



Research articles

Spontaneous magnetization-induced phonons stability in γ' -Fe₄N crystalline alloys and high-pressure new phase



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ABSTRACT

The stability of lattice dynamics and the magnetism of the ordered γ' -Fe₄N crystalline alloy at high pressures were studied by first-principle calculations based on density-functional theory. The dynamical stable new phase P2/m-Fe₄N at high pressures was found by conducting the softening phenomenon at the point M (0.5 0.5 0) of the acoustic phonon at 10 GPa in the γ' -Fe₄N via soft-mode phase transition theory. Compared to the phonon spectrum of γ' -Fe₄N without considering electronic spin polarization, the ground-state lattice dynamical stability of the ferromagnetic phase γ' -Fe₄N is induced by the spontaneous magnetization at pressures below 1 GPa. However, P2/m-Fe₄N is more thermodynamically stable than γ' -phase at pressures below 1 GPa, and the magnetic moments of the two phases are almost the same. The ground-state structure of P2/m phase is more stable than that of γ' -phase in the pressure range from 2.9 to 19 GPa. The magnetic moments of the two phases are almost the same in the pressure range from 20 to 214 GPa, but the ground-state structure of γ' -phase is more stable than that of P2/m phase in the pressure range from 143.8 to 214 GPa. On the contrary, the ground-state structure of P2/m phase is more stable when the pressure is above 214 GPa. In the pressure range from 214 to 300 GPa, the magnetic moment of P2/m phase is lower than that of γ' -phase, and the magnetic moments of the two phase tend to be consistent when the pressure exceeds 300 GPa.

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1. Introduction

Among iron nitrogen compounds, γ' -Fe₄N has received much attention of researchers for its excellent magnetic properties and chemical stability [1–8]. As γ' -Fe₄N has cubic structure, and the nitrogen atoms are dissolved into the octahedral interstitial (body center of γ -Fe) constructed by the six Fe atoms located in the face centers of γ -Fe, the lattice constant of the face-centered γ -Fe expands [1–5]. The space group of the γ' -Fe₄N is Pm $\bar{3}$ m. Kokado et al. [6] studied the energy dependence of the spin-polarization ratio and the electronic structure by first-principle calculations, and analyzed the conductivity using the Kubo formula and the Slater-Koster tight-binding model. Results showed that in the vicinity of the Fermi energy, the spin polarization ratio takes almost 1.0, which is 5.0 times as large as that of bcc-Fe. In recent years, based on the crystal structure of γ' -Fe₄N, the electronic structure, chemical bonding, elastic properties etc. were studied with the atom-substituting method at nonequivalent positions

[9–15]. These work is very helpful for understanding the mechanism of the mechanical and chemical stability, and high saturation magnetization of γ' -Fe₄N.

Rebaza et al. [16] reported ab-initio studies of the magnetic property variations with pressure of both iron sites in the structure of γ' -Fe₄N, by using full-potential linearized augmented plane wave method and the Perdew-Burke-Ernzerhof functional [17] and generalized gradient approximation to describe the exchange-correlation potential. They showed that when lattice parameter is varied, the magnetic moment of Fe2 at corners is almost constant while that of Fe1 at face centers place presents a discontinuity. This variation is due to the distribution difference of spinning up and spinning down electronic density of states, and the magnetic-moment variation of Fe1 arises mainly from changes in the d_{xy}, d_{xz}, d_{yz}, and d_(x²-y²) orbitals. Wenxu Zhang [18] studied the magnetic moment-induced phonon in the γ -Fe by using density-functional theory, which attracts our attention, for the phonon stability and its analysis of γ' -Fe₄N at high pressures has not been reported. In order to further reveal the macroscopic and microscopic features of γ' -Fe₄N, we systematically

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studied the relation between the magnetic moment and the phonons in γ' -Fe₄N, and calculated the phonons at high pressures.

The experimental researches on the pressure-induced soft-mode transition in ferromagnetic crystal alloys have been rarely reported. The main reason is that it is quite difficult to determine the phonon dispersions in the whole Brillouin zone by inelastic-neutron scattering experiments or Raman scattering experiments, and it is more difficult to determine the magnetism and crystal structure of the system. Using first principles based on density-functional theory, we can calculate the phonon dispersions in the whole Brillouin zone, which provides computing technology (PHONOPY [19]) to study the soft-mode transition of crystalline alloys [20–25]. We reference the above theory and computing technology to calculate the acoustic phonon softening of γ' -Fe₄N at the point M at 10 GPa, and find the new phase of P2/m-Fe₄N.

2. Computational details

The calculation adopts the Vienna Ab initio Simulation Package (VASP) based on the plane wave pseudo-potential method of density-functional theory (DFT) [26–28]. The exchange interaction between electrons adopts Perdew-Burke-Ernzerhof (PBE) [17]. The projector augmented wave (PAW) [29] method is used to calculate the electron-core interactions. For Fe and N atoms, the electron configurations are $3p^63d^74s^1$ and $2s^22p^3$, respectively. The integral in Brillouin zones adopts Monkhorst-Pack method to take samples, the integration grid is $10 \times 10 \times 10$, and the cutoff energy of plane-wave basis function is 800 eV. The relaxation of atoms adopts first-order Methfessel-Paxton smearing method, and the smearing width is 0.2 eV. The calculation of total energy adopts modified linear tetrahedron method of Blöchl to obtain higher precision [30]. The convergences precision for the relaxation of electrons and ions is 1.0×10^{-6} eV and 1.0×10^{-4} eV respectively, and that of force is -1.0×10^{-7} eV. The calculation of phonon adopts supercell of $3 \times 3 \times 3$, the integral in Brillouin zones adopts Monkhorst-Pack method to take samples, and the integration grid is $2 \times 2 \times 2$.

The dispersion of longitudinal and transverse acoustic phonons of γ' -Fe₄N under 10 GPa display imaginary frequency at the symmetrical point M (0.5 0.5 0), which is processed with the software PHONOPY [19]. The details are as the followings. Displacements are made for Fe and N atoms along the direction of polarized vector on XY plane ((0 0 1) plane) relative to the expanded cell $2 \times 2 \times 1$ (The lattice parameters are $a = b = a_0 = 7.40857 \text{ \AA}$ and $c = 0.5a_0$) of the primitive cell. Table 1 shows the displacements of Fe and N atoms according to each relative displacement of 0.1, indicating that the displacement direction (the angle relative to the [1 0 0] crystal direction on XY plane) is constant, and this is displacement-type phase transition. The lowest total free energy

appeared when the relative displacement is 0.9, which corresponds to the space group of P2/m.

The calculating details and precision for P2/m-Fe₄N are the same as those of γ' -Fe₄N, but the integration grid adopts $5 \times 7 \times 5$, and the phonon calculation adopts supercell of $2 \times 3 \times 2$.

After optimization, the information of the crystal structure are shown in Table 2, indicating the calculations fits well with the date in Refs. [10,31–33], and that our results is reliable Fig. 1.

