Theoretical prediction of a phase transition in gold

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(Received 17 July 2000; revised manuscript received 23 January 2001; published 30 April 2001)

We performed theoretical investigations on gold under high pressure through first principles self-consistent total-energy calculations within the local-density approximation as well as generalized gradient approximation using full-potential muffin-tin-orbital method and found a phase transition from fcc-type to hcp-type of structure at 241 GPa. The stability of this phase has been explained through electronic density of state.

DOI: 10.1103/PhysRevB.63.212101 PACS number(s): 61.66.Bi, 64.30.+t, 62.50.+p

Gold is a well-known primary internal high-pressure calibration standard, which can be used by evaluating its lattice parameters at certain pressures (if the temperature is known).[1] Gold is also important due to its properties such as chemical inertness and availability in pure form. Additionally, it has stable crystal structure up to high pressures (>100 GPa) and temperatures and its simple structure and high atomic number make it relatively easy to constrain the lattice parameter by x-ray diffraction. Considerable amount of data on gold is available to constrain its equation of state.[1–4] The compressibility of gold is quite high (isothermal bulk modulus K_T and its pressure derivative K_T' at zero pressures are 167 ± 5 GPa and 5.5 ± 0.8).[2] Using the available data on gold (ultrasonic and Hugonoit) Jamieson *et al.*[1] predicted a series of isochors in the pressure-temperature planes. Heinz and Jeanloz[2] verified experimentally the 300-K isotherms predicted by Jamieson *et al.*[1] from high-temperature Hugoniot data. They measured the compression of gold experimentally at room temperature to 70 GPa using x-ray diffraction through digital-to-analog converter (DAC) and ruby fluorescence scale. The thermal equation of state was derived by a simultaneous inversion of all equation-of-state data and the gold calibration standard was extended up to 200 GPa in pressure and 3000 K in temperature.

Godwal and Jeanloz[5] calculated the equation of state of gold up to a pressure of 200 GPa at 5000 K by using the linear-muffin-tin-orbital (LMTO) method in atomic sphere approximation (ASA) with approximate corrections for lattice vibrational and electronic contributions to the pressure. Their calculations indicate that the electronic contribution to the high-temperature equation of state is negligibly small and under compression, gold shows virtually no change in the electronic structure. Besides gold, copper and silver are noble metals and candidates for the high-pressure measurement scale. Numerous investigations have been performed to evaluate equation of state of these metals. By the use of indirect and direct laser driven shocks, the copper equation-of-state measurements have been performed up to 40-Mbars-pressure range.[6–13] We used the full-potential linear muffin-tin orbital (FPLMTO) method[14] in order to deduce the equation of states (EOS) of gold, whereas the method used in an earlier report[5] to calculate EOS was based on ASA. To our knowledge, no structural phase transformation in gold, copper, and silver at ultrahigh pressures has been reported. To locate possible phase transformation at multi-megabar pressures, we investigated gold up to a pressure of 250 GPa.

Prima facie, we briefly describe here the *ab initio* method to solve the Dirac equation (for the core electrons) or (modified) Schrödinger equation (for the valence and semicore electrons). The total energy of the system was obtained within the local density approximation (LDA) as well as generalized gradient approximation (GGA). The Hedin-Lundqvist[15] parametrization for the exchange and correlation potential in case of LDA and Perdew, Burke, and Ernzerhof[16] parametrization for the exchange and correlation potential in case of GGA have been used. The wave functions are expanded by the means of linear muffin-tin orbitals inside the nonoverlapping muffin-tin spheres that surround each atomic site in the crystal. No geometrical approximation was employed to evaluate the basis function, electron densities, and potentials. The expansion of these parameters was performed in such a way that it is a combination of spherical harmonic functions (with $l_{max}=6$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and a Fourier series in the interstitial region. The muffin-tin radius was consistently chosen such that the muffin-tin spheres occupied 66% of the total volume. We make use of a so-called double-basis set since we allow the two tails with different kinetic energy for each muffin-tin orbital with a given *l*-quantum number. In the present calculations, we make use of following parameters: pseudocore $5s$, $5p$ and valence band $6s$, $6p$, $5d$, and $5f$ basis functions with corresponding two sets of energy parameters, appropriate for semicore $5s$, $5p$ state and valence states, respectively. It results in the formation of a single and fully hybridizing basis set with a well-converged basis.[14] For sampling the irreducible wedge of the Brillouin zone, we used a uniform mesh of k points[17] and in final convergence 195 and 320 k points in the irreducible Brillouin zone were used for fcc and hcp structure, respectively. In order to speed up the convergence, each calculated eigen value was associated with a Gaussian broadening of 20 mRy wide.

