The first-row transition metal doped germanium clusters $Ge_{16}M$: Some remarkable superhalogens

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Abstract

Geometric and electronic structures, stability and magnetic property of both neutral and anionic $Ge_{16}M^{0/-}$ clusters with M being a first-row 3*d* transition metal atom, are investigated using quantum chemical approaches. Both isoelectronic $Ge_{16}Sc^-$ anion and $Ge_{16}Ti$ neutral that have a perfect Frank-Kasper tetrahedral T_d shape and an electron shell filled by 68 valence electrons, emerge as magic clusters with an enhanced thermodynamic stability that can be rationalized by the simple Jellium model. Geometric distortions from Frank-Kasper tetrahedron of $Ge_{16}M$ having more or less than 68 valence electrons can be understood by a Jahn-Teller effect. Remarkably, DFT calculations reveal that both neutral $Ge_{16}Sc$ and $Ge_{16}Cu$ can be considered as *superhalogens* as their electron affinites ($\geq$ 3.6 eV) exceed the value of the halogen atoms and even that of the icosahedral Al_{13}. A detailed view of the magnetic behavior of $Ge_{16}M^{0/-}$ clusters shows that when M goes from Sc to Zn, the total magnetic moment of $Ge_{16}M^{0/-}$ increases steadily and reaches the maximum value of $4\mu_B$ at M = Mn before decreasing towards the end of the first-row 3*d* block metals. Furthermore, the IR spectra of some tetrahedral $Ge_{16}M$ are also predicted.