3. Results of calculation and discussion

From the enthalpy-difference curves shown in Fig. 2(a), compared with the γ' -Fe₄N without considering electron spin polarization, it is more stable when considering the electron spin polarization at pressures below 237 GPa. The enthalpy-difference between γ' -Fe₄N with and without considering the electron spin polarization is decreased gradually with the increasing pressure, which is almost the same at pressures over 237 GPa. From Fig. 2 (b) and (c), the critical pressure (P_c) for the magnetic collapse of the γ' -Fe₄N is 237 GPa. From Fig. 2(b), the magnetic moment of Fe2 at corners changes slowly with pressure, and only changes sharply near the critical pressure. The magnetic moment of Fe1 at face centers decrease rapidly at pressures below 40 GPa. However, when the pressure is over 40 GPa, the magnetic moment of Fe1 decreased linearly till the magnetic collapse. These results agree with Ref. [16]. From Fig. 2 (c), it is the 3d electron of Fe1 and Fe2 that makes contribution to the magnetic moments of γ' -Fe₄N.

From Fig. 3(a) and (b), in the entire Brillouin area, there appears no imaginary frequency in the phonon spectrum of the ferromagnetic γ' -Fe₄N crystalline alloy at the pressure of 0 GPa. From Fig. 3(b), it can be seen that N atoms at the body centers make no contribution to the phonon-state density in low-energy phonon spectral region, and the main contribution is from Fe1 at face centers and Fe2 at corners. Due to the static magnetic forces of Fe1 and Fe2, N atom located at the body center is in a stably equilibrium state at 0 GPa, in which the magnetic potential exerted on the body centered N by Fe1 and Fe2 is minimum. Phonons in the low frequency region ($\nu < 2.5 \text{ THz}$ in Fig. 3(a) and (b)) belong to acoustic branches, which represent the vibrational modes of mass center (i.e. the equilibrium position of N). The atomic weight of Fe is far larger than that of N. Based on the above considerations, the contribution of body centered N to the phonon density of states approximate to zero.

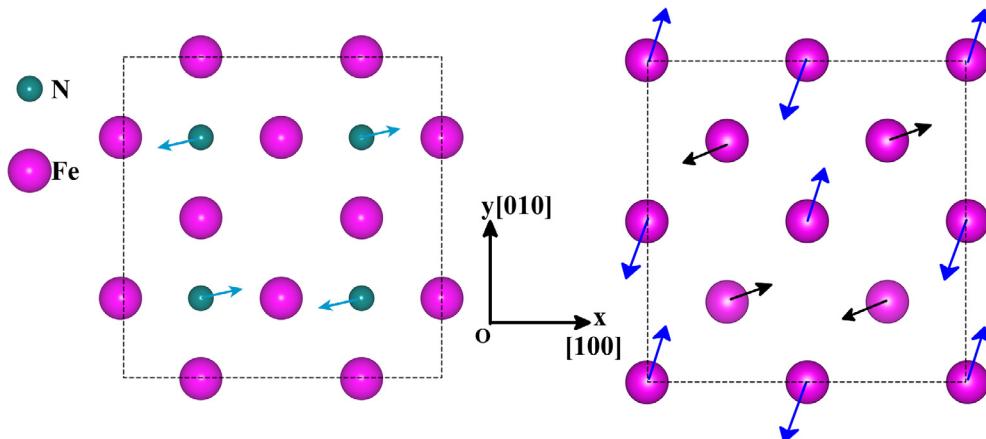
The light atoms make less contribution to the phonon-state density in low-frequency region, which indicates that γ' -phase in the crystalline alloy Fe₄N is ground-state stable. From the optical phonon-state density in high-frequency (near 20 THz) region, the contribution is mainly from the relative vibration of N and Fe1

Table 1
The angle relative to the crystal orientation of [1 0 0] and relative displacement Δd relative to the lattice parameters a_0 of the expanded cell $2 \times 2 \times 1$ for the primitive cell with Pm 3 m structure when the relative movement is 0.1 at 10 GPa.

Atoms	The initial position	After the mobile position	Angle	$\Delta d (\text{\AA})$
Fe1	(0.25, 0.25, 0.0)	(0.2520, 0.2503, 0.0)	9.52°	0.000038072
Fe1	(0.25, 0.75, 0.0)	(0.2480, 0.7497, 0.0)	189.52°	0.000038072
Fe1	(0.75, 0.25, 0.0)	(0.7480, 0.2497, 0.0)	189.52°	0.000038072
Fe1	(0.75, 0.75, 0.0)	(0.7520, 0.7503, 0.0)	9.52°	0.000038072
Fe2	(0.0, 0.0, 0.0)	(0.0002, 0.0013, 0.0)	80.48°	0.000015187
Fe2	(0.0, 0.5, 0.0)	(0.9998, 0.4987, 0.0)	260.48°	0.000015187
Fe2	(0.5, 0.0, 0.0)	(0.4998, 0.9987, 0.0)	260.48°	0.000015187
Fe2	(0.5, 0.5, 0.0)	(0.5002, 0.5013, 0.0)	80.48°	0.000015187
N	(0.25, 0.25, 0.5)	(0.2501, 0.2500, 0.5)	9.52°	0.000000134
N	(0.25, 0.75, 0.5)	(0.2499, 0.7500, 0.5)	189.52°	0.000000134
N	(0.75, 0.25, 0.5)	(0.7499, 0.2500, 0.5)	189.52°	0.000000134
N	(0.75, 0.75, 0.5)	(0.7501, 0.7500, 0.5)	9.52°	0.000000134

Table 2Crystal structures, lattice parameters, atomic positions and magnetic moments of Fe₄N at 0 and 10 GPa.

Crystal structures	Lattice parameters (Å)	Atomic position	Magnetic moment (μB)
Pm $\bar{3}$ m 0 GPa	$a = 3.795$ (3.780 ^a , 3.797 ^b , 3.790 ^c , 3.748 ^d)	Fe1: 3c (0.5, 0, 0.5) Fe2: 1a (0, 0, 0) N: 1b (0.5, 0.5, 0.5)	Fe1: 2.336 (2.307 ^a , 2 ^b) Fe2: 2.951 (2.972 ^a , 3 ^b) N: 0.026 (0.050 ^a) Tot: 9.983 (10.01 ^a)
Pm $\bar{3}$ m 10 GPa	$a = 3.70463$	Fe1: 3c (0.5, 0, 0.5) Fe2: 1a (0, 0, 0) N: 1b (0.5, 0.5, 0.5)	Fe1: 1.746 Fe2: 2.935 N: -0.007 Tot: 8.164
P2/m 10 GPa	$a = 5.24780$ $b = 3.71980$ $c = 5.24780$	Fe1: 1e (0.5, 0.5, 0.0) Fe2: 2m (0.72940, 0.0, 0.72930) Fe3: 2m (0.76405, 0.0, 0.23587) Fe4: 1b (0.0, 0.5, 0.0) Fe5: 1f (0.0, 0.5, 0.5) Fe6: 1h (0.5, 0.5, 0.5) N: 2h (0.74894, 0.5, 0.74893)	Fe1: 1.989 Fe2: 1.939 Fe3: 2.927 Fe4: 1.965 Fe5: 1.976 Fe6: 1.577 N: 0 Tot: 17.240

