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## Phase stability in nickel phosphides at high pressures

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Phosphorus – one of the light elements of the Earth's core and planets. High-pressure behaviour of phosphorus compounds with nickel and iron attracts considerable attention due to their findings in meteorites and mantle xenolites (Константин, поправь меня, если я не прав). In the present work, with modern methods of crystal structure prediction we investigate structures and stability of compounds in Ni-P system at pressures of 100-400 GPa. As the result the series of (Ni,P) solid solutions, presents by compounds Ni<sub>14</sub>P, Ni<sub>12</sub>P, Ni<sub>10</sub>P, Ni<sub>8</sub>P, Ni<sub>7</sub>P, Ni<sub>5</sub>P, and Ni<sub>3</sub>P, is revealed. Phosphorus show sufficient solubility in *fcc* structure of Ni, and up to 25 mol.% of this element can be dissolved at low temperatures. Based on the comparison of compounds in Ni-P and Fe-P systems we suggest, that at high pressures Ni facilitates phosphorus dissolution in closed-packed structure of *d*-metals, and dissolution of P in (Ni,P) alloy will be higher, than in pure Fe. For the Ni<sub>3</sub>P compound, a new high-pressure phase with *Cmca* symmetry is revealed. This structure can be described as deformed *fcc* packing and also belongs to the series of (Ni,P) solid solutions. The transition from the low-pressure phase of Ni<sub>3</sub>P-*I*4̄ to the *Cmca* phase occurs at a pressure of 62 GPa, regardless of the external temperature. Ni<sub>2</sub>P is stabilised at pressure above 200 GPa in the form of allabogdanite structure. The transition from barringerite to allabogdanite is predicted to occur in the range of 78–88 GPa at temperatures 0-2000 K.

## Introduction

Phosphides play a significant role in the mineralogy of iron meteorites as the components of the ternary Fe-Ni-P system. Although being rare, accessory minerals with composition (Fe,Ni)<sub>x</sub>P, they give important information about phosphorus geochemistry on the early stages of the universe formation.<sup>1–10</sup> The occurrence of these minerals in meteoritic samples is believed to originate either from the equilibrium condensation of protoplanetary materials taking place in the solar nebulae or from crystallization processes in the cores of parent bodies.

Iron-rich end-members of Fe-P system were intensively studied using both experimental and theoretical techniques. So far, most of the high-pressure investigations on iron phosphides have been restricted on Fe<sub>4</sub>P,<sup>11</sup> Fe<sub>3</sub>P,<sup>12</sup> Fe<sub>2</sub>P<sup>13,14</sup>, and FeP.<sup>15</sup> Sev-

eral structural and magnetic phase transitions have been revealed as the result. Dera et al. observed that on heating at 8 GPa phase of Fe<sub>2</sub>P transforms to a high-pressure modification, which could be quenched to ambient conditions.<sup>13</sup> Theoretical modelling demonstrates that the stable phase of Fe<sub>2</sub>P should be the *Pnma* with the lowest total energy in the low pressure region, and the *P6̄2m* and *Pnma* phases would transform to the *P3̄m* phase with larger coordination number of iron at 125 GPa and 153 GPa, respectively.<sup>14</sup> Theoretical studies have shown that Fe<sub>3</sub>P could decompose into Fe<sub>2</sub>P and Fe<sub>4</sub>P at pressures higher than 214 GPa<sup>16</sup>, and Fe<sub>3</sub>P and Fe would react with formation of Fe<sub>4</sub>P at ~100 GPa.<sup>11</sup> Fe<sub>3</sub>P exhibits a structural phase transition from *I4* to *P4/mnc* at 64 GPa and 1600 K accompanied with an electronic state transition from high-spin to low-spin at around 20-40 GPa.<sup>17,18</sup> Upon compression, Fe<sub>4</sub>P undergoes transition from ferromagnetic to nonmagnetic state at 80 GPa.<sup>11</sup> Britvin et al. reported two new structures of FeP (*Pnma*) and FeP<sub>2</sub> (*Pnnm*), found in the pyrometamorphic rocks.<sup>8,9</sup>

Alloying effect of Ni on physical properties and structure of Fe and it's alloys with light elements is also of geological interest. From the analysis of iron meteorites and the observation of Earth's moment of inertia, it is known that the primary constituent of Earth's inner core is an iron-nickel alloy<sup>7</sup> with

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Table 1 Structural data for the found phases of Ni–P system at P=100 GPa . The pressures at which the structures were predicted are indicated in the corresponding column

