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Quantum architecture of novel solids

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Abstract. 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?

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1 Introduction

Nature exhibits a remarkable selectivity in the crystal structure it adopts for solids. This is evident by considering even the simplest case of binary A-B inorganic phases: If one considers a hypothetical crystallographic unit cell with N sites, each occupied either by an A or a B atom, there can be an astronomically large number (2^N) of possible crystal configurations, e.g., $\sim 10^{10}$ for a 34-atom unit cell. Yet, since the discovery around the turn of the century of x-ray diffraction, *only* $\sim$ 4000 *inorganic crystal structures* have been observed in the enormous effort, encompassing checking of over 200,000 crystal phases [1]. The combination of the *diversity* of possible crystal forms (2^N options) with the remarkable *specificity* by which nature selects but a few stable structures defines one of the outstanding enduring challenges in the quantum theory of solids. Today, at the 100th birthday of quantum-mechanics, one has to admit that despite great advances in quantum theory or solids and the advent of large computers, we have still failed to *predict* which crystal structure is adopted by a given A-B compound, even if it is a binary system. This article will review the current status of this challenge.

Most crystalline materials adopt structures that represent the lowest thermodynamic energy (either locally or globally) of any of the 2^N possible configurations. This simple statement has formed the basis for historic efforts in metallurgy, inorganic chemistry, and solid state physics aimed at understanding, systematizing and predicting the structure of crystals in terms of the innate propensities of the specific atom pair A and B to select a structure. While our solid state chemistry and physics text books pretend that they know the answer (ionic binary crystals are said to select the NaCl structure, covalent crystals “select” the diamond or zincblende structure, simple metals are close-packed, etc.), the simple truth is that such descriptions do not confront the many (2^N) possible structural alternatives.

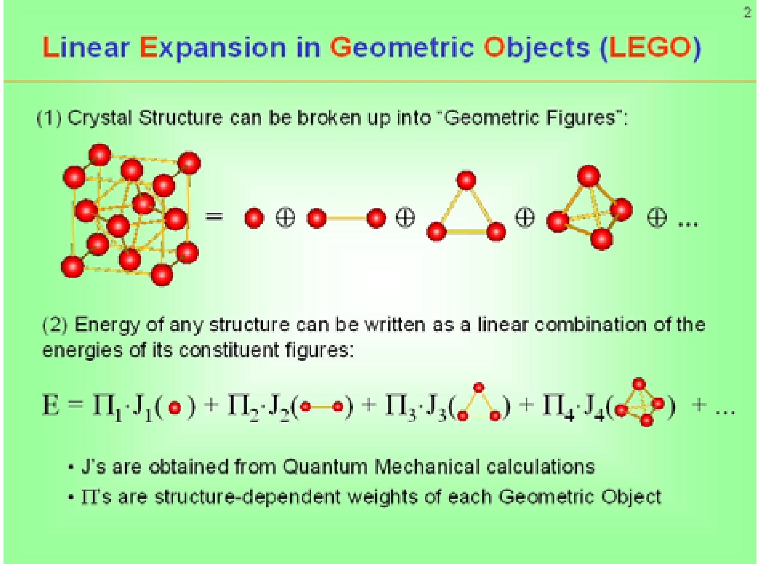
What makes this challenge not only scientifically intriguing but also technologically existential is the fact that the *function* of crystals (e.g., useful properties) reflects their *form*, i.e., structure. In *semiconductor superstructures,* the particular sequence of atomic layers defines “quantum confinement” of electrons, hence the optical properties of the solid. For example, a certain sequence of GaP/InP layers enables high-efficiency solar cells, while another sequence of GaN/InN enables blue lasers. In *insulating crystals*, certain atomic arrangements of the binary system C-N are said to lead to super-hardness, while other C-N forms are predicted to be remarkably soft. In *metallic crystals*, some crystal forms are brittle, others are ductile (examples of alluminides); some structures form material-hardening precipitates (“super alloys”) and others do not. This dualism of structure vs. property sets the stage for the vision of designing materials with desired properties. We share this vision with the alchemists of the 15th century who were exploring ways of enticing materials to transform into forms that create value (and luster) through new functionality. But while alchemists had a total disregard for the number of protons and the electronic structure, these features are the centerpiece of our current dreams of quantum-architecture. This article will thus emphasize the recent development of “first-principles” quantum mechanical approaches to the problem, using the Local Density Approximation (LDA). We will see that the efforts in theoretical “first-principles” structure predictions has recently shown significant successes, to be reviewed here, but that at the same time, these successes have exposed a central weakness in the fundamental strategy used. Thus, the field is at a juncture, offering exciting new challenges and opportunities.

