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Spin-polarized electronic properties of $NiHe_{0.25}$ under pressure*

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This paper studies the effects of He atom on the spin-polarized electronic properties of nickel under pressures using *ab initio* pseudopotential plan-wave method. Under high pressures, the compound of $NiHe_{0.25}$ can exist and helium-bubble can not create in Ni. A pressure-induced ferromagnetic to paramagnetic phase transition has been predicted in $NiHe_{0.25}$ at about 218 GPa. It is found that under pressures, the magnetic property of Ni atoms is more strongly affected by He atom than by H atom and that the behaviour of He atom in Ni are completely different from that of H atom, like the bonding characteristics and the electron transfer.

Keywords: plane-wave method, interaction potential, electronic structure
PACC: 7115A, 3520J

1. Introduction

As we know, understanding the fundamental behaviour of hydrogen and helium in metals is a primary issue in the research and development of fusion reactor materials. No matter whether the chemically active H or inert gas He, the impurity leads to a strong electronic interaction with the host metal.[1] The addition of H in metal can dramatically change the bulk properties of metal, such as the magnetic,[2] superconducting[3−5] and mechanical properties.[6] As for the addition of He in metal, many experimental[7−10] and theoretical[11−16] results indicate that a helium-bubble creates and grows in metals, while less is known of the effect of pressure on it and the modifications in the metallic characteristic produced by the addition of helium. By studying the spin-polarized electronic properties of $NiHe_{0.25}$, we expect to make clear if the ferromagnetism of metal nickel is reduced by the doped helium atom. This study is of interest, because He holds a closed electronic shell, completely different from the chemically active H atom.

The results indicate that under high pressures, the compound of $NiHe_{0.25}$ can exist and the helium-bubble cannot be created in Ni. The pressure-induced ferromagnetic–paramagnetic (FM–PM) phase transition in $NiHe_{0.25}$ occurs at 218 GPa, but within the pressure range of our investigation up to 220 GPa, $NiH_{0.25}$ maintains the ferromagnetism.[17] The effect of helium atom on metal nickel is more intense than that of hydrogen atom under high pressures.

2. Modelling and methods

Among allowing self-trapping states in fcc lattice, the octahedral site is clearly more favourable than the tetrahedral site.[1] The unit cell of the crystal structure contains four Ni atoms in the fcc Bravais lattice sites and one helium located in the interstitial site which is the biggest-octahedron site as shown in Fig.1(a). In order to check the interaction between the doped

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He and its mirror image, one $2 \times 2 \times 1$ supercell constructed with the unit cell are used to realize $Ni_{16}He_4$, and one He atom is removed to different sites in the high symmetry axis as shown in Fig.1(b) to investigate the effect of He–He relative displacement on the interaction potential. The effect of pressure on the interaction potential along the special axis is shown in Fig.2. At 0 GPa, the height of T point is lower than that of S point and the potential barrier along $T-O-T$ direction is close to the average vibration energy at room temperature (0.026 eV), which indicates that the helium-bubble is created more easily in this path. With the increase of pressure, the height of T and S sites increases largely, and after 10 megabar the potential barrier along $T-O-T$ direction is higher than 0.8 eV, which means that the helium can not traverse this potential barrier unless it heats up to about 8000°C. Furthermore, the saddle point X between O and T is higher than T, which indicates that under this chemical proportion in Ni–He system, the helium atom stably locates at O site. But the distribution of this interaction potential is not changed obviously by compression.

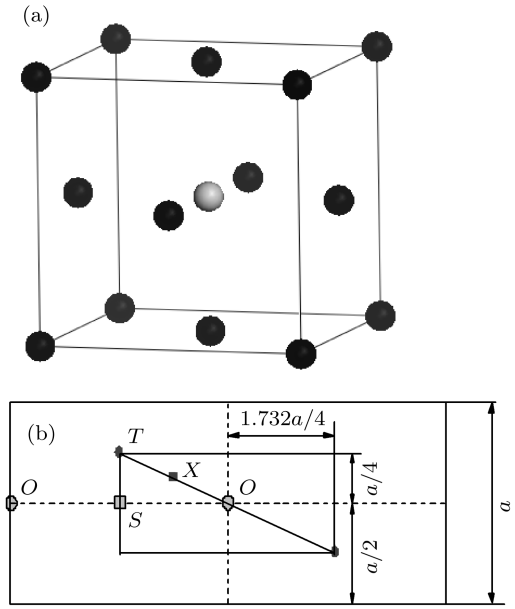


Fig.1. The modelling structure. (a) The crystal structure, (b) The testing sites of He atom.

