High-Pressure Synthesis: A New Frontier in the Search for Next-Generation Intermetallic Compounds

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CONSPECTUS: The application of high pressure adds an additional dimension to chemical phase space, opening up an unexplored expanse bearing tremendous potential for discovery. Our continuing mission is to explore this new frontier, to seek out new intermetallic compounds and new solid-state bonding. Simple binary elemental systems, in particular those composed of pairs of elements that do not form compounds under ambient pressures, can yield novel crystalline phases under compression. Thus, high-pressure synthesis can provide access to solid-state compounds that cannot be formed with traditional thermodynamic methods. An emerging approach for the rapid exploration of composition−pressure−temperature phase space is the use

of hand-held high-pressure devices known as diamond anvil cells (DACs). These devices were originally developed by geologists as a way to study minerals under conditions relevant to the earth's interior, but they possess a host of capabilities that make them ideal for high-pressure solid-state synthesis. Of particular importance, they offer the capability for in situ spectroscopic and diffraction measurements, thereby enabling continuous reaction monitoring—a powerful capability for solid-state synthesis. In this Account, we provide an overview of this approach in the context of research we have performed in the pursuit of new intermetallic compounds. We start with a discussion of pressure as a fundamental experimental variable that enables the formation of intermetallic compounds that cannot be isolated under ambient conditions. We then introduce the DAC apparatus and explain how it can be repurposed for use as a synthetic vessel with which to explore this phase space, going to extremes of pressure where no chemist has gone before. The remainder of the Account is devoted to discussions of recent experiments we have performed with this approach that have led to the discovery of novel intermetallic compounds in the Fe−Bi, Cu−Bi, and Ni−Bi systems, with a focus on the cutting-edge methods that made these experiments possible. We review the use of in situ laser heating at high pressure, which led to the discovery of $FeBi_2$, the first binary intermetallic compound in the Fe−Bi system. Our work in the Cu−Bi system is described in the context of in situ experiments carried out in the DAC to map its high-pressure phase space, which revealed two intermetallic phases ($Cu_{11}Bi_7$ and CuBi). Finally, we review the discovery of β-NiBi, a novel high-pressure phase in the Ni−Bi system. We hope that this Account will inspire the next generation of solid-state chemists to boldly explore high-pressure phase space.
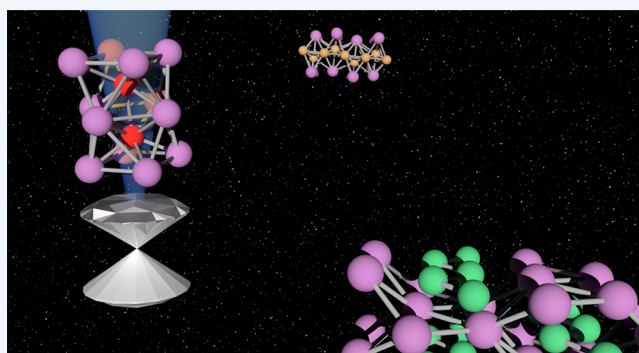
■ PRESSURE IS THE NEW TEMPERATURE

The pressure scale of the universe is vast, spanning around 50 orders of magnitude. The lowest measurable pressure exists in the intergalactic voids, where values are on the order of 10^{-26} GPa. On Earth, pressure ranges from 10^{-4} GPa at the surface to around 360 GPa at the core. Moving beyond Earth and into our solar system, Jupiter, the most massive planet, has a core pressure of around 4000 GPa, while the pressure at the core of our sun is 2.6×10^7 GPa. The highest calculable pressure in the universe is that at the center of a neutron star,[1] where the pressure is on the order of 10^{25} GPa (Figure 1).

Despite this enormous range, virtually all synthetic chemistry is carried out in a relatively narrow region of pressures. For many chemists, the phrase "high pressure" invokes the Haber−Bosch process (3×10^{-3} GPa) and steel autoclave reactions (10^{-2} GPa). However, pressures on the order of 10^2 GPa are now readily achievable with specialized equipment such as multianvil presses (MAPs)[2] and diamond anvil cells (DACs).[3] These additional 4 orders of magnitude greatly extend our reach into composition−pressure−temperature phase space and bring within our grasp chemical phases that simply do not form at lower pressures but often form quite readily under compression.