Under compression, the calculation shows that gold undergoes a structural phase transition from fcc-type to hcp-type of structure. Our calculated transition pressure in LDA is around 241 GPa, whereas in GGA it is around 200 GPa.

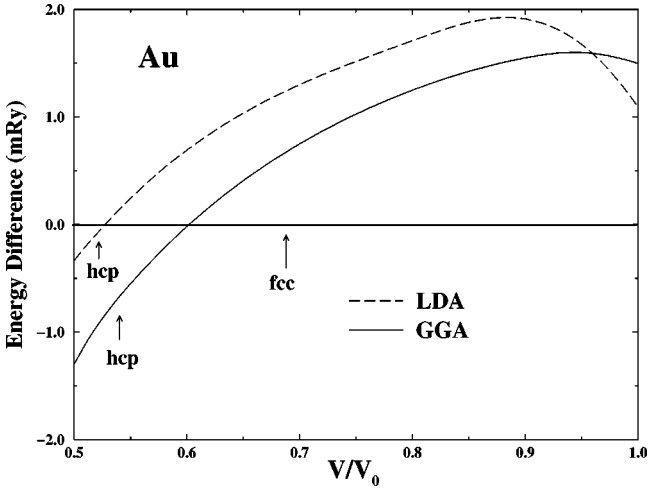

FIG. 1. Energy difference between the fcc and the hcp structure for gold as a function of volume (V/V_0), where V_0 is the experimental equilibrium volume. The fcc structure is used as the zero-energy reference level.

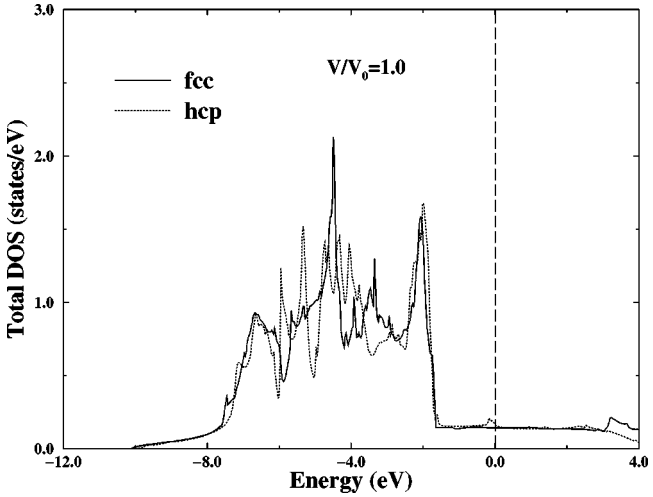

FIG. 2. Calculated density of states (DOS for gold at $V/V_0 = 1.0$). The full and dotted lines indicate DOS for fcc and hcp phase, respectively. The Fermi level is set at zero-energy level and marked by a vertical dashed line.

Present calculations are performed at 0 K and the experiment will be done at 300 K, so an entropy difference is estimated between the fcc and hcp structures. At very high pressure, this difference is very small and less than 0.05 mRy,[18] so entropy contribution will not effect the transition pressure. In previous studies no phase transformation has been reported to pressures as high as 200 GPa and at temperature to 5000 K.[5] Figure 1 depicts the difference in the total energy between the pertinent crystallographic structures of gold as a function of volume. We compared the fcc-type (low-pressure phase) structure and hcp type (high-pressure phase) of gold by taking the energy of the fcc-type structure as a reference. We observed that the theoretical equilibrium volume is slightly bigger for the fcc-type structure than for the hcp-type structure. The only difference between the cubic close packing (fcc) and hexagonal close packing (hcp) is having an *abab* versus an *abc* stacking along (111). Figure 1 also indicates that the hcp structure is more stable than the low-pressure phase beyond $V/V_0 = 0.55$ in LDA and $V/V_0 = 0.60$ in GGA. In Table I, we list the unit-cell volume, bulk modulus, and pressure derivative of bulk modulus of two phases of gold. We have optimized the c/a ratio for the new hcp phase. Our calculated value is very close to that for ideal hcp structure. In Table I we also compared our calculated values of unit-cell volume, bulk modulus, and pressure derivative of bulk modulus for fcc phases of gold with the respective values as reported earlier.[2,5] A significant difference between our and the reported values can be attributed to the use of the atomic sphere approximation, which exhibits a high degree of inaccuracy as compared to the full potential *ab initio* method of the present investigation.