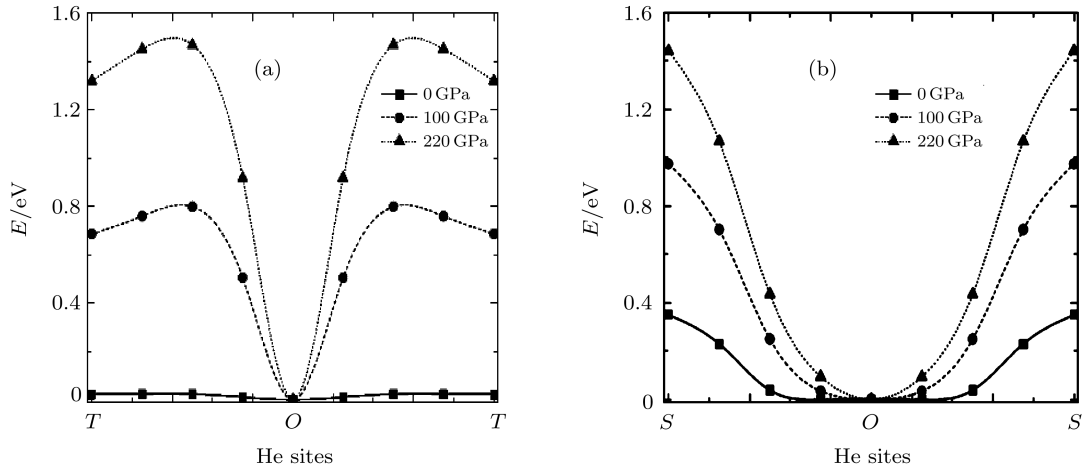


Fig.2. The effect of pressure on the interaction potential in the special axis: (a) along $T-O-T$ axis; (b) along $S-O-S$ axis.

Figure 3 shows the density of state (DOS) of different He atom in the supercell $Ni_{16}He_4$ at 220 GPa. The DOS of the removed He atom located at T, S or O site and of the other fixed He atom is shown in Figs.3(a) and 3(b), respectively. The results indicate that under pressures the other fixed He atom aren't affected by the removed He atom. So we can deduce that under pressures, the interaction among He atoms in $NiHe_{0.25}$ is very small and the $NiHe_{0.25}$ compound can exist.

Pseudopotential plane-wave *ab initio* calculations[18] are performed within the framework of density functional theory through the CASTEP code.[19] The total energy is obtained for the electron states, by using the Perdew–Wang (PW91) generalized gradient-approximation (GGA).[20] The interaction of the valence electrons with the core electrons is described by ultrasoft pseudopotential[21] which is generated with an atomic electronic configuration of $3d^8 4s^{1.27} 4p^{0.73}$ for Ni. A cutoff energy of 600 eV and a k mesh of $16 \times 16 \times 16$ are used to obtain convergence of the total energy and pressure with respect to basis set size for $NiHe_{0.25}$. Spin-polarization is applied in all the calculations.

