PHYSICAL REVIEW B VOLUME 38, NUMBER 11 15 OCTOBER 1988-I

Structural stability of rhenium as a function of lattice compression: Theory

R. E. Watson, J. W. Davenport, M. Weinert, and G. Fernando
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

(Received 18 March 1988)

Total-energy, linearized augmented Slater-type orbital calculations have been done for rhenium as a function of lattice volume in response to recent experiments addressing the issue of whether the hcp phase of Re becomes unstable, with respect to the bcc phase, at high pressures. The calculations indicate that the hcp, in fact, becomes more stable, relative to the bcc, under compression.

Rhenium is a transition element sitting just to the right of tungsten in the 5*d* row. Having roughly half-filled *d* bands, it has a high cohesive energy and melting temperature, is of high density, and is one of the least compressible of all metals. Re crystallizes in the hcp structure and retains this structure up to its melting temperature. Nevertheless there are questions, as with transition metals in general, as to the competition of the other close-packed phases, the bcc and fcc at high temperatures and/or at high pressures. Recently, Vohra, Duclos, and Ruoff studied[1] Re at pressures up to 2.16 Mbar, yielding a volume fraction V/V_0 of 0.734. They detected no change in structure and observed that the hcp c/a ratio stayed constant within experimental error. From their observations, they concluded that Re would be a suitable gasket material for ultrahigh-pressure experiments. From some suggestions in the literature, they had been concerned with whether Re would tend to the bcc structure under compression and they voiced regret that no first-principles calculations had been carried out concerning the crystal-phase stability of Re under pressure. This Brief Report endeavors to fill that void.

There are some hints in the literature about the competition between the bcc and the other close-packed phases for a metal such as Re. Of particular concern to Vohra *et al.*, was the work[2,3] of Kaufman and Bernstein who, considering the phase diagrams of Re alloyed with elements such as Nb and Ta, concluded that the bcc form of Re, though unstable, would be denser than the hcp. This suggests the possibility that the bcc phase becomes more competitive when Re is compressed. There are other, less relevant matters raised in the literature. For example, Alexander and McTague applied[4] Landau theory to the problem of what possible ordered structures a liquid might condense into at temperatures below the melting point and concluded that the bcc would be favored over the other close-packed phases. (More recently, applying a more general parametrization of the theory, Bak obtained[5] that icosahedral "quasicrystalline" ordering would be even more stable.) There is, of course, also the question of what happens at elevated temperatures where a number of elemental metals transform from fcc or hcp to bcc. This has traditionally been associated[6,7] with phonon contributions to the crystal entropy (it has been also noted[8] that electron-excitation contributions to the entropy are also of experimental significance). Even if Vohra *et al.* failed to observe the bcc phase for Re under pressure, it is still of interest as to whether the bcc structure becomes less unstable upon compression. The calculations of the present paper indicate the reverse.

The self-consistent, scalar relativistic, linearized augmented Slater-type orbital (LASTO) method[9] has been applied to obtain total energies for bcc and hcp Re at varying volumes with a fixed c/a ratio (equal to the observed value of 1.6145) for the hcp lattice. Local density muffin-tin potentials were used. A set of 64 special k points in the hcp Brillouin zone (and 70 in the bcc) was employed and this more than suffices for the relative accuracy needed in the total crystal energy obtained at some lattice volume and structure as compared to that at another. The LASTO computational method has been described elsewhere[9-12] and will not be repeated here, but there are some features of such calculations that are important to the case at hand. These are associated with the crystal potential and with the atomic core when making as much as aa 30% change in the lattice volume. Like other augmented basis set methods, nonoverlapping atomic spheres of radius r_s are employed, inside of which Schrödinger's equation or its relativistic counterpart is integrated to obtain wave functions that are then matched to an analytic basis set in the interstitial region. This basis set may be plane waves, Gaussians, or, as is the case at hand, Slater-type orbitals. One problem with such a scheme is that of the core electrons, which in the present calculations are dealt with self-consistently (and fully relativistically). The treatment of how the core-electron tails extend outside of an atomic sphere is somewhat arbitrary. The best and correct treatment would be to take those "semicore" electrons, having significant tailing, and treat them as band states in a full band-structure calculation. This involves a significant increase in computational effort and has not been done here. For the closed-packed structures considered here, 1–3 % of the semicore 5*p* density lies outside the spheres (depending on the r_s used) and the resulting wave-function tails are adequately treated using an atomiclike approximation in which the potential outside the spheres is set equal to the muffin-tin potential. So as to minimize any variation in the core-electron contributions to the errors in the total energies, results will be reported for calculations with a fixed sphere radius r_s at varying volume and structure. This, of course, implies that a varying fraction of the crystal volume is in the interstitial region. For such a case it would be better to employ full rather than muffin-tin potentials (with their constant potential in the interstitial region). Use of the latter is not expected to qualitatively affect the energy differences to be reported here, although the actual numbers would differ between the two treatments.

