

Trends of the Elastic Constants of Cubic Transition Metals

J. M. Wills,⁽¹⁾ Olle Eriksson,⁽¹⁾ Per Söderlind,⁽²⁾ and A. M. Boring⁽¹⁾

⁽¹⁾Center for Materials Science and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

⁽²⁾Department of Physics, Uppsala University, Uppsala, Sweden

(Received 23 January 1992)

We show for the first time, using *ab initio* calculations, that the trend exhibited by the elastic constants in the transition metals can be simply understood. In particular, we show that the trend of the elastic constants of cubic transition metals is determined by the energy difference between the fcc and bcc structures of a given element, which in turn is determined by band filling. Our results suggest indirectly that the reason for the disagreement between calculated "experimental" data for crystal energy differences does not lie in the calculated results.

PACS numbers: 62.20.Dc, 71.10.+x, 71.25.Pi

Many of the ground-state properties of the transition metals are now well characterized and understood. For example, the equilibrium volumes (V_{eq}) show a parabolic trend with a minimum in approximately the middle of the series. The bulk modulus (B) and the cohesive energy (E_c) have similar trends, but with a maximum approximately where the volume has a minimum. The trends of V_{eq} and E_c are roughly given by the Friedel model [1], in which one is occupying bonding d orbitals in the first half of the series and then filling antibonding d orbitals in the second half of the series. In this model these d orbitals form a narrow d band that is pinned at the Fermi energy (E_F), and assuming only nearest-neighbor hopping Pettifor [2] demonstrated that the Friedel model connects the maximum in the bulk modulus with the maximum in the cohesive energy, as well as with the minimum in the equilibrium volume. A more quantitative picture of the trends of all three quantities is given by the universal bonding model [3] based upon local density approximation (LDA) calculations. An important feature of the LDA calculations is that B , V_{eq} , and E_c can be determined at the 90% accuracy level independent of crystal structure, indicating that these quantities are independent of the arrangement of the atoms as long as they are rather closely packed (fcc, bcc, or hcp). It is this blend of detailed calculations (LDA results) and descriptive concepts (Friedel model) that has given a deeper understanding of these average properties of solids.

The elastic constants (C_{11} , C_{12} , and C_{44}) of the cubic transition metals stand in contrast to the clear parabolic trends shown by V_{eq} , B , and E_c . However, the observed elastic constant trends for the $3d$, $4d$, and $5d$ series are similar, and for simplicity we shall concentrate only on one, the $5d$ series. To illustrate the problem we show in Fig. 1 the tetragonal shear constant C' and the bulk modulus B [$C' = (C_{11} - C_{12})/2$ and $B = (C_{11} + 2C_{12})/3$]. We have chosen C' instead of C_{11} or C_{12} because this constant is obtained from the curvature of a tetragonal distortion of a cubic lattice (see below). Despite the fact that C' and B are both linear combinations of C_{11} and C_{12} , they do not follow a similar trend; the shear constants of W and Ir are highly anomalous while the shear

constants of Cs, La, Ta, Pt, and Au follow approximately the same trend as B . The lack of simple parabolic behavior when the crystal symmetry is broken as in C_{11} or C_{12} has led to the belief that there is no simple explanation of elastic constant behavior in the transition-metal elements.

Previous studies of elastic properties of transition-metal elements have mainly demonstrated the complexity of the behavior. For example, the high shear constant of Ir yields unusual brittle cleavage of that material, and it was argued on this basis that Ir has very strong directional atomic binding forces [4]. Similarly, using interatomic central force potentials, it has been argued that the bcc transition elements have strong directional covalent bonds, since C' and E_c could not both be fitted [5]. The directionality in the bonds of bcc metals was also used as an argument for the similar behavior of ΔE_0 and K_b [5] (ΔE_0 is the deviation between the predicted cohesive energies with and without the presence of covalent bonds, and K_b is proportional to the difference between calculated and experimental C' values). Moreover, the covalent bond strength was suggested to decrease with increasing $|n_d - 5|$, where n_d is the number of d electrons [5].

