Three new crystal structures in the Na–Pb system: solving structures without additional experimental input

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The structures of three Na–Pb compounds, γ, δ and δ', have remained incompletely solved for nearly 60 years. The space group, lattice parameters and positions of the Pb atoms of these three structures have been determined, but the positions of the Na atoms are still unknown. In this work, the First-Principles Assisted Structure Solution (FPASS) method [Meredig & Wolverton (2013). *Nat. Mater.* **12**, 123–127] has been used to complete the description of these three structures using only experimental information available from the literature as input. The paper also discusses the relative advantages of constrained crystal structure prediction tools, like FPASS, in comparison to conventional crystal structure prediction methods in reference to their abilities to complete the solution of other unsolved structures.

1. Introduction

While modern tools for determining crystal structures are quite advanced, it is not uncommon that the structure of a compound cannot be determined with the available experimental data. In fact, thousands of entries in the Powder Diffraction File (PDF) are not associated with a crystal structure. Each of these incomplete entries represents a gap in the scientific knowledge and a material whose properties cannot be better understood by assessing their atomic scale structures. In many of these cases, it was possible to determine at least some information about the crystal, such as its composition and symmetry group. As an example, Weston and Shoemaker attempted to solve the structures of three Na–Pb compounds in 1957 and failed (Weston & Shoemaker, 1957). They were able to determine the lattice parameters, space group, and even the positions of the Pb atoms, but were unable to solve the positions for the Na atoms and, to this day, the structures have yet to be solved.

In the case of these unsolved Na_xPb_y compounds, the diffraction data are no longer available. Rather than repeating the diffraction experiments required for conventional crystal structure solution techniques, we propose that these structures can be solved using crystal structure prediction algorithms. Crystal structure prediction (CSP) algorithms are designed to determine the lowest-energy crystal structure when provided with at least the composition of the structure in question (Woodley & Catlow, 2008). These CSP algorithms have the advantage of requiring no experimental input to determine the ground-state structure of a compound, which makes them ideal for solving the Na_xPb_y structures considered in this work and, possibly, useful tools in addressing the large number of other unsolved structures.
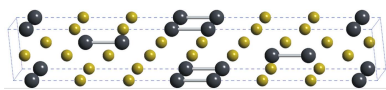
Table 1
Structures for the γ, δ and δ' phases, as determined using FPASS.

The composition, lattice parameters, space group and Pb positions were originally determined by Weston & Shoemaker (1957).

Phase	δ	δ'	γ
Composition	Na_5Pb_2	Na_9Pb_4	$Na_{13}Pb_5$
Space group	$R\bar{3}m$ (166)	$P6_3/mmc$ (194)	$P6_3/mmc$ (194)
Lattice parameters	$a = b = 5.54$, $c = 23.15$ Å	$a = b = 5.47$, $c = 30.41$ Å	$a = b = 5.51$, $c = 40.39$ Å
Atom positions	Na (0 0 0.5)	Na (0 0 0.183)	Na (0 0 0)
	Na (0 0 0.785)	Na (1/3 2/3 3/4)	Na (1/3 2/3 0.211)
	Na (0 0 0.357)	Na (1/3 2/3 0.635)	Na (0 0 0.083)
	Pb (0 0 0.070)	Na (1/3 2/3 0.091)	Na (1/3 2/3 0.617)
		Na (1/3 2/3 0.519)	Na (0 0 0.167)
		Pb (0 0 0.050)	Na (1/3 2/3 0.710)
		Pb (1/3 2/3 0.2)	Na (1/3 2/3 0.531)
			Pb (0 0 1/4)
			Pb (1/3 2/3 0.05)
			Pb (1/3 2/3 0.13)

As the number of possible crystal structures for a given composition is too large to be exhaustively evaluated (Oganov & Glass, 2006), CSP algorithms rely on evaluating a subset of these possibilities that is likely to contain the true ground state, and are quite varied in their approaches to determining that subset. For instance, there are a wide variety of CSP methods that employ specially designed global optimization algorithms to search efficiently through the space (Lonie & Zurek, 2011; Majzoub & Ozoliņš, 2008; Michel & Wolverton, 2014; Oganov & Glass, 2006; Pickard & Needs, 2011; Revard *et al.*, 2014; Togo & Tanaka, 2013; Wang *et al.*, 2010). Alternatively, one could assume that the ground-state structure is similar to a structure that has already been observed experimentally and evaluate a list of already known crystal structure types as potential solutions (Curtarolo *et al.*, 2003; Fischer *et al.*, 2006; Hautier *et al.*, 2010; Kong *et al.*, 2012). Both of these classes of CSP techniques have been used extensively in the literature to determine the structure of compounds when it was impractical to do so experimentally (Hautier *et al.*, 2010; Oganov & Ono, 2004; Pickard & Needs, 2007; Woodley & Catlow, 2008).