Phase	Pressure (GPa)	Space group	Lattice parameters (Å, degree)			Atomic coordinates			
						Atom	x	y	z
Ni <sub>14</sub> P	400	C2/m (#12)	$a=7.538$ $\alpha=90$	$b=6.816$ $\beta=120$	$c=5.567$ $\gamma=90$	Ni1	0.000	0.169	0.000
						Ni2	0.099	0.000	0.397
						Ni3	0.301	0.000	0.198
						Ni4	0.703	0.335	0.800
						Ni5	0.599	0.166	0.398
						P1	0.000	0.500	0.000
Ni <sub>12</sub> P	400	$R\bar{3}(\#148)$	$a=8.032$ $\alpha=90$	$b=8.032$ $\beta=90$	$c=5.261$ $\gamma=120$	Ni1	0.539	0.384	0.001
						Ni2	-0.029	0.409	0.332
						P1	0.000	0.000	0.000
Ni <sub>10</sub> P	300	$P\bar{1}(\#2)$	$a=3.932$ $\alpha=107.5$	$b=5.074$ $\beta=105.0$	$c=5.079$ $\gamma=97.4$	Ni1	0.0450	0.4101	0.1803
						Ni2	0.5902	0.3191	0.3592
						Ni3	0.1372	0.2285	0.5468
						Ni4	0.2267	0.0494	-0.0910
						Ni5	0.6776	0.1381	0.7281
						P1	0.5000	0.5000	0.0000
Ni <sub>8</sub> P	200	$P\bar{1}(\#2)$	$a=3.927$ $\alpha=75.0$	$b=3.932$ $\beta=82.6$	$c=5.076$ $\gamma=80.5$	Ni1	0.22148	0.11048	0.56082
						Ni2	0.67093	0.33311	0.66740
						Ni3	0.44401	0.21845	0.11085
						Ni4	0.11116	0.55650	0.78047
						P1	0.00000	0.00000	0.00000
Ni <sub>7</sub> P	100	$P\bar{1}(\#2)$	$a=3.755$ $\alpha=73.0$	$b=3.777$ $\beta=90.0$	$c=4.393$ $\gamma=79.9$	Ni1	0.5020	0.0003	0.2477
						Ni2	0.0000	0.0000	0.5000
						Ni3	0.7539	0.4984	0.1244
						Ni4	0.2490	0.5069	0.3713
						P1	0.0000	0.0000	0.0000
Ni <sub>5</sub> P	200	$P6_3/mcm(\#193)$	$a=3.934$ $\alpha=90$	$b=3.934$ $\beta=90$	$c=7.372$ $\gamma=120$	Ni1	0.3333	0.6667	0.0000
						Ni2	0.6710	0.0000	0.2500
						P1	0.0000	0.0000	0.0000
Ni <sub>3</sub> P	100	$Cmca(\#64)$	$a=13.1666$ $\alpha=90$	$b=4.4854$ $\beta=90$	$c=4.4851$ $\gamma=90$	Ni1	0.3814	0.0000	0.0000
						Ni2	0.0000	0.1818	0.8180
						Ni3	0.2500	0.7473	0.2500
						P1	0.1365	0.0000	0.0000
Ni <sub>2</sub> P	100	$Pnma(\#64)$	$a=4.271$ $\alpha=90$	$b=3.307$ $\beta=90$	$c=6.247$ $\gamma=90$	Ni1	0.4537	0.2500	0.7890
						Ni2	0.8260	0.2500	0.0589
						P1	0.8021	0.2500	0.3870

Fe/Ni~16.<sup>??</sup> Addition of nickel to iron phosphides affect the structure and phase stability. The example of Fe<sub>2</sub>P shows, that even a small addition of Ni and Co stabilise the structure of allabogdanite against [barringerite](#)<sup>3,4,19</sup>, and also slightly increases the bulk modulus of the allabogdanite phase.<sup>19</sup> **А может здесь сослаться на нашу статью по алабогданиту (Bekker, Sagatov et al., 2020)?** The incorporation of Ni in nonmagnetic Fe<sub>4</sub>P results in reduction of the compressional and shear wave velocities enhancing their anisotropy.<sup>11</sup>

