Electronic and structural properties of ununquadium from first principles

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Using first-principles techniques, the electronic and structural properties of ununquadium are investigated. These properties are compared to the known experimental and theoretical properties of Pb which lies in the same column above Uuq in the periodic table. Within the limits of density-functional theory, we find that solid Uuq is expected to be metallic and crystallize in an fcc structure.

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In recent decades, there has been considerable interest in the creation and study of superheavy elements.[1–5] A large portion of this interest is because of the prediction of the so-called "island of stability" which suggests that there are several stable very heavy elements.[6,7] The hypothetical shore of this island is projected to begin at the element with doubly closed shells of protons ($Z=114$) and neutrons ($N=184$), namely, ^{298}Uuq. Hence, particular interest abounds regarding the recent detection of the element historically known as "eka" lead. The monatomic sample of Uuq was observed to exist for longer than 30 s.[8,9] It was seen to have atomic weight 289 and was created by the collision of ^{48}Ca and ^{244}Pu.

Motivated by the current interest in Uuq and in the spirit of laying the framework for new materials,[10] we have considered the solid-state properties of a hypothetical collection of these atoms. While all-electron calculations have been performed on atomic Uuq,[11] no theoretical work on solid Uuq is present in the literature. Therefore, we apply modern computational methods to a crystalline solid composed of Uuq to determine its ground-state crystal structure, high-pressure phase transitions as well as expected electronic properties. Because of the valence structure of Uuq, it is expected to most resemble the homolog element Pb,[1] therefore, we have applied our techniques[12,13] to both elements.

In this Brief Report, we report the results of total-energy calculations for Pb and Uuq for various crystal structures and lattice constants corresponding to a wide range of hydrostatic pressures. Additionally, the electronic structures and Fermi surfaces are reported. Density-functional-theory[14] calculations were performed within the generalized gradient approximation[15] incorporating scalar-relativistic effects while nonlinear core corrections and semicore states were included in the pseudopotentials.[16] These states included the $5d$, $6s$, and $6p$ of Pb and the $7s$, $5f$, $6d$, and $7p$ of Uuq. Spin-orbit effects were not included in this first-generational study of the Uuq system. They should be included in the next generation studies, especially if experimental data become available. Total energies and electronic band structures were calculated using a plane-wave basis with a kinetic-energy cutoff of 70 Ry in the case of Pb. A rather large cutoff of 180 Ry was necessary when performing calculations with element 114 because of the inclusion of the localized $5f$ electrons. In each case cubic structures were calculated on a $14\times14\times14$ Monkhorst-Pack grid[17] while hexagonal structures employed a grid of equivalent sampling density.

The total energy as a function of volume for the fcc, bcc, simple cubic (sc), hcp, and diamond structures was least-squares fitted to Eq. (1), the Murnaghan equation of state.[18] In this equation E_0 is the minimum total energy, B_0 and B_0' are the bulk modulus and its derivative, respectively, while V_0 is the volume at E_0. Figure 1 displays the results of these fits along with *ab initio* data points while data for the difference between the total minimum energy per atom for each structure is enumerated in Table I,

$$E(V)=E_0-\frac{B_0V_0}{B_0'-1}+\frac{B_0V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0'-1}\right]. \qquad (1)$$

Clearly, of the given choices, the fcc structure is the most

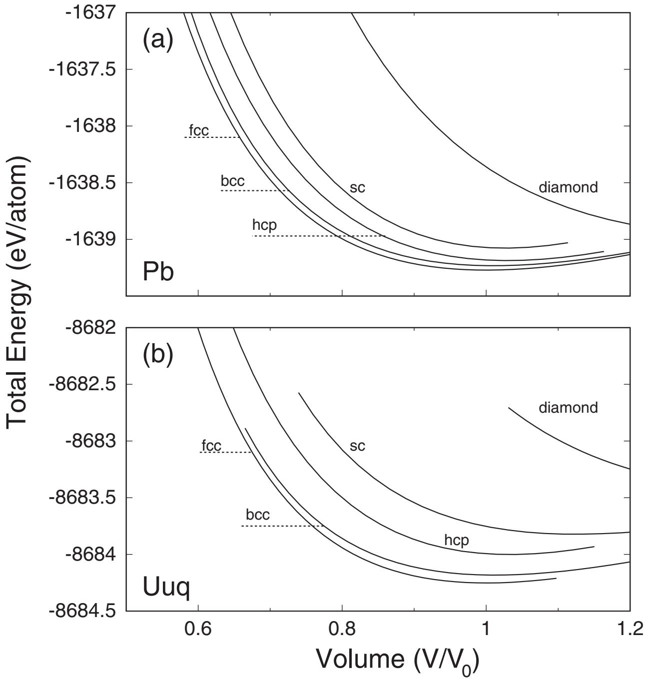

FIG. 1. Total energy as a function of volume for (a) Pb and (b) Uuq. The volume in each box is normalized to the volume at the absolute minimum energy of the fcc structure. Each solid line which gives the total-energy plot for the different structures is the result of a least-squares fit to the Murnaghan Equation. First-principles data points are not plotted to prevent obstruction of the data.

TABLE I. Minimum energies and volumes per atom for five different structures of Pb and Uuq. The volume is normalized in each case to the ground-state volume at E_{min} in the fcc structure.