A third, computationally more efficient, approach is to use information that is already known about a crystal structure to constrain the search for the correct solution and employ a CSP algorithm to locate the lowest-energy structure within those constraints (Lanning *et al.*, 2000; Meredig & Wolverton, 2013; Putz *et al.*, 1999). The concepts behind such constrained methods are that (i) employing these constraints speeds the calculation by reducing the number of possible candidates and (ii) evaluating candidates based on both energetic feasibility and consistency with experimental measurements (*e.g.* lattice parameters, diffraction patterns) will eliminate spurious, low-energy solutions that are inconsistent with experimental observation (Putz *et al.*, 1999). One such combined method, the First-Principles Assisted Structure Solution (FPASS) method, uses a genetic algorithm to search for materials that both match a powder diffraction pattern and have minimum energy according to *ab initio* density functional theory (DFT) calculations. This method has been used previously for struc-

tures that proved difficult to solve with conventional crystal structure prediction and solution techniques (Meredig & Wolverton, 2013), and has the ability to constrain based on symmetry. Given that the space group, lattice parameters and Pb atomic positions are known for the compounds studied in this work, FPASS is a suitable tool for solving their structures. In this work, we present the solutions to three long-unsolved Na–Pb crystal compounds, the γ, δ and δ' phases (Hultgren, 1973). Additionally, we investigate the effect of supplying FPASS with different amounts of experimental information and discuss the relative advantages of constrained methods compared to crystal structure prediction strategies with reference to their ability to be used to solve incompletely determined structures.

2. Methods

2.1. Experimental data

The three structures of interest in this work are Na-rich binary Na_xPb_y compounds originally discovered by Weston and Shoemaker (W&S) in 1957 (Weston & Shoemaker, 1957). W&S were able to determine some information about the structures and published these data as an abstract for a presentation at the fourth IUCr Congress, which is the only source of data used for solving these structures. Since then, these structures have remained incompletely solved. For clarity, we describe them using the notation used in the phase diagram reported by Hultgren (1973).

γ-$Na_{13}Pb_5$. This phase was originally reported to have a stoichiometric composition of Na_5Pb_2. W&S were able to determine the space group, lattice parameters and positions of Pb atoms (shown in Table 1) using a combination of powder and single-crystal X-ray diffraction techniques (Weston & Shoemaker, 1957). The authors were unable to determine the positions of Na atoms. This phase is known to have a composition of approximately 71.4 at.%Na – Na_5Pb_2 – at its melting temperature (Weston & Shoemaker, 1957). W&S were also able to determine that the Na positions are likely to be partially occupied and the composition of γ with all sites fully occupied is 72.2 at.%Na ($Na_{13}Pb_5$). In this work, we used this information to simplify the solution process by assuming all sites are fully occupied and the composition of γ is $Na_{13}Pb_5$.

δ-Na_5Pb_2. This is a high-temperature phase with a composition near Na_9Pb_4. This phase is known to have a space group of $R\bar{3}m$ with lattice parameters and Pb positions shown in Table 1. As with the γ phase, the positions of Na atoms are yet unknown. As with the γ structure, W&S hypothesized that the Na positions are partially occupied and proposed that the structures had a composition of 71.4 at.%Na (Na_5Pb_2). As with the γ phase, we assume all sites are fully occupied and the composition is Na_5Pb_2 when solving the structure of δ.

δ'-Na_9Pb_4. This low-temperature hexagonal phase ($P6_3/mmc$) has a composition of Na_9Pb_4. As with δ and γ, the lattice parameters, Pb positions (but not those of the Na atoms) and space group were also determined using X-ray diffraction techniques, and are shown in Table 1.