Like most augmented basis set band calculations, the present calculations are also linearized, that is the sphere integrations are done at some specific orbital energy parameter ε_l (which may be different for differing orbital angular momentum l). Mattheiss and Hamann have very nicely shown, in their investigation[13] of Cr, Mo, and W, that an incorrect choice of the energy parameter can lead to collapse of the valence states into the core thereby causing a spuriously large binding value for the calculated crystal energy. This collapse is the result of not maintaining the orthogonality between the semicore and valence states. (For core states completely contained within the spheres, the orthogonality is guaranteed.) The $5p$ levels of $5d$ transition metals, such as Re, are the troublesome cores even if they lie some 30 eV below the conduction bands and as Mattheiss and Hamann have shown for W, the calculated total crystal energy has a plateau as a function of ε_1 and one must assure oneself the ε_1 is chosen so as to lie in the top of the plateau. We have observed that this choice depends on the atomic sphere radius r_s and depends slightly, if at all, on lattice volume. Calculations will be reported here for two widely different sphere sizes with the higher-lying ε_1 required for the smaller sphere.

Total energies are plotted as a function of V/V_0, where V_0 is the observed Re crystal volume, in the top panel of Fig. 1. The zeros of the plot are taken to be the total energies (at the two different sphere radii) of hcp Re with $V/V_0=1$. If plotted on some absolute energy scale, the total energies for both bcc and hcp Re at $V/V_0=1$ as obtained with the larger sphere radius would lie below those for the smaller radius. Those with the larger radius have a smaller fraction of the crystal in the poorly described muffin-tin region and, in the process of providing a better description of the crystal potential, the calculations with the larger r_s happen to also provide the better total energies. The arrow indicates the volume to which Vohra *et al.* compressed Re. The two sphere radii were chosen so that there were touching spheres in the bcc structure for V/V_0 of 1.0 and of 0.712, respectively. Calculations employing the larger sphere could not be taken to smaller volumes than those plotted without having the spheres overlap.[14] (Calculations were done at intermediate values of the radii yielding results consistent with what is shown here.)

The result of most immediate concern, in light of the recent experiments, is summarized in the bottom panel of the figure where the difference between the hcp and bcc total energies is plotted. There is a clear indication that the hcp phase becomes increasingly stable, relative to the bcc, as the lattice is compressed. If one employs the largest possible spheres (i.e., the x point for $V/V_0=1$) in the calculations, the energy separation has increased by a factor of 2 over the range of volume compression shown here while the predictions employing a common r_s indicate an increase which is somewhat less.

Perhaps the most striking feature of the upper panel is the fact that the calculated minima in the total energies do not occur at the observed lattice volume V_0, but instead at somewhat smaller volumes. This is a characteristic of band-theory predictions employing muffin-tin potentials. The $r_s=2.256$ a.u. calculations have the energy minimum at $V/V_0 \sim 0.93$ while those for $r_s=2.526$ a.u. have it at ~ 0.96. The latter calculations, with a larger fraction of the crystal volume in the atomic spheres, have a better representation of the crystal potential and, as a result, do a markedly better job in predicting the lattice volume.

