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Xiuwen Zhang and Alex Zunger

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(Received 3 March 2010; published 15 June 2010)

We show how pressure fundamentally alters the repulsive nature of the nonreactive Li-Cs mixture, converting it from strongly phase separating at ambient pressure to strongly long-range ordering at high pressures. The ordered phases found via a global space group optimization within the density-functional theory are Li_7Cs in the *Cmmm* structure, LiCs in the *B*2 structure, and Li_7Cs in the *C*2LiSm structure. These structures are remarkably stabilized by a pressure-induced increase in charge transfer from Cs to Li unit, an unusual effect concerning two elements from the same group (isovalent). These high-pressure phases exhibit interesting behaviors: (i) LiCs (*B*2) has its Cs 5*p* core states nearl

merge [11 16]. Phase-diagram studies at ambient pressure [11 13] and our density-functional-calculated formation enthalpies (ΔH's) summarized in Fig. 1 show that Na

$_2$Cs, Na_2K, and K_2Cs form ordered Laves phase ($MgZn_2$ type). Yet, the Li interalkalies clearly exhibit only phase-separation behavior with concomitant calculated formation enthalpies that are positive and rapidly increase with the size mismatch, i.e., 56, 179, 215, and 227 meV/atom for Li-Na, Li-K, Li-Rb, and Li-Cs, respectively. Li-Cs with its largest positive ΔH is the paradigm phase-separation interalkali due to its large atomic size mismatch of $\Delta V/\bar{V}$ ¼ 142%. Pressure can change nonreactivity tendencies [17] as illustrated by Li-Be (which, however, is a nonisovalent combination more prone to reactivit 3(Press79.4(3ee1e6ginc4(-a0tio6(Cs)Tj/F21Tf1.53920TD(()Tj/F51Tf0.33060TD(C)Tj/F41Tf0.68830TD(2)Tj/F51Tf0.4986

Li, the *hR*1 structure transforms to the *cI*16 structure at about 35 GPa, then at about 75 GPa it transforms to the *C*2 structure, and then at about 98 GPa it transforms to the *Aba*2 structure, which persists up to at least 160 GPa; for Cs, the *Cmca* structure transforms to the *dhcp* structure at about 60 GPa, which persists up to at least 200 GPa. The transition pressures are in agreement with the experimental results [3 5]. Random search techniques [24] and the evolutionary algorithm method [25,26] were previously applied to search the ground states of elemental lithium by Pickard et al. [8], Yao et al. [9], and Ma et al. [7], respectively, who all Cchand3.4(experimental)]TJ

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$$\Delta H_{\mathrm{VD}} = [H(\mathrm{Li}, V_m) - H(\mathrm{Li}, V_1)] + [H(\mathrm{Cs}, V_m) - H(\mathrm{Cs}, V_2)]. \tag{1}$$

The charge-transfer energy ΔH_{CT} is the enthalpy change when combining bcc Cs and bcc Li at the constant volume V_m to form LiCs ($B2$),

$$\Delta H_{\mathrm{CT}} = H(\mathrm{LiCs}, V_m) - H(\mathrm{Li}, V_m) - H(\mathrm{Cs}, V_m). \tag{2}$$

ΔH_{VD} and ΔH_{CT} are shown as the red line and the green line in Fig. 4(a), respectively. We see that ΔH_{VD} is positive and increases rapidly as pressure increases, the main effect coming from the $P(V_2 - V_1)/2$ term (dashed line). At zero pressure, ΔH_{VD} (+520 meV/atom) is large enough to make the Li-Cs system phase separating. In contrast, ΔH_{CT} is negative and decreases rapidly as pressure increases. At 160 GPa, $\Delta H = -258$ meV/atom and ΔH_{CT} is large enough to induce ordering in Li-Cs.

The electronic structures of LiCs ($B2$) are shown in Figs. 4(b) and 4(c). At zero pressure the dispersions of the Li($1s$), Cs($5s$), and Cs($5p$) bands are all small. At 160 GPa, the Li($1s$) band still has negligible dispersion, while the dispersion of the Cs($5s$)

high-pressure compounds between two elements in the same column of the periodic table (Li-Cs) is perhaps reminiscent of compound formation and charge transfer between Ag-K [27] or Li-Be [17], although the latter two cases are perhaps less surprising than Li-Cs as they represent a far larger chemical disparity (hence, reactivity) between the constituent elements that belong to different columns in the periodic table.

Li$_7$Cs (*Cmmm*) *[illegible] 1D-[illegible].* The electronic structure of Li$_7$Cs (*Cmmm*) at 80 GPa exhibits interesting features of 1D-like bands. Its density of states at the Cs$(5s)$ and Cs$(5p)$ bands [see Fig. 6(a)] displays a remarkable feature of typical 1D electronic structure, the emergence of which in a three-dimensional environment is rather unexpected. Figure 6(b) shows the band structure of Li$_7$Cs (*Cmmm*) at 80 GPa. The Cs$(5s)$ and Cs$(5p)$ bands display strong dispersion only along the Γ-X direction, but are nearly dispersionless along other directions. The 1D band structure is caused by the unique crystal structure of Li$_7$Cs (*Cmmm*) [see the inset of Fig. 3(a)]. The Cs chains are embedded in the three-dimensional Li networks and are separated from each other. Along the chain direction, the Cs atoms are close to each other and their cores overlap.