The tetragonal shear constant C' is obtained from the curvature of the total energy under a volume-conserving

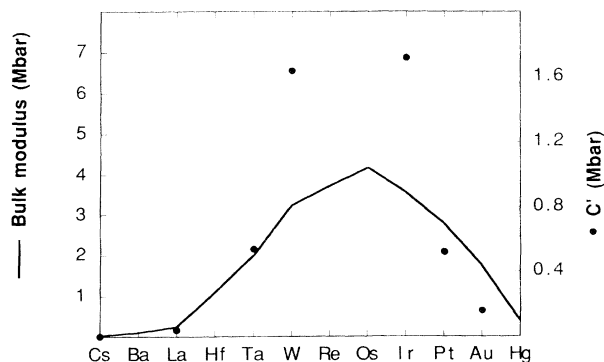


FIG. 1. Experimental data for the tetragonal shear constant (solid circles, right-hand scale) and for the bulk modulus (solid line, left-hand scale) of the $5d$ transition metals.

strain that modifies the c axes but keeps the a and b axes equal [6–8]. C' is obtained from the curvature around the energy minimum, i.e., for very small shears. However, the same shear (tetragonal), although larger, can transform a bcc crystal to a fcc crystal and vice versa. Hence, both the fcc and the bcc crystal can be described as body-centered tetragonal with $c/a = \sqrt{2}$ and 1, respectively. This kind of shear is referred to as the Bains transformation path [9]. It is therefore illustrative to study the total energy as a function of not only small shears (the C' values), but also shears of the same magnitude that bring a bcc crystal to the fcc structure and vice versa. These considerations indicate that an understanding of C' is tied up with an understanding of crystal structure trends in the transition metals.

The crystal structure stabilities of almost all transition metals have been calculated from first principles [10–12]. The trend of the crystal structure stabilities was again shown to be determined by the d electrons, and it was even demonstrated that the eigenvalues [and therefore the density of states (DOS)] of the “canonical d bands” [13,14] (which only depend on the crystal structure, with no potential or volume dependence) describe these trends [10,11]. Also, it was shown that the dominant term which minimizes the total energy of a given structure is associated with the shape, and the filling (number of valence electrons) of the partial d DOS. This is essentially described by the canonical d bands, which are unique to that particular arrangement of the atoms. Another feature given by these studies is that the energy difference between fcc and hcp is normally small, whereas the difference between fcc and bcc structures can be substantially higher. As mentioned above there is a path (the Bains path [9]), involving one parameter, that describes the bcc to fcc transition. The situation is more complicated for the hcp structure, but the so-called Burgers path [15] takes a bcc crystal to a hcp crystal. The bcc \rightarrow hcp transition can be described as a shear together with atomic displacements corresponding to the zone-boundary [110] T_1 phonon mode [16]. For this reason we will consider the bcc and fcc structures only, neglecting the hcp structure. The argument then for the crystal structure trends (bcc versus fcc) is based upon the difference between the double-peak structure of the bcc d DOS and the broad roughly featureless fcc d DOS structure [10]. As one goes across the $5d$ series, the occupied fcc d DOS has a larger energy moment (La,Hf). After passing the first bcc peak the bcc band energy is greater (Ta,W). For the rest of the series, the fcc DOS moment dominates. This same trend is seen in the $4d$ series, but in the $3d$ series this trend is modified by magnetism [10].

We turn to the detailed LDA calculations of the elastic constants themselves which indicate the level of accuracy obtained. The first *ab initio* calculation of elastic constants of transition metals was presented by Dacorogna, Ashkenazi, and Peter [6] who calculated the C' constants for thirteen fcc and bcc transition metals, using the linear

muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) [13,14]. These results compared fairly well with experiments, with the largest disagreement being $\sim 50\%$ too large in fcc Pd, $\sim 60\%$ too large in fcc Ag, as well as $\sim 60\%$ too large in bcc Mo. Christensen [7], on the other hand, found good agreement for both fcc Pd and fcc Au, using LMTO-ASA calculations. Moreover, Shimizu [17] and Ohta and Shimizu [18] found fairly poor agreement in their calculated C' constants of V and Cr. The only full potential treatment of elastic constants of transition elements, that we are aware of, were published by Alouani, Albers, and Methfessel, who obtained good agreement with experiment for bcc Mo [19].

In this Letter, results for both the total energies and the shear constants are given. We have used a full-potential linear muffin-tin orbital method (FP-LMTO) [20] as well as a LMTO-ASA [13,14] method. The details of both FP-LMTO as well as LMTO-ASA calculations will be given in a longer paper. The accuracy of the total energy needed for calculating the elastic constants is on the order of 0.01 mRy. Shown in Table I are the results for C' and C_{44} (details about the trends of C_{44} will also be given in a longer paper) from the full-potential calculations. In order to establish trends we have performed the calculations for all $5d$ transition elements in the true crystal structures, except for the hexagonal ones where we have used a hypothetical fcc structure. Except for La (which is fcc only at elevated temperatures) we have agreement between experiment and theory at the $\sim 90\%$ level. This gives one confidence that these calculations can be used to explain these trends. Next, in Fig. 2 the total energies (obtained from LMTO-ASA) are shown for all $5d$ elements as a function of the c/a ratio, i.e., the calculated Bains path [with the reference energy set to zero for $c/a = \sqrt{2}$ (fcc) for all elements]. From Fig. 2 it is clear that systems that have a large energy difference between the bcc and fcc structures show a large curvature of the total energy around the energy minimum (for both bcc and fcc crystals) and should show large C' values. Therefore from Fig. 2 one deduces that