There are numerous phases were revealed in Ni–P system at ambient pressure. Among them are Ni<sub>3</sub>P, Ni<sub>8</sub>P<sub>3</sub>, Ni<sub>12</sub>P<sub>5</sub>, Ni<sub>2</sub>P, Ni<sub>5</sub>P<sub>4</sub>, NiP, NiP<sub>2</sub>, and NiP<sub>3</sub>. **Вижу здесь NiP3, Ni5P4, Ni12P5. Возникает вопрос, а почему мы их на выпуклую оболочку не нанесли? Ni8P3 и NiP2 нанесли, а эти нет? Какой принцип для выбора фаз? По-хорошему следовало бы для всех этих составов провести предсказания, как мы это делали с гидридами. В Методику нужно обязательно добавить, что какие-то фазы мы брали из литературных данных и просто протягивали их по давлению. Подумайте, может имеет смысл запустить эти расчёты на предсказание, пока статья будет на рецензии они досчитаются и мы это**

**включим в статью** However, the data on this system at high-pressures, especially above 100 GPa, are limited. Donohue et al.<sup>20</sup> studied P-rich compositions (NiP<sub>2.2–2.5</sub>) at 1.5–6.5 GPa. Dera et. al.<sup>21</sup> synthesized a cubic NiP<sub>2</sub> phase at 6.5 GPa during heating at 1200°C and subsequent cooling to 900°C. Incongruent melting associated with formation of pyrite-type NiP<sub>2</sub> and amorphous Ni–P alloy was found at an intermediate pressure range, between 6.5 and 40 GPa. The phase transitions in Ni<sub>2</sub>P were not observed in these experiments at pressures up to 50 GPa consistently with theoretical predictions.<sup>19</sup> Several reversible phase transitions were established in NiP at ambient temperature: (a) from *Pbca* to *Cmc*<sub>21</sub> at 3.5 GPa, (b) to *Pnma*-phase at 8.5 GPa and to another *Cmc*<sub>21</sub>-phase, but with different crystal structure at 25 GPa.<sup>22,23</sup> [Litasov et.al. studied the melting processes and subsolidus phase relations in the Ni–Ni<sub>2</sub>P system at 6 GPa and 900–1600°C. At 6 GPa and 900–1600°C the Ni–Ni<sub>2</sub>P system has four stable phosphides: Ni<sub>3</sub>P nickelphosphide, Ni<sub>8</sub>P<sub>3</sub>/Ni<sub>5</sub>P<sub>2</sub>, Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P transjordanite. The Ni<sub>12</sub>P<sub>5</sub> phase becomes unstable at 900°C and decomposes into Ni<sub>5</sub>P<sub>2</sub> and Ni<sub>2</sub>P.](#)<sup>24</sup>

The phase stability, elastic properties, hardness and related

electronic structures of Ni–P crystal phases at ambient pressure and zero temperature were studied theoretically in Ref. <sup>25,26</sup>. The equations of state and structural parameters of Ni<sub>2</sub>P, NiP<sub>2</sub> (pyrite type) and Ni-doped Fe<sub>2</sub>P (allabogdanite) at high pressures were determined with first-principles calculations. <sup>19</sup> There was not found barringerite-allabogdanite phase transition in Ni<sub>2</sub>P at pressures up to 50 GPa. Bulk modulus of (Fe<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>P (allabogdanite) increases with Ni concentration. Increasing the concentration of Ni decreases the stability of structure and suppresses the total magnetic moment of the system.

In present research, we theoretically investigate Ni–P compounds in the pressure range from 100 to 400 GPa. A search for new crystalline structures is carried out. The relative stability of all predicted and well-known experimentally observed structures of the Ni–P system is investigated. The phase diagram of the Ni<sub>2</sub>P system is calculated, where barringerite-allabogdanite structural phase transition occurs at pressures of 77–87 GPa depending on temperature. Similar calculations of the phase equilibrium between the new high-pressure Ni<sub>3</sub>P phase and the schreibersite structure are also performed.

## Computation Details

The structure predictions were performed using USPEX code based on evolutionary algorithms <sup>27–29</sup> and AIRSS based on a random sampling method. <sup>30,31</sup> Crystal structure prediction calculations were divided into two stages. At the first stage, the search for stable structures of intermediate compositions was performed using the USPEX package. At the second stage, the predictions were performed for the fixed compositions represented on the convex hull constructed at the first stage using USPEX and AIRSS. При каких давлениях осуществлялись предсказания структур? В случае AIRSS для какого количества формульных единиц? Хорошо бы указать и сколько структур было просчитано. The calculations of the electronic structure were carried out within the DFT using the VASP 5.4 package. <sup>32,33</sup> The exchange-correlation interaction was taken into account in the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional <sup>34</sup> in a plane-wave basis set along with projector augmented-wave (PAW) pseudopotentials. <sup>35</sup> For all studied structures, calculations were performed, taking into account the spin polarization. It was found that in all cases, except for the new predicted phases Ni<sub>10</sub>P, Ni<sub>12</sub>P, and Ni<sub>14</sub>P, the magnetic moment is equal to zero. The computation parameters were as follows: energy cut-off – 450 eV; the density of the grid of Monkhorst-Pack k-point mesh – 0.5 Å<sup>-1</sup>. The most promising predicted structures were then optimized with higher accuracy at various pressures. In these calculations, the cut-off energy was 700 eV and the density of k-points was 0.2 Å<sup>-1</sup>. Тут, как уже было отмечено, нужно добавить про оптимизацию структур, взятых из литературных источников.