2.2. Structure solution method

We employed the recently developed FPASS method to solve each structure (Meredig & Wolverton, 2013). FPASS works by using a genetic algorithm to locate the lowest-energy crystal structure out of all structures that match any known structural information, which can include lattice parameters and space group. In cases where diffraction data are available, this search is further guided by preferentially evaluating candidate structures that are better matches to the powder diffraction pattern of the compound. The inclusion of both diffraction pattern matching and constraining searches to a certain symmetry group has been shown to allow FPASS to resolve the correct structure when both conventional crystal structure solution and crystal structure prediction methods are unable to determine the correct crystal structure with certainty (Meredig & Wolverton, 2013).

We used the results from a study by W&S as a starting point for our solution process (Weston & Shoemaker, 1957), as described in the previous section. For all three cases (γ, δ and δ'), the space group, lattice parameters and the positions of the Pb atoms were known. Unless otherwise mentioned, all of this information was employed to define the space of possible crystal structures evaluated using FPASS. While both single-crystal and powder X-ray diffraction were used to characterize each compound in the original study from 1957, the diffraction data were not reported in the original papers, and therefore are not available to help solve the structures.

We used a population size of ten structures for the genetic algorithm and the optimization was halted once the energy of the optimal structure failed to change by more than 5 meV per atom after five generations. At each generation, the best performing structure from the previous generation was kept in the population. Mutation and crossover operations were slightly different to those used in the original FPASS paper, and are described in detail in other work (Ward *et al.*, 2015). Mutation probabilities of 50% were used for both the Wyckoff site combinations and atom positions. Wyckoff site biasing, as described in Meredig & Wolverton (2013), was not found to be necessary for solving these structures. FPASS was run ten times with different random number seeds for each compound, and the structure with the lowest energy out of all runs was selected to be the candidate solution. The software used to perform FPASS is available under an open-source licence from http://github.com/materials/mint.

3. Energy calculations

We used DFT (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), as implemented in the Vienna *ab initio* software package (*VASP*) (Kresse & Hafner, 1993; Kresse & Joubert, 1999), to evaluate the energy of each candidate crystal structure. In particular, we employed the projector augmented-wave method (Blöchl, 1994) with the Perdew–Burke–Ernzerhof generalized-gradient approximation for the exchange-correlation energies (Perdew *et al.*, 1996). We used pseudopotentials for Na and Pb that treat the $3s^1$ and $6s^2 6p^2$ electrons as valence, respectively, with a cutoff energy of 102 eV and a gamma-centered mesh of 1000 k-points per reciprocal atom in all calculations (Blöchl, 1994; Kresse & Joubert, 1999).

When comparing the energy of our proposed solutions against those of other $Na_x Pb_y$ compounds, we used the same DFT settings as the Open Quantum Materials Database (OQMD) (Saal *et al.*, 2013). These more accurate parameters include a higher cutoff energy of 520 eV and a k-point mesh of 8000 points per reciprocal atom. Additionally, performing energy calculations with these settings made it possible to use energies available in the OQMD directly in the analysis of our results without repeating any calculations. It is worth noting that, while these DFT settings are more accurate, they are too computationally expensive to be practical for use with FPASS.

4. Results and discussion

4.1. δ Phase

The δ phase is a high-temperature phase with a rhombohedral structure that reversibly transforms into hexagonal δ' below 463 K (Hultgren, 1973; Weston & Shoemaker, 1957) (below, we consider the δ' phase). W&S found that the stoichiometry of this structure is $Na_5 Pb_2$ with space group $R\bar{3}m$ (166). They found that all the Na sites were fully occupied and they determined the locations of all Pb atoms in the structure. The only missing piece of information about the structure is the positions of the Na atoms. To find these positions, we used FPASS to locate the structure with the lowest energy that satisfies all of the known information about the structure (*i.e.* lattice parameters, Pb positions and space group). Each FPASS solution requires evaluating between 120 and 200 candidate structures, which required only 3 h for all ten runs of FPASS on two eight-core, 2.6 GHz processors. All ten runs returned the same structure: a crystal that is isostructural with $Li_5 Tl_2$ and $Li_5 Sn_2$ (Frank *et al.*, 1975; Stöhr & Schafer, 1979). The structural parameters of our proposed solution are listed in Table 1.

