Phase stability in nickel phosphides at high pressures

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Supporting Information

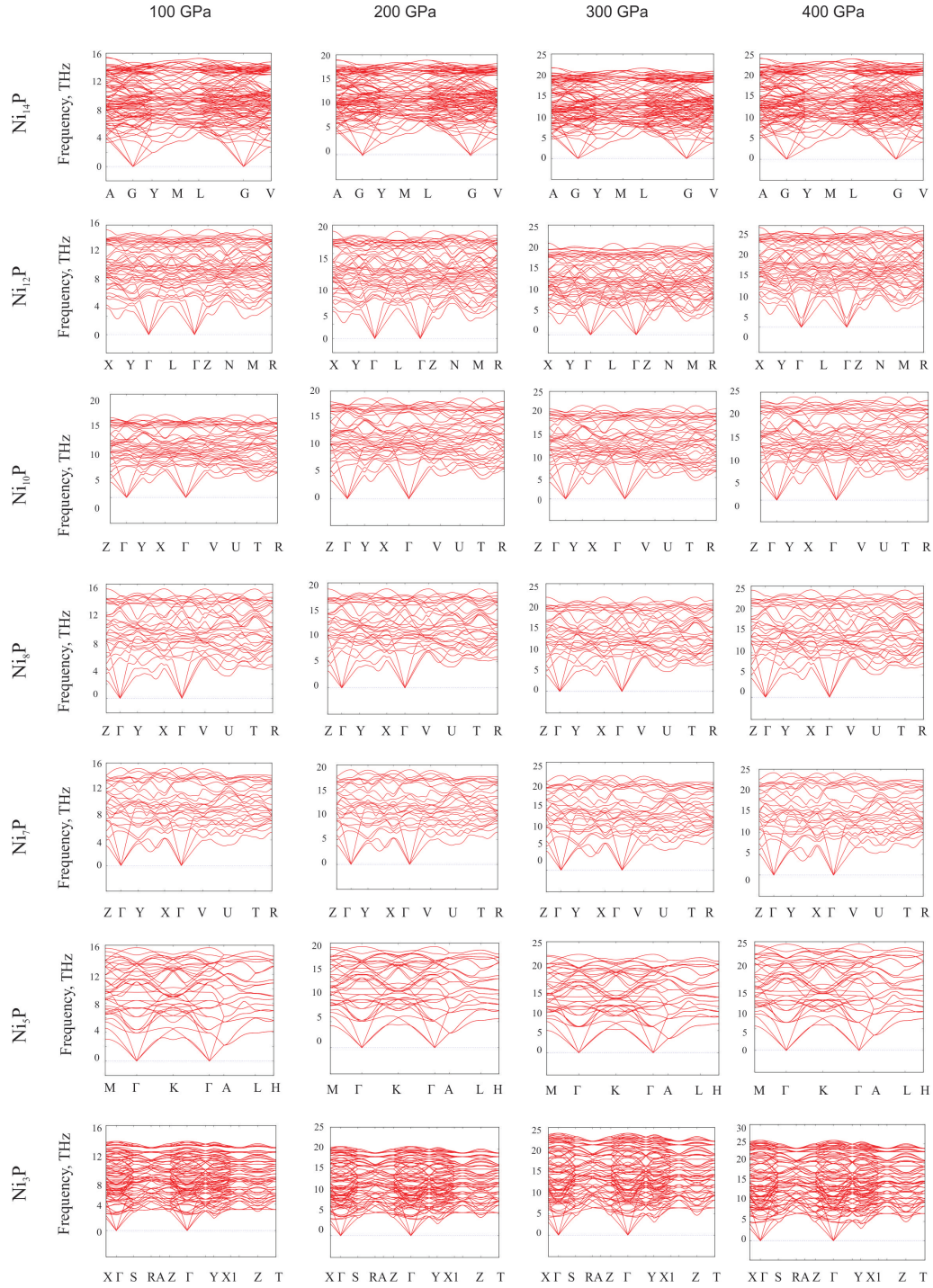## Phonon spectra for predicted Ni–P structures

Figure 1 Calculated phonon spectra for predicted Ni–P compounds.