To take into account the temperature effect and predict the phase diagrams, we used the method of lattice dynamics within the quasi-harmonic approximation (QHA). For this task, the phonon frequencies were calculated with the PHONOPY code. <sup>36</sup> Coordination polyhedrons for predicted structures were

visualized with VESTA software? <sup>7</sup>

## Results and Discussion

The analysis of HP crystal structures

Structural data of the new phases predicted with USPEX and AIRSS codes are summarized in Table 1 and shown in Fig. 1. All found structures are dynamically stable, the corresponding phonon spectra presented in Supporting Information (SI) in Fig. S1. New structures were predicted at different pressures. Table 1 shows the unit cell parameters after the optimization of the volume of unit cells corresponding to an external pressure of 100 GPa.

The structures of Ni<sub>14</sub>P, Ni<sub>12</sub>P, Ni<sub>10</sub>P, Ni<sub>8</sub>P, Ni<sub>7</sub>P, Ni<sub>5</sub>P, and Ni<sub>3</sub>P are characterized by *fcc* packing, with Ni atoms partially substituted by P atoms. The pure Ni also present in the *fcc* form up to 400 GPa. Thus, the found structures can be considered as (Ni,P) solid solutions. This type of isomorphism between *d*-metal and light element is unusual at ambient pressures. At extreme pressures of the Earth's core, when elements which are typical non-metals like sulfur adopt metallic properties <sup>37</sup>, this isomorphism became widespread. Isomorphic replacement of iron on S, Si and C within *hcp* or *bcc* crystal structures can be given as an example <sup>38</sup>. Добавил ссылку, но bibtex ее не видит. Как и некоторые другие выше. Phosphorus atoms in found structures tend to be homogeniously spread through the structure, without clustering or group formation.

Ni<sub>14</sub>P, Ni<sub>12</sub>P, Ni<sub>10</sub>P, Ni<sub>8</sub>P, Ni<sub>7</sub>P, Ni<sub>5</sub>P structures are characterised by almost ideal *fcc* packing, with both Ni–Ni and Ni–P bonds are of the same length, equal to 2.7 Å at 100 GPa. The Ni–Ni bond in the pure Ni is characterised by the same length. Ni<sub>3</sub>P structure is sufficiently deformed, as shown on Figure 1, the Ni–P bond is equal to 2.25 Å while length of Ni–Ni bonds vary in the range 2.25–2.35 Å. The found Ni<sub>2</sub>P–*Pnma* structure is the analogue of allabogdanite mineral with composition Fe<sub>2</sub>P. Allabogdanite is of cottunite-type, does not having close-packing of atoms, in contrast to *fcc* structure which is 3-layered close-packing. The calculations, which results will be presented below, show that experimentally synthesised at ambient pressure Ni<sub>8</sub>P<sub>3</sub> structure is also stable up to 400 GPa. As well as Ni<sub>2</sub>P, the structure of this phase are not of closed packing type. Thus, at nearly 25 mol.% of P content in (Ni,P) alloy, the change of the structural type takes place. This value can be accepted as the estimation for the phosphorus solubility in Ni structure at high pressures and low temperatures. As temperature increases the limits of isomorphism, this value can be sufficiently higher for the conditions of the cores of the Earth or planets. The fact, that similar isomorphism was not found in Fe–P systems, likely shows that solubility of P in (Fe,Ni) alloy will be higher than in the pure Fe.