We were able to verify that our structure matches other quantitative characteristics determined by the original investigators. According to W&S, the $Na_5 Pb_2$ structure should have six atoms on the lines $[0, 0, z]$, $[\frac{1}{3}, \frac{2}{3}, z]$ and $[\frac{2}{3}, \frac{1}{3}, z]$ (Weston & Shoemaker, 1957). Our final structure satisfies this geometric constraint. However, we should note that every structure that matches the number of atoms in the unit cell, Pb positions and space group from W&S automatically fits this requirement. W&S also proposed that this structure is a supercell of body-centered cubic (b.c.c.), which we were able to confirm using the newly solved Na positions. We found that the (110) plane of this structure is parallel to the (110) plane of the underlying b.c.c. lattice, which has a lattice parameter of $a \sim 3.9$ Å. While each Pb atom in the structure features exactly one Pb nearest neighbor (as originally suggested by W&S), the structure features Na atoms with between zero and four Pb nearest neighbors.

As a further test of our solution, we performed a test where we provided FPASS with a space group of lower symmetry than that which was determined experimentally ($P\bar{3}m1$) and a second test where no symmetry information was provided. By easing the symmetry requirements, we allow the algorithm to test a larger number of possible configurations to see whether there are any lower-energy solutions that do not fit all of the provided constraints. Even though it was possible for Na atoms to be located off the lines predicted by W&S in these tests, the FPASS result in both cases was identical to the result found when FPASS was provided with full symmetry information. Finding the correct structure in these cases both supports the space-group determination of W&S and demonstrates how FPASS can be used with incomplete symmetry information. We also found that FPASS predicts the same structure when the Pb positions from W&S were not used and the space group was assumed to be $R\bar{3}m$. As with the tests with reduced symmetry information, finding the same structure as the fully constrained test supports our conclusion that we have found the correct structure for the δ phase.

The fact that FPASS returns the same structure in each test shows that the algorithm is capable of finding the solution even with limited initial data. However, the real advantage of being able to employ already known information about a crystal in FPASS is reduced computational time. When using only the Pb positions and lattice parameters, a single FPASS calculation to solve this structure requires approximately

10.5 h of computing time. By incorporating only lattice parameters and symmetry (*i.e.* no Pb positions), the required time decreases to 1.3 h. If we provided FPASS with all of the known information about the structure, we could increase the speed of the solution to only 22 min per calculation – an acceleration of over $30\times$ the test without symmetry information and $3.5\times$ faster than without Pb positions.

4.2. γ Phase

The crystal structure of the γ phase was determined by W&S to have the symmetry group of $P6_3/mmc$ (194) and a stoichiometry of $Na_{13}Pb_5$ with 36 atoms in the unit cell when all sites are fully occupied. Additionally, they were able to determine the positions of all ten Pb atoms. In this work, we completed the description of this structure by solving for the lowest-energy positions of the Na atoms in structures that fit these constraints using FPASS (see Fig. 1a and Table 1). Three out of ten FPASS calculations found this structure, which had the lowest DFT energy of all candidate structures for this phase. Each solution required, on average, 6 h on two eight-core, 2.6 GHz processors.

We were able to validate our solution using a few characteristics of the structure that were determined by W&S: (i) 12 atoms exist along the $[0, 0, z]$, $[\frac{1}{3}, \frac{2}{3}, z]$ and $[\frac{2}{3}, \frac{1}{3}, z]$ lines through the unit cell, and (ii) four-fifths of the Pb atoms have exactly one Pb nearest neighbor. Our structure meets both criteria. The second criterion is satisfied by the Pb positions provided as input to FPASS, and our proposed solution trivially meets this requirement as a result. In contrast, the fact that our structure satisfies the first criterion (which was not predetermined by the input parameters) shows that our solution matches the experimental data first determined by W&S and provides validation of the structure's accuracy. We found that this structure, like the δ phase, is based on a distorted b.c.c. superstructure, as was originally hypothesized by W&S. In this case, the lattice is not only distorted but also contains a defect from the ideal lattice, as shown in Fig. 2.