In order to understand the mechanism behind this phase transition, we calculated the density of states (DOS) in LDA for both phases at two different volumes. Figures 2 and 3 depict such plot for the fcc and hcp phase at two volumes ($V/V_0 = 0.5$ and 1). The DOS for hcp structure is for two atoms, whereas for fcc phase it is for one atom. The density of state below the Fermi level is mainly composed of *d*-bands. The bandwidth of *d*-band for both phases is around 10 eV at equilibrium volume. We observed that the hcp phase at this volume is unstable as compared to the fcc phase, reflected by a peak at the Fermi level. It is to be noted that the Fermi level lies at the onset of this peak, implying the instability of this phase as compared to the fcc phase. Further at this volume total DOS for fcc phase is 0.14 states per eV per atom and 0.17 states per eV per atom for hcp phase. On compression up to 50% of the equilibrium volume, we found that the bandwidth increases from 10 eV to

TABLE I. Properties of the fcc and the hcp gold at ambient conditions.

	Volume (Å^3)	K_T (GPa)	K_T'	c/a
Present calculation (fcc-LDA)	16.76	193.0	4.8	
Present calculation (fcc-GGA)	17.52	219	3.74	
Present calculation (hcp-LDA)	16.50	191.0	4.7	1.63
Present calculation (hcp-GGA)	17.32	216	3.75	1.63
Calculation (fcc-LDA)[a]	15.94	16.5	6.4	
Experiment (fcc)[b]	16.96	166.7	5.48	

[a]LMTO-ASA calculations by Godwal and Jeanloz (Ref. 5).
[b]Heinz and Jeanloz (Ref. 2).

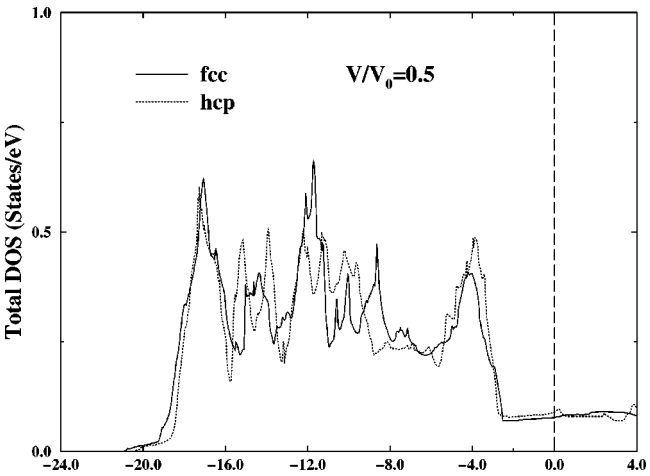

FIG. 3. Calculated density of states (DOS for gold at $V/V_0 = 0.5$). The full and dotted lines indicate DOS for fcc and hcp phase, respectively. The Fermi level is set at zero-energy level and marked by a vertical dashed line.

22 eV. Additionally, the shift of Fermi level to the minima of peak implies the stability of hcp phase at this volume. The total DOS for fcc phase is 0.08 states per eV per atom and 0.09 states per eV per atom for hcp phase. Still at this compression, the DOS of fcc phase is lower by 0.01 states per eV per atom in comparison to hcp structure. One can notice that at $V/V_0 = 1$, the DOS of fcc phase was lower by 0.03 states per eV per atom in comparison to hcp structure. This suggests increasing stability of hcp phase in comparison to fcc phase with decreasing volume. Keeping in the mind that DOS is just sum of one-electron eignvalue and there are other contributions to total energy also, so may be one has to compress little bit more to see the stability of hcp phase in terms of DOS.

In summary, we observed a pressure-induced phase transition in gold at 241 GPa. The values of volume, isothermal bulk modulus, and its pressure derivative of the new polymorph of gold in LDA are evaluated to be 16.50 $Å^3$, 191 GPa, and 4.7 respectively. The high-pressure polymorph of gold has hcp structure. We explained the stability of the new phase through electronic density of state.

The authors (R.A. and B.J.) wish to thank the Swedish Natural Science Research Council (NFR), ATOMICS (SSF), and TFR for financial support. We are also grateful to J. M. Wills for letting us use his FPLMTO code.

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