Altered Reactivity and the Emergence of Ionic Metal Ordered Structures in Li-Cs at High Pressures

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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 Li₇Cs in the *Cmmm* structure, LiCs in the *B*2 structure, and Li₇Cs in the *C*2/*m* 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 nearly merged with the valence Cs(6*s*) states, indicating that core states can become valence states at high pressures; (ii) Li₇Cs (*Cmmm*) structure exhibits an interesting 1D electronic structure within a 3D crystal structure.

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The different phases that elemental alkali metals take up under pressure have attracted a lot of attention [1-10]because such single valence electron systems (along with hydrogen) provide a natural laboratory for the physics of interelectronic interactions between simple s electrons in the field of simple geometric ionic lattices. Studies of binary combinations of alkali metals, also offering a glimpse at the chemistry of such systems, are, however, less common [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 Na₂Cs, Na₂K, and K₂Cs form ordered Laves phase (MgZn₂ 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 $\Delta V/\bar{V} = 142\%$. Pressure can change nonreactivity tendencies [17] as illustrated by Li-Be (which, however, is a nonisovalent combination more prone to reactivity). Since ordering under pressure of an otherwise phase-separating system can manifest unsuspected stoichiometries and geometries [17], we have used the composition (x)-dependent global space group optimization (X-GSGO [18]) within the density-functional theory. This allows us to explore the ground states of Li-Cs systems starting from a random selection of both lattice vectors and atomic positions. We find that as pressure is increased, the initially positive ΔH of Li-Cs lattices decreases rapidly, and unsuspected ordered structures emerge: the Li₇Cs (space group Cmmm) at 80 GPa and the LiCs (B2) and Li₇Cs (C2/m) at 160 GPa. This is remarkable because it is the first isovalent metal system (two elements of the same group) that is immiscible under ambient pressure and has ordered stoichiometric comPACS numbers: 61.50.Ah, 62.50.-p, 71.20.Lp

pounds under high pressure. The mechanism of alloying such highly mismatched metals under high pressure is studied in detail. We find that the $Cs \rightarrow Li$ charge transfer increases significantly at high pressures in these structures. Remarkably, the Li₇Cs in *Cmmm* structure exhibits an interesting 1D electronic structure.

Theoretical method.—The X-GSGO method allows for the simultaneous optimization of the $A_{1-x}B_x$ structures $(0 \le x \le 1)$, which are stable against phase disproportionation, without any *a priori* constraints on stoichiometry. The method combines genetic-algorithm selection with density-functional total-energy calculation [19–23]. Overall convergence of total energy is ~5 meV/atom, and the uncertainty of transition pressure is about ±6 GPa.

Figure 2 shows the phases that elemental Li [Fig. 2(a)] and elemental Cs [Fig. 2(b)] attain under pressure, as found by calculating E + PV versus pressure *P*. We see that for



FIG. 1 (color online). Summary of phase behavior of binary combinations of alkali metals. Top symbols indicate the experimentally observed [11–13] phases: phase separation (PS), solid solutions (SS), and ordering (A_2B). Bottom numbers are the calculated formation enthalpies ΔH (in meV/atom), using the *B*2 structure type for Li-M, K-Rb, and Rb-Cs, and the MgZn₂-Laves structure type for Na-K, Na-Rb, Na-Cs, and K-Cs.



FIG. 2 (color online). (a) Enthalpies of Li at high pressure. (b) Enthalpies of Cs at high pressure. (c) Pressure range of stable ordered structures of the Li-Cs system.

Li, the hR1 structure transforms to the cI16 structure at about 35 GPa, then at about 75 GPa it transforms to the C2 structure, and then at about 98 GPa it transforms to the Aba2 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 found the experimentally observed *cI*16 structure [3–5] in the pressure range 50–70 GPa.

Structures of ordered Li-Cs phases.—Figure 3 shows the evolution of the enthalpies of the Li-Cs system during the global space group optimization (black squares). The thick line in Fig. 3 is the ground state line (convex hull), which connects the lowest energy configurations at given compositions (solid spheres) that are stable with respect to disproportion into two configurations at neighboring compositions. We see from Figs. 3(a) and 3(b) that numerous structures with negative formation enthalpies emerge at high pressure. Not all are ground states: at 80 GPa only one Li:Cs structure at composition 7:1 is a ground state; at 160 GPa, there are two ground states: the 1:1 LiCs (B2) structure and the 7:1 Li₇Cs (C2/m) structure. Figure 2(c) shows the range of stability of these Li-Cs phases: The Li₇Cs (Cmmm) structure is stable between 53 and 116 GPa. The Li₇Cs (C2/m) structure is stable above 116 GPa, whereas LiCs (B2) is stable above 101 GPa. The structures of the emerging ordered phases are unsuspected by the ordinary knowledge of intermetallic bonding:

Calculated Li₇Cs (*Cmmm*) structure.—The Li₇Cs (*Cmmm*) structure at 80 GPa has calculated lattice parameters a = 4.83 Å, b = 9.38 Å, c = 2.90 Å and Wyckoff positions Cs 2a (0, 0, 0), Li 8q (0.284, 0.138, 1/2), Li 2b (1/2, 0, 0), and Li 4i (0, 0.760, 0). This structure [see inset



