeed occur in vanadium under pressure and, furthermore, that at a pressure of about 84 GPa the rhombohedral structure is more stable (has a lower energy) than the bcc structure. It was also revealed that at pressures above 280 GPa the bcc lattice again becomes energetically more favorable than the rhombohedral lattice.

A useful tool for understanding structural transformations in elementary metals under a high degree of compression is Landau's phenomenological theory of phase transitions as applied to situations where a lattice loses its stability when under pressure. Table 1 below summarizes the structural transformations a cubic lattice can undergo with loss of its stability against shear deformations. The results were obtained by group-theoretical analysis for Bravais lattice symmetry [22] in the framework of the fourth-order model

(in the sense of retaining fourth-order terms in the thermodynamic potential expansion in the components of the Lagrange finite deformation tensor). The stability conditions for the new low-symmetry phases are expressed in terms of the third- and fourth-order elastic constants. At the next level of complexity—which is the sixth-order model—less symmetric and more complex structures appear, including modulated ones [23].

Experimental data on the high-pressure phases of alkali and alkali-earth metals [3] reveal that at high degrees of compression ( $V/V_0 = 0.2-4$ ) the most often observed phases are the body-centered tetragonal phase (Bravais lattice  $\Gamma_q^v$ ) and the orthorhombic phase ( $\Gamma_o, \Gamma_o^v, \Gamma_o^f$ ) with a different number of atoms in a unit cell. It is precisely these structures which are listed in the table as being due to the crystal losing its stability against shear deformation related to the elastic constant  $(C_{11} - C_{12})/2$ .

Let us be reminded that, for sodium, the stability criterion (2) related to the elastic constant  $(C_{11} - C_{12})/2$  is violated at compression ratios close to an estimated 0.2 (see Fig. 1). The pressure-induced cubic-to-rhombohedral ( $\Gamma_{rh}$ ) transition observed in vanadium [20] corresponds to the lattice losing its stability against  $C_{44}$  shear deformation (see Table 1).

Thus, by applying the Landau theory of phase transitions to crystal lattice stability analysis at high degrees of compression, new equilibrium structures can be predicted, making the search for high-pressure phases much easier.

## 4. Conclusions

In this paper, crystal lattice stability and possible elastic phase transitions have been analyzed for a number of simple and transition metals under high degrees of compression, leading to the conclusion that high-pressure low-symmetry phases are due to the anharmonicity (nonlinear elasticity) of the crystal lattice: the structure and stability of a new phase are in the simplest cases determined by the second-, third-, and fourth-order elastic constants. The inclusion of higher-order anharmonicity allows new, more complex structures to be obtained. The approach we have outlined, while revealing nothing about the mechanisms behind the formation of high-pressure phases, turns out to be useful for predicting new structures at high degrees of compression and is therefore of particular relevance to current research into materials at high pressures.

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**Table 1.** Deformation phase transitions in cubic crystals.

Transition conditions	Order parameter *	Transition-induced change of Bravais lattice
$C_{11} - C_{12} - 2P = 0$	$\eta_1 = -\eta_2 = \eta$	$\Gamma_c \rightarrow \Gamma_o;$ $\Gamma_c^f, \Gamma_c^v \rightarrow \Gamma_o^v, \Gamma_o^f$
	$\eta_3 = -2\eta_2 = -2\eta_1 = \eta$	$\Gamma_c \rightarrow \Gamma_q; \Gamma_c^f, \Gamma_c^v \rightarrow \Gamma_q^v$
$C_{44} - P = 0$	$\eta_4 = \eta_5 = \eta_6 = \eta$	$\Gamma_c, \Gamma_c^f, \Gamma_c^v \rightarrow \Gamma_{rh}$
	$\eta_4 = \eta$	$\Gamma_c \rightarrow \Gamma_o, \Gamma_o^b;$ $\Gamma_c^v, \Gamma_c^f \rightarrow \Gamma_m^b$

\* The remaining components of the deformation tensor are zero.

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