There is no other structure in the ICSD that has the same stoichiometry ($A_{13}B_5$), number of atoms in the unit cell (36) and space group ($P6_3/mmc$) as the one found we found. The
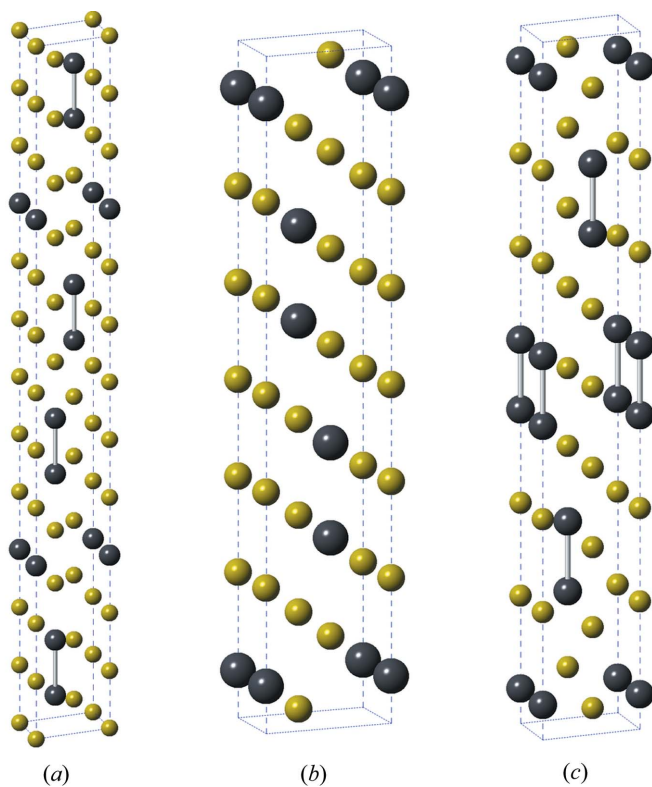

Figure 1
Proposed solution for (*a*) γ, (*b*) δ and (*c*) δ', as determined using FPASS. As hypothesized by Weston & Shoemaker (1957), atoms lie along the $\langle 0, 0, z \rangle$, $\langle \frac{1}{3}, \frac{2}{3}, z \rangle$ and $\langle \frac{2}{3}, \frac{1}{3}, z \rangle$ lines in all three cases.
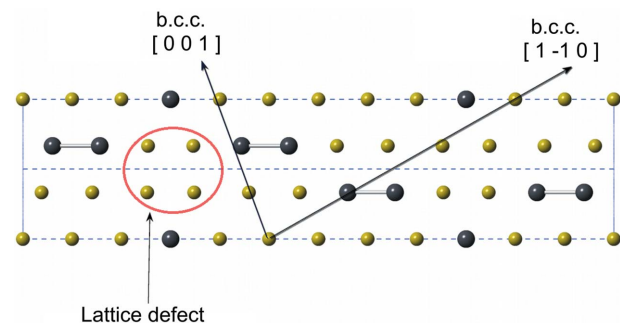

Figure 2
(110) plane of the γ structure. The black lines indicate the approximate [001] and [1$\bar{1}$0] directions in the underlying Na b.c.c. lattice, which is heavily distorted by the presence of the Pb atoms. The region containing a defect from this b.c.c. lattice is indicated with a red ellipse.

only other structure with $A_{13}B_5$ stoichiometry that matches the second criterion (80% of the Pb atoms present in pairs) given by W&S is that of $Li_{13}Sn_5$, which was found to be nearly degenerate ($\sim$2 meV per atom lower in energy) with the γ structure we determined (with Na/Pb replacing Li/Sn). However, the space group of $Li_{13}Sn_5$ and the positions of the Pb atoms are different than found by W&S. Additionally, while the $Li_{13}Sn_5$ structure is also a superstructure of b.c.c. (Frank & Müller, 1975), it lacks the deviation from perfect packing found in our solution. Assuming that the original space-group determination was correct, the solution of the γ-phase structure shows the unreliability of simply relying on energy and searching only known prototypes when solving a crystal structure. Had we relied only on evaluating the energy of known structures, we would have incorrectly concluded the $Li_{13}Sn_5$ structure was the solution for the γ-phase structure.

4.3. δ' Phase

The δ' phase is stable at low temperatures and has a composition of Na_9Pb_4. The space group of its structure ($P6_3/mmc$), lattice parameters and Pb positions were determined by W&S and we found the Na positions using FPASS. Our solution for the structure of δ', shown in Fig. 1(c) and Table 1, fits the descriptions supplied by W&S: eight atoms along the $[0, 0, z]$ line, nine atoms along the $[\frac{1}{3}, \frac{2}{3}, z]$ and $[\frac{2}{3}, \frac{1}{3}, z]$ lines, and all Pb atoms have exactly one Pb nearest neighbor. Each solution required, on average, 1.6 h on two eight-core, 2.6 GHz processors. Four out of ten FPASS solutions found the same ground-state structure. Our proposed solution for δ' is not isostructural to any other phase in the ICSD, so simply searching a database of known crystal structure prototypes would have failed to correctly solve this compound. The other A_4B_9 hexagonal crystals in the ICSD do not match the criteria given by W&S and, according to DFT calculations, are higher in energy by at least 100 meV per atom than our solution.