2 Outline of the solution: Linear Expansion in Geometric Objects (LEGO)

The reason we cannot explore quantum-mechanically the 2^N possible ordered phases of A_xB_{1-x} is that a calculation of the quantum-mechanical total energy

$$E = \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$$

scales unfavorably with the system's size N. (Even linear-scaling algorithms currently have an unfavorable large pre-factor). One approach to this problem is to map the quantum-mechanical total energy $E_{LDA}(\sigma)$ of configuration σ into a readily-calculable linear expansion $E_{LEGO}(\sigma)$. Figure 1 illustrates an expansion in terms of “Geometric Objects” (GO) such as atom-pairs (1st to m-th nearest-neighbors), atomic triangles, squares, etc. Each GO has a (yet unknown) characteristic energy J_{GO} and a frequency of occurrence $B_{GO}(\sigma)$ in configuration σ. In principle there are 2^N configurational energies $E(\sigma), \sigma = 1 \ldots 2^N$ and 2^N geometric figures J_{GO}, $GO = 1 \ldots 2^N$. However, if in some sense the interactions between widely-separated atoms is less important



Linear Expansion in Geometric Objects (LEGO)

(1) Crystal Structure can be broken up into "Geometric Figures":

(2) Energy of any structure can be written as a linear combination of the energies of its constituent figures:

$$E = \Pi_1 \cdot J_1(\bullet) + \Pi_2 \cdot J_2(\bullet\!-\!\bullet) + \Pi_3 \cdot J_3(\triangle) + \Pi_4 \cdot J_4(\ ) + \ldots$$

- J's are obtained from Quantum Mechanical calculations
- Π's are structure-dependent weights of each Geometric Object

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

than the interaction between nearer atoms, then the expansion of $E(\sigma)$ could require fewer than 2^N interaction energies J_{GO}. Thus, an LDA calculation of the total energies $E_{LDA}(\sigma)$ of N_σ ordered configurations could be used to determine N_σ interaction energies [2], thus affording examination of the rate of convergence of the series $E_{LEGO}(\sigma)$. If the series converges after $\approx 10 - 20$ terms (as it does in many cases, see below) then one can calculate $E(\sigma)$ for ***any*** configuration σ by just summing over that many terms. Furthermore, one could combine such an expansion $E_{LEGO}(\sigma)$ with statistical-mechanics "ground state search" algorithim (e.g., simulated-annealing) and readily locate out of 2^N possibilities the configuration of lowest energy. By viewing the expansion as a generalized Ising-type Hamiltonian one can apply to it any of the statistical mechanics lattice-gas techniques (cluster-variation-method; finite temperature expansion, Monte-Carlo) and calculate finite-temperature free-energies of various phases and microstructures. Figure 1 illustrates the idea graphically.

Our past research revealed [3] that the simple-minded expansion [2] has a few problems, such as (i) slow convergence for highly size-mismatched alloys (Cu-Au, GaP-InP), (ii) difficulty to include ***all*** forms ("cell-internal" as well as "cell external") of atomic relaxation, (iii) the "k=0 singularity problem" (dependence of the energy on the direction of approach to the Brillouin zone center), and (iv) the limitation of the number of interactions to the number of trial structures. All of these problems could fortunately be overcome by developing a ***"mixed basis" expansion***, [4, 5] in which (i) the analytic strain energy is subtracted from the LDA energy before the expansion is attempted; (ii) pair-figures to arbitrary order are calculated in *reciprocal-space* whereas man-body figures are calculated in *real space*, etc. The final LEGO expression allows us to calculate the excess energy $\Delta E(\sigma)$ 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 ΔE_{LDA} of 20-30 ordered compounds A_pB_q consisting of only 2-16 atoms per unit cell. The excess energy $\Delta E(A_pB_q, (\sigma)$ of such ordered A_pB_q bulk compounds is defined as the energy gain or loss with respect to the bulk constituents at their equilibrium lattice constants:

$$\Delta E_{LDA}(A_pB_q;\sigma) = E^{tot}(A_pB_q,\sigma) - xE^{tot}_A(a_A) - (1-x)E^{tot}_B(a_B). \qquad (1)$$