In the context of solid-state chemistry and, in particular, the synthesis of intermetallic compounds, the potential of high
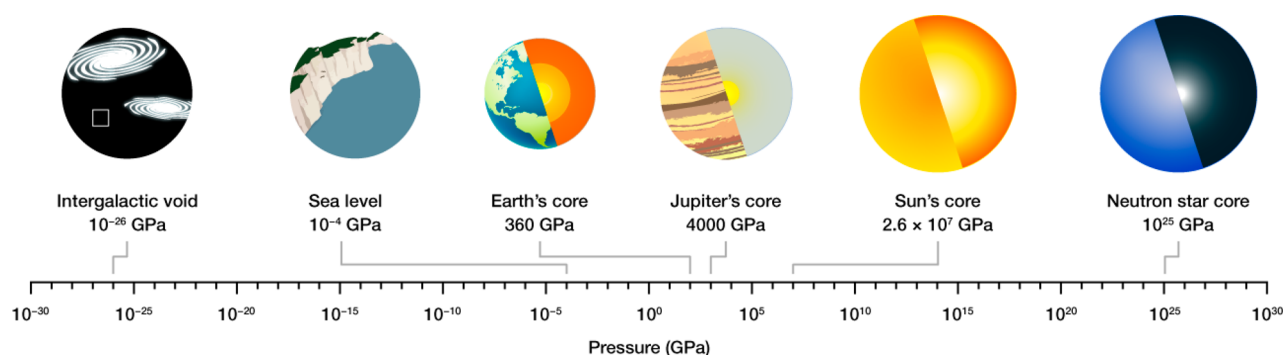
Figure 1. Scale of the pressures found throughout the universe. The range of pressures spans roughly 50 orders of magnitude, and yet most chemistry is performed below 10^{-2} GPa. We are using DACs to explore the effect of extreme pressures on the ability to synthesize intermetallic compounds.

pressure has been recognized for decades.[4−7] As an illustrative example, we can consider the A_3B family of superconductors.[8] Interest in these compounds flourished in the 1950s after the discovery of superconductivity at relatively high temperatures in the A_3B compounds V_3Si (T_c = 17 K)[9] and Nb_3Sn (T_c = 18 K).[10] Although a large number of vanadium and niobium compounds in the same structure type were pursued and isolated in the years that followed these initial discoveries, many of the targeted compounds remained inaccessible by conventional solid-state methods. The challenge was eventually surmounted using high pressures and temperatures (2−7 GPa, 800−2200 °C) to isolate some of the undiscovered compounds.[11] It is worth noting that although high pressures were required to access these compounds, they remained stable (technically *metastable*) after decompression back to ambient conditions. Indeed, it is not uncommon for high-pressure phases to remain intact after the pressure and temperature are quenched, and a subset of these compounds can persist indefinitely, with diamond being a prominent example of such a material. Thus, high-pressure synthesis is not merely a way to detect nonambient phases; it can be a viable method for the ambient-pressure isolation of kinetically stabilized phases.

In an era where many in the field of solid-state chemistry are turning their attention toward metastable materials, high pressure is a promising and underused vector, especially considering how straightforward it is to equip a solid-state synthesis laboratory with high-pressure apparatus. A single DAC, along with multiple diamond anvils and all of the consumables required for dozens of reactions, has a cost comparable to that of a conventional tube furnace and its accompanying consumables. Furthermore, the footprint of a DAC is about the size of a coffee mug. The main drawback of DACs is the inherently small sample size, which is miniscule compared with those used in MAPs. However, the sample sizes are appropriate for in situ methods, especially those using high-brilliance high-focus beamline techniques, laboratory-based lasers, and current-generation silver microsource diffractometers. Indeed, such methods are being used to discover exotic metastable phases across a variety of chemical systems, including hydrides,[12−17] nitrides,[18−22] carbides,[23−26] high-density C−N−H compounds,[27,28] and even intuitively impossible compounds such as the recently discovered $XeFe_3$ and $XeNi_3$ binaries.[29]

In this Account, we will describe our research using DACs for the rapid exploration of high-pressure synthetic phase space in binary elemental systems and demonstrate how it has

enabled the discovery of novel intermetallic compounds in elemental systems that previously had none.

■ THE NEXT GENERATION OF SOLID-STATE SYNTHESIS

The creation of new binary intermetallic compounds is foundational for discovery and technological growth, given that they underpin our global infrastructure. Wind energy is harnessed by turbines that rely on intermetallic permanent magnets, medical imaging technology is enhanced by intermetallic superconductors, and the electronics industry is advanced through the incorporation of new intermetallic compounds.[30]

Historically, transformative advances in materials science have been enabled by the discovery of new compounds with unprecedented bonding and/or structure. Inspired by this, we and others are pursuing the discovery of new binary intermetallic compounds in search of fundamentally novel chemical interactions, with an emphasis on the isolation of binary compounds in systems with no known intermetallics, since these compounds offer a unique opportunity to study fundamentally new chemical interactions.

