$BaBiO_3$ at high pressure: metal, insulator or superconductor?

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At zero pressure and temperature $BaBiO_3$ is an insulator with a structural *dimerization*, equivalent to a static valence *disproportionation* of the two Bi ions per cell from 4^+ to $3^+/5^+$. Under pressure one would expect an insulator-metal transition and the eventual disappearance of the dimerization. Moreover, the metallic phase should be superconducting, in analogy the metal doped $Ba_{1-x}K_xBiO_3$ compounds. To date, there are no accurate ab initio predictions under pressure, essentially because LDA or GGA fail to stabilize an insulating phase with the correct distortion and electronic gap.

We carried out first principles LDA+U calculations by determining the effective Hubbard U self-consistently at every pressure, and found that the presence of U is mandatory for a correct description of the zero-pressure state. Upon increasing pressure, we found an insulator to metal transition at ~20 GPa. By further increasing the pressure, we predict the appearance of a superconducting phase, characterized by quantum melting of the weakly dimerized CDW lattice.

However, recent electrical resistivity measurements on $BaBiO_3$ display a decrease of resistivity up to ~18 GPa followed by a sudden increase at higher pressures, in contrast with the hypothesis of high-pressure superconductivity. By using a genetic-algorithm based search (USPEX) and ab-initio calculations, we identified a manifold of novel $BaBiO_3$ crystal structures, characterized by the migration of one oxygen ion from one BiO_6 octahedron to the nearest, forming chains of BiO_5-BiO_7 polyhedra. This *strong* disproportionation is responsible for the opening of a ~2 eV band gap at high pressure.