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Structure prediction and targeted synthesis: A new Na_nN_2 diazenide crystalline structure

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Significant progress in theoretical and computational techniques for predicting stable crystal structures has recently begun to stimulate targeted synthesis of such predicted structures. Using a global space-group optimization (GSGO) approach that locates ground-state structures and stable stoichiometries from first-principles energy functionals by objectively starting from randomly selected lattice vectors and random atomic positions, we predict the first alkali diazenide compound Na_nN_2 , manifesting homopolar N–N bonds. The previously predicted Na_3N structure manifests only heteropolar Na–N bonds and has positive formation enthalpy. It was calculated based on local Hartree–Fock relaxation of a fixed-structure type (Li_3P -type) found by searching an electrostatic point-ion model. Synthesis attempts of this positive ΔH compound using activated nitrogen yielded another structure (anti- ReO_3 -type). The currently predicted (negative formation enthalpy) diazenide Na_2N_2 completes the series of previously known BaN_2 and SrN_2 diazenides where the metal sublattice transfers charge into the empty N_2 Π_g orbital. This points to a new class of alkali nitrides with fundamentally different bonding, i.e., homopolar rather than heteropolar bonds and, at the same time, illustrates some of the crucial subtleties and pitfalls involved in structure predictions versus planned synthesis. Attempts at synthesis of the stable Na_2N_2 predicted here will be interesting. © 2010 American Institute of Physics. [doi:10.1063/1.3488440]

I. INTRODUCTION

Laboratory synthesis and characterization of compounds are the ultimate reality tests for theoretical crystal-structure predictions. Indeed, it is not surprising that the theoretical prediction¹ and subsequent synthesis and structure determination^{2–4} of a new alkali nitride Na_3N have understandably featured prominently in a recent review article on structure prediction⁵ and on planned synthesis in solid-state chemistry.^{6,7} Nitrides of alkali metals offer a fruitful arena for finding new crystal-structure types because of the subtlety of the competing chemical interactions. The nitrogen atom is a poor electron acceptor (having unusually low electron-affinity due to its stable half-filled p^3 shell) making it difficult to form a heteropolar $\text{M}^+ - \text{N}^-$ bond with alkali metals M ; yet, the nitrogen atom has a large affinity to other nitrogen atoms with which it can form the highly stable molecular N_2 . This sets up a competition between homopolar N–N and heteropolar $\text{M}^+ - \text{N}^-$ bonding within metal frameworks. Indeed, with the exception³ of Li (forming Li_3N in the Li_3N structure having no N–N bonds), no other alkali metal was known to form any nitride from $\text{M} + \text{N}_2$ under ambient conditions. This failure of the homology principle²—the existence of Li_3N , but absence of Na_3N , and K_3N —stimulated the theoretical search and eventual prediction¹ of a new Na_3N crystal-structure. The predicted metastable structures¹ manifested only heteropolar M–N

II. METHOD

A. Strategies of structure optimization

With the advent of first-principles total-energy computational methods for *periodic* solids,^{8–10} two leading types of structure prediction approaches based on such calculations have developed. In the *inductive* approach (e.g., data mining,¹¹ or diagrammatic orbital-radii structure separation),¹² one offers a guess for the crystal structure of a given compound by analogy with known structures of other compounds, an approach that generally works very well except if one encounters a new prototype structure that is matchless (as is the case for Na–N here). In the *deductive* approach, one explicitly varies the structural degrees of freedom (SDFs) of a (say, A_pB_q) compound in search of a minimum of a given energy functional. The latter can be either a “first-principles” functional based on a microscopic Hamiltonian with explicit electronic coordinates (e.g., Hartree–Fock; density-functional), or an empirical “force field,” in which the electronic coordinates are integrated out and one focuses on a subset of the chemical interactions deemed important (e.g., a point-ion electrostatic potential with some repulsive walls is used).¹

The selection of the SDF being optimized divides the energy minimization methods into different optimization classes illustrated in Fig. 1. (i) In one common approach one fixes at the outset the type of unit cell lattice vectors (e.g., orthorhombic or monoclinic) and the occupancy of the space-group specific (Wyckoff) atomic sites, (e.g., NaCl versus fluorite site occupation of the $Fm\bar{3}m$ space-group) and optimize the remaining SDFs, i.e., the magnitude of the lattice parameters and cell-internal parameters not decided by symmetry. Such “local optimization”^{13–15} (Fig. 1) is ubiquitous and has been implemented in most standard solid-state total-energy packaged codes.^{10,16} This approach requires *a priori* knowledge of the structure type appropriate for a given compound and thus affords but a limited “surprise factor” in identifying unsuspected structures. (ii) In the “global space-group optimization” approach one starts from randomly selected lattice vectors and random Wyckoff positions and uses global optimization and search methods, (e.g., evolutionary algorithm¹⁷ and simulated annealing)¹⁸ to zoom-in in an unbiased manner to the minimum energy. Unlike the local relaxation (a positional optimization), in the global crystal-structure search (both a positional and configurational optimization) A and B atoms can swap positions during the calculation and the lattice-type can change (e.g., bcc to fcc) in search of lower energy topologies. In a recent

development,¹⁹ such approaches were generalized to optimize the stable stoichiometries (p, q) in A_pB_q “on the fly.” The different combinations of energy functionals with either local or global structure optimization (Fig. 1) define the various classes (1, 2, or 3) of deductive structure predictions. As we will see below the selection of such a class can critically control the qualitative and quantitative outcome of the structure prediction.

B. Search for heteropolar Na–N structures

Jansen and Schön¹ (see also reviews in Refs. 5–7) used an empirical point-ion electrostatic force field in conjunction with a global optimization technique (method 1 in Fig. 1) identifying candidate structures for Na_3N , with energies shown in Fig. 2(a). Since an electrostatic point-ion energy functional can not stabilize like-charge (homopolar) bonds, all structures found (shown in Fig.

fed to it. The ensuing HF formation enthalpies are shown in Fig. 2(b). The lowest-energy structure of Na_3N is now the Li_3P structure type. Notably, the order of stability is very different in Fig. 2(a) (electrostatics) and Fig. 2(b) (Hartree–Fock) [e.g., see the energy order of the Al_3Ti and Li_3N structure types in (a) versus (b)], reflecting the limited ability of the simple point-ion electrostatic force field to describe chemistry. Given the positive formation enthalpies of all heteropolar structures predicted in Fig. 2(b) with respect to metallic Na and free-space N_2

sitions. Significantly, none of the heteropolar Na–N structures discussed before^{1,2,6} emerged here as ground-state structures. Instead, we find numerous structures with negative ΔH

tional charge elongates the N–N bond (the N–N bond length of the free-space N_2 molecule is 1.10 Å in LDA). The main part of the Na 3s state is above E_F (i.e., empty). The $2\Pi_g(2p)$ state consists of the p_x, p_y states of dinitrogen and looks like two toruses surrounding the two N atoms. The additional charge filling the $2\Pi_g(2p)$ state is distributed in these two toruses [see the inset figure of Fig. 5(a)]. This electronic structure is similar to that of BaN_2 (Ref. 28) and SrN_2 (Ref. 29) diazenides. We have estimated the charge transfer from the metal sublattice to the nitrogen diatomic units by integrating the difference between the charge density of the solid minus the charge densities of the M atoms and N_2 molecules at the respective positions in the solid [inset to Fig. 5(a)], finding $Q=0.60e$ for Na_2N_2 ; $Q=0.79e$ for Na_6N_2 compared with $Q=0.51e$ in SrN_2 . These values are smaller than the idealized $Q=2e$ value assigned classically.

C. M–N versus M– N_2 structures

Are the molecular structures [e.g., Fig. 4(d)] always more stable than the nonmolecular ones (e.g., Fig. 3)? To answer this question, we show in Fig. 6 the calculated formation enthalpies of the Na_3N and Li_3N compounds both in the Na_6N_2 (*Cm*) structure [see Fig. 4(d)] and in the atomic anti- ReO_3 and Li_3N -type structures. We see that whereas in the Na_3N compound the molecular phase is more stable (both in LDA and GGA), in the Li_3N compound the atomic phases are more stable (both in LDA and GGA). This agrees with experimental phase diagram³¹ of Li_3N .

D. Lithium-nitrogen system

The Li_3N (Ref. 31) and LiN_3 (Ref. 25) are the two known phases in the Li–N system. We calculate the formation enthalpy of Li_2N_2 in the Na_2N_2 (