Our primary focus is the creation of new binary compounds incorporating bismuth. Bismuth, which is the heaviest element stable toward radioactive decay ($t_{1/2}$ = 1.9 × 10^{19} years[31]), offers tremendous promise for creating exotic materials. Many classes of emergent materials rely on spin−orbit coupling to realize their unusual properties. Since spin−orbit coupling increases with Z_{eff}^4, bismuth is perfectly positioned to serve as a source of orbital angular momentum. Indeed, several ambient-pressure phases incorporating bismuth serve as excellent proofs of concept for this idea. Most prominent are the topological insulator Bi_2Te_3[32] and the permanent magnet $MnBi$.[33] The key factor enabling both of these phenomena is orbital angular momentum. In the former it leads to a band inversion, thereby enabling surface-trapped states, while in the latter it gives rise to a high coercivity, leading to a wide hysteresis loop and in turn to more desirable magnetic properties. Outside of explicit contributions from orbital angular momentum, binary compounds of bismuth offer additional promise for alternate applications, such as superconductivity in $NiBi$[34] and $NiBi_3$[35] and thermoelectric behavior in Bi_2Se_3.[36]

We are primarily focused on systems with no known intermetallic compounds and in some instances with no known bonds between the given pair of elements in the solid state. Within this framework, we can separate our research into three

subclasses, delineated by the location of the second element within the periodic table (Figure 2).

Figure 2. Periodic table with regions highlighted to illustrate the classes of compounds we are targeting for bismuth binaries. Notable compounds from each class are shown below the table, as discussed in the main text.

Our primary interest is in creating bismuth–magnetic first-row transition metal binary compounds. Specifically, we seek to integrate bismuth with spin-bearing metals to induce an orbital moment at the spin center through reconstitution of the separated spin and orbital angular momenta. By coupling the spin of a transition metal (S) with the orbital angular momentum of bismuth (L), we hope to create a ground-state total angular momentum (J) term. By engendering a powerful spin–orbit-coupled moment, it may be possible to create hard magnetic materials of technological importance. Toward those ends, open-shell mid-transition metals are our targets of interest.

A second class of materials of interest to us are bismuth–main group binary compounds. A particularly noteworthy compound in this class is bismuth telluride, Bi_2Te_3—a widely studied thermoelectric material and topological insulator.[16,20] The recent discovery of superconductivity in $Cu_xBi_2Te_3$—where the copper atoms intercalate between the $\{Bi_2Te_3\}$ layers—suggests that materials could be engineered to house physical interfaces between seemingly disparate emergent physical phenomena.[37] Thus, new metastable compounds in these systems could exhibit similarly exciting topological properties involving novel emergent phenomena.

A subclass of compounds within the class of main group binaries are the alkali/alkaline-earth metal binaries of bismuth. The A_3Bi alkali metal pnictides exhibit unusual electronic properties that include protected three-dimensional Dirac states[38,39] and transformations from Dirac semimetals to trivial insulators.[40] Having such a range of exotic phenomena within a small area of phase space offers tremendous promise for future exploration.

A third class of interest are the binary compounds of late transition metals and bismuth. This class of compounds, as mentioned above, are promising candidates for superconductivity since the presence of bismuth is known to engender nonconventional and topological superconductivity. Such compounds can also inspire the future synthetic design of undiscovered bismuth-based pnictide superconductors that would be of urgent interest to the scientific community. Furthermore, the potential to create exfoliable phases offers

promise for the development of new low-dimensional materials with exotic properties.

The creation of novel phases within this unexplored phase space of bismuth binary compounds is enabled by the application of high pressure, which can be envisioned as an added dimension in the phase diagram, as depicted in Figure 3.
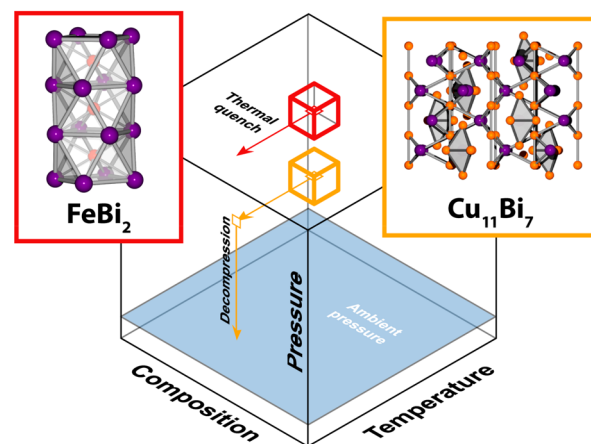

Figure 3. Phase space opened up by the addition of pressure as an experimental variable, with the phase area accessible by traditional solid-state chemistry highlighted in blue. Arbitrary regions of phase space (boxes) can be accessed using a specific combination of composition, temperature, and pressure, sometimes yielding new intermetallic compounds. In some cases, thermal quenching and decompression steps can then be used to recover the phase to ambient conditions.

One can consider an arbitrary region of unexplored phase space that can now be accessed using a combination of composition, temperature, *and* pressure. Our exploration of phase space has so far enabled us to synthesize a number of novel intermetallic compounds, some of which have formed in binary systems having no known intermetallic phases at ambient pressure. In this Account, we will describe the synthesis of the first intermetallic compounds in the Fe–Bi and Cu–Bi systems as well as the discovery of a new high-pressure phase in the Ni–Bi system. This research will be described through the lens of the diamond anvil cell, which can be viewed as a new form of synthetic vessel with potential wide applicability within the solid-state and materials synthesis communities.