Here, σ 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. $E^{tot}(a_A)$ and $E^{tot}(a_B)$ 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 (LDA) using either pseudopotential plane-waves or the all-electron LAPW approach. These 20-30 LDA calculated energies are used to fit the coefficient of LEGO, in which any configuration σ is defined by specifying the occupations of each of the N lattice sites by a B-atom ($S_i = -1$) or an A-atom ($S_i = +1$). The excess energy of any configuration σ is then given by

$$\Delta E_{LEGO}(\sigma) =$$

$$\sum_k J_{pair}(k)|S(k,\sigma)|^2 + \sum_f^{MB} D_f J_f \overline{\Pi}_f(\sigma) + \frac{1}{4x-1}\sum_k \Delta E^{eq}_{cs}(\hat{k},x)|S(\hat{k},\sigma)|^2 \qquad (2)$$

The first term includes all pair figures, where $J_{pair}(k)$ and $S(k,\sigma)$ are, respectively lattice Fourier transforms of real space interactions and spin-occupation variables. The second sum represents many-body (MB) interactions and runs over symmetry in equivalent clusters consisting of three or more lattice sites. D_f is the number of equivalent clusters per lattice site, and $\Pi_f(\sigma)$ are structure-dependent geometrical coefficients. The last summation involves the “constituent strain energy,” ΔE_{cs} which is defined as the strain energy of bulk A and B required to maintain coherency along an interface with orientation k. ΔE_{cs} can be calculated by deforming the bulk elements from their equilibrium lattice constants a_A and a_B to a common lattice constant a perpendicular to k. Once we determined $J_{pair}(k)$, J_f and E_{cs} from 20-30 LDA calculations on simple ordered structures, we can calculate $E_{lego}(\sigma)$ for **any** σ (even containing 100,000 atoms) essentially effortlessly. Then Eq. (2) is subjected to (i) “ground state search” identifying the lowest-energy $T = 0$ K structures out of $\sim 2^N$ possibilities, and to a Monte-Carlo calculation of (ii) phase-diagrams, (iii) precipitate shapes, and (iv) various forms of short range order. We can thus obtain “LDA accuracy” for as many as 100,000 atom alloys and extend LDA to finite temperatures.

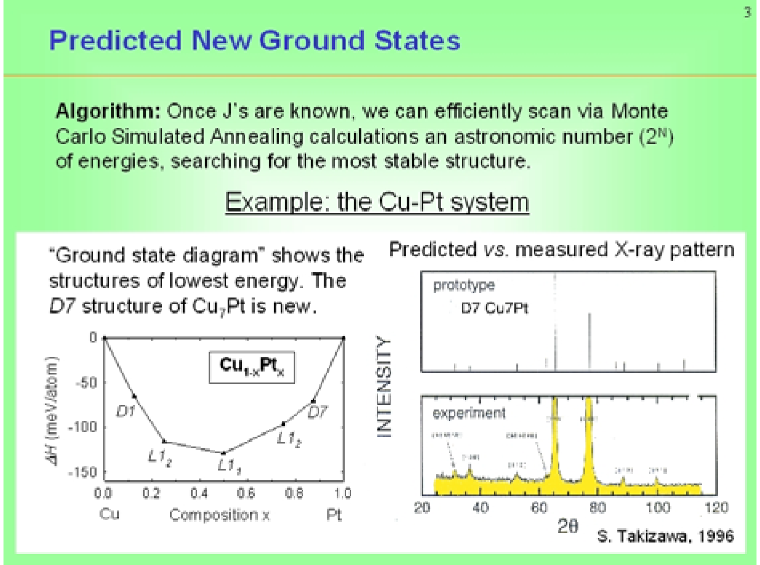
3 Applications

This method was used to predict the stablest $T = 0$ structures of a number of “classic” binary systems such as those listed in Table 1.

Table 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.

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

The new Cu_7Pt "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!



Predicted New Ground States

Algorithm: Once J's are known, we can efficiently scan via Monte Carlo Simulated Annealing calculations an astronomic number (2^N) of energies, searching for the most stable structure.

Example: the Cu-Pt system

"Ground state diagram" shows the structures of lowest energy. The *D7* structure of Cu_7Pt is new.

Predicted *vs.* measured X-ray pattern

S. Takizawa, 1996

Fig. 2 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 sohesion into a predictive theory of new materials!

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