^a Ref. [10].^b Ref. [31].^c Ref. [32].^d Ref. [33].**Fig. 1.** For γ' -Fe₄N after expansion of the primitive cell $2 \times 2 \times 1$, the moving diagram of Fe and N atoms along the polarization direction corresponded by virtual frequency on XY plane ((0 0 1) crystal plane) (See Table 1).

atoms, and that of N is large, while the vibration of Fe2 atoms almost makes no contribution. The reason is that the bond length of Fe1-N at face centers is smaller than that of Fe2-N at corners, and the strong vibration of the N atom only causes the vibration of the nearest neighbor Fe1 atoms but almost has no effect on the vibration of Fe2 in this frequency region. From Fig. 3 (c) and (d), without considering magnetism, there appears low-frequency phonon softening phenomenon in the phonon spectrum of γ' -Fe₄N crystalline alloy, that is to say, imaginary frequency appears. From Fig. 3(c), the three acoustic phonons do not display softening at the point G (See Σ line), and only optical phonons display imaginary frequency, and there are 6 imaginary frequencies appeared near the R point along the line S, which indicates that imaginary frequency must appear in the low-frequency optical phonon. From Fig. 3(d), it can be seen that the vibration of Fe1 at face centers causes the imaginary frequency of low-energy phonon, while that of Fe2 at corners has no contribution to the imaginary frequency. Moreover, N atoms at body center also have contributions, which one more time proves that the imaginary frequency must appear in the low-energy optical phonon. As the atomic weight of N is much smaller than that of Fe, Fe atoms makes main contribution to acoustic phonon, and the contribution of N can be ignored. This indicates that in Fig. 3(d), the contribution of N atom to imaginary frequency is caused by the optical phonons

which have relations with the relative vibration between Fe1 at face centers and N at body centers. This also indicates that when not considering the magnetism of the system, Fe1 and N locate at the equilibrium positions of the system, which is in instable equilibrium state.

Wenxu Zhang [18] studied the phonon spectrum of γ -Fe, and found that without considering the magnetic moment of Fe, imaginary frequency does not appear in phonon spectrum, while when considering the magnetic moment, imaginary frequency appears. They thought that the magnetic moment of Fe induced the phonon softening of γ -Fe. When considering the magnetic moment of Fe, the phonon spectrum of γ' -Fe₄N is stable and there is no imaginary frequency, indicating that Fe atoms are in lattice dynamical instability equilibrium state in γ -Fe (considering magnetic moment of Fe). The spontaneous magnetization of γ' -Fe₄N causes the redistribution of magnetic moment of Fe atoms after interstitial atom N fills body center, and this induces the stable phonon spectrum of the system. Thus, we think that the stability of the phonon spectrum of γ' -Fe₄N has close relations with the interaction of magnetic oscillator and phonon [34].

We calculate the pressure dependence of bond lengths of γ' -Fe₄N. As shown in Fig. 4, Fe1-N bond is the shortest and the difference relative to zero pressure varies slowly, Fe2-N bond is the longest and the difference changes more rapidly, while the bond

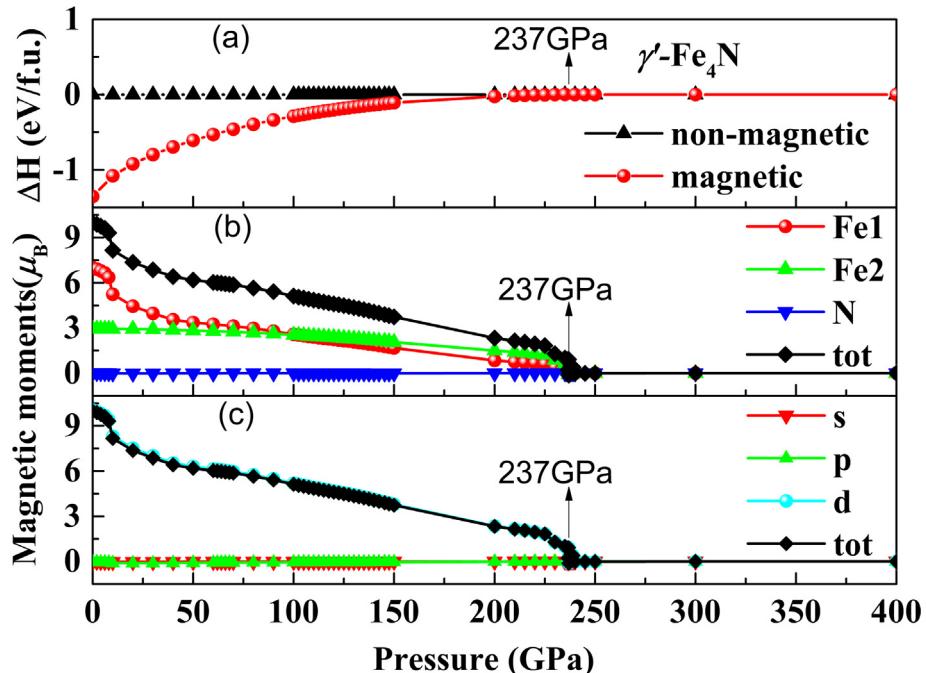


Fig. 2. The variation of enthalpy difference and magnetic moments of γ' -Fe₄N with pressure. (a) The enthalpy difference of γ' -Fe₄N with and without considering the electron spin polarization. (b) The contribution of unequal atoms to the magnetic moments and the total magnetic moments. (c) The contribution of electrons in different orbits to the magnetic moments and the total magnetic moments.