	V_{min}/V_0		ΔE_{min} (meV/atom)	
Phase	Pb	Uuq	Pb	Uuq
fcc	1.00	1.00	0	0
bcc	1.01	1.01	39	69
hcp	1.03	1.03	84	251
sc	1.03	1.12	194	430
Diamond	1.38	1.48	308	792

stable for both Uuq and Pb. This is in agreement with experimental results for Pb and is consistent with the expected similarities between Pb and Uuq. The relaxed lattice constant for fcc Uuq was found to be 5.101 Å as compared to 4.873 Å for fcc Pb, which differs from experiment by −1.5%. Using the above values and estimating that a more stable isotope of Uuq might have a mass number of 298,[19] it is found that the expected density of solid Uuq would be 44% greater than that of lead. Additionally, the fitting parameters from the Murnaghan equation of state give a theoretical bulk modulus of 52 GPa for Pb where the experimental value is 46 GPa while in the case of Uuq the bulk modulus is estimated to be 48 GPa, in close accord with the Pb value.

We have calculated the zero-temperature Gibbs free energy, $G_{T=0}=E+PV$, as a function of pressure for Pb and Uuq to ascertain the structural phase diagram of these two elements as was done earlier for group IV elemental solids.[20,21] Experimental phase changes from fcc to hcp are observed in Pb at 15 GPa while a transformation to bcc is seen to take place at a pressure between 127 and 174 GPa.[22] The wide range of pressures for the latter phase change results from a small volume change leading to a small free-energy difference. Our theoretical calculations on metallic Pb predict a transformation to hcp near 20 GPa and to bcc at about 90 GPa. For the case of Uuq we find that at pressures below 250 GPa Uuq will not transition from the fcc structure to one of the candidate structures chosen.

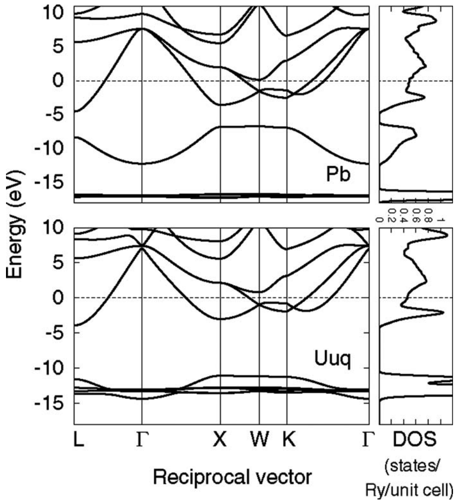

FIG. 2. Electronic band structures and densities of states of (top) Pb and (bottom) Uuq in the ground-state fcc structure. The character of the bands crossing the Fermi level and densities of states for both materials closely resemble each other.

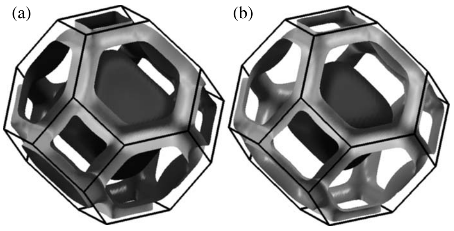

FIG. 3. Multisheeted Fermi surfaces of (a) Pb and (b) Uuq. The surfaces are shown for zero pressure and zero temperature in the ground-state fcc structures. Given that they share very similar geometries arising from bands with the same character, it is therefore expected that material properties of Uuq which depend on the details of the Fermi surface may resemble those of Pb.

The electronic band structures and electronic densities of states are plotted for both Pb and Uuq in Fig. 2. Our results indicate that solid Uuq is distinctly metallic, confirming the similarity of our approach on the material to that taken on Pb and similar metals.[23] Near the Fermi level the similar character of the electronic bands is striking. However, the highest occupied p states of these materials differ in both bandwidth and hybridizational characteristics. The $6p$ bands of Pb are isolated from higher energy states and have a bandwidth of 12.2 eV; the $7p$ orbitals of Uuq span 10.9 eV while mixing at Γ with the states of higher energy bands. Also of interest are the localized d-like states located several electron volts below the Fermi level in either case with differences arising in the relative location of the highest occupied s band. Additionally, the densities of states at the Fermi level have similar values. In the case of Pb, $N(\epsilon_F)=0.497$ states/Ry/unit cell while the value at the Fermi level in Uuq is 7% lower at 0.462 states/Ry/unit cell. Given the similar densities of states at the Fermi level, we expect that solid Uuq might be an elemental superconductor like Pb.[24] Using the ratio of the masses to estimate an average phonon frequency, we expect that the transition temperature would be reduced from the Pb value by ~20% to 5 K.

The Fermi surfaces corresponding to the band structures of Fig. 2 are shown in Fig. 3. Uuq exhibits the same "jungle-gym"-like Fermi surface as Pb.[25] The only variations in Fermi-surface geometry between the two materials can be connected to the somewhat lower density of states in Uuq leading to a smaller zone-center Fermi-surface sheet as well as thinner pipes on the jungle gym.

In summary, it is predicted that within the limits of density-functional theory the zero-temperature ground state of solid Uuq is metallic and the crystal structure is most likely fcc. In addition to sharing the same ground-state crystal structure, the Fermi surfaces and electronic structure of Uuq are similar to Pb. Thus, we predict that a solid composed of a long-lived isotope of Uuq would behave much like a dense variant of Pb.

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