Supporting Information: Similarities between structural distortions under pressure and chemical doping in superconducting BaFe$_2$As$_2$

**Collapsed phase in AFe$_2$As$_2$ materials with small A-site cations.**

In the wider 122 family of compounds, an alternative groundstate is also found for compounds with a small A-site cation such as CaFe$_2$As$_2$. This so-called ‘collapsed phase’ is driven by the formation of As-As bonds between Fe$_2$As$_2$ layers, and the associated structural deformations.$^1$ To assess the extent of such a contribution in BaFe$_2$As$_2$, a plot of As-As distances versus the c/a ratio is shown$^2$ in S1 for the AFe$_2$As$_2$ compounds. At 6 GPa the c/a ratio for BaFe$_2$As$_2$ is still larger than SrFe$_2$As$_2$ at ambient pressure. In contrast, the collapsed phase in CaFe$_2$As$_2$ has an As-As distance which approaches that of elemental As (2.52 Å), inferring a $\sigma$-bonding contribution.

![S1 Diagram](image)

**S1 Details of collapsed phase in AFe$_2$As$_2$ materials with small A-site cations.** (a) Plot of As-As bond distance against c/a ratio for AFe$_2$As$_2$ materials, points for high pressure CaFe$_2$As$_2$ and BaFe$_2$As$_2$ are also shown, dashed line shows bond distance in elemental As. (b) As–As $\sigma$-bonding pathway in 122 compounds.

**Plot of As z coordinate as a function of pressure for BaFe$_2$As$_2$.**

The only internal degree of freedom in the BaFe$_2$As$_2$ structure is the As z coordinate. The value of this parameter controls the As-Fe-As bond angles and distances. Here we show the refined values from neutron powder diffraction at 75 and 150 K.
S2 Refined As z-coordinate. Refined values on increasing pressure at 150 K and decreasing pressure at 75 K are shown. Error bars represent standard uncertainties from Rietveld refinement of powder neutron diffraction data.

S3 Electronic Band Structures. Electronic band structure for (a) BaFe$_2$As$_2$ at ambient pressure (b) BaFe$_2$As$_2$ at 6 GPa (c) Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ obtained within DFT in the GGA approximation and performing VCA in the doped case. The band character near E$_F$ is shown in red (d$_{x^2}$), red (d$_{x^2}$-d$_{y^2}$), blue (d$_{z^2}$) and green (d$_{xy}$,d$_{yz}$). The orbital notation is given in the local coordinate frame x = a and y = b. The main bandstructure features near E$_F$ evolve similarly under pressure and doping. Note the similar shape of the band structure near E$_F$ for the 6 GPa structure and the Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ structure.
**S4 Calculated Density of States.** Density of states (DOS) for \( \text{BaFe}_2\text{As}_2 \) at various pressures (upper panel) and dopings (lower panel). The DOS at \( E_F \) increases almost linearly as a function of doping and pressure.

**References:**