■ USING THE DAC AS A NEW SYNTHETIC ENTERPRISE

Our synthetic vessel of interest, the diamond anvil cell, can be traced back to the invention of the opposed-anvil device by Percy Bridgman in the early 20th century.[41] Although numerous refinements and redesigns have been made in the decades since, the fundamental concept has remained the same.[42] The basic principle of the cell is to drive two large single-crystal diamonds into each other. The diamonds are cut in such a way that they have an extremely small circular facet at the base of the pavilion, known as the culet facet, and these facets act as the contact points between the diamonds. The small sizes of the culets, which are on the order of 0.1−1 mm in diameter, enable the application of very high loads across an area much less than 1 mm^2, resulting in extremely high pressures across a sample held at the contact point. To prevent

the sample from being squeezed out of the space between the diamonds and to enable a more uniform pressure, a gasket with a circular hole smaller in diameter than the culet faces is placed between the diamonds. The sample to be pressurized is then loaded inside the laser-drilled[43] gasket hole, which collapses inward as the load on the diamonds is increased.

Reimagining the DAC as a vessel for solid-state synthesis (Figure 4), one can consider the DAC sample space as a
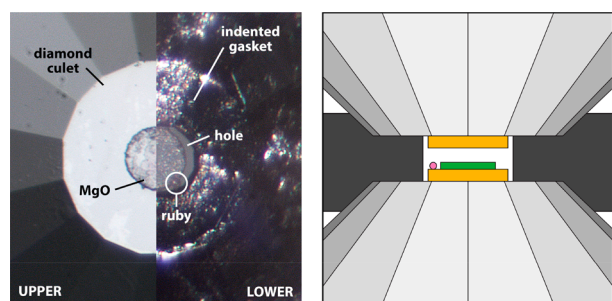

Figure 4. Sample space preparation for laser heating synthesis experiments. Left: composite photograph showing both anvils of an open DAC loaded with laser-cut MgO discs on each side. Right: side-view schematic of a closed cell. MgO discs (yellow) sandwich the sample (green). Ruby spheres (pink) are often included as pressure calibrants because of the known dependence of their fluorescence lines on pressure.

cylindrical vessel having diamond surfaces as the top and bottom and gasket material (e.g., steel or rhenium) as the sides. In a practical sense, this is essentially identical to the sample environment in the sealed reaction vessels commonly used in solid-state reactions, where the vessel walls are also made from comparatively inert materials such as platinum or fused silica. From this perspective, a DAC reaction is simply a miniaturized version of a conventional sealed-tube reaction, where the major difference is the ability to considerably reduce the sample volume to induce high pressures.

The DAC is a modular piece of equipment with interchangeable anvil sizes, support seat dimensions, and gasket materials, thus enabling a range of target experimental conditions. To permit anaerobic chemistry, we fabricate laser-cut discs of magnesium oxide that can be set into place within the sample space prior to glovebox loading (Figure 4), leaving only the final sample loading step to be performed in the box itself.

As the sample hole collapses during pressurization, the MgO fills the sample space, surrounding the sample and acting as the pressure-transmitting medium. There are additional specific benefits of using MgO for chemical synthesis: (i) it exhibits transparency under pressure, enabling optical access during experiments and thus facilitating laser heating; (ii) it acts as a reliable in situ pressure calibrant on account of its well-known equation of state;[44] (iii) it is thermally[45] and structurally[46] stable up to extremely high pressures, limiting its participation in reactions; and (iv) it provides excellent thermal insulation between the heated sample and the highly thermally conductive diamond anvils. Full details of the MgO disc creation procedure can be found elsewhere.[47]

Diamonds are the anvil material of choice because of their exceptional hardness, which allows them to survive very large loads without breaking. An incidental benefit of diamond is its transparency, which facilitates in situ measurements by allowing the sample space to be easily located and tracked using optical

methods as well as allowing for laser irradiation heating methods. Indeed, this transparency gives DACs a unique advantage over conventional solid-state synthetic approaches that rely on opaque containers and therefore do not offer the ability to monitor reaction progression. With the DAC method, it is possible to perform diffraction measurements even while one or more of the reactants are present as a molten flux.

In the context of intermetallic compounds, arguably the most powerful experimental technique for detecting the formation of new phases during heating is powder X-ray diffraction (PXRD), since this is a direct probe of the new crystalline domains that arise. Conveniently, DACs have been optimized over the years by geoscientists for the in situ collection of XRD data at high pressures and temperatures, and the development of in situ laser heating methods now enables us to simultaneously access wide ranges of temperature and pressure.

Chemical reaction is induced through laser heating, where the sample space is irradiated with a high flux of photons. This is facilitated in the case of intermetallic reactions by the fact that metals generally couple well to the incident optical radiation. A major benefit of this approach is that a small spot size can be achieved with an optically focused laser, allowing us to attain tremendously high local temperatures on the scale of thousands of kelvins. The pressures required for reaction are usually a priori unknown and must be found experimentally by carrying out in situ heating at incrementally higher pressures. We typically use steps of 1−2 GPa during our explorations.

The increase in spatial resolution made possible by the highly focused X-ray probe and laser heating spot allows us to heat different regions of larger samples independently and at different cell pressures, yielding many data points in pressure−temperature phase space using only a single cell. This high-throughput approach, when combined with real-time feedback in the form of ultrafast XRD analysis, is particularly powerful as a method for the rapid exploration of phase space.

GOING BOLDLY WHERE NO CHEMIST HAS GONE BEFORE

Iron−Bismuth: FeBi$_2$

In the search to create new magnetic binary compounds, iron is the most intuitive candidate for a spin-bearing metal. Throughout recorded history, iron has been featured in magnetic materials, from the once mystifying magnetic properties of lodestone (naturally magnetized Fe_3O_4) to the more recent incorporation of iron in our strongest permanent magnet material, $Nd_2Fe_{14}B$. Within our goal of harnessing bismuth's orbital angular momentum in conjunction with spin from a transition metal, iron is the ultimate candidate metal.

The study of iron−bismuth intermetallic compounds is stymied by the absence of stable intermetallic compounds within the iron−bismuth system at ambient pressure.[48] Even more remarkably, Fe−Bi bonds are completely absent from the solid state. The closest Fe−Bi interaction in any solid-state compound is that in $BiFeO_3$, where the two atoms lie on distinct coordination sites within the perovskite structure and are considered nonbonding. This lack of reactivity is reflected in the Fe−Bi temperature−composition phase diagram, which reveals an almost complete lack of miscibility of the two elements even up to the highest measured temperatures. In other words, even as molten liquids, iron and bismuth are immiscible. Given the propensity of bismuth to form compounds with exotic bulk properties and our desire to

seek out new magnetic or superconducting properties, we pursued the hitherto elusive iron–bismuth intermetallics.

We explored the reactivity of iron and bismuth at elevated pressures using the laser-heated DAC approach outlined in the previous section as our synthetic vector. Our experimental strategy was to take a pressed flake of 1:1 Fe/Bi to incrementally higher pressures, laser-heat the sample at each pressure step, and monitor the XRD pattern in real time. The laser power was controlled remotely, and spectral imaging of the sample space allowed for the determination of the sample temperature by fitting the optical emission from the glowing sample to the Planck function.

Figure 5 shows the XRD data collected and visualized in real time during laser heating in the Fe–Bi system. The experiment
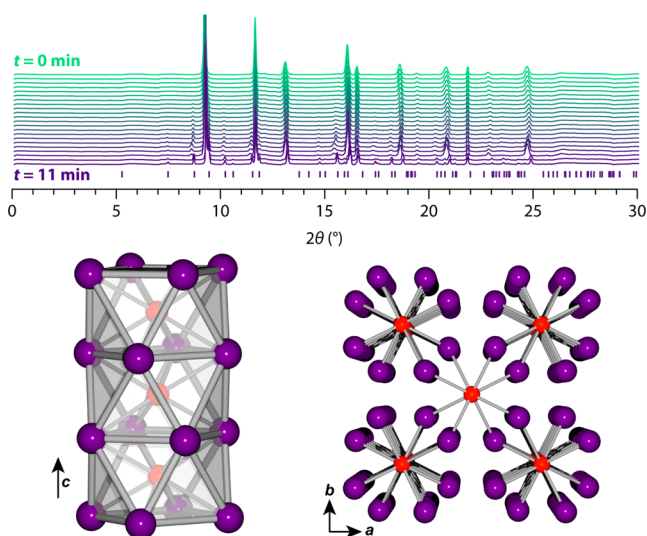

Figure 5. Top: Real-time XRD patterns collected during the laser heating experiment that led to the discovery of $FeBi_2$ ($\lambda = 0.40663$ Å). The sample was at 32.2 GPa and held at 1400 K. The synthesis of the new phase was signaled by the appearance of new diffraction peaks over time (positions indicated by purple ticks below the plots). Bottom: Crystal structure of $FeBi_2$, showing the connectivity between iron (red) and bismuth (purple) atoms.

was run on beamline 16-ID-B of HPCAT at the Advanced Photon Source, which is optimized for exploratory synthesis reactions in the DAC and is equipped with a double-sided laser heating system that uses two independent YLF:Nd lasers (1053 nm) with a total operating power of 170 W.[49,50] The stacked PXRD plots show the evolution of the background-corrected diffraction patterns over time while the sample temperature was held at 1400 K under a pressure of ~32 GPa. The exposure time for each pattern was 1 s, with a delay time of 10 s between each collection. The data were integrated and visualized automatically using the Dioptas software package,[51] providing real-time feedback on the reaction progress.

The starting XRD pattern was that of the reactants (in this case the high-pressure polymorphs of bismuth and iron: Bi(V) and ε-Fe) as well as the MgO pressure medium. As the laser power was increased, the temperature at the heating spot began to rise, and after the sample was held at 1400 K for a few minutes, new peaks began to appear in the XRD pattern (new phase peak positions are indicated by vertical purple bars below the plots). Because of the real-time nature of the experiment, we knew within a matter of seconds that we were at reaction conditions, and we chose to hold the temperature steady to

allow the reaction to proceed. Once the peaks for the new phase were no longer growing in intensity, we thermally quenched the reaction by cutting the power to the lasers.

The use of in situ XRD as described above is a demonstration of how powerful this method is for exploring the new phase space opened up by pressure. The ability to quickly vary both pressure and temperature allows us to visit multiple *PT* coordinates within minutes of each other, and real-time diffraction enables us to rapidly detect the formation of any crystalline products as we enter conditions favorable to reaction.

The new peaks that we observed at 32 GPa and 1400 K were readily indexed in space group $I4/mcm$ with parameters $a = 6.3121(3)$ Å and $c = 5.4211(4)$ Å. These are a match for the Al_2Cu structure type, and Rietveld refinement confirmed that the new phase is $FeBi_2$. The iron atoms are coordinated by eight bismuth atoms in a square-antiprism arrangement, with these prisms stacking along the c axis to form columns (Figure 5). The Fe–Bi distance at 30 GPa is 2.72 Å, while the Bi–Bi interaction between the columns is 2.95 Å. Both of these interactions are within the expected range for a bonding interaction and are likely important in stabilizing this structure.

One experiment we can readily perform on phases synthesized in the DAC is to see how the lattice parameters vary as a function of pressure; this allows us to assess the compressibility of the compound, which is an indirect measure of the strength of the bonding network. Plotting the lattice parameters of $FeBi_2$ as a function of pressure after decompression down to ambient pressure reveals that the structure is more compressible along the a and b axes than along the c axis, as is typical for this structure type.[52] However, the overall compressibilty is significantly lower than would be expected from the trend of the iron–pnictide $FePn_2$ binaries, possibly as a result of the relativistic effects in bismuth. Our current efforts are focused on isolating this compound under ambient pressure and performing in situ methods of characterization under very high pressure so that we can examine the magnetic and electronic structure of this exotic compound.

Copper–Bismuth: $Cu_{11}Bi_7$ and CuBi

A promising candidate for studying the impact of spin–orbit coupling on conduction electrons is the noble metal copper, whose $[Ar]3d^{10}4s^1$ electron configuration in the pure metal state enables superlative electrical conductivity.[53] Thus, binary intermetallics containing copper offer the opportunity to study the impact of heavy metals on free electron carriers. While copper is the canonical conductor, in its elemental form copper does not exhibit superconductivity,[54] yet in some systems it can lead to high-temperature superconductivity, most notably in the cuprates.[55] Fusing copper with bismuth thus offers the potential to create new superconductors, potentially including those with exciting topological properties.

The copper–bismuth system is similar to the iron–bismuth system in that it has no known stable intermetallic compounds under ambient pressures. However, unlike the Fe–Bi system, the Cu–Bi system exhibits miscibility of its liquid elements at modest temperatures (below 1100 K for 1:1 mixtures). We interpreted this miscibility as an indication that the reactivity of these two elements should be comparatively more favorable than in the Fe–Bi system, and indeed, we discovered that the first two intermetallic compounds in the Cu–Bi system— $Cu_{11}Bi_7$[56] and CuBi[57,58]—require much lower pressures than those required to synthesize $FeBi_2$.

We wanted to investigate the high-pressure phase diagram of the Cu−Bi system to gain deeper insight into the comparative stability of these two phases as a function of pressure and temperature. The DAC was the ideal vessel with which to perform the required in situ diffraction experiments since it allowed us to sweep the temperature at fixed pressures to detect phase boundaries.

Our experiments revealed that between 3.2 and 4.8 GPa and at temperatures below the melting point of bismuth, CuBi is the thermodynamically stable phase. The CuBi crystal structure can be described as a derivative of the NiAs structure type wherein an ordered vacancy of Cu chains leads to a layered structure (Figure 6, left). Each bonded layer can be described as a triangular 2D net of Cu atoms sandwiched between two rhombic 2D nets of bismuth.
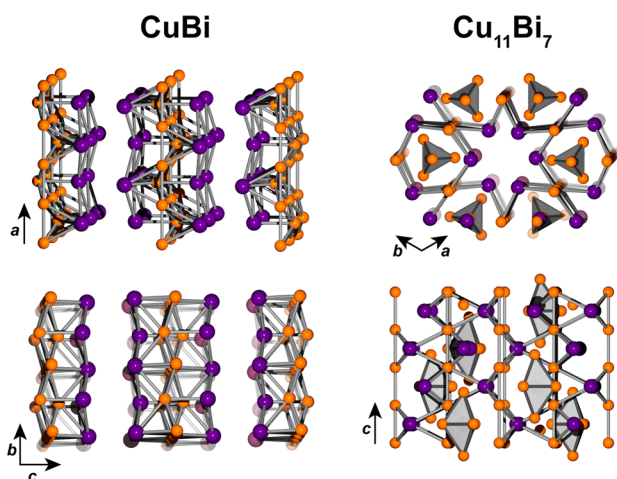

Figure 6. Crystal structures of CuBi and $Cu_{11}Bi_7$, showing the connectivity between copper (orange) and bismuth (purple) atoms. CuBi exhibits a clear partitioning of the elements into layers, with void planes existing between bismuth layers. In $Cu_{11}Bi_7$, a similar separation of the elements arises, with open bismuth channels running along the c axis and clustering of copper atoms into {Cu_5} moieties.

At 4.2 GPa and higher and at temperatures above the melting point of bismuth, $Cu_{11}Bi_7$ becomes the thermodynamically stable phase. The crystal structure of $Cu_{11}Bi_7$ is also derived from the NiAs structure type, but it is clearly much more complex, with bismuth sites sometimes being completely unoccupied to form channel voids along the c axis while at other times being replaced by unusual trigonal-bipyramidal {Cu_5} moieties (Figure 6, right).

Because these compounds can be synthesized at relatively low pressures (i.e., below 15 GPa), the reactions can be scaled up and performed in a multianvil press. This allows us to recover pellets of these compounds with sizes on the order of cubic millimeters, which in turn opens up the possibility of a number of bulk characterization methods. Performing the reaction in larger volumes also facilitates the growth and recovery of single crystals on the order of tens of microns in each direction, which is sufficient to perform single-crystal X-ray diffraction (SCXRD). Single crystals recovered from a MAP reaction of $Cu_{11}Bi_7$ were studied using conventional laboratory SCXRD, and weak first-order commensurate satellite reflections revealed that the crystal structure of $Cu_{11}Bi_7$ is actually even more complex than assumed from the initial in situ PXRD studies, with the {Cu_5} moieties and Bi atoms exhibiting an unusual ordering that results in a tripling along the b axis. This level of complexity is quite remarkable for a binary compound and hints at an untapped reservoir of structural diversity in other binary systems at higher pressures.

Larger sample sizes also permit the measurement of electrical resistivity, which for both compounds reveals type II superconductivity with T_c = 1.3 K (CuBi) and 1.36 K ($Cu_{11}Bi_7$).[32,35] These results add to the growing library of bismuth-containing superconductors and encourage further exploration of the Cu−Bi system.

Nickel−Bismuth: β-NiBi

Another powerful aspect of high-pressure research is the ability to capture and study phases that are accessible only under elevated pressures. The study of these nonequilibrium phases is reminiscent of the experiments performed by spectroscopists seeking to study reaction intermediates using ultrafast techniques. Indeed, we propose that extending the ability to measure intermediate states to the field of solid-state chemistry will lead to a deeper understanding of reaction kinetics in a field traditionally dominated by thermodynamic considerations. Toward this end, we investigated the Ni−Bi system to study the reaction dynamics in the transformation from one solid-state phase into another. Unlike the Fe−Bi and Cu−Bi systems, the Ni−Bi system forms intermetallic compounds under ambient pressures. The two known ambient-pressure compounds, NiBi[59] and NiBi$_3$,[60] are both superconducting, with T_c values of 4.25 K[18] and 4.06 K,[19] respectively.

We took a large single-crystal sample of NiBi and ground it to create an atomically mixed precursor. We then used this sample to perform in situ XRD studies in the Ni−Bi system at varying pressures and temperatures using the laser-heated DAC method.[61] At a pressure of 39.3(1) GPa and a temperature of around 700 °C, new diffraction peaks appeared that correspond to a new high-pressure phase of NiBi that we denote as β-NiBi (Figure 7). Peaks from β-NiBi grew at the expense of those of
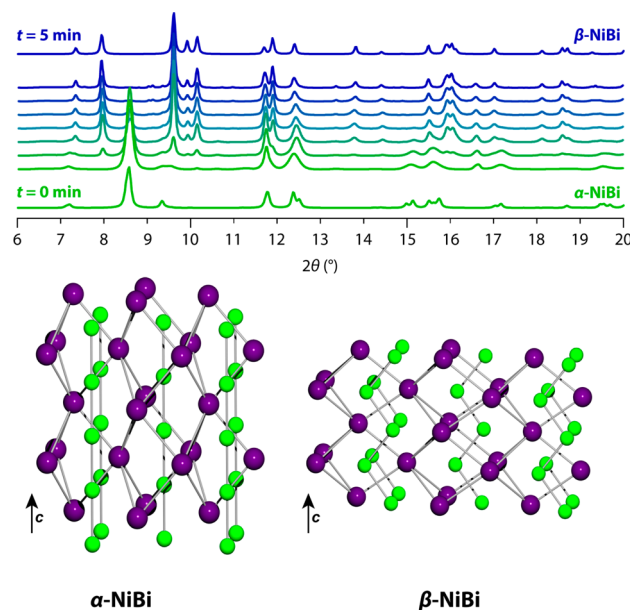

