

A Pressurized Exploration of Intermetallic Chemistry

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Intermetallic phases have been known as a realm of “endless wonders”,¹ whose expansion can be tracked first through the thick volumes of *Pearson's Handbook of Crystal Data on Intermetallic Phases*² of the 1990s to online crystal structure databases whose scale is measurable only in disk space. The structural data in these resources has shaped many of our views about the solid state. For example, we consider some elements such as bismuth and indium being relatively unreactive based on the large number of binary systems in which they show little interest in interacting with the second element. Along these lines, the Fe–Bi system combines elements that are essentially immiscible at atmospheric pressure—so much so that melts of the two elements stubbornly segregate into separate liquid phases. Sometimes this nonreactivity is quite inconvenient: in this case, Fe–Bi compounds would be expected to display intriguing magnetic properties and could provide insights into the iron–pnictide family of superconductors.³

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All of these perceived hurdles, however, derive from the wisdom acquired predominantly from intermetallic structures synthesized at ambient pressure. Chemical bonding can work very differently as pressure is increased.⁴ The work of Walsh et al.⁵ demonstrates the salience of this point strikingly. Motivated by a strong desire to realize Fe–Bi bonding in the solid state, they subjected a mixture of Fe and Bi to increasingly high pressures and temperatures (using a diamond anvil cell and laser heating, respectively), monitoring for structural changes in real time via synchrotron X-ray diffraction. Above 30 GPa, such changes took place, as revealed by the growth of new peaks in the diffraction pattern. The powder pattern of the new phase, FeBi₂, hinted at an atomic arrangement first observed for CuAl₂, and such

The discovery of FeBi₂ could lead to further investigation of other materials unobservable at ambient pressure.

The Structure of FeBi₂

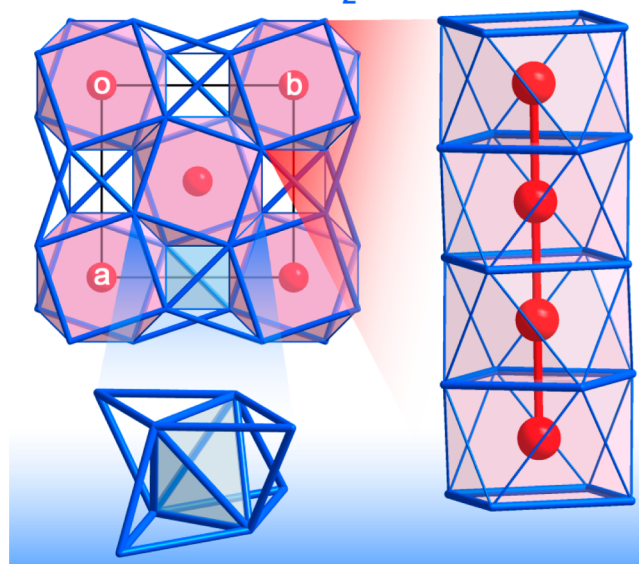


Figure 1. The CuAl₂-type crystal structure of the FeBi₂ phase, the first binary compound in the Fe–Bi system only obtained after heating a mixture of the elements to ca. 1500 K at pressures greater than 30 GPa. The columns of square antiprisms and flattened stella quadrangula formed by the Bi sublattice are highlighted.

an analogous structure for the new material was confirmed through its refinement against the diffraction data.

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Curiously, for being such an exotic species, the structure of FeBi₂ should be quite familiar to intermetallic chemists. It shares the same tetragonal structure type with about

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60 other binary structures. Of these, about 20 also have a TE_2 stoichiometry, where T is a transition metal and E = p-block main group element (Figure 1). Characteristic features of these TE_2 compounds include T-filled columns of E square antiprisms, which share edges to make flattened versions of the stars of tetrahedra known as stella quadrangula.⁶ The bonding in other T–E $CuAl_2$ -type phases has been interpreted in terms of the 18 electron rule,⁷ and from its electron count alone, $FeBi_2$ appears to fit nicely within this bonding scheme. Such an observation raises a tantalizing question: why is $FeBi_2$ so unstable without the application of pressure? An answer to this question would not only help us understand the poor reactivity of some elements toward intermetallic phase formation at ambient pressure but also provide guidance to which systems are likely to exhibit new structural chemistry at elevated pressures.

Another intriguing query is the relationship between $FeBi_2$ and the Bi-III phase which is stable between about 3 and 8 GPa.⁸ Both phases appear to share the same framework of Bi-based square antiprisms. The main difference is their occupation: in $FeBi_2$ each square antiprism is occupied by an Fe atom. In Bi-III these columns instead host chains of Bi atoms with a spacing that is irrational compared to that of the rest of the structure, leading to an arrangement which is aperiodic along the channel axis.⁸ Can intermediate structures be synthesized between $FeBi_2$ and Bi-III with the channels having different combinations of Bi and Fe?

More generally, the discovery of $FeBi_2$ foretells of many other exciting results to emerge from the exploration of the high-pressure chemistry of intermetallics using diamond anvil cells.

Finally, it will be exciting to learn whether the $FeBi_2$ phase exhibits the unique magnetic and/or electrical properties that formed the original motivation for this work. The authors' first attempts to release the pressure led to the degradation of the $FeBi_2$ phase once the pressure fell below 2.9 GPa, preventing the characterization of its properties at ambient conditions. In the future, the authors will try to circumnavigate this problem using sophisticated mechanisms for pressure release and lowering the temperature. The hope is to trap $FeBi_2$ as a metastable phase at atmospheric pressure, but they are not taking any chances: we can also look forward to seeing the results of *in situ* property measurements on $FeBi_2$ at the high pressures at which it is most at home.

More generally, the discovery of $FeBi_2$ foretells of many other exciting results to emerge from the exploration of the high-pressure chemistry of intermetallics using diamond anvil cells. These are devices that can generate incredible pressures of >100 GPa, yet are available to researchers at costs affordable as a line item in a single investigator grant. The growth of new structural observations that will arise from the wider spread use of this technique is very timely, as it coincides with a vibrant effort on the theoretical side to predict new phases and phenomena at high pressures.⁹

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