Chemical Bonding Across the Periodic Table at High and Ambient Pressures

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Primary CNF Tools Used: CNF computer cluster

Abstract:

We address problems of bonding, structure, and emergent properties such as superconductivity in a wide range of materials — from discrete molecules through polymers to extended solids. The behavior of matter under high pressure is of special interest, as it forms a fruitful collaboration with the group of Neil Ashcroft in Physics. The specific project addressed in 2017-18 was the design of a new phase in the Si/C system, stoichiometry Si_3C.

Summary of Research:

As the second most abundant element in the Earth's crust, relatively low cost and an intrinsic semiconductor that can be both *n*- and *p*-doped, silicon has been widely used in the electronic industry. The well-known diamondoid Si(d-Si) structure is a semiconductor with an indirect gap of 1.2 eV and a much larger direct gap of 3.4 eV. As a consequence of the indirect gap nature of d-Si, Si solar cell absorber layers need to be relatively thick to absorb low energy photons. Much theoretical and experimental work has been directed toward the design and synthesis of direct band gap silicon allotropes, at 1 atm and under high pressure, preferably with a band gap value around optimal (~1.4 eV) for effective solar light conversion.

Si_3C is predicted to take on a diamondoid structure (space group: I-42d), at P = 1 atm, consistent with the experimental results on a cubic $Si_{0.75}C_{0.25}$ alloy. This structure is computed to be a semiconductor with a direct band gap of about 1.3 eV, a desired value. Under pressure, Si_3C may transform to metastable metallic R.3m-2 and R-3m-3 structures at about 25 and 250 GPa, respectively. Both are layered structures with six-coordinate Si and unusual six-coordinate carbon atoms.

The R-3m-1 and R-3m-2 structures (shown in Figure 1, along with the diamondoid structure) are both estimated to be superconductors with T_c of a few Ks. This is the first time that superconductivity in undoped silicon carbides is calculated.

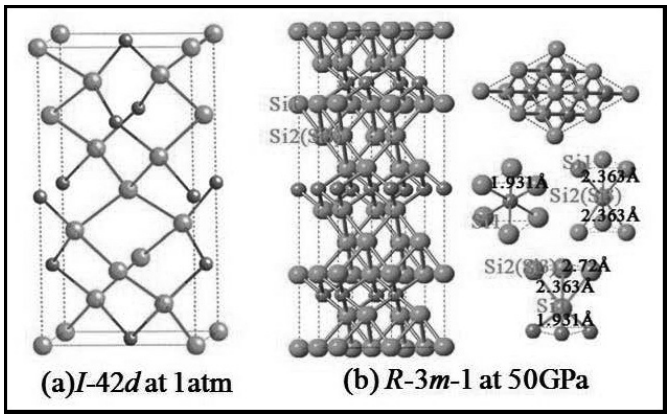

Figure 1: Predicted I-42d, and R-3m-1 structures for Si_3C at 1 atm, and 50 GPa, respectively. Orange, large balls are Si; grey, small balls carbon. The right panel of (b) presents the top view of the R-3m-1 structure and Si-or C-centered octahedra within the structure. See full color version on pages xxviii-xxix.