Figure 7. Top: Real-time in situ PXRD patterns showing the complete conversion of α-NiBi to β-NiBi while heating to 700 °C at a pressure of ~37−39 GPa (λ = 0.40663 Å). Bottom: Comparison of the crystal structures of α-NiBi and β-NiBi, showing the connectivity between nickel (green) and bismuth (purple) atoms.

the ambient-pressure phase—which we now denote as α-NiBi—and continued to grow until the phase had been completely converted (i.e., undetectable diffraction intensity from the α-NiBi phase). At this point the reaction was thermally quenched by turning off the lasers.

After cooling to ambient temperature, the pressure had dropped to 36.8(1) GPa, but the peaks from the new phase remained and could be indexed to the orthorhombic space group $Cmcm$ with lattice parameters $a = 3.3873(2)$ Å, $b = 9.4079(9)$ Å, and $c = 3.7587(2)$ Å. β-NiBi is modeled well in the TlI structure type ($B33$). Comparison of α-NiBi (commonly reported as NiAs-type, $B8_1$, but in reality a more complex modulated supercell thereof[62,63]) with β-NiBi (TlI-type, $B33$) suggests that a displacive transformation takes place at elevated pressures, with a buckling of the nickel chains (Figure 7, bottom). The phase transformation is reversible, with complete conversion back to the α-NiBi phase after decompression below 11.6(1) GPa. β-NiBi is the first binary pnictide compound to crystallize in the TlI type and the first example of a pressure-induced transition from $B8_1$ to $B33$. In view of the ubiquity of the NiAs type, these results have important implications for the ability to modify common structure types with the application of high pressures.

The fact that β-NiBi is nonquenchable means that in situ methods were crucial to its discovery, and the DAC was the ideal vessel with which to perform the experiment given that the target pressure was not already known. Rapid exploration of phase space in this manner is likely to lead to the discovery of many novel phases in systems that are currently considered to be well-explored. This is particularly exciting in the context of elemental systems that already exhibit compounds with remarkable properties.

■ CONCLUSIONS

The diamond anvil cell is an extremely powerful tool for the rapid exploration of pressure–temperature phase space in search of novel intermetallic compounds and is an indispensable asset to the adventurous solid-state chemist embarking on a journey into high-pressure phase space. We have provided examples of some of our early successes with this technique, outlining the discovery of new intermetallic compounds in a number of binary elemental systems. For the Fe–Bi and Cu–Bi systems, the uncovered compounds represent the first intermetallics in their respective classes and hint at the enormous promise of this method as a way to isolate families of currently "impossible" compounds. Future targets for our group include new bismuth binary compounds, specifically those involving the alkali/alkaline-earth and main group elements. We are also developing experimental methods that will allow us to target selected ternary compounds of interest.

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Notes

The authors declare no competing financial interest.

Biographies

James P. S. Walsh was born in Billinge, England. He carried out his undergraduate and postgraduate studies at the University of Manchester, receiving his Ph.D. in 2014 after working with Professors David Collison, Eric McInnes, and Richard Winpenny on a project studying magnetic exchange interactions between highly anisotropic ions in molecular nanomagnets. He was then a postdoc with Jacob Overgaard at Aarhus University in Denmark, where he worked on charge density studies of single-molecule magnets. In 2015, he moved to Northwestern University to work with Professor Danna Freedman, using molecular magnetism to perform a gravity assist into the field of solid-state chemistry. His current projects center on the high-pressure synthesis of novel intermetallic compounds.

Danna E. Freedman is an Assistant Professor in the Chemistry Department at Northwestern University. She began her scientific career as a high school student working at a local observatory. She was an undergraduate researcher in Prof. Hongkun Park's laboratory at Harvard University. She received her Ph.D. from UC Berkeley in 2009, where she studied magnetic anisotropy in molecules under the supervision of Prof. Jeffrey Long. She performed her postdoctoral research in Prof. Daniel Nocera's lab at MIT, probing geometric spin frustration in kagomé lattices. The Freedman laboratory's research focuses on applying inorganic chemistry toward questions in physics. Current research topics are magnetism, superconductivity, and quantum information science. Unsurprisingly, Danna enjoys the television show *Star Trek: The Next Generation*.

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