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Electronic structure and magnetism of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys

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An *ab initio* linearized augmented plane-wave method has been employed to calculate the electronic and magnetic structures of both face-centered-cubic and body-centered-cubic $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys with $x=0.25$, 0.50, and 0.75, respectively. Decreasing the Pd content in $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloy from $x=1$, the magnetic ordering of fcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ changes from paramagnetism to ferromagnetism, ferrimagnetism, and finally to antiferromagnetism. However, the magnetism of bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ changes simply from paramagnetism to ferromagnetism.

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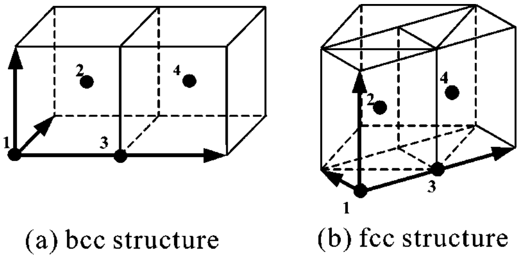
According to the itinerant electron model, ferromagnetism of transition metals occurs basically because of the spatial localization of d orbitals near the top of the d band.[1] This localization produces both a large density of states at the Fermi energy $\rho(\varepsilon_F)$ and a relative large exchange integral I, fulfilling the Stoner condition of ferromagnetism, $I\rho(\varepsilon_F)>1$. The Stoner condition can indeed explain the existing fact that only some transition metals are ferromagnetic but others are not in the periodic table. The reason behind is that the product $I\rho(\varepsilon_F)$ is large enough for ferromagnetism at the end of the $3d$ series (Fe, Co, and Ni), but not the $4d$ series or the light elements in the $3d$ series.

It has long been noticed that Pd is a special case in the transition metals. The electronic configuration of Pd in its atomic state is $4d^{10}5s^0$ and the atomic magnetic moment is zero. However, in its metallic state the electronic configuration of Pd changes to an unfilled d band $4d^{10-\delta}5s^{\delta}$ ($\delta\sim0.6$) because of the strong s-d hybridization, resulting in a net atomic moment.[2] Although the Stoner condition of ferromagnetism is not yet satisfied, fcc Pd does show strong paramagnetism with large susceptibility because of the fairly large product $I\rho(\varepsilon_F)$.[3] It is thus possible and hopeful to drive the paramagnetic Pd to a ferromagnetic state with some well-controlled perturbations such as the proximity effect with a ferromagnet. In fact, there have been already some experiments done towards this direction during the last decade, especially in the system of Fe/Pd.[4–8] Nevertheless, the results were all interpreted based on a sharp-interface assumption, which might not be necessarily true in reality because of the interface intermixing. A very recent experiment on Fe/Pd(100) prepared with two different epitaxial growth techniques—thermal evaporation and pulsed laser ablation—does indicate that the magnetism of this system depends strongly on the interface mixing.[9] Therefore it is interesting and motivated from a theoretical point of view to investigate the consequences of the interface mixing between Fe and Pd by exploring the electronic and magnetic properties of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys. This work is also motivated by the fact that different (either thermