Revealing Unusual Chemical Bonding in Planar Hyper-Coordinate Ni_2Ge and Quasi-Planar Ni_2Si Two-Dimensional Crystals

Supporting Information

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1. Dynamical stability of Ni_2X monolayer

The dynamical stability of the Ni_2X monolayer was tested by calculating the phonon dispersion along the high-symmetry lines in the Brillouin zone (Fig. S1). The absence of imaginary frequencies clearly indicates that these Ni_2X 2D crystals are minima on the potential energy surface with high kinetic stability.

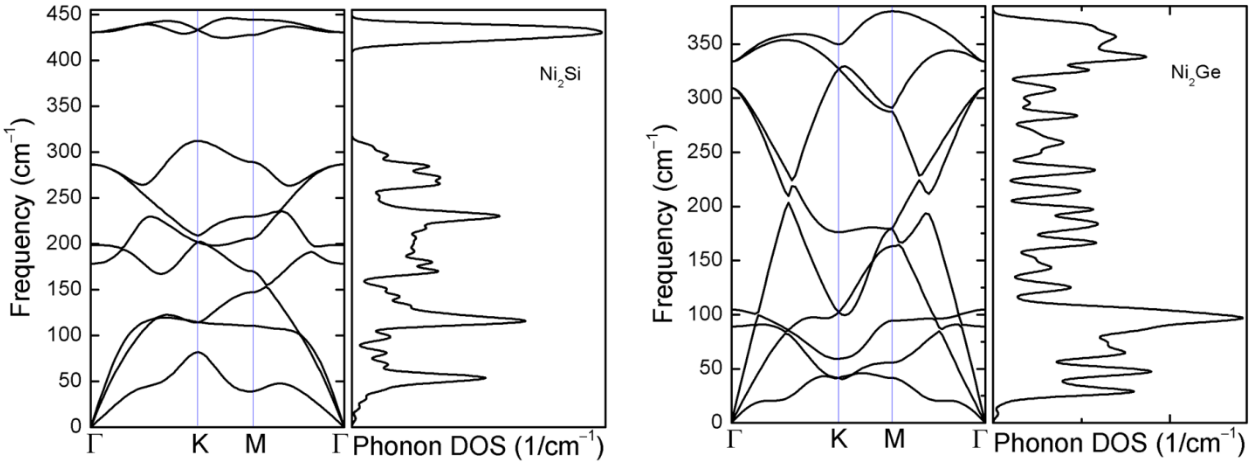

Figure S1. Phonon dispersion and phonon density of states (Phonon DOS) of the monolayer Ni_2Si (left panel), and Ni_2Ge (right panel).

2. Thermal stability of Ni_2X monolayer

To test the stability of these new materials at elevated temperatures, we have performed a series of 10 ps *ab initio* molecular dynamics simulations. A periodic 4 × 4 supercell was used in the MD simulations. For Ni_2Si, simulations were run 600, 1200, 1500, and 1800 K. The framework was maintained up to 1500 K, but melted by 1800 K after 4 ps. Bond length extensions of 17%, 26% and 30% were observed for 600, 1200 and 1500 K simulations respectively. RMSD values of 0.12 and 0.16 were calculated at 600 and 1200 K. Snapshots taken at the end of each simulation are shown in Figure S2. For Ni_2Ge, simulations were run at 600, 900, and 1500 K. The framework was maintained up to 900 K, but melted by 1500 K. Bond length extensions of 39 % and 43 % were observed for 600 and 900 K simulations respectively. RMSD values of 0.20 and 0.21 respectively were measured. The figure at 600 K shows that the Ni_2Ge surface has an unusual low energy excitation. We see that some atoms can pop up while neighbor atom pops down. At 900 K we see an unusual wrinkling or bending of the surface. This allows two next neighbor nickel atoms to bond together temporarily (in this snapshot two next nearest Ni atoms have a bond length of 2.48 Å).

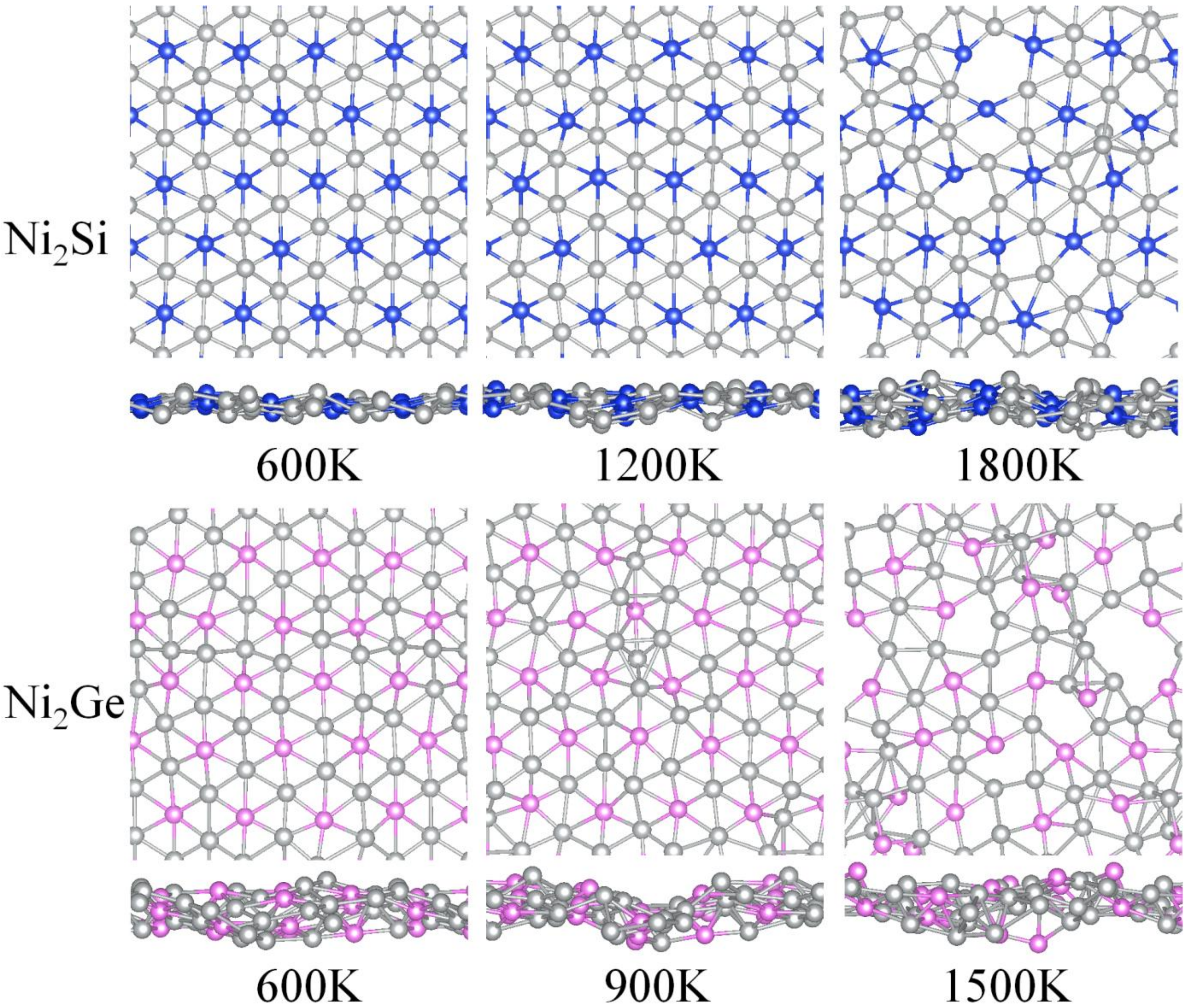

Figure S2. Snapshots of the final frame of each molecular dynamics simulation from Ni$_2$Si and Ni$_2$Ge at various temperatures (top and side views).

3. Electronic structures of 2D crystal Ni_2X

To get insight into electronic properties, we have computed the electronic band structure (Figure S3), which indicates that both 2D crystals are metallic. The partial density of states (PDOS) analysis shows that below the Fermi energy the major contribution comes from Ni 3*d*-states. For Ni_2Si, the states at the Fermi level are dominated by the Si-3*p*, Ni-4*p* and, most importantly, Ni-3*d* states, indicating apparent hybridization between Si 3*p*- and Ni 4*p*-, 3*d*-states. This is consistent with the chemical bonding analysis of the Ni_2Si monolayer. Contrary to Ni_2Si, the major components in Ni_2Ge at the Fermi level are the 4*p* electrons of Ge and Ni-4d states. A striking difference is that the *d*-band of Ni is shifted to higher energy, so that it is split by the Fermi level. In general we see a larger density of states at the Fermi level for Ni_2Ge compared to Ni_2Si, indicating higher electronic conductivity of Ni_2Ge compared with Ni_2Si.

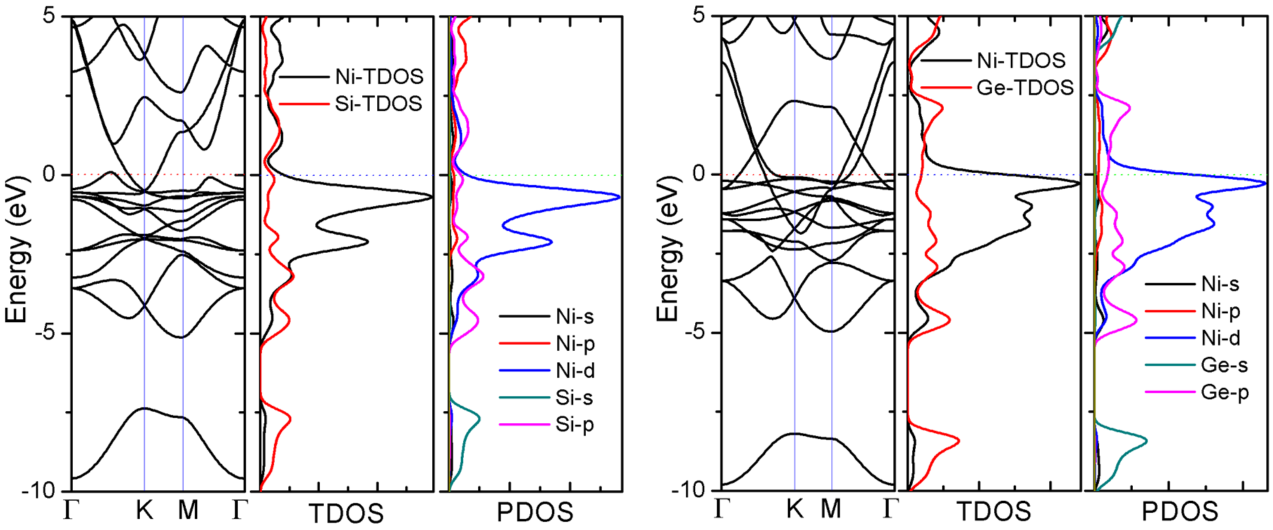

Figure S3. Electronic structure of Ni_2Si (left panel) and Ni_2Ge (right panel). For each panel, band structure (left), total density of states (DOS) (middle), and partial density of states (PDOS) (right) are shown. The Fermi level is at 0 eV.

The band structure indicates these materials are diamagnetic and metallic with a large DOS at the Fermi level, as confirmed by a spin-polarized computation. This is in contrast with the Group 14 Xenes (i.e., graphene, silicene and germanene) that are gap-less semiconductors.