Elementary substances of Ni and P

Before exploring the binary Ni-P system, we examined each of the components separately. Nickel crystallizes in the face-centered-cubic structure,[1] and no experimentally structural phase transitions are found in it. In the case of phosphorus, several pressure-induced structural phase transitions are experimentally observed. The most stable form at ambient conditions is the so-called black phosphorus which has the A17 (orthorhombic, space group: *Cmca*)

structure.[2] It has been well known that the A17 structure transforms to the A7 rhombohedral: $R\bar{3}m$) structure at 5 GPa and further into the simple cubic (sc: $Pm\bar{3}m$) structure at 10 GPa.[3,4] A phase transition from the simple cubic to the simple hexagonal structure was observed at 137 GPa via an intermediate phase P-IV.[5] At pressure 260 GPa hexagonal structure transforms to the body-centered cubic structure[6] Later it was shown that this structure forms a 2×2×2 superlattice of the bcc structure [cI16 (space group: I-43d)].[7] Phase P-IV has an incommensurately-modulated crystal structure described by the four-dimensional superspace group $Cmmm(00\gamma)s00$.[8,9] In the present study, we approximated the P-IV phase with the eight-atom-cell commensurate structure of $Cmcm$ symmetry.[9]

The calculated dependencies of enthalpy on pressure at 0 K are presented in Fig. S2 The theoretical phase diagram qualitatively agrees with the sequence of phase transformations in phosphorus crystals. Some quantitative difference is caused, on the one hand, by the neglect of thermal effects, on the other hand, the difference between the calculated enthalpy values of bcc and I-43d phases in the pressure range of 250-300 GPa is small. It does not exceed 0.02 eV per formula unit, which is consistent with the experiment where a sluggish phase transition was observed with the coexistence of these phases in a wide pressure range of 262-322 GPa.[7] The data obtained were used further to calculate the enthalpy of formation of various crystalline modifications of the Ni–P system.

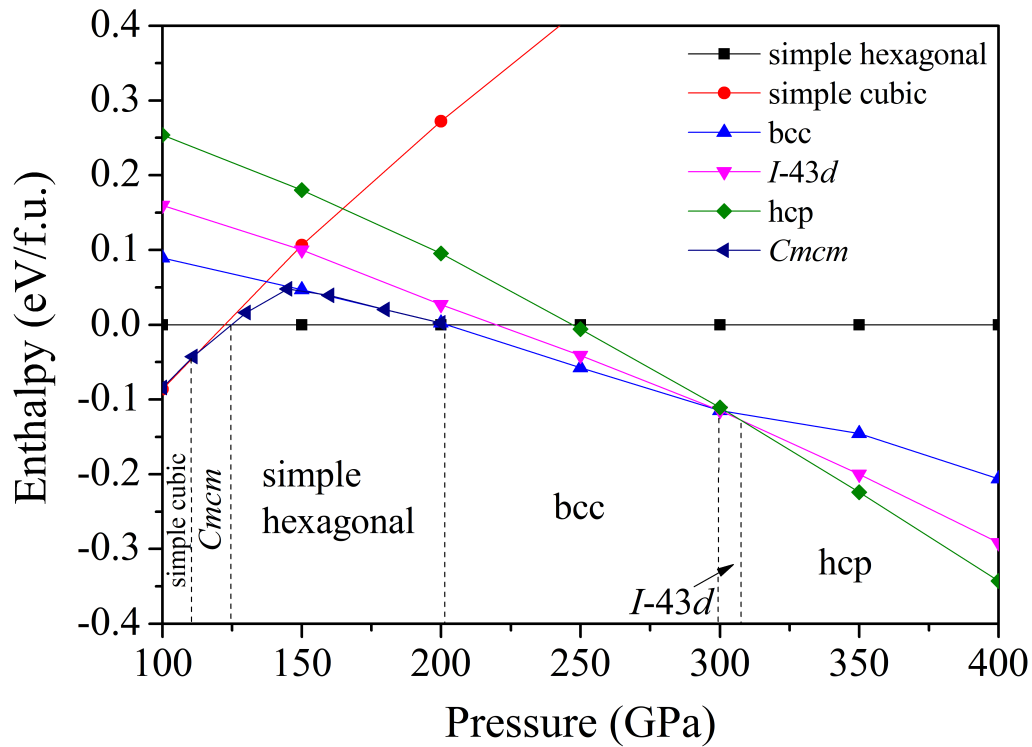Figure 2 Pressure phase diagram of the elementary P.

Notes and references

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