Comment on "Theoretical prediction of phase transition in gold"

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The structural properties of compressed gold are studied from first-principles theory. A new bcc phase is predicted to be stable as the ultimate high-pressure phase and not the hcp phase that was suggested by Ahuja *et al.* [Phys. Rev. B **63**, 212101 (2001)]. Semicore $5p$ states are broadened under high pressures and begin to hybridize with the $5d$ band and this modification of the electronic structure favors the bcc over the fcc and hcp structures at megabar pressures.

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In this Comment we address the recent theoretical study of gold at high pressures by Ahuja *et al.*[1] These authors calculated the total energies, using Wills' version[2] of the full potential linear muffin-tin orbitals (FP-LMTO) method, for fcc and hcp gold up to megabar pressures. These calculations indicated a phase transition, fcc→hcp, at about 60% compression of gold. Their argument for this phase transition was the small changes in the electronic density of $5d$ states in the vicinity of the Fermi level that stabilized hcp over fcc gold with increasing compression. However, at multimegabar pressures of gold it is not sufficient to only consider the valence $5d$ band because band broadening effects as well as shifts of bands relative to each other could be very significant. These effects sometimes lead to surprising results. For instance, Pt (gold's nearest left neighbor in the periodic table) adopts a bcc structure[3] at extreme compressions although the bcc structure is know to exist only for the central *d* transition metals at ambient pressure. Knowing this, it seems necessary to at least also consider the bcc phase of gold at very high compressions.

In this Comment we investigate the bcc phase in addition to the fcc and hcp phases of gold. Details of the present calculations are very similar to those by Ahuja *et al.*[1] We also employ an FP-LMTO method[2] but include spin-orbit coupling in a variational manner as suggested by Andersen.[4] Other technical differences are that here we adopt the PW91 (Ref. 5) exchange-correlation functional and also add $4f$ basis functions as semicore states such that $5s$, $5p$, and $4f$ are semicore states and $6s$, $6p$, $5d$, and $5f$ comprise valence states. The number of k points in the irreducible part of the Brillouin zone was about 3000 for the fcc and bcc structures and about 1500 for the hcp structure. To each eigenvalue a Gaussian was associated with a width of 15 mRy. Other details of the calculations were identical to those of Ahuja *et al.*[1]

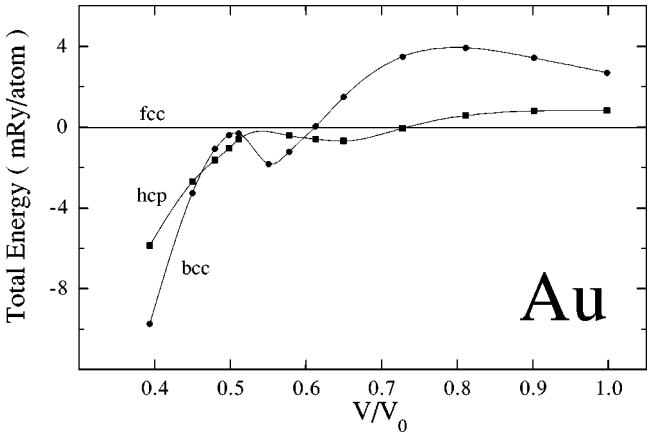

FIG. 1. Total energies (mRy/atom) for bcc and hcp (ideal c/a ratio) relative to the fcc total energy as a function of compression for gold. Here V_0 is the experimental equilibrium volume, 16.79 Å^3.

Notice in Fig. 1 that the fcc and hcp energies are very close up to about 50% compression when hcp is increasingly stable over fcc. Here we chose an ideal c/a ratio for the hcp structure. Optimizing this axial ratio lowered the total energy less than 0.4 mRy/atom at $0.5V/V_0$. Ahuja *et al.*[1] found an fcc→hcp transition at about 60% compression but here we obtain this transition already at about 70% compression, which corresponds to a calculated pressure of 1.51 Mbar. The very small energy difference between the hcp and the fcc phases, however, makes the actual transition pressure very sensitive to details of the calculation. We speculate that inclusion of spin-orbit coupling, which is known to significantly improve the equation of states for Ta,[6] is responsible for this slight disagreement. More importantly is that the bcc phase becomes very competitive at about 60% compression and at higher compressions the bcc phase is clearly stable over both fcc and hcp. The calculated pressure for the stabilization of the bcc phase is 4.0 Mbar. The reason for this latter transition was shown to be related to hybridization between semicore $5p$ states and valence $5d$ states.[3] In this earlier paper by Ahuja *et al.*,[3] canonical band theory was used to show that bcc will be the ultimate high-pressure phase for most *d* transition metals including gold as a consequence of $5p$-$5d$ hybridization. The present calculations indeed support this view.

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