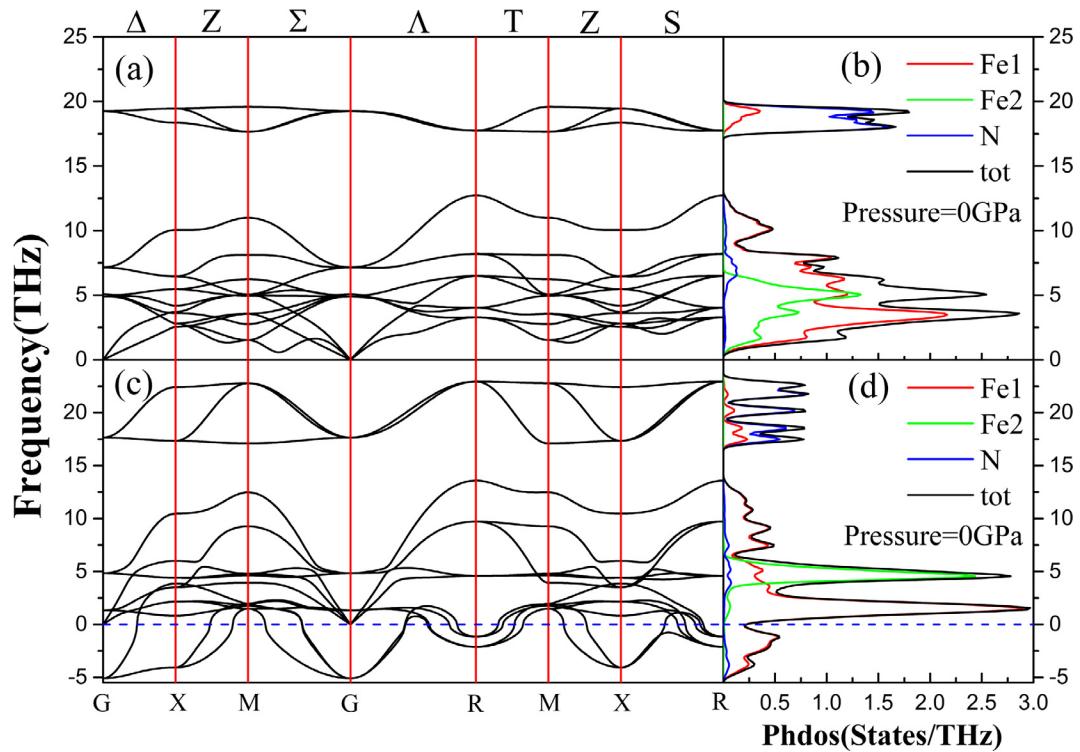


Fig. 3. The phonon spectrum and the corresponding phonon-state density of γ' -Fe₄N crystalline alloy at 0 GPa. (a) The phonon spectrum of the system considering electron spin polarization, (b) The corresponding phonon-state density. (c) The phonon spectrum of the system without considering electron spin polarization, (d) The corresponding phonon-state density.

length of Fe1-Fe2 and the difference present a moderated decrease. These calculated results suggest that the effect of N on Fe1 is stronger than that on Fe2, leading to the pressure dependent magnetic moments (see Fig. 2) and phonon frequencies. To this end, pressure induced phonon spectrum of γ' -Fe₄N is calculated.

From Fig. 5, it can be seen that there is no imaginary frequency in the phonon spectrum of γ' -Fe₄N when the pressure is below 1 GPa, so γ' structure is the ground-state structure of dynamic stabilization. When the pressure is larger than 1.03 GPa, the point (0.37 0.37 0) on the Σ line appears imaginary frequency which

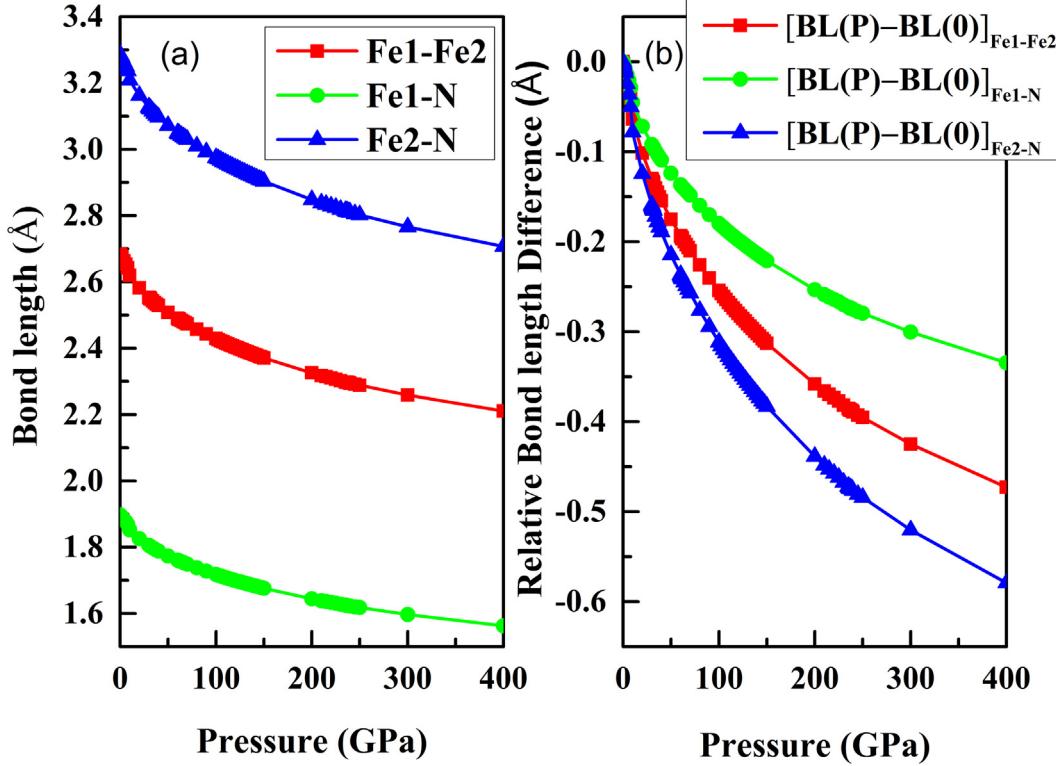


Fig. 4. (a) The bond length of Fe1-Fe2, Fe1-N and Fe2-N as a function of pressure; (b) the bond length of Fe1-Fe2, Fe1-N and Fe2-N relative to the bond length ones in 0 GPa as a function of pressure.

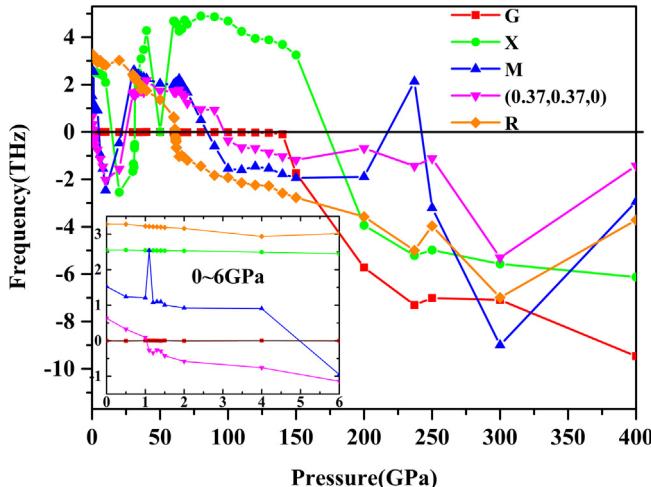


Fig. 5. The variation of low-energy phonon modes of γ' -Fe₄N crystalline alloy with pressure in the main symmetry points (points G, X, M and R) and the point (0.37, 0.37, 0) in the Brillouin zone.

approximately meets the critical pressure P_c determined by Landau's theory [20–23,25] of pressure-induced soft-mode phase transition. The P_c meets the relation of $v^2 - v_0^2 = c(P - P_c)$, where v_0 is the phonon frequency under normal pressure and c is the proportional coefficient. When the pressure is about 5 and 14.5 GPa, imaginary frequencies appear at the points M and X respectively. For the points M, (0.37 0.37 0) and X, the imaginary frequency disappears near 21.6 GPa, 25 GPa and 31.5 GPa respectively. And as the imaginary frequency disappears at the point X, the pressure-induced phonon-spectrum stability appears. In the pressure range from 31.5 to 60.8 GPa, the lattice dynamics of the system is stable.

