Prediction of ordered structures in the bcc binary systems of Mo, Nb, Ta, and W from first-principles search of approximately 3,000,000 possible configurations

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We predict ground states of the refractory alloys Nb-Mo, Nb-W, Ta-Mo, and Ta-W by combining first-principles calculated energies of □ 50 configurations for each system with a "mixed-basis cluster expansion,"

gies of structures not in the fit, and (iii) strain energies of the long-range elastic limit, via the "constituent strain" term.[17] (i)–(iii) ensure that the number, range, and type of interactions needed to fit and predict LDA energies is determined as objectively as possible. Human subjectivity as to which interactions are needed (e.g., concepts such as "locally complete sets," (Ref. 23) or cluster variation method aufbau-like hierarchy that forces all subclusters if a given cluster is used[24]) is avoided. In fact, the interactions that are identified by our approach do not follow any of these *ad hoc* principles. Once a MBCE is available, it can be easily evaluated for each of the 2^N

ground states are prominently absent on the (Nb/Ta)-rich side. Remarkably, the ground-state line segments of Mo-rich Nb-Mo, W-rich Ta-W, and Mo-rich Ta-Mo are densely decorated by structures on or near the ground-state line. Such dense sequences can arise as "adaptive structures," (Refs. 27 and 28) where long-ranged competing interactions allow stable structures at immediately adjacent x, creating a continuous convex curve $\Delta H^{(O)}(x)$. In contrast, the dilute (Nb/Ta)-rich regimes, beyond the complex Mo_4Ta_9-like structures, are devoid of truly stable structures altogether. The complexity of all three ground-state lines shows the need of realistic, first-principles-based interactions whose predictive power is carefully checked. For Mo-Ta and Ta-W, this complexity is missed entirely by the simpler scheme of Turchi *et al.*[15,16] Very recently, Curtarolo *et al.*[29] used a fixed library of 176 different structures within a data-mining[30] density functional theory-based series study of binary ground states. They predict for Nb-Mo correctly the Mo-rich $C11_b$ and $D0_3$ structures, but incorrectly the $B2$ and Nb-rich $C11_b$ structures. Our results [Fig. 3(a)] agree with the data-mining approach where the actual ground states happen to be among the 176 preselected structures (Mo-rich $C11_b$ and $D0_3$). However, ground-state configurations such as $B2_3$ and Nb-rich Mo_4Ta_9 are outside any conventional structure library, and will almost inevitably be missed in a prediction scheme based on human-compiled structure lists.

Ground states of Nb-W. The ordering behavior of Nb-W is completely different from the other three systems, despite qualitative indicators that would have suggested similarities (e.g., the close proximity in the periodic system of elements, similar $\Delta\Delta$ and lattice mismatch). The key ground state structures of Nb-W are illustrated in Fig. 4. The central ground state (NbW) is $B32$ (the NaTl structure), the A_2B_2 superlattice of (111

low ground-state structure in LDA (Nb_4W_2), which is in principle the *B*32 structure, but with pure Nb (100) planes inserted after every second plane.

All pair and many-body interactions are shown in Fig. 5. The difference between Nb-W and the other three systems is found in the smaller pairs beyond the first-nearest-neighbor interaction (which is always attractive). In contrast, three of the four many-body figures that characterize Nb-W are also found for Ta-W and Ta-Mo, and their relative magnitude is even quantitatively similar between the three systems. Figure 2(b) shows the calculated energy of ideally random ($T\rightarrow\Box$) solid solutions, $\Box H^{(\mathrm{R})}(x)$ (solid line), and that of short-range ordered solid solutions at $T=1200$ K, $\Box H^{(\mathrm{SRO})}(x)$ (dashed line). The shape of each calculated curve is confirmed quantitatively by direct LDA calculations, using large-cell special quasirandom structures[20,31] [Fig. 2(b)]. We use canonical Monte Carlo simulations[32] to calculate order-disorder transi-