FIG. 3 (color online). Evolution of the formation enthalpies of Li-Cs system during the global space group optimization (black squares) at (a) 80 GPa and (b) 160 GPa. Insets: The structures of the ground states. Li, small sphere; Cs, large sphere.

of Fig. 3(a)] contains chains of Cs atoms with Cs-Cs distance along the chain direction of 2.90 Å. Around each Cs chain there are eight Li chains arranged approximately as a square. Two of the eight Li chains are shared by two Cs chains. The Li chains form a three-dimensional network, within which the Cs chains are embedded. The sublattice of Cs atoms is base-centered orthorhombic, which can be translated to the base-centered orthorhombic sublattice of edge sharing Li_{10} octahedra (consist of common-base up-down roofs).

Calculated Li₇Cs (C2/m) structure.—The Li₇Cs (C2/m) structure at 160 GPa has calculated lattice parameters a = 4.16 Å, b = 6.41 Å, c = 3.83 Å, $\beta = 101.1^{\circ}$ and Wyckoff positions Cs 2b (0, 1/2, 0), Li 2a (0, 0, 0), Li 4i (0.244, 0, 0.471), and Li 8j (0.122, 0.233, 0.736). This structure has a simple triangular arrangement as in two-dimensional close packing of chains of corner sharing Li₈ parallelepipeds, with Cs atoms located at the interstitial sites.

The bonding mechanisms we find for interalkali compounds are equally surprising.

Mechanisms of ordering.—To understand the electronic factors governing the stability of LiCs (B2), we decompose its excess enthalpy with respect to bcc Li + bcc Cs into a volume-deformation part $\Delta H_{\rm VD}$ and a charge-transfer part $\Delta H_{\rm CT}$. Here, $\Delta H_{\rm VD}$ is the enthalpy change upon deforming bcc Li at its equilibrium volume V_1 and bcc Cs at its equilibrium volume V_2 into the equilibrium volume V_m of LiCs (B2),

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

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

 $\Delta H_{\rm VD}$ and $\Delta H_{\rm CT}$ are shown as the red line and the green line in Fig. 4(a), respectively. We see that $\Delta H_{\rm VD}$ 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, $\Delta H_{\rm VD}$ (+520 meV/atom) is large enough to make the Li-Cs system phase separating. In contrast, $\Delta H_{\rm CT}$ is negative and decreases rapidly as pressure increases. At 160 GPa, $\Delta H = -238$ meV/atom and $\Delta H_{\rm CT}$ is large enough to induce ordering in Li-Cs.

The electronic structures of LiCs (*B*2) 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) band is about 5 eV, and the Cs(5p) band has a dispersion of about 10 eV which almost touches the valence s bands [consisting of Li(2s) and Cs(6s)]. This indicates that the core states partially become valence states and contribute in the reactivity of Li with Cs. The huge difference of dispersions of core bands between Li and Cs stems from the large overlap of Cs cores and small overlap of Li cores which forces electrons away from Cs to the surrounding area of Li, thus enhancing the



FIG. 4 (color online). (a) Components of excess enthalpies of LiCs (*B*2) with respect to bcc Li + bcc Cs as shown in Eqs. (1) and (2) as functions of pressure. (b),(c) Densities of states of LiCs (*B*2) at (b) 0 GPa and (c) 160 GPa in a common unit eV^{-1}/nm^3 for comparison. Fermi level is shown by a vertical dashed line.

charge transfer and decreasing the charge-transfer energy $\Delta H_{\rm CT}$.

Figures 5(a) and 5(b) show the 2D contour plot of the charge density of the solid LiCs (B2) structure minus the superposition of atomic charge densities $\Delta \rho = \rho_{\text{solid }AB} - \rho_{\text{solid }AB}$ $\sum \rho_{\text{atomic }A} - \sum \rho_{\text{atomic }B}$ (in eÅ⁻³). We see that, as the pressure increases, the charge transfer (indicated by the white arrows) increases significantly. At 0 GPa, the pseudosphere of negative charge difference around the Cs atom has small amplitude, but at 160 GPa it is very strong. In Fig. 5(b), we see that the Li atom is surrounded by a small negative $\Delta \rho$ "core" and a large positive $\Delta \rho$ "shell," the total charge difference surrounding Li being positive. For LiCs (B2) at 0 GPa, the total integrated charge difference in the sphere surrounding Cs is -0.009 e, but as pressure increases to 160 GPa, this decreases to -0.3 e. The LiCs (B2) at 160 GPa can be approximately viewed as consisting of positively charged Cs spheres and negatively charged Li spheres.

Charge density and stability of Li₇Cs.—The 2D contour plots of $\Delta \rho$ of Li₇Cs structures are shown in Figs. 5(c) and 5(d). The Cs atoms are surrounded by strong negative $\Delta \rho$ pseudospheres, and there are strong positive $\Delta \rho$ inside the Li₈ parallelepiped in Li₇Cs (C2/m) and the Li₁₀ octahedra in Li₇Cs (*Cmmm*) (the large spaces inside these Li units are effective acceptors of electrons). The integrated $\Delta \rho$ in the sphere surrounding Cs is -0.57 e for Li₇Cs (C2/m) at 160 GPa and -0.47 e for Li₇Cs (*Cmmm*) at 80 GPa, which are comparable to that in LiCs (*B*2) at 160 GPa. The large charge transfer contributes to ordering in the Li-Cs system at high pressures, and indicates that the ordered compounds are strongly *ionic metals*. The existence of stable



FIG. 5 (color online). 2D contour plot of the charge density difference $(\Delta \rho)$ of Li-Cs structures with respect to atomic Li and atomic Cs (in e Å⁻³). (a) LiCs (*B*2) at 0 GPa in (101) plane. (b) LiCs (*B*2) at 160 GPa in (101) plane. (c) Li₇Cs (*C*2/*m*) at 160 GPa in (010) plane. (d) Li₇Cs (*Cmmm*) at 80 GPa in (010) plane.



FIG. 6 (color online). (a) Density of states and (b) band structure of Li_7Cs (*Cmmm*) at 80 GPa.

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.

Li₇Cs (Cmmm) exhibits 1D-like bands.—The electronic structure of Li₇Cs (*Cmmm*) at 80 GPa exhibits interesting features of 1D-like bands. Its density of states at the Cs(5s)and $C_{s}(5p)$ 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 Li₇Cs (*Cmmm*) at 80 GPa. The Cs(5s) and Cs(5p) bands display strong dispersion only along the Γ -X₃ direction, but are nearly dispersionless along other directions. The 1D band structure is caused by the unique crystal structure of Li₇Cs (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. We see from Fig. 6(b) that, at Γ point, the Cs(5*p*) states split into two groups due to the strong anisotropy of the crystal structure. The crystal field splitting of Cs(5p) states is about 5 eV.

In summary, we show that pressure fundamentally alters the reactivity of the isovalent metals Li and Cs, converting it from strongly phase separating at ambient pressure to strongly long-range ordering at high pressures, which is the first such case of isovalent metal alloys. We find unsuspected ionic metal ordered structures and a remarkable 1D electronic structure within a 3D crystal structure.

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- J. B. Neaton and N. W. Ashcroft, Nature (London) 400, 141 (1999).
- [2] M. Hanfland, K. Syassen, N.E. Christensen, and D.L. Novikov, Nature (London) 408, 174 (2000).
- [3] M. I. McMahon, R. J. Nelmes, and S. Rekhi, Phys. Rev. Lett. 87, 255502 (2001).
- [4] K. Shimizu et al., Nature (London) 419, 597 (2002).
- [5] T. Matsuoka and K. Shimizu, Nature (London) 458, 186 (2009).
- [6] Y. Ma et al., Nature (London) 458, 182 (2009).
- [7] Y. Ma, A. R. Oganov, and Y. Xie, Phys. Rev. B 78, 014102 (2008).
- [8] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. 102, 146401 (2009).
- [9] Y. Yao, J. S. Tse, and D. D. Klug, Phys. Rev. Lett. 102, 115503 (2009).
- [10] Y. Yao et al., Phys. Rev. B 79, 092103 (2009).
- [11] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
- [12] R. Hultgren et al., Selected Values of The Thermodynamic Properties of Binary Alloys (American Society for Metals, Metals Park, OH, 1973).
- [13] T.B. Massalski et al., Binary Alloy Phase Diagrams (American Society for Metals, Metals Park, OH, 1986), Vol. 1.
- [14] R.F. Berg et al., J. Phys. F 17, 1861 (1987).
- [15] G.K. Moiseev, Russ. J. Inorg. Chem. 48, 1889 (2003).
- [16] A.M. Vora, Physica (Amsterdam) 450C, 135 (2006).
- [17] J. Feng et al., Nature (London) 451, 445 (2008).
- [18] G. Trimarchi, A. J. Freeman, and A. Zunger, Phys. Rev. B 80, 092101 (2009).
- [19] We use the Perdew-Burke-Ernzerhof exchange-correlation functional [20] as implemented in the Vienna *ab initio* simulation package (VASP) [21], the projector-augmented wave pseudopotential [22], energy cutoff of 350–900 eV, and *k*-point density of $2\pi \times 0.034$ Å⁻¹. We treat 1*s* and 2*s* electrons for Li, 2*s*, 2*p*, and 3*s* electrons for Na, 3*s*, 3*p*, and 4*s* electrons for K, 4*s*, 4*p*, and 5*s* electrons for Rb, 5*s*, 5*p*, and 6*s* electrons for Cs as valence. For Li we get exactly the same phases as Yao *et al.* [9]. See supplementary material [23].
- [20] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [21] G. Kresse and J. Furthműller, Comput. Mater. Sci. 6, 15 (1996).
- [22] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
- [23] See supplementary material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.104.245501 for details and performance of pseudopotentials.
- [24] D.C. Karnopp, Automatica 1, 111 (1963).
- [25] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. 75, 288 (1995).
- [26] A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006).
- [27] J.S. Tse et al., Phys. Rev. Lett. 82, 4472 (1999).