When the pressures are about 61.1, 84.7, 97.2, 139.9 and 172.6 GPa respectively, the points R, M, (0.37 0.37 0) on the Σ line, G and X begin to appear imaginary frequencies respectively. The magnetism of the system disappears when the pressure is over 237 GPa, when the phonon spectrum coincides with that of γ' -phase without considering magnetism. This indicates that the pressure changes the interatomic distance and the distribution of electric charge among atoms, which provides favorable conditions to offset the interatomic forces. The competition between the role of pressure and the spontaneous magnetostriction of ferromagnetism γ' -Fe₄N causes the above softening of the low-energy phonons and the stable phonon spectrum. The spontaneous magnetostriction makes the dynamic stabilization of the system, and the effect of the pressure makes the system dynamic unstable. When the pressure is under 1 GPa, the effect of the spontaneous magnetostriction is more than that of the pressure which makes all atoms at stable equilibrium places. While when the pressure is over 1.03 GPa, the pressure effect destroys the equilibrium of the system, and makes the system appear low-energy phonon softening (Figs. 5–7). When the pressure is between 31.5 and 60.8 GPa (Figs. 5–9), the pressure effect and spontaneous magnetostriction meet the stable equilibrium. All the atoms of the system have restoring force and vibrate at its stable equilibrium position which makes the phonon spectrum stable. However, our calculation on the phonon spectrum of the γ' -Fe₄N without considering spin polarization shows that the phonon spectrum is more and more unstable with the increasing pressure. This once more time indicates that the spontaneous magnetostriction induced the dynamic stabilization of the ferromagnetism γ' -Fe₄N. When the pressure is over 61.3 GPa (Figs. 5, 8 and 9), the pressure effect offset the stable equilibrium of the system. Some atoms are at unstable equilibrium position and the interatomic forces are offset by the pressure effect, which makes the phonon spectrum appear imaginary frequency. When the pressure is over 61.3 GPa, the phonon spectrum is more and more unstable with the increasing

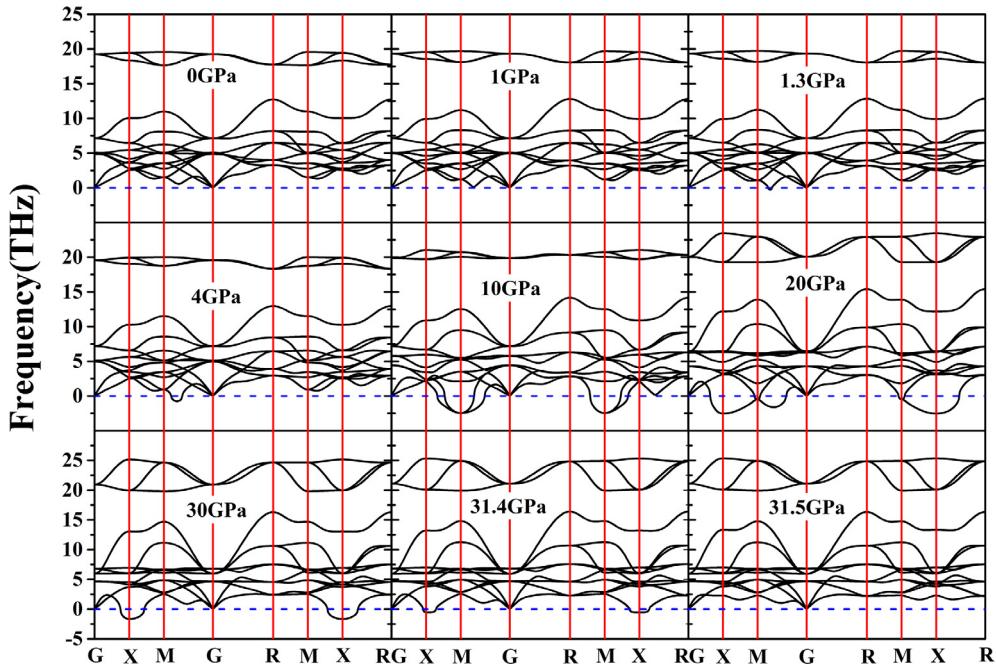


Fig. 6. The phonon spectrum of γ' -Fe₄N crystalline alloy at different pressures (0, 1, 1.3, 4, 10, 20, 30, 31.4 and 31.5 GPa).

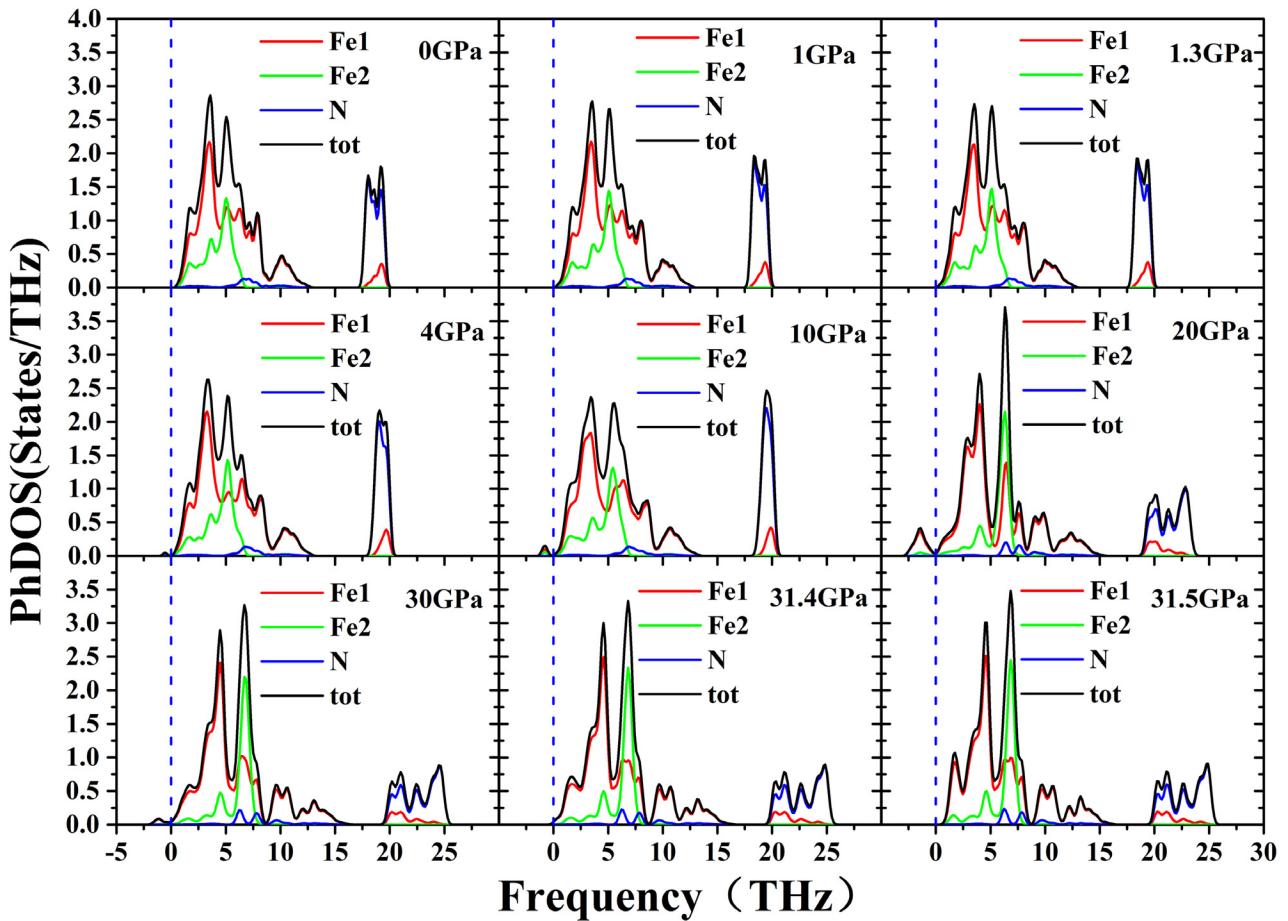


Fig. 7. The phonon-state density of γ' -Fe₄N crystalline alloy at different pressures (0, 1, 1.3, 4, 10, 20, 30, 31.4 and 31.5 GPa).

pressure. And when the pressure is over 237 GPa, the lattice kinetic instability of the system is the same with that without considering

magnetism. This indicates that for γ' -Fe₄N, the pressure effect makes the system dynamic instable.

