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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.

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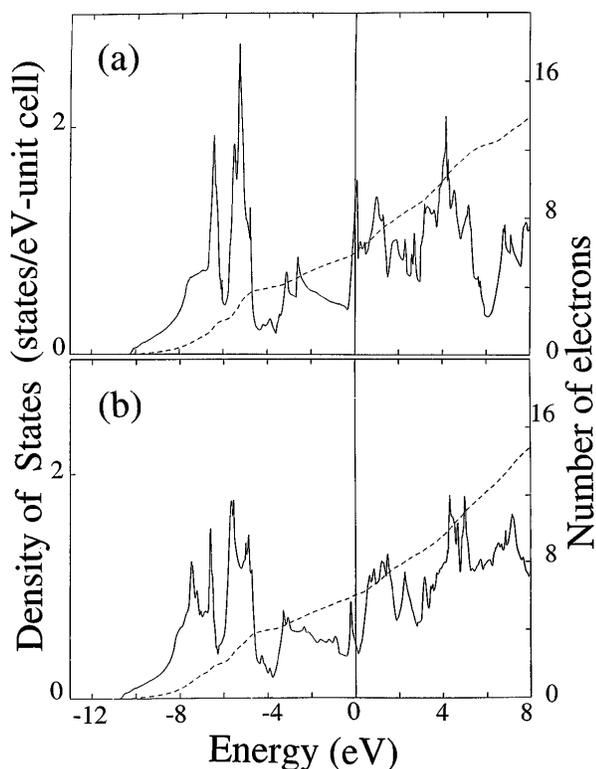


FIG. 1. The total densities of states (full curve) and the number of electrons (dashed curve). The Fermi energy is chosen as the origin: (a) cubic ZrH_2 ; (b) tetragonal ZrH_2 .

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