Spin-polarized calculations show the presence of a magnetic moment in structures with a relatively high nickel content from Ni<sub>14</sub> to Ni<sub>8</sub>P, as shown in Fig. 2. In all other cases, the magnetic order is absent. The magnetic moment per nickel atom decreases with an increase in the specific phosphorus content in the system. With increasing pressure, the magnetic moment

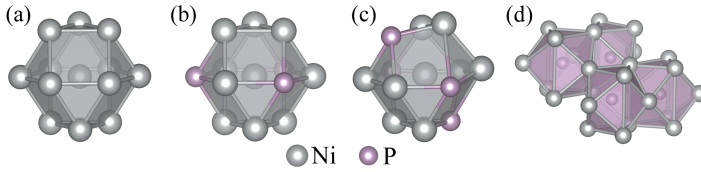


Fig. 1 Coordination polyhedrons in fcc-Ni (a), Ni<sub>5</sub>P (b), Ni<sub>3</sub>P (c), and Ni<sub>2</sub>P structures (d).

and magnetic ordering completely disappear at a pressure of 315, 360, 350, and 115 GPa for the Ni<sub>14</sub>P, Ni<sub>12</sub>P, Ni<sub>10</sub>P, and Ni<sub>8</sub>P lattices, respectively. Unlike the considered phosphides, the magnitude of the magnetic moment in pure nickel weakly depends on external pressure. With an increase in pressure from 100 to 200 GPa, the magnetic moment per nickel atom decreases from 0.58  $\mu_B$  to 0.5  $\mu_B$  and then remains practically unchanged.

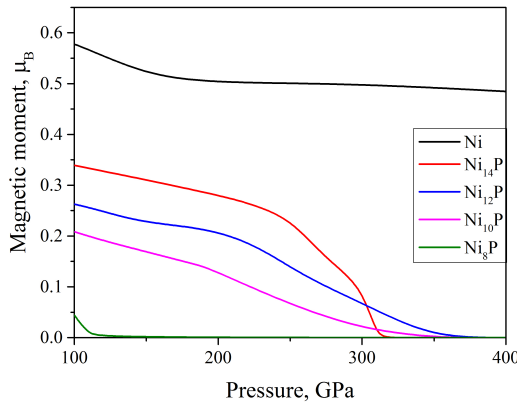


Fig. 2 Pressure dependence of magnetic moment (in Bohr magneton,  $\mu_B$ ) per Ni atom for predicted Ni-P crystal structures. The dependence of the magnetic moment on pressure for pure nickel is given for comparison.

#### Thermodynamic of Ni-P compounds

Both sets of the predicted and experimentally observed Ni-P binary compounds were used to evaluate the formation enthalpy  $\Delta H$  with respect to the elemental solids Ni and P according to Eq. 1, in order to explore the thermodynamic stability of Ni-P:

$$\Delta H(\text{Ni}_n\text{P}_m) = \frac{H(\text{Ni}_n\text{P}_m) - nH(\text{Ni}) - mH(\text{P})}{Z(n+m)}, \quad (1)$$

where  $H = U + PV$  is the enthalpy of each compound,  $Z$  is a number of formula units in the unit cell of the structure and  $\Delta H$  is the enthalpy of formation per formula unit. Herein,  $U$ ,  $P$ , and  $V$  are internal energy, pressure and volume, correspondingly. Detailed information about the element solids can be found in SI. Ссылка на рисунок.

The relative stabilities of the considered compositions at the selected pressures of 100, 200, 300, and 400 GPa, with  $\Delta H$  evaluated per atom, are shown in the form of the co-called convex hull Fig. 3, useful for assessing of the phases thermodynamic stability. Points corresponding to the phases with enthalpy lower

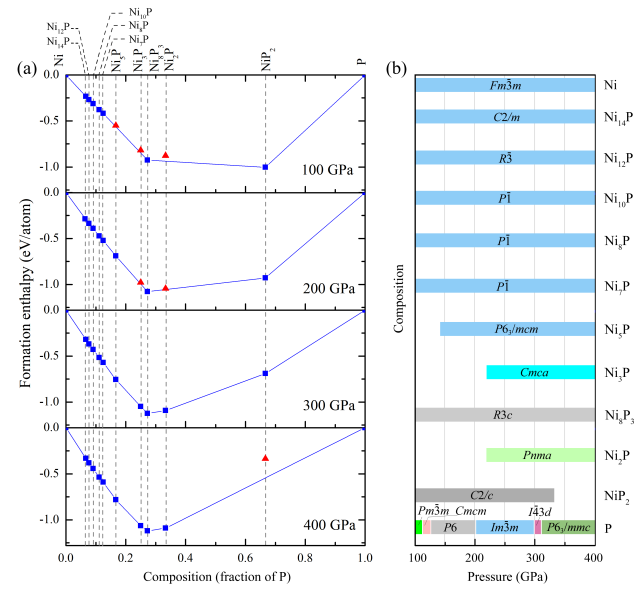


Fig. 3 Global stability convex hulls of the Ni-P system at the pressure range 100-400 GPa (a) and predicted pressure-composition phase diagram for the Ni-P system. Blue squares denote stable structures, red triangles - metastable structures.