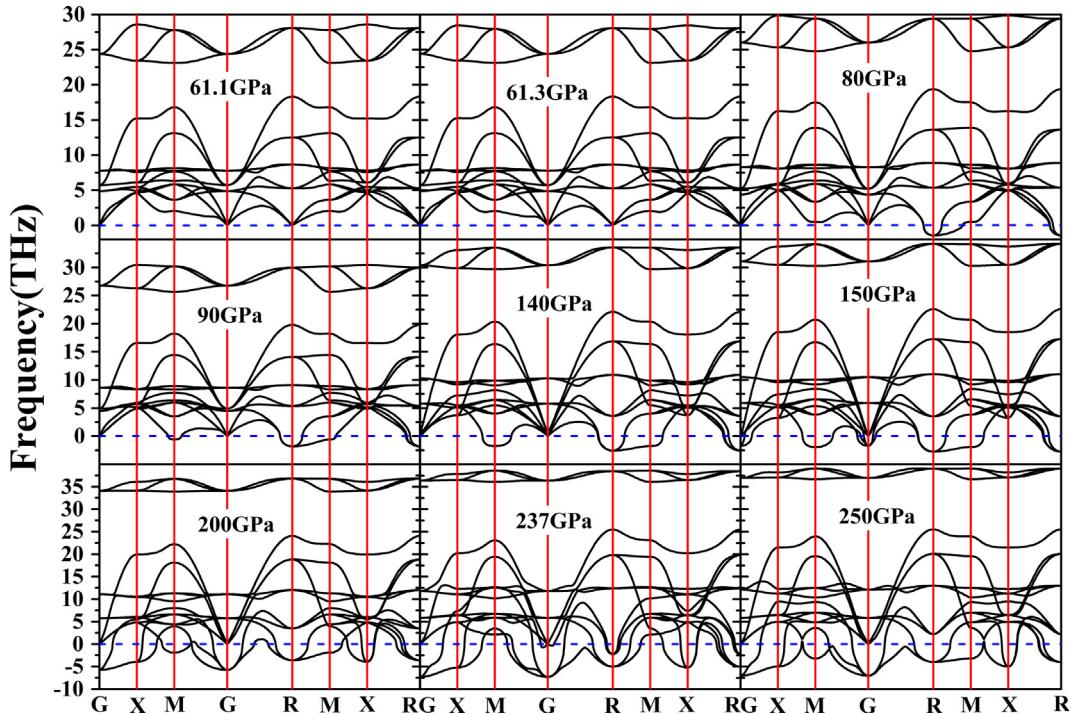


Fig. 8. The phonon spectrum of γ' -Fe₄N crystalline alloy at different pressures (61.1, 61.3, 80, 90, 140, 150, 200, 237, 250 GPa).

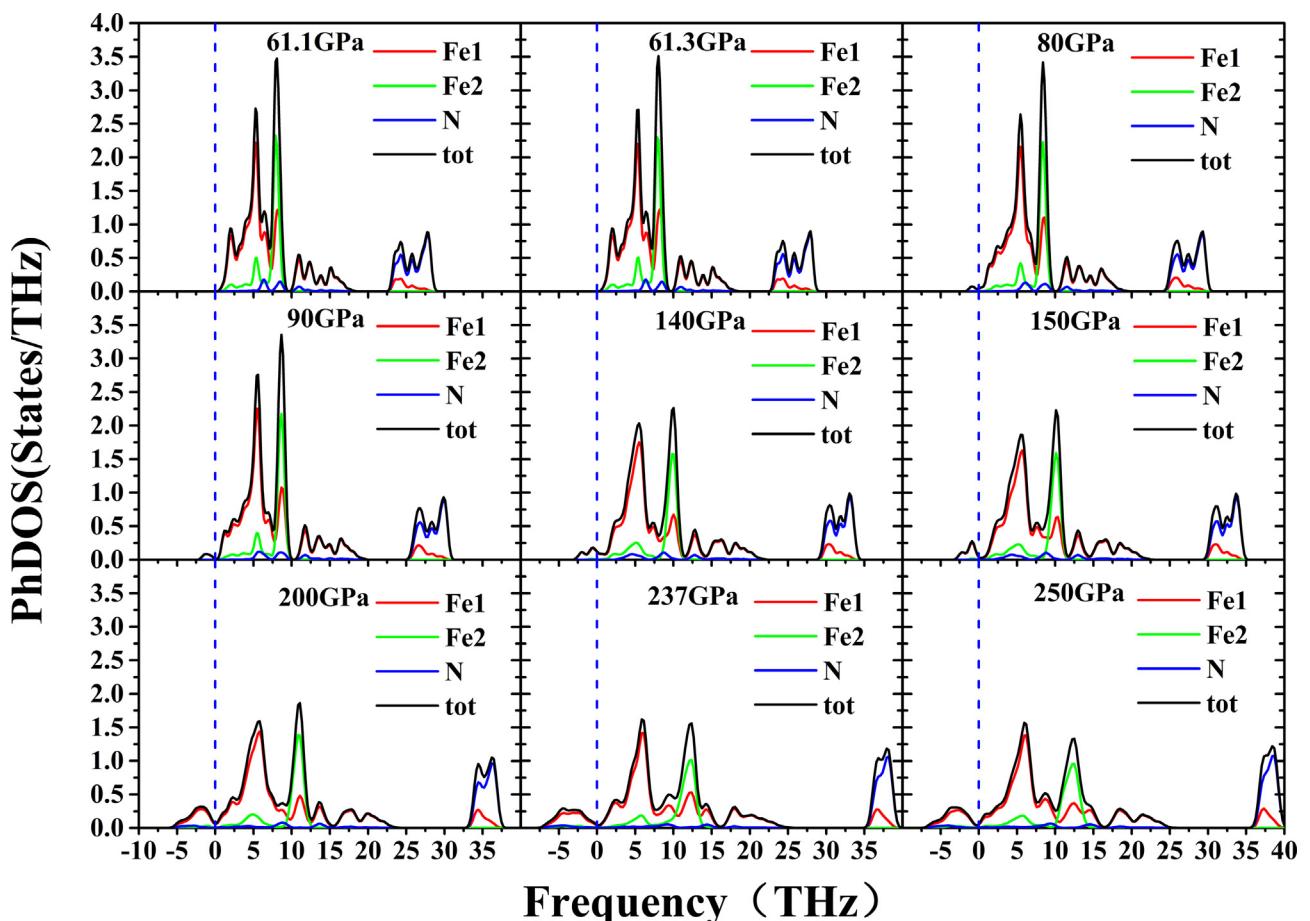


Fig. 9. The phonon-state density of γ' -Fe₄N crystalline alloys at different pressures (61.1, 61.3, 80, 90, 140, 150, 200, 237, 250 GPa).