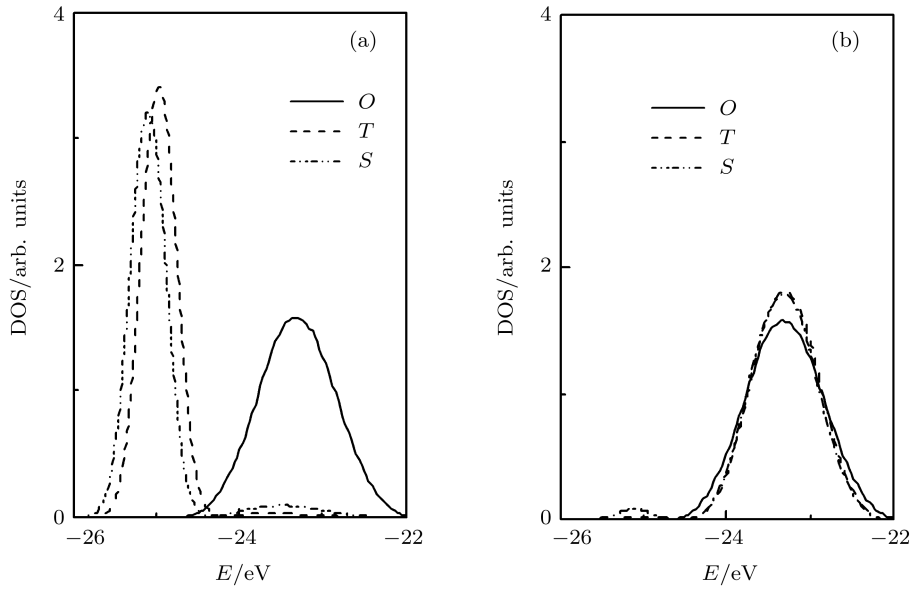


Fig.3. The density of state (DOS) of different He atom in the supercell $Ni_{16}He_4$ at 220 GPa: (a) the removed He atom located at T, S or O point; (b) the other fixed He atom.

3. Results and discussion

Figure 4 shows the spin-polarized band structure for $NiHe_{0.25}$ at 100 and 218 GPa. The majority and minority-spin band is represented by the solid and dashed lines, respectively. At 100 GPa, the bands show majority and minority-spin band splittings. The doped He atom makes the bands below the Fermi level compressed. Especially, in the centre of Brillouin zones (G), the width of the second lowest energy band reduces. With the addition of the doped He atom, there is an ionic band located at the lowest energy area. As for the ionic band, the gap between the ionic band and the second lowest energy band is about 10 eV in $NiHe_{0.25}$. With the increase of pressure, the real gap of $NiHe_{0.25}$ increases. As we have investigated in nickel-hydrides,[17] with the increase of pressure, the splittings between the majority and minority-spin band reduce, and up to 220 GPa, the splittings in Ni and $NiH_{0.25}$ still exist, while the splittings in $NiHe_{0.25}$ vanish at 218 GPa.

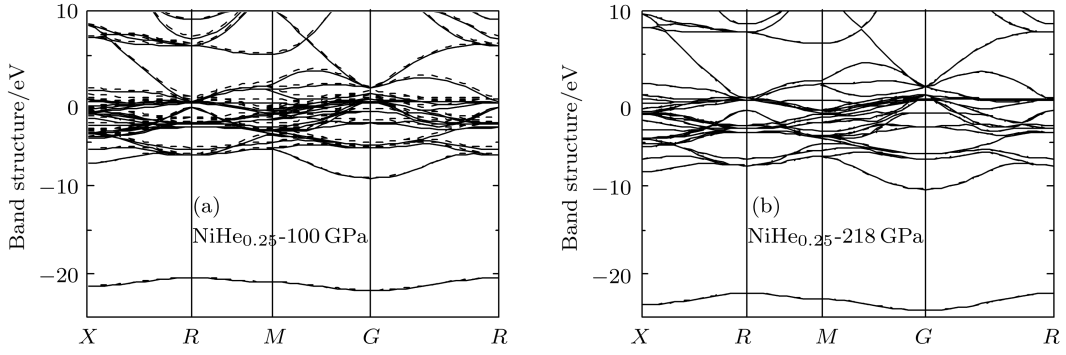


Fig.4. Calculated spin-polarized band structure for $NiHe_{0.25}$ at 100 and 218 GPa.

The bond overlap population (BOP) in $NiH_{0.25}$ and $NiHe_{0.25}$ by Mulliken population scheme[22,23] is listed in Table 1, in which Ni 2 and Ni 3 represent the second-nearest-neighbour and the nearest-neighbour Ni atoms to H or He atom, respectively. As we know, there are three nearest-neighbour Ni atoms in $NiH_{0.25}$ and $NiHe_{0.25}$, so we make Ni 3' represent the equivalent nearest-neighbour Ni atoms. At 100 GPa, Ni 2 with He can form a weak bonding states, and Ni 3 with He can form a weak antibonding states, while Ni