Bulk moduli have also been calculated and, again, the

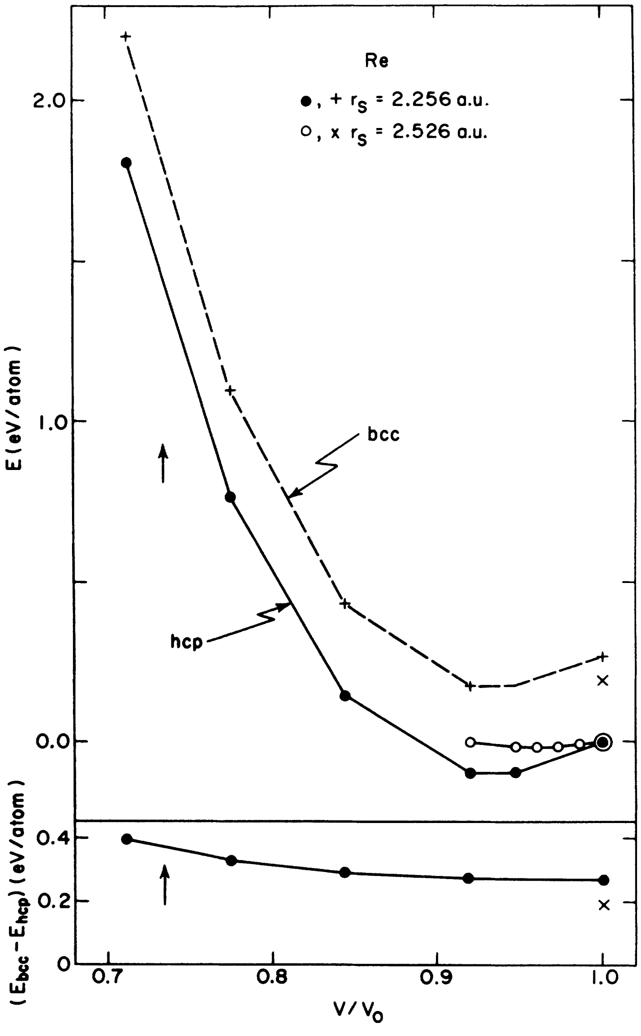

FIG. 1. Total energies calculated for bcc and hcp Re as a function of reduced volume V/V_0 (where V_0 is the experimentally observed lattice volume) as calculated for two fixed atomic sphere radii, $r_s=2.256$ and 2.526 a.u. The zeros of the top panel are the energies for hcp Re (for the two sphere radii) as calculated for $V/V_0=1$. The bottom panel shows the calculated energy differences between the bcc and hcp phases at common V/V_0. The vertical arrows show the volumes to which Vohra *et al.* (Ref. 1) experimentally compressed Re.

calculations employing the more nearly volume-filling spheres do better. A value of 5.3±0.1 Mbar is obtained employing the total energies associated with the smaller r_s while a value of 3.9±0.2 Mbar is obtained with $r_s = 2.526$ a.u. The larger spread in the latter value is associated with the fact that much smaller energy differences were involved in the estimate. These computed quantities are to be compared with quoted experimental values which range between 3.72 and 3.79 Mbar. The large-sphere result of 3.9 Mbar is in reasonable accord with this and is closer to experiment than the result[15] of Andersen *et al.* which is 4.4 Mbar. Their calculations involve the atomic-sphere approximation (ASA) where the interstitial region is done away with by taking overlapping atomic spheres whose volumes equal the crystal lattice's atomic volume (hence some of the crystal is dealt with twice, where spheres overlap, and some of it not at all, where there are no spheres). The ASA predictions may be inferior but tremendous computational economies attend the implementation of the method.

The main point of the present communication is comparison with the recent experiments and here theory is in accord with experiment: the bcc phase is not expected to prevail over the hcp. If some phase transition does occur upon still further compression, the calculations indicate that it will not be to the bcc phase. Re is a strongly bonded transition metal with close to half-filled *d* bands and it would appear that any ideas concerning a bcc compressed state for such a metal simply do not apply.

The research at Brookhaven National Laboratory has been supported by the Division of Materials Sciences U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

---

[1] Y. K. Vohra, S. J. Duclos, and A. L. Ruoff, Phys. Rev. B **36**, 9790 (1987).

[2] L. Kaufman in *Phase Stability in Metals and Alloys,* edited by P. S. Rudman, J. Stringer, and R. I. Jaffee (McGraw-Hill, New York, 1967), p. 125.

[3] L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams* (Academic, New York, 1970).

[4] S. Alexander and J. P. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[5] P. Bak, Phys. Rev. B **32**, 5764 (1985).

[6] C. Zener, Phys. Rev. **71**, 846 (1947); in *Phase Stability in Metals and Alloys,* edited by P. S. Rudman, J. Stringer, and R. I. Jaffee (McGraw-Hill, New York, 1967), p. 25.

[7] J. Friedel, J. Phys. (Paris) Lett. **35**, L59 (1974).

[8] R. E. Watson and M. Weinert, Phys. Rev. B **30**, 1641 (1984).

[9] J. W. Davenport, Phys. Rev. B **29**, 2896 (1984).

[10] J. W. Davenport, M. Weinert, and R. E. Watson, Phys. Rev. B **32**, 4876 (1985); **32**, 4883 (1985).

[11] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **34**, 8421 (1986).

[12] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **35**, 508 (1987).

[13] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).

[14] The packing of atoms in the hcp (or fcc) lattice allows the introduction of nonoverlapping atomic spheres of larger radius than is allowed for a bcc lattice having the same atomic volume. As a result, the calculations done at some given r_s can be extended to smaller V/V_0 for the hcp than for the bcc. This is the case in the figure for $r_s = 2.526$ a.u.

[15] O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed Matter Theory,* edited by F. Bassani, F. Fumi, and M. Tosi (North-Holland, Amsterdan, 1985), p. 59.