Embrittlement and the Bistable Crystal Structure of Zirconium Hydride

In a recent Letter [1] Ackland proposed that the delayed hydride cracking (DHC) in zirconium alloys can be attributed to a mechanical instability of the cubic phase in an external strain field with respect to a tetragonal distortion, which leads to uniaxial misfit strains and causes DHC. This suggestion is based on *ab initio* electronic structure calculations using norm-conserving nonlocal pseudopotentials carried out for cubic fluorite structure ZrH_2 and for tetragonal distortion of the cubic cell over a range of values of the a and c parameters. He finds that ZrH_2 is an insulator in both the cubic and tetragonal phases. This result is in complete contradiction with both theoretical calculations [2–4] which are not cited in Ackland's Letter and experimental data which include electronic specific heat [5,6], magnetic susceptibility [6,7], thermoelectric power [6,8], and nuclear magnetic resonance [9–11], where ZrH_2 is found to be metallic.

To confirm this contradiction, we have performed new band structure calculations for ZrH_2 in both cubic and tetragonal forms ($c/a = 0.893$) within the local density approximation (LDA) using the linear muffin-tin orbital in the atomic sphere approximation method with combined correction terms. The total densities of states (DOS) calculated using the linear energy tetrahedron method are plotted in Fig. 1 for the cubic and tetragonal structures. In agreement with previous LDA calculations [2–4], the zirconium dihydrides are characterized by two low-energy bands due to metal-hydrogen bonding and H-H interactions. These bands which correspond to the two peaks in the DOS observed below -4 eV in Fig. 1 overlap the Zr-d states extending above -4 eV. The Fermi energy E_F of cubic ZrH_2 is located on a peak of high DOS which is associated with a dispersionless doubly degenerate band in the [111] ΓL direction of the fcc Brillouin zone. This degeneracy is lifted by the tetragonal distortion leading to a decrease of the DOS at E_F in the tetragonal phase; this result is in agreement with suggestions based on experimental observations [5–11] and previous calculations [2–4]. The hydrides in the two phases are clearly metallic. The DOSs obtained by LDA calculations bear no common features with those plotted by Ackland in Fig. 3 of his Letter. A close examination of Fig. 1 of Ackland's Reply shows that this figure is not simply "a backward tracing" of Fig. 3 of his Letter. We therefore believe that there is a serious mistake in his band structure calculations which invalidates his suggestions concerning embrittlement and DHC in zirconium.

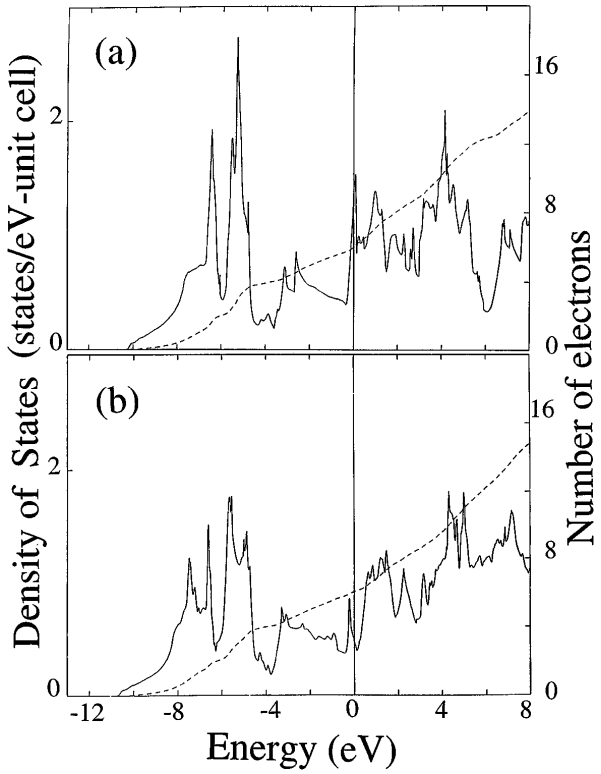

FIG. 1. The total densities of states (full curve) and the number of electrons (dashed curve). The Fermi energy is chosen as the origin: (a) cubic ZrH_2; (b) tetragonal ZrH_2.

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