From Figs. 6, 7 and 10, it can be seen that both longitudinal and transverse acoustic phonons display softening at the point M for γ' -Fe₄N at the pressure of 10 GPa (see Figs. 6 and 7). Using the soft-mode phase transition theory, we process the soft modes of the two acoustic phonons, and first discover the new high-pressure phase of P2/m-Fe₄N which is dynamic stable (see Fig. 10(a), (b), (c) and Table 1). At zero pressure, the magnetic moments of the unit formula of the new phase is 9.930 μ_B /f.u., which is almost the same to that of γ' -Fe₄N (9.983 μ_B /f.u.) (see Fig. 11(b)). The new high-pressure phase of P2/m-Fe₄N is thermodynamic stable at the pressure below 1 GPa (see Fig. 11(a)), and the magnetic moments of P2/m- and γ' -Fe₄N is almost the same (The magnetic moments of P2/m phase is only 0.05 μ_B /f.u smaller than that of γ' -phase) (see Fig. 11(b)). The magnetic moments of P2/m-Fe₄N is decreased sharply near 1.1 GPa, and linearly decreased with the pressure increasing from 1.2 to 20 GPa. However, the magnetic moment of γ' -Fe₄N is decreased sharply at about 8.77 GPa. The magnetic moment of γ' -Fe₄N is bigger than that of P2/m-Fe₄N at pressures below 8.77 GPa and is smaller than that of P2/m-Fe₄N at pressures between 8.79 and 19.5 GPa (See Fig. 11(b)). The structure of γ' -Fe₄N is more stable than that of P2/m-Fe₄N at pressures between 1.1 and 2.87 GPa, but is less stable between 2.9 and 19 GPa (See Fig. 11(a)). In the pressure range of 20–214 GPa, the two phases almost have the same magnetic moment. But at 143.8–214 GPa, the ground-state structure of γ' -phase is more stable than that of P2/m-Fe₄N phase. And, when the pressure is greater than 214 GPa, the ground-state structure of P2/m phase is more stable. At 214–300 GPa, the magnetic moment of P2/m phase is less than that of γ' -phase, and when the pressure is over 300 GPa, the two phases have the tend to have consistent magnetic moment. The magnetic properties of the new phase P2/m are mainly related to the distance between the Fe atoms, and Fe3 atoms make significant contributions to the magnetic moments of the system. Moreover, the magnetic moment of system decreases with the decreasing of the acoustic phonon-state density in low-frequency region, and the corresponding optical phonon-state density increases.

4. Conclusion

Through the first-principle calculations of the magnetism, lattice dynamics and soft-mode phase transition of Fe₄N crystalline alloy, the following conclusions can be drawn.

- (1) When the pressure is over 237 GPa, the enthalpy of the system with and without considering spin polarization is the same. The critical pressure P_c is 237 GPa for the magnetism collapse of the γ' -Fe₄N. The magnetic moment of Fe2 at corners varies slowly with pressure and is only sharply decreased near the collapse pressure. When the pressure is below 40 GPa, the magnetic moment of Fe1 at face centers is sharply decreased with the increasing pressure, and is almost linearly decreased up to the magnetism collapse with the pressure increasing from 40 GPa.
- (2) Fe atoms are in lattice dynamical instability equilibrium state in γ -Fe. The spontaneous magnetization of γ' -Fe₄N causes the redistribution of magnetic moment of Fe atoms after interstitial atom N fills body center, and this induces the stable phonon spectrum of the system.
- (3) For γ' -Fe₄N crystalline alloy, when the pressure is below 1 GPa, the effect of the spontaneous magnetostriction is more than that of the pressure which makes all atoms at stable equilibrium places. When the pressure is between 31.5 and 60.8 GPa, the pressure effect and spontaneous magnetostriction meet the stable equilibrium. All the atoms of the system have restoring force, and vibrate at its stable equilibrium position which makes the phonon spectrum stable. When the pressure is over 61.3 GPa, the pressure effect offset the stable equilibrium of the system. Some atoms are at instable equilibrium position and their restoring force disappears due to the pressure effect, which causes the imaginary frequency of phonon spectrum. The dynamic instability is more and more obvious with the increasing pressure at pressures over 61.3 GPa.
- (4) Through soft-mode transition theory, the high-pressure new phase of crystalline P2/m-Fe₄N is first discovered, which is thermodynamic stable at pressures below 1 GPa, and whose

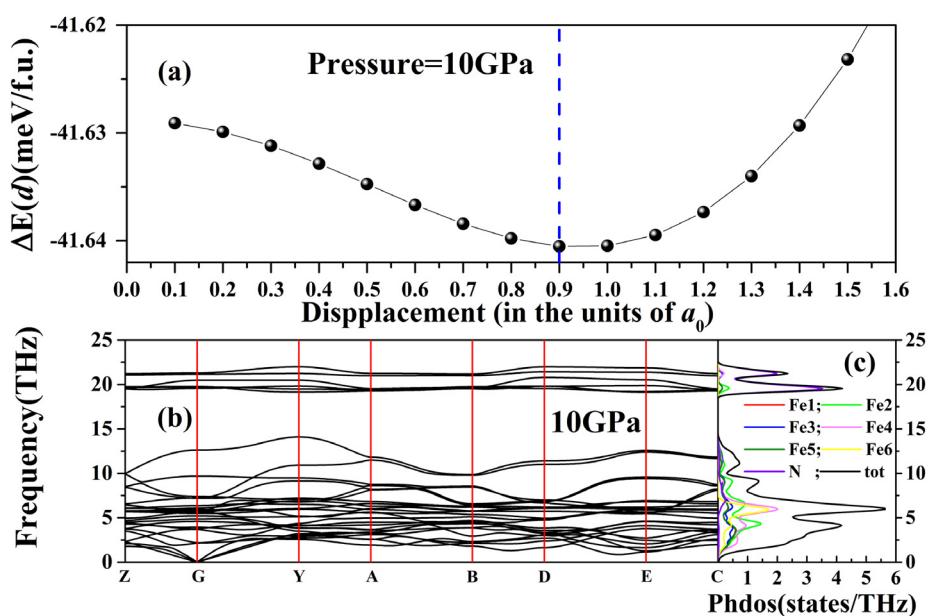


Fig. 10. (a) Energy evolution curve resulted from the displacements of Fe and N atoms in (0 0 1) crystal plane along the direction of the soft mode of the point M at 10 GPa. (b) The phonon spectrum of the crystalline alloy Fe₄N with P2/m structure at 10 GPa. (c) The corresponding phonon-state density at 10 GPa.

