Supplementary Information
Structural Evolution, Photoelectron Spectra and Vibrational Properties of Anionic GdGeₙ⁻ (n=5-18) Nanoalloy Clusters: A DFT Insight

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Figure S1. Lowest energy structure and isomers of GdGe\(_n^-\) \((n=1-4)\) anionic clusters, point group, electronic state and relative energy (in eV) calculated at mPW2PLYP/aug-cc-pVTZ,def2-TZVP//mPW2PLYP/cc-pVTZ-PP,def2-TZVP level. The blue and red circles stand for germanium and gadolinium atoms, respectively.

Figure S2. Size dependences of average atomization energy (AAE) for GeGe\(_n^-\) and LuGe\(_n^-\) \((n=5-17)\) clusters. The values of LuGe\(_n^-\) clusters are taken from Ref. 11.
Figure S3. Size dependences of HOMO-LUMO energy gap ($E_{\text{gap}}$) for GeGe$_n^-$ and LuGe$_n^-$ ($n=5$-$17$) clusters. The values of LuGe$_n^-$ clusters are taken from Ref. 11.
Table S1. Total energies (a.u.) of GdGeₙ (n=5-18) clusters in octuplet and decuplet calculated by using mPW2PLYP/(aug-cc-pVTZ,def2-TZVP)//mPW2PLYP/(cc-pVTZ-PP,def2-TZPV) scheme.

| Isomer | Octuplet       | Decuplet       | Isomer | Octuplet       | Decuplet       |
|--------|----------------|----------------|--------|----------------|----------------|
| 5A1    | -11148.59661   | -11148.54910   | 11A4   | -23609.02991   | -23609.00713   |
| 5A2    | -11148.58321   | -11148.57607   | 12A1   | -25685.78992   | -25685.74058   |
| 6A1    | -13225.35432   | -13225.31848   | 12A2   | -25685.78645   | -25685.72747   |
| 6A2    | -13225.32490   | -13225.29891   | 12A3   | -25685.77560   | -25685.73268   |
| 6A3    | -13225.31069   | -13225.31720   | 12A4   | -25685.77503   | -25685.75326   |
| 7A1    | -15302.07925   | -15302.02559   | 13A1   | -27762.53028   | -27762.49715   |
| 7A2    | -15302.07592   | -15302.03822   | 13A2   | -27762.52556   | -27762.48418   |
| 7A3    | -15302.07234   | -15302.07213   | 13A3   | -27762.52522   | -27762.48141   |
| 7A4    | -15302.06729   | -15302.01301   | 13A4   | -27762.51718   | -27762.45367   |
| 8A1    | -17378.82419   | -17378.77772   | 14A1   | -29839.27081   | -29839.21985   |
| 8A2    | -17378.82139   | -17378.79228   | 14A2   | -29839.26963   | -29839.21702   |
| 8A3    | -17378.82024   | -17378.77767   | 14A3   | -29839.25949   | -29839.24956   |
| 8A4    | -17378.81909   | -17378.80639   | 14A4   | -29839.24836   | -29839.22125   |
| 8A5    | -17378.81916   | -17378.78227   | 15A1   | -31916.02109   | -31915.96955   |
| 9A1    | -19455.59466   | -19455.53751   | 15A2   | -31916.01794   | -31915.96750   |
| 9A2    | -19455.57832   | -19455.51909   | 15A3   | -31916.00826   | -31915.95910   |
| 9A3    | -19455.57191   | -19455.51415   | 15A4   | -31916.00582   | -31915.96282   |
| 9A4    | -19455.55727   | -19455.51576   | 16A1   | -33992.78627   | -33992.71106   |
| 10A1   | -21532.30723   | -21532.25069   | 16A2   | -33992.76593   | -33992.72447   |
| 10A2   | -21532.30063   | -21532.27283   | 16A3   | -33992.72899   | -33992.68894   |
| 10A3   | -21532.29482   | -21532.26481   | 17A1   | -36069.50557   | -36069.44537   |
| 10A4   | -21532.27367   | -21532.26768   | 17A2   | -36069.47500   | -36069.43183   |
| 11A1   | -23609.04865   | -23608.99830   | 18A1   | -38146.23920   | -38146.18444   |
| 11A2   | -23609.04476   | -23609.00664   | 18A2   | -38146.23532   | -38146.21333   |
| 11A3   | -23609.03997   | -23608.98703   |        |                |                |
Table S2. Natural population analysis (NPA) charge (in a.u.), valence configuration, magnetic moment (μB) of 6s, 4f, 5d, 6p, and total of Gd atom, and total magnetic moment of the global minima GdGe$_n^-$ ($n$=5-18) compounds calculated at the mPW2PLYP level.

| Compound | Charge (a.u.) | Electron Configuration | Magnetic Moment of Gd Atom | Molecule Total (μB) |
|----------|--------------|------------------------|---------------------------|-------------------|
| GdGe$_5^-$ | 0.16 | [core]6s$^{0.81}$f$^{0.05}$d$^{0.17}$p$^{0.32}$ | 0.01 6.98 0.24 0.01 | 7.24 7 |
| GdGe$_6^-$ | 0.25 | [core]6s$^{0.70}$f$^{0.00}$d$^{0.12}$p$^{0.32}$ | 0.00 6.98 0.24 0.00 | 7.22 7 |
| GdGe$_7^-$ | 0.15 | [core]6s$^{0.57}$f$^{0.00}$d$^{0.03}$p$^{0.25}$ | 0.03 6.98 0.17 0.00 | 7.18 7 |
| GdGe$_8^-$ | 0.15 | [core]6s$^{0.50}$f$^{0.00}$d$^{0.03}$p$^{0.33}$ | 0.01 6.98 0.25 0.01 | 7.25 7 |
| GdGe$_9^-$ | 0.37 | [core]6s$^{0.57}$f$^{0.00}$d$^{0.13}$p$^{0.26}$ | 0.02 6.98 0.28 0.01 | 7.29 7 |
| GdGe$_{10}^-$ | -0.02 | [core]6s$^{0.43}$f$^{0.00}$d$^{0.09}$p$^{0.51}$ | 0.01 6.98 0.23 0.01 | 7.23 7 |
| GdGe$_{11}^-$ | 0.11 | [core]6s$^{0.39}$f$^{0.00}$d$^{0.15}$p$^{0.65}$ | 0.01 6.98 0.18 0.01 | 7.18 7 |
| GdGe$_{12}^-$ | -0.26 | [core]6s$^{0.36}$f$^{0.00}$d$^{0.11}$p$^{0.78}$ | 0.00 6.98 0.17 0.01 | 7.16 7 |
| GdGe$_{13}^-$ | -0.04 | [core]6s$^{0.46}$f$^{0.00}$d$^{0.10}$p$^{0.49}$ | 0.01 6.98 0.22 0.01 | 7.22 7 |
| GdGe$_{14}^-$ | 0.25 | [core]6s$^{0.37}$f$^{0.00}$d$^{0.12}$p$^{0.58}$ | 0.01 6.97 0.18 0.02 | 7.18 7 |
| GdGe$_{15}^-$ | -4.10 | [core]6s$^{0.46}$f$^{0.00}$d$^{0.13}$p$^{0.77}$ | 0.00 6.97 0.19 0.01 | 7.17 7 |
| GdGe$_{16}^-$ | -4.87 | [core]6s$^{0.47}$f$^{0.00}$d$^{0.30}$p$^{0.05}$ | 0.01 6.97 0.20 0.01 | 7.19 7 |
| GdGe$_{17}^-$ | -4.07 | [core]6s$^{0.44}$f$^{0.00}$d$^{0.64}$p$^{1.76}$ | 0.00 6.97 0.20 0.01 | 7.18 7 |
| GdGe$_{18}^-$ | -3.17 | [core]6s$^{0.38}$f$^{0.00}$d$^{0.33}$p$^{1.43}$ | 0.00 6.97 0.19 0.01 | 7.17 7 |