

# Quantum architecture of novel solids

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The current status of our understanding of Quantum Mechanics is that if one specifies the chemical formula of a compound (e.g., CuAu, or GaAs, or NiPt) it is still impossible to predict if this material is a superconductor or not, but it is now possible to predict its crystal structure. This is a nontrivial accomplishment for there are as many as  $2^N$  possible structures for a binary compound. This article reviews this classic question of structural chemistry and condensed matter physics: How can one figure out which of the astronomic number of possible crystal structures is selected by Nature?

Crystal structures, Local Density Approximation, cluster expansion, structural selectivity

61.50.Ah, 64.10.+h, 71.15.Ap

## 1 Introduction



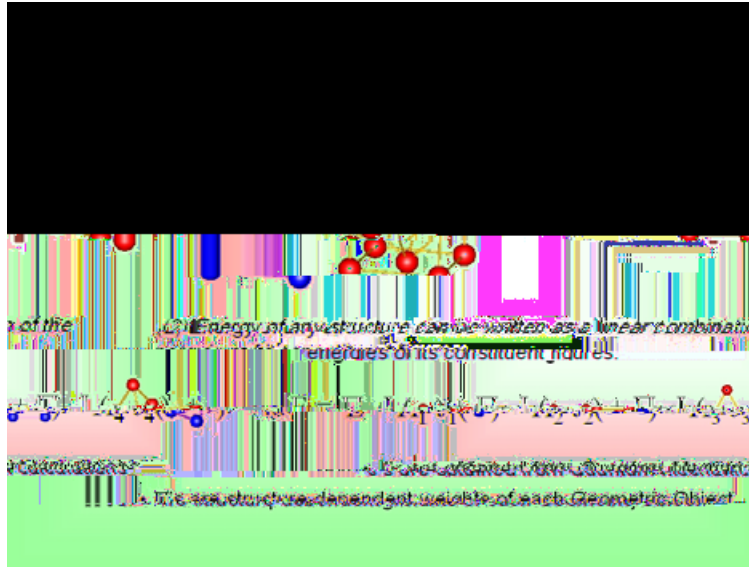


Fig. 1 Schematic illustration of how the LEGO idea works. See Refs. [4, 5]

than the interaction between nearer atoms, then the expansion of  $E(\mathbf{r})$  could require fewer than  $2^N$  interaction energies  $J_G$ . Thus, an LDA calculation of the total energies  $E_{LDA}(\mathbf{r})$  of  $N_\sigma$  ordered configurations could be used to determine  $N_\sigma$  interaction energies [2], thus a ordering examination of the rate of convergence of the series  $E_{LEG}(\mathbf{r})$ . If the series converges after  $\approx 10 - 20$  terms (as it does in many cases, see below) then one can calculate  $E(\mathbf{r})$  for *any* configuration by just summing over that many terms. Furthermore, one could combine such an expansion

allows us to calculate the excess energy  $E(\gamma)$  of any arbitrary atomic configuration, (even consisting of more than 100,000 atoms) and it includes automatically the energy lowering due to atomic relaxations. Formulation of the method requires as input the  $T = 0$  K excess energies  $E_{LDA}$  of 20-30 ordered compounds  $A_p B_q$  consisting of only 2-16 atoms per unit cell. The excess energy  $E_{LDA}(A_p B_q; \gamma)$  of such ordered  $A_p B_q$  bulk compounds is defined as the energy gain or loss with respect to the bulk constituents at their equilibrium lattice constants:

$$E_{LDA}(A_p B_q; \gamma) = E_{\gamma}(A_p B_q; \gamma) - x E_A(a_A) - (1-x) E_B(a_B). \quad (1)$$

Here,  $\gamma$  denotes the type of ordered structure,  $x = p/(p+q)$ , and  $a_A$  and  $a_B$  are the equilibrium lattice constants of the bulk elements A and B.  $E_A(a_A)$  and  $E_B(a_B)$  are the total energies of A and B, respectively. The formation energies of such small unit cell structures can be easily calculated within the local-density approximation

• 1 These calculations provide comprehensive state-of-the-art first-principles description of *ground state structures*, *phase stability*, and *short-range order* in these systems.

<b>Pd-Pt</b>	[6]	<b>Ni-V</b>	[7, 8]	<b>Cu-Pt</b>	[12, 13]
<b>Rh-Pt</b>	[6]	<b>Ag-Au</b>	[9, 10]		
<b>Cu-Au</b>	[11]	<b>Ni-Au</b>	[11]		

The new Cu Pt “D7-type” ground state structure was predicted [12,13], and subsequently found experimentally by S. Takizawa (1996). This is illustrated in Fig. 2 and demonstrates the power of first-principles theory to predict previously unsuspected structures!

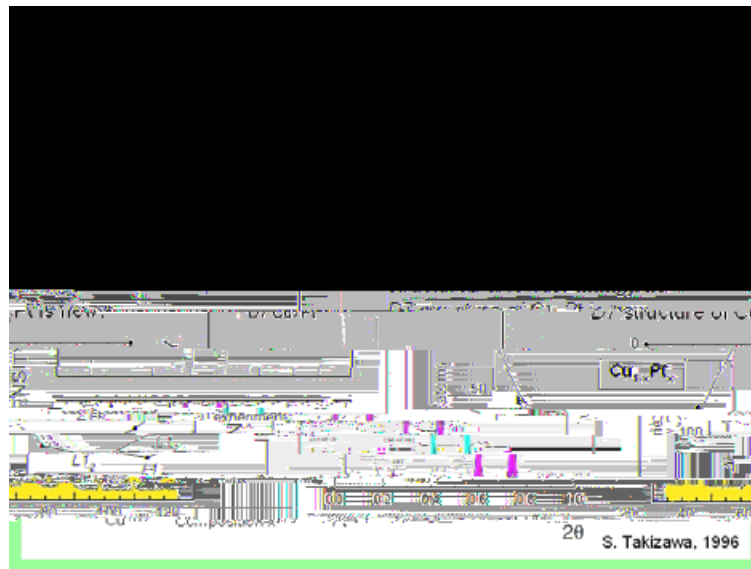


Illustration for prediction (Ref. [12,13]) and subsequent verification of a new structure for Cu-Pt.

We are now at the beginning of the process of solving one of the classic problems of Quantum Theory of Solids: We are transforming our qualitative and semi-quantitative understanding of cohesion into a predictive theory of new materials!

## References

- [1] P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Amer. Soc. Metals, Metals Park, OH (1985)
- [2] J. W. Connolly and A. R. Williams, *Phys. Rev.* (1983) 5169