2 with H form antibonding states, and Ni 3 with H form bonding states. In the other point of view, this indicates that under lower pressures, the interaction between Ni and He is mainly embodied by repulsion, while that between Ni and H mainly by hybridization. Furthermore, the antibonding states between the equivalent nearest-neighbour Ni atoms and between Ni 2 and Ni 3 in $NiH_{0.25}$ and $NiHe_{0.25}$ are formed. With the increase of pressure, the bonding states between Ni 3 and H, and the antibonding states between Ni 2 and H decrease, while the antibonding states between Ni 3 and He, and the bonding states between Ni 2 and He increase largely, which illuminates that in the lower–energy range, the repulsion presented between Ni and He is reduced by compression, and under higher pressures, the interaction between them also embodied by hybridization. Furthermore, the intensity of the antibonding states between the equivalent nearest-neighbour Ni atoms, and between the inequivalent Ni atoms in $NiH_{0.25}$ and $NiHe_{0.25}$ is enhanced with the increase of pressure, which is more obvious for the antibonding states between the inequivalent Ni atoms in $NiHe_{0.25}$. So, we can see that the largest difference between $NiH_{0.25}$ and $NiHe_{0.25}$ is focused on the bonding characteristics between the doped atom and nickel atoms. Under higher pressures, the bonding characteristics are more obvious in $NiHe_{0.25}$ than in $NiH_{0.25}$, which indicates that the chemical activity of He is enhanced by compression and even stronger than that of H. Combined with Fig.4, we find that the electrons of He is quite localized, so, for the electrons in the lower-energy range, the hybridization between Ni and He is enhanced, while the repulsion between Ni and He also exists in the higher-energy range.

Table 1. Distance [BL(nm)] and bond overlap population (BOP) between Ni atoms and doped H or He atom, and between different Ni atoms.

		100 GPa		218 GPa	
		BOP	BL	BOP	BL
$NiH_{0.25}$					
	H – Ni 2	–0.19	0.2850	–0.14	0.2714
	H – Ni 3	0.15	0.1645	0.09	0.1568
	Ni 2 – Ni 3	–0.05	0.2327	–0.48	0.2216
	Ni 3 – Ni 3'	–1.18	0.2327	–2.14	0.2216
$NiHe_{0.25}$					
	He – Ni 2	0.10	0.2898	0.32	0.2750
	He – Ni 3	–0.09	0.1673	–0.17	0.1588
	Ni 2 – Ni 3	–0.33	0.2367	–1.07	0.2246
	Ni 3 – Ni 3'	–1.05	0.2367	–2.01	0.2246

For further investigation, we also display the partial density of states (PDOS) in $NiH_{0.25}$ and $NiHe_{0.25}$ as shown in Fig.5. The Fermi level is mainly contributed by Ni 3d electrons. In $NiHe_{0.25}$, the hybridization mainly exists among He 1s, Ni 4s, Ni-2 4p and Ni-3 3d, while in $NiH_{0.25}$, the hybridization mainly exists between H 1s and Ni 4s, and all these hybridizations are enhanced by pressure, especially in $NiHe_{0.25}$. Besides that, the effect of pressure on Ni atoms is mainly focused on Ni-2 4p.

Figure 6 shows the electron transfer induced by pressure in $NiHe_{0.25}$. The dotted lines represent the doped He 1s, and the squares, triangles and circles represent the 4s, 4p and 3d of Ni, respectively. The Mulliken charge population analysis[22,23] indicates that He is as a cation and there are electron transfers from nearest-neighbour Ni 4p to second-nearest-neighbour Ni 4s and from 4p to 4s and 3d inside each Ni atom. As we have investigated in Nickel-hydrides,[17] all the above mentioned electron transfers among Ni atoms existed in $NiH_{0.25}$, but the difference between $NiH_{0.25}$ and $NiHe_{0.25}$ is that H is as an anion and accepts electrons from the nearest-neighbour Ni atoms.

The charge (Q) and magnetic moment (m) for the inequivalent atoms in $NiHe_{0.25}$ under different pressures is listed in Table 2. In Ni–H system, it is Ni atoms which provide electrons to H atom, as investigated in Ref.[17], but in Ni–He system, it is He atom which provide electrons to Ni atoms, and merely complete to the nearest-neighbour Ni atom. Under pressures, in Ni–H system, H atom obtains more electrons from the nearest-neighbour Ni atom. At the same time, the second-nearest-neighbour Ni atom also obtains electrons from the nearest-neighbour Ni atom.