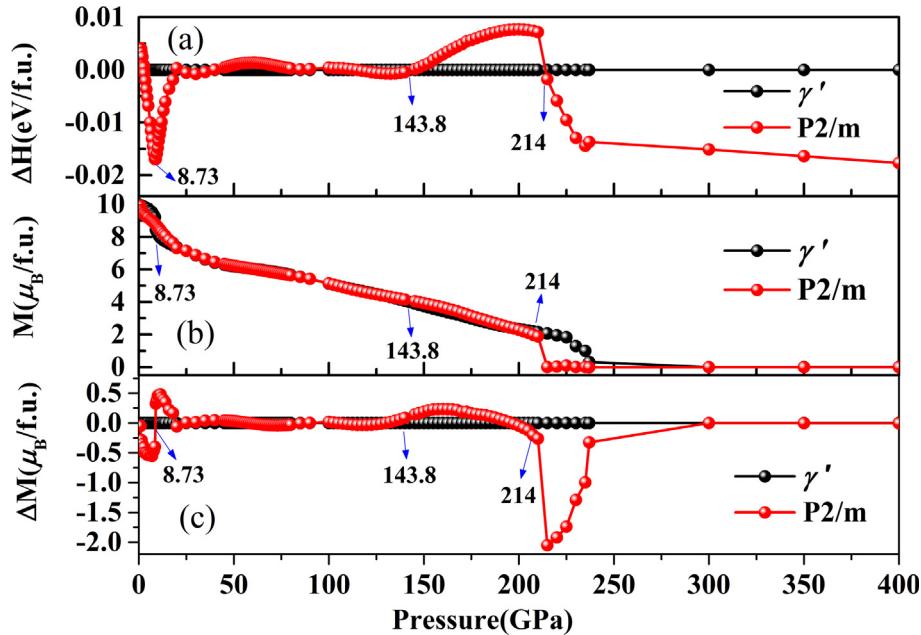


Fig. 11. (a) The enthalpy-difference change of Fe_4N between the P2/m and γ' structure with pressure. (b) The magnetic-moment change of Fe_4N with the P2/m and γ' structure with pressure. (c) The relative magnetic moment of P2/m phase as compared to the γ' -phase varies with pressure.

magnetic moment has little difference with that of γ' - Fe_4N . The thermodynamic stability of P2/m phase is better than that of γ' -phase in the pressure range between 2.9 and 19 GPa, and at pressures between 20 and 214 GPa, the magnetic moments of the two phases are almost the same. However, the ground-state structure of γ' -phase is more stable than that of P2/m phase at pressures from 143.8 to 214 GPa, and is less stable when the pressure is above 214 GPa. The magnetic moment of P2/m phase is lower than that of γ' -phase at pressures from 214 to 300 GPa, and the magnetic moments of the two phases tend to be consistent when the pressure exceeds 300 GPa.

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References

- [1] T. Yamaguchi, M. Sakita, M. Nakamura, T. Kobira, J. Magn. Magn. Mater. 215–216 (2) (1994) 529.
- [2] S.K. Chen, S. Jin, T.H. Tiefel, Y.F. Hsieh, E.M. Gyorgy, D.W. Johnson Jr., J. Appl. Phys. 70 (10) (1991) 6247.
- [3] N. Elliott, Phys. Rev. 129 (3) (1963) 1120.
- [4] J.M. Gallego, D.O. Boerma, R. Miranda, F. Yndurain, Phys. Rev. Lett. 95 (13) (2005) 136102.
- [5] N.D. Telling, G.A. Jones, C.A. Faunce, P.J. Grundy, H.J. Blythe, D.E. Joyce, J. Vac. Sci. Technol. A19 (2) (2001) 405.
- [6] S. Kokado, N. Fujima, K. Harigaya, H. Shimizu, A. Sakuma, Phys. Stat. Sol. (c) 3 (9) (2006) 3303.
- [7] S. Kokado, N. Fujima, K. Harigaya, H. Shimizu, A. Sakuma, Phys. Rev. B 73 (17) (2006) 172410.
- [8] E.P. Blanca, J. Desimoni, N.E. Christensen, H. Emmerich, S. Cottenier, Phys. Status Solidi B 246 (5) (2009) 909.
- [9] Y. Kong, R.J. Zhou, F.S. Li, Phys. Rev. B 54 (8) (1996) 5460.
- [10] Z.Q. Lv, Y. Gao, S.H. Sun, M.G. Qv, Z.H. Wang, Z.P. Shi, W.T. Fu, J. Magn. Magn. Mater. 333 (2013) 39.
- [11] D. Music, J.M. Schneider, Appl. Phys. Lett. 88 (3) (2006) 031914.
- [12] Z.J. Wu, J. Meng, Appl. Phys. Lett. 90 (24) (2007) 241901.
- [13] E.J. Zhao, H.P. Xiang, J. Meng, Z.J. Wu, Chem. Phys. Lett. 449 (26) (2007) 96.
- [14] Y. Takahashi, Y. Imai, T. Kumagai, J. Magn. Magn. Mater. 323 (23) (2011) 2941.
- [15] P. Monachesi, T. Bjorkman, T. Gasche, O. Eriksson, Phys. Rev. B 88 (5) (2013) 054420.
- [16] A.V.G. Rebaza, J. Desimoni, E.P. Blanca, Physica B 404 (1) (2009) 2872.
- [17] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (18) (1996) 3865.
- [18] W.X. Zhang, J. Magn. Magn. Mater. 323 (16) (2011) 2206.
- [19] A. Togo, F. Oba, I. Tanaka, Phys. Rev. B 78 (13) (2008) 134106.
- [20] L.D. Landau, Phys. Z. Soviet. 11 (1937) 26.
- [21] L.D. Landau, JETP 7 (1937) 19.
- [22] L.D. Landau, E.M. Lifshitz, Statistical Physics (Part I), third ed., Butterworth-Heinemann, Oxford, 2007, pp. 446–516.
- [23] J.F. Scott, Rev. Mod. Phys. 46 (1) (1974) 83.
- [24] G. Shirane, Rev. Mod. Phys. 46 (3) (1974) 437.
- [25] S. Baroni, S.d. Gironcoli, A.D. Corso, P. Giannozzi, Rev. Mod. Phys. 73 (2) (2001) 515.
- [26] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (16) (1996) 11169.
- [27] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1) (1996) 15.
- [28] G. Kresse, D. Joubert, Phys. Rev. B 59 (3) (1999) 1758.
- [29] G. Kresse, J. Hafner, Phys. Rev. B 47 (1) (1993) 558.
- [30] P.E. Blöchl, Phys. Rev. B 50 (24) (1994) 17953.
- [31] B.C. Frazer, Phys. Rev. 112 (3) (1958) 751.
- [32] H. Jacobs, D. Rechenbach, U. Zachwieja, J. Alloys Compd. 227 (1) (1995) 10.
- [33] C.M. Deng, C.F. Hou, L.L. Bao, X.R. Shi, Y.W. Li, J.G. Wang, H.J. Jiao, Chem. Phys. Lett. 448 (5) (2007) 83.
- [34] R. Silberclitt, Phys. Rev. 188 (2) (1969) 786.