Recently, Ellis et al. proposed that δ' has the orthorhombic $Na_{13}Sn_5$ structure (which has a fully occupied stoichiometry of A_4B_9) – a distorted version of our solution (Ellis et al., 2014). In order to determine whether this distortion is real or just an artifact of an incomplete structure refinement from X-ray data, we first relaxed the atomic positions and lattice parameters of the Ellis et al. structure to their minimum DFT energy values. Then, we adjusted the atomic positions in the structure so that they matched the positions of our higher-symmetry solution. Next, we calculated the energy of several structures whose atomic positions interpolated between those of our higher-symmetry structure and Ellis's solution. As shown in Fig. 3, we found that our structure is more stable and that the energy of the structure increases with larger displacements. Consequently, we conclude that the structure proposed by Ellis et al. is dynamically unstable and that our solution – an undistorted version of the $Na_{13}Sn_5$ structure – is a better representation of the δ' phase.

4.4. $T = 0$ K Na–Pb ground-state phase diagram

As an additional step of validation, we compared the energy of each structure at 0 K (computed using DFT) to that of every other known compound in the Na–Pb binary system. The energies of the other compounds (Na, $Na_{15}Pb_4$, NaPb, $NaPb_3$ and Pb) were taken directly from the OQMD or computed using its associated toolkit (Saal et al., 2013). The DFT-calculated formation enthalpies are shown in Fig. 4 along with the convex hull (solid black line), which represents the
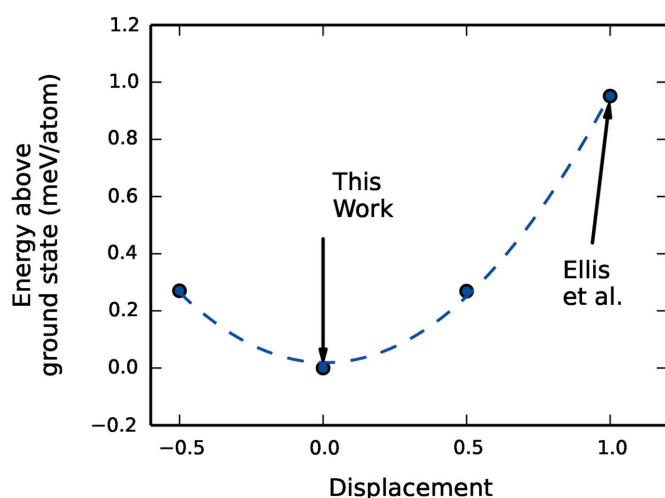

Figure 3
DFT energy of structures that interpolate between the structure for δ' determined in this work and a distorted version proposed by Ellis et al. (2014). A displacement of 0.0 corresponds to our hexagonal solution, and 1.0 to the orthorhombic structure of Ellis et al. Energy is shown to increase with displacement, which demonstrates that the structure proposed by Ellis et al. is dynamically unstable.
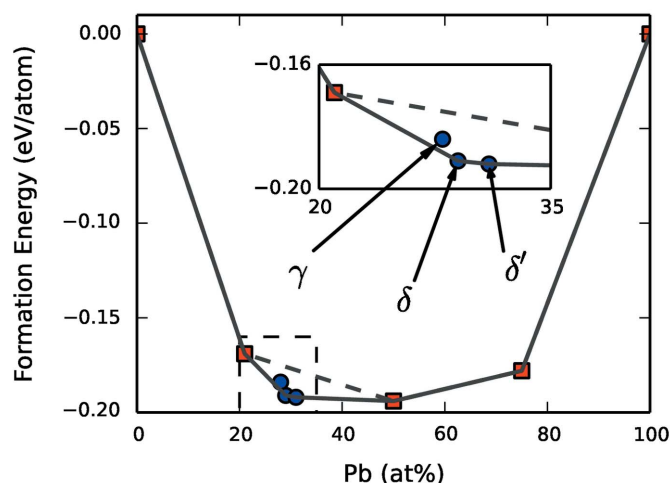

Figure 4
Phase diagram of Na–Pb calculated using DFT showing the formation energies of compounds with already known structures (red squares) and those solved in this work (blue circles). The solid line indicates the convex hull for this system. The dashed line represents the convex hull before introducing the compounds solved in this work. The region highlighted by the inset is shown in black dashed lines. All three of the structures that were solved in this work were found to be either stable (i.e. on the solid black line) or close to it, which suggests they are energetically feasible.

energy of the lowest-energy combination of phases at a certain composition.