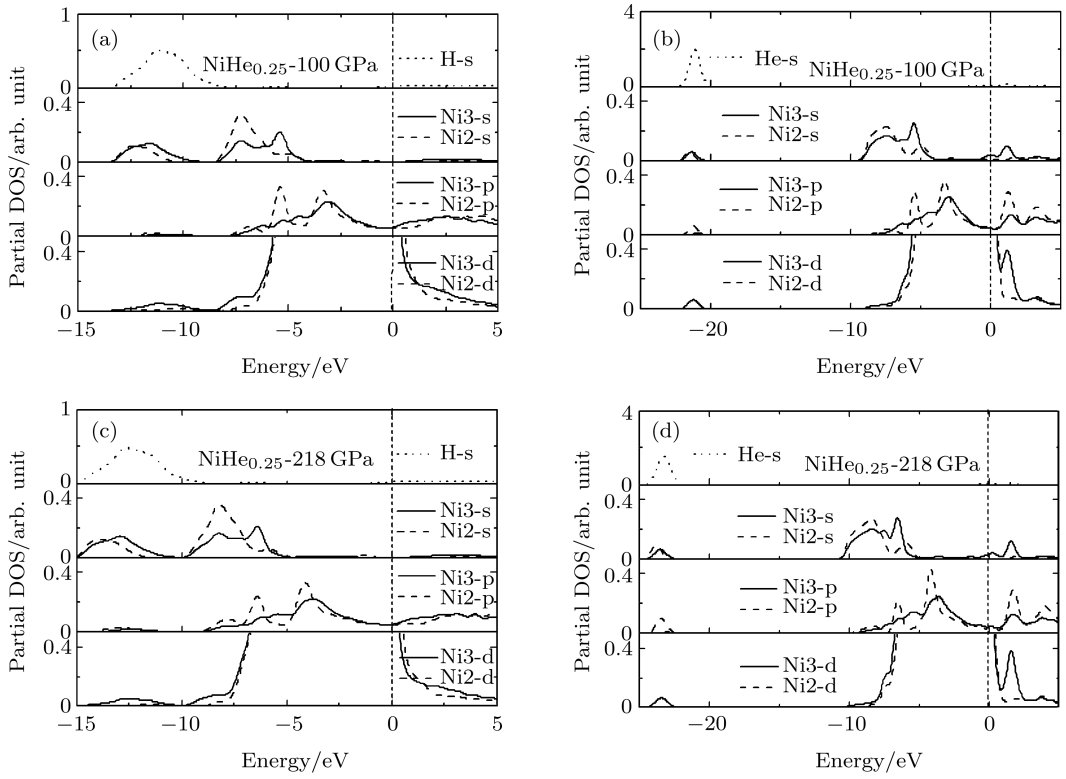


Fig.5. Calculated PDOS for $NiH_{0.25}$ and $NiHe_{0.25}$ at 100 and 218 GPa. The Fermi level is set at zero energy and marked by a vertical dotted line.

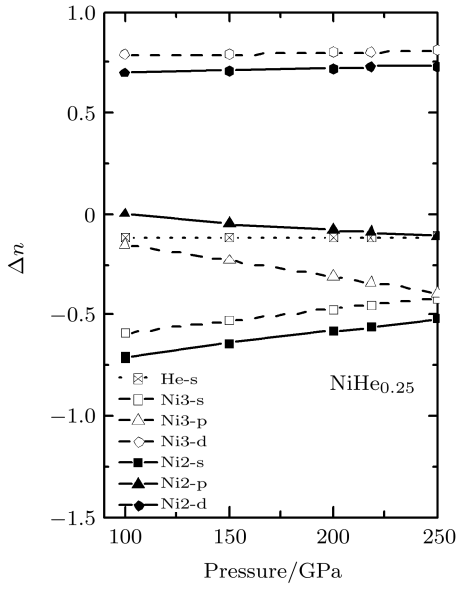


Fig.6. The electron population for Ni 3d, 4s, 4p and H 1s in $NiHe_{0.25}$ under different pressures. The charge spilling parameter is below 3×10^{-3} under all the investigated pressures.