than the enthalpy of mechanical mixture of the neighbouring compounds forms the convex hull on such a plot. All points above the convex hull corresponds to the unstable phases, decomposing on the mixture of neighbouring compounds. In addition to the predicted and described above Ni<sub>14</sub>P, Ni<sub>12</sub>P, Ni<sub>10</sub>P, Ni<sub>8</sub>P, Ni<sub>7</sub>P, Ni<sub>5</sub>P, Ni<sub>3</sub>P, and Ni<sub>2</sub>P structures, we have also considered Ni<sub>8</sub>P<sub>3</sub> and NiP<sub>2</sub> structures, synthesised experimentally at ambient pressure.

Predicted solid solutions Ni<sub>14</sub>P – Ni<sub>7</sub>P are stable within all pressure range from 100 to 400 GPa, while solid solution enriched with phosphorus are stabilised with pressure. Ni<sub>5</sub>P became stable from 200 GPa and above, while Ni<sub>3</sub>P from 300 GPa and above. Allabogdanite-Ni<sub>2</sub>P is also stabilised against decomposition at 200 GPa. Experimental phase Ni<sub>8</sub>P<sub>3</sub> is stable in all pressure range, while NiP<sub>2</sub> destabilised above 300 GPa.

It has to be emphasized, that the results presented in Fig.3 are obtained neglecting thermal effects. In order to account for the effect of temperature on Gibbs energy, we use method of lattice dynamic. Within this method, it is necessary to calculate the vibrational spectra of all the structures considered. We performed phonon mode calculations for all predicted structures, described above. Experimentally synthesised Ni<sub>8</sub>P<sub>3</sub> was not considered in this context, due to the large size of the unit cell, containing 132 atoms. Speculatively we assume thermodynamic instability of such a low symmetric structure in the field of high temperatures, due to effect of entropy.

Due to natural occurrence of schreibersite-Ni<sub>3</sub>P, allabogdanite-Ni<sub>2</sub>P, and transjordanite-Ni<sub>2</sub>P phases and their findings in meteoritic rocks, we determined PT phase diagrams for these compounds, presented in Fig. 4. The diagrams shows, that transition from barringerite to allabogdanite structure in the Ni<sub>2</sub>P system occurs in the pressure range 77-88 GPa at temperatures

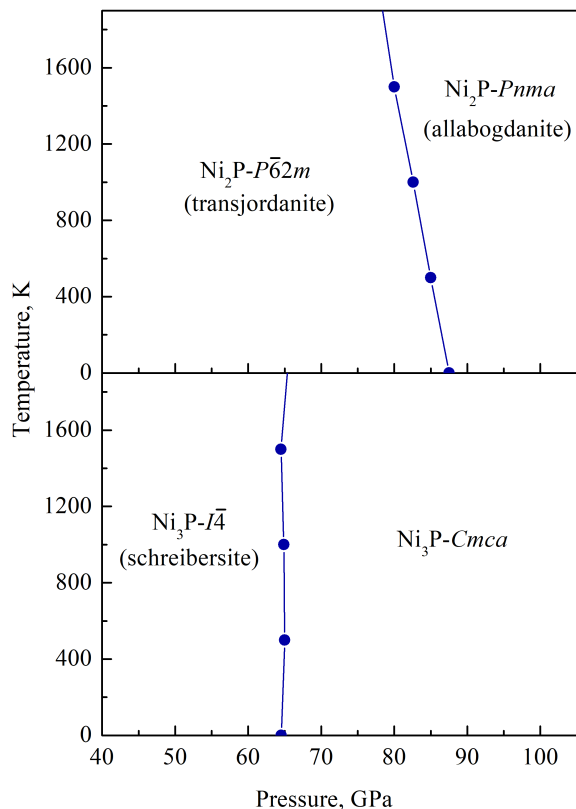


Fig. 4  $P$ - $T$  diagram of (a)  $\text{Ni}_2\text{P}$  and (b)  $\text{Ni}_3\text{P}$

0–2000 K. The transition from schreibersite to the found  $Cmcm$  structure occurs at 62 GPa and pressure of phase transition is almost independent from temperature.

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