Rotational Rehybridization and the High Temperature Phase of UC2

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Abstract

The screened hybrid approximation (HSE) of density functional theory (DFT) is used to examine the structural, optical, and electronic properties of the high temperature phase, cubic UC2. This phase contains C-2 units with a computed C-C distance of 1.443 angstrom which is in the range of a CC double bond; U is formally 4+, C-2 4-. The closed shell paramagnetic state (NM) was found to lie lowest. Cubic UC2 is found to be a semiconductor with a narrow gap, 0.4 eV. Interestingly, the C-2 units connecting two uranium sites can rotate freely up to an angle of 30 degrees, indicating a hindered rotational solid. Ab-initio molecular dynamic simulations (HSE) show that the rotation of C-2 units in the low temperature phase (tetragonal UC2) occurs above 2000 K, in good agreement with experiment. The computed energy barrier for the phase transition from tetragonal UC2 to cubic UC2 is around 1.30 eV per UC2. What is fascinating about this system is that at high temperature, the phase transformation to the cubic phase is associated with a rehybridization of the C atoms from sp to sp(3).

Keywords

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