However, in Ni–He system, under pressures, there is not electron transfer in He atom, and the electron transfer mainly exists from the nearest-neighbour Ni atom to the second-nearest-neighbour Ni atom. Therefore, the positive electricity of He atom is not changed, the negative electricity of the nearest-neighbour Ni atom reduces and the negative electricity of the second-nearest-neighbour Ni atom increases. As for the magnetism in $NiHe_{0.25}$, the magnetic moments are mainly contributed by Ni atoms, furthermore the nickel atoms are away from the doped He atom, the larger their magnetic moments are, which is the same as that in nickel-hydrides.[17]

Table 2. The charge $Q(e)$ and magnetic moment m (μ_B) for two Ni atoms (Ni 2 and Ni 3) and one He atom in the unit cell of $NiHe_{0.25}$ under different pressures. Ni 2 and Ni 3 represent the second-nearest-neighbour Ni atom and the nearest-neighbour one, respectively. The charge spilling parameter for majority and minority-spin components is below 3×10^{-3} under all the investigated pressures.

	100 GPa		218 GPa	
	Q	m	Q	m
He	0.12	0.021	0.12	0.00
Ni 2	0.00	0.665	–0.08	0.00
Ni 3	–0.04	0.312	–0.01	0.00

Figure 7 shows the theoretical value of the average magnetization of per Ni atom in $NiH_{0.25}$ and $NiHe_{0.25}$, in comparison with that in pure Ni system.[24] The average magnetization of per Ni atom is decreased by

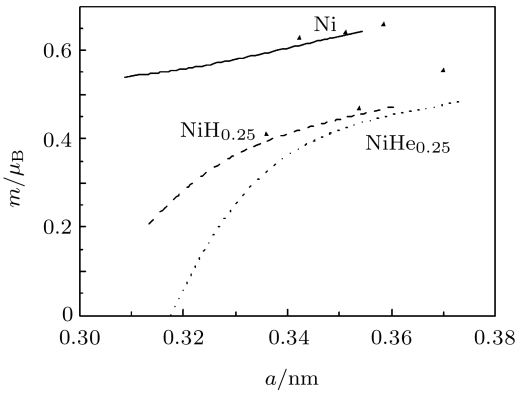


Fig.7. Theoretical value of the average magnetization of per Ni atom in Ni, $NiH_{0.25}$ and $NiHe_{0.25}$.

the addition of the doped atom. With the increase of pressure, the average magnetization of per Ni atom reduces in both $NiHe_{0.25}$ and $NiH_{0.25}$, especially in $NiHe_{0.25}$, the value even equals to zero. See Table 2 again, the added He atom enhances the magnetic moment attributed to Ni 2 atom, while reduces that attributed to Ni 3 atom. With the increase of pressure, the magnetic moments of all the Ni atoms reduce, and up to 218 GPa, those in $NiHe_{0.25}$ are all zero. It indicates that under pressures, the magnetic property of Ni atoms is more strongly affected by He atom than by H atom, and that at 218 GPa, there is a pressure-induced FM–PM transition in $NiHe_{0.25}$. The similar transition in $NiH_{0.25}$ will occur under higher pressure.[17]

The LMTO results (Ref.[24]) represented by the triangles are shown for comparison.

4. Conclusions

We have investigated the effect of He on metal nickel under pressures using *ab initio* pseudopotential plane-wave method. Under high pressures, the compound of $NiHe_{0.25}$ can exist and the interaction among He atoms in $NiHe_{0.25}$ is very small. In the pressure range from 100 to 220 GPa, a pressure-induced FM to PM phase transition has been found in $NiHe_{0.25}$ at 218 GPa. It indicates that under pressures, the effect of He atom on Ni is stronger than that of H atom. Under lower pressures, in $NiHe_{0.25}$, the bonding behaviours between He and Ni is much weak. However, with the increase of pressure, the bonding characteristics between He and Ni enhance. Up to certain pressure, the behaviours of bonding or antibonding states are quite stronger in $NiHe_{0.25}$ than in $NiH_{0.25}$.

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