Two of the three proposed structures (δ and δ') are stable at 0 K with respect to any combination of all other known phases. Since the δ' phase is known to be stable at low temperatures, the fact that we found its structure to be the 0 K ground state supports the assertion that we have found the correct structure. The δ phase is only known to be stable at elevated temperatures and is observed to exist at an off-stoichiometric composition near $Na_{0.69}Pb_{0.31}$. We did find this structure to be stable at 0 K at its stoichiometric composition of Na_5Pb_2, which suggests that it is energetically feasible for it to form at high temperature. The fully occupied structure of the third phase, γ, was found to be unstable at 0 K, which is consistent with the fact that it is only known to be stable at high temperatures, and it is observed to have a composition of Na_5Pb_2. Even so, the γ-phase structure is only unstable by 4 meV per atom, which is not unfeasibly large. Given that kT at room temperature is around 25 meV per atom, it is possible for γ to be stabilized by entropic contributions to the free energy at modest temperatures. As a result, we conclude that our solution for the structure of the γ phase is also energetically reasonable.

Finding additional stable compounds in the Na–Pb system affects the calculated phase diagram and the corresponding chemical potentials in that composition region, which affects both the accuracy and feasibility of atomistic simulation-based studies. For example, these chemical potentials are of great importance when determining defect energies with DFT – calculations which have been used to guide the doping of Na into PbTe thermoelectric materials (He *et al.*, 2012). Additionally, Pb has recently been studied as a possible anode material for non-aqueous sodium-ion batteries (Ellis *et al.*, 2014). A more complete database of Na–Pb structures now makes it possible to study electrochemical reactions in this battery system with atom-scale modeling.

5. Advantages of constraining structure search

The solution of the Na–Pb compounds in this work demonstrates that FPASS is a suitable tool for solving crystal structures when limited information about the structure is already available and, in general, highlights the advantages of constraining a CSP algorithm using that information. While originally designed to solve structures given diffraction data, we have shown that FPASS is robust enough to solve structures lacking this information and, in some cases, even lacking complete symmetry information about the structure. Furthermore, we found that it is possible to solve the structure of phases that are only stable at high temperatures using FPASS, as demonstrated by the solution of the structure of the γ phase. By restricting the search to only structures that match experimental measurements, spurious solutions that happen to be lower in energy at 0 K are avoided – which could be a recurring problem during the solution of high-temperature phases (as suggested by the solution of the structure of the γ phase).

The solution of the Na–Pb compounds in this work also highlights the deficiencies of using crystal structure prediction techniques that do not enforce consistency with experimental observations. In the solution of the structure of the γ phase, a prediction method that only considers energy would have found the $Li_{13}Sn_5$ structure because it is lower in energy, even though this structure does not match the experimentally determined space group. Additionally, by constraining based on space group and lattice parameter, the next lowest energy solution is at least 50 meV per atom higher in energy than the best solution in each case, which is sufficiently large to confidently select that solution as the true ground state. In contrast, finding several, nearly degenerate ground states (*e.g.* at least $Li_{13}Sn_5$ and our solution when solving γ) would complicate selecting the true solution.

Furthermore, techniques that do not consider already available information about a crystal structure could be drastically slower. As an example, the solution of the δ structure required 30× more time when the experimental symmetry group was not used – and this figure would only increase if the Pb positions and lattice parameters were also ignored. These results suggest that constraining a structure search using symmetry and known positions could have performance benefits in other methods.

6. Conclusion

In this work, we demonstrate how the First-Principles Assisted Structure Solution (FPASS) method can be used to solve incompletely determined crystal structures. In particular, we used FPASS to solve the structures of three Na–Pb compounds (γ, δ and δ') that had remained unsolved since 1957 (Weston & Shoemaker, 1957). Through these solutions, we show that FPASS is able to solve structures that are unstable at 0 K and can be used to determine the correct structure even with incomplete symmetry information and without a diffraction pattern.

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