TABLE I. Experimental and theoretical values of the C' and C_{44} constants (in Mbar). The experimental value of fcc La was obtained at elevated temperatures ($\sim 600^\circ\text{C}$).

	C'^{expt}	C'^{theor}	C_{44}^{expt}	C_{44}^{theor}
La	0.041	0.064	0.165	0.158
Hf	...	0.190	...	0.659
Ta	0.541	0.646	0.873	0.836
W	1.638	1.729	1.631	1.781
Re	...	1.480	...	2.619
Os	...	1.821	...	3.323
Ir	1.719	1.776	2.682	2.655
Pt	0.522	0.592	0.774	0.847
Au	0.160	0.164	0.454	0.311

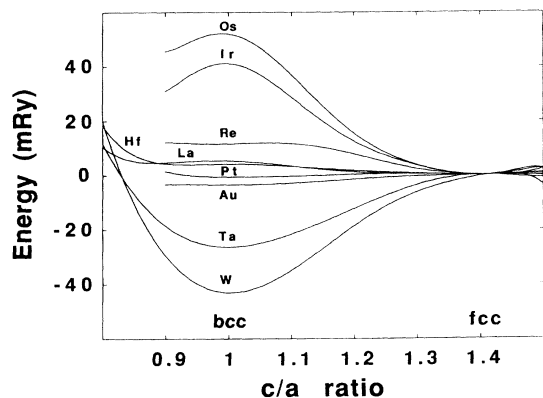


FIG. 2. Calculated Bains path for the 5d transition metals.

the C' values scale with the energy difference between the bcc and fcc structures. To test this hypothesis, shown in Fig. 3 are the calculated C' values, as well as (the magnitude of) the energy difference between the bcc and fcc crystals, for all 5d metals. The data shown in Fig. 3 were obtained from FP-LMTO calculations (the LMTO-ASA calculations yield similar trends). We have also plotted the experimental data for the cubic metals in Fig. 3. Notice that the anomalously high shear constants of W and Ir simply reflect a very large difference in crystal structural energies. The reasons for these large differences in crystal structure energies have previously been demonstrated to be governed by the d -band filling, and in particular the shape of the "canonical" d bands [10,11]. For example, the bcc structure is energetically very unfavorable on the low side of the second peak in the bcc d DOS curve, where the bcc energy moment is smaller than the fcc moment (Os, Ir). Notice also that the scaling between the crystal structure energy and C' depends on the shape of the Bains path for a particular system. However, it is seen that (except for the high-temperature phase of La) there is agreement to approximately (80–90)%.

If we put all the pieces together we arrive at a simple explanation for the trend in C' for the cubic transition-metal elements. From the calculation of the Bains path one obtains not only the crystal structure stability, but its "excited" state (bcc-fcc energy difference) and the fact that C' is related to its excited-state structure. Therefore, unlike V_{eq} , B , and E_c , the crystal structure energies determine the trends in C' and one does not get a parabolic trend. Because both the stable crystal structure and its excited state can be correlated with d -band filling we arrive at a simple explanation for the values of C' , i.e., those crystals for which band-filling arguments dictate a large bcc-fcc energy difference will have large C' values. The physical explanation for this is that it is precisely these systems for which the bcc-fcc transformation is difficult and hence the C' values high.

Turning the argument around, since we are able to reproduce the experimental C' data very well, one would

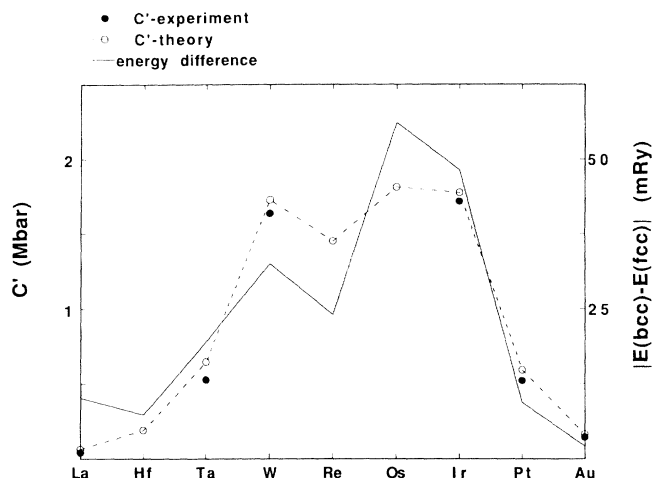


FIG. 3. Theoretical data for the absolute value of the energy difference between the fcc and bcc structures, as well as the calculated tetragonal shear constant, C' . The experimental data for C' are also shown. The fcc energy is lowest for all elements except Ta and W.

therefore also expect the same kind of accuracy when comparing calculated [10,12] (Fig. 3) and measured [21] values of the bcc-fcc energy difference. However, the calculated data [10,12] (Fig. 3) are sometimes a factor of 3–5 larger than the "experimental" data. There is some modeling associated with extracting the experimental data, and we use the good agreement between our calculated and experimental C' data as an argument for experimentalists to try and refine the experimental data for the bcc-fcc energy difference.

Finally we speculate that similar correlations should exist between the hcp-bcc energy difference and the zone-boundary [110] T_1 phonon mode of the bcc crystal, since the atomic displacement that brings a bcc crystal to hcp corresponds to this mode, together with a shear (the Burgers path [15]).

Duane Wallace, Börje Johansson, and R. Schwarz are acknowledged for critical reading of the manuscript. Valuable discussions with Bengt Nöläng, Bob Albers, Barry Cooper, and Matthew Steiner are acknowledged.

- [1] J. Friedel, *The Physics of Metals*, edited by J. M. Ziman (Cambridge Univ. Press, New York, 1969).
- [2] D. G. Pettifor, *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 43.
- [3] R. C. Albers, A. M. Boring, and J. C. Boettger, in *Advances in Quantum Chemistry* (Academic, New York, 1990), Vol. 21, p. 365; J. R. Smith, J. Fernante, and J. H. Rose, *Phys. Rev. B* **25**, 1419 (1982).
- [4] S. S. Hecker, D. L. Rohr, and F. Stein, *Metall. Trans. A*

- 9a, 481 (1978); D. L. Rohr, L. E. Murr, and S. S. Hecker, *Metall. Trans. A* **10a**, 399 (1979).
- [5] E. S. Machlin and J. Shao, *J. Phys. Chem. Solids* **44**, 435 (1983).
- [6] M. Dacorogna, J. Ashkenazi, and M. Peter, *Phys. Rev. B* **26**, 1527 (1982).
- [7] N. E. Christensen, *Solid State Commun.* **49**, 701 (1984); **50**, 177 (1984); *Phys. Rev. B* **29**, 5547 (1984); *Ψ_k -Newslett.* **8**, 2 (1984).
- [8] Duane C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
- [9] I. C. Bain, *Trans. AIME* **70**, 25 (1924).
- [10] H. L. Skriver, *Phys. Rev. B* **31**, 1909 (1985).
- [11] J. C. Duthie and D. G. Pettifor, *Phys. Rev. Lett.* **38**, 564 (1977).
- [12] G. W. Fernando, R. E. Watson, M. Weinert, Y. J. Wang, and J. W. Davenport, *Phys. Rev. B* **41**, 11 813 (1990); R. E. Watson, G. W. Fernando, M. Weinert, Y. J. Wang, and J. W. Davenport, *Phys. Rev. B* **43**, 1455 (1991).
- [13] O. K. Anderson, *Phys. Rev. B* **12**, 3060 (1975).
- [14] H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
- [15] W. G. Burgers, *Physica (Utrecht)* **1**, 561 (1934).
- [16] Y. Chen, C.-L. Fu, K.-M. Ho, and B. N. Harmon, *Phys. Rev. B* **31**, 6775 (1985); Y. Chen, K.-M. Ho, and B. N. Harmon, *Phys. Rev. B* **37**, 283 (1988).
- [17] M. Shimizu, *Physica (Amsterdam)* **159B**, 26 (1989).
- [18] Y. Ohta and M. Shimizu, *J. Phys. F* **13**, 761 (1983).
- [19] M. Alouani, R. C. Albers, and M. Methfessel, *Phys. Rev. B* **43**, 6500 (1991).
- [20] J. M. Wills (unpublished).
- [21] A. R. Miedema and A. K. Niessen, *Comput. Coupling Phase Diagrams Thermochem. (CALPHAD)* **7**, 27 (1983).