Ordering Tendencies in Pd-Pt, Rh-Pt, and Ag-Au Alloys

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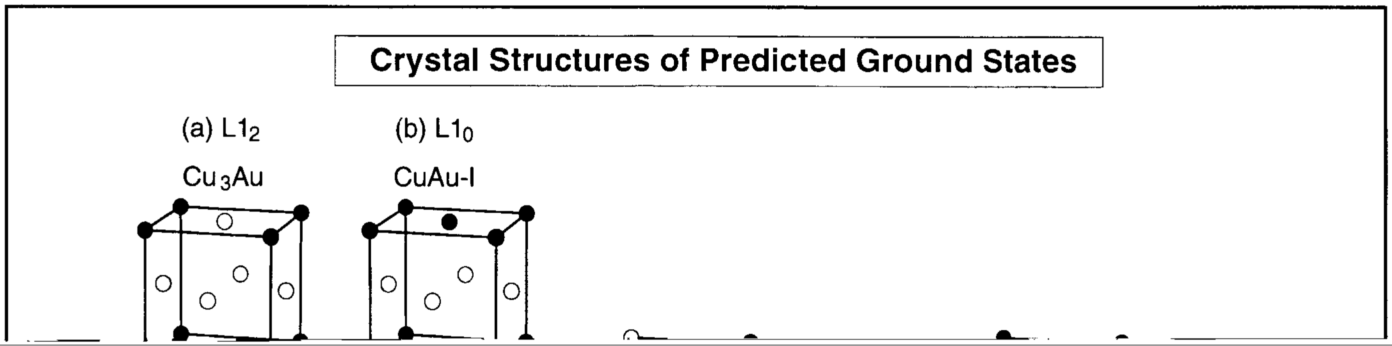
First-principles quantum-mechanical calculations indicate that the mixing enthalpies for Pd-Pt and Rh-Pt solid solutions are negative, in agreement with experiment. Calculations of the diffuse-scattering intensity due to short-range order also exhibits ordering tendencies. Further, the directly calculated enthalpies of formation of ordered intermetallic compounds are negative. These ordering tendencies are in direct conflict with a 1959 prediction of Raub that Pd-Pt and Rh-Pt will phase-separate below ~760 °C (hence their mixing energy will be positive), a position that has been adopted by all binary alloy phase diagram compilations. The present authors predict that $Pd_{1-x}Pt_x$ will order in the $L1_2$, $L1_0$, and $L1_2$ structures ([001] superstructures) at compositions $x = \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$, respectively, while the ordered structures of $Rh_{1-x}Pt_x$ are predicted to be superlattices stacked along the [012] directions. While the calculated ordering temperatures for these intermetallic compounds are too low to enable direct growth into the ordered phase, diffuse-scattering experiments at higher temperatures should reveal ordering rather than phase-separation characteristics (i.e., off-Γ peaks). The situation is very similar to the case of Ag-Au, where an ordering tendency is manifested both by a diffuse scattering intensity and by a negative enthalpy of mixing. An experimental reexamination of Pd-Pt and Rh-Pt is needed.



Crystal Structures of Predicted Ground States

4. Conclusion

Using a first-principles quantum-mechanical method (which properly includes the terms that were neglected by the previous theories, such as simplified tight-binding Hamiltonian models, neglect of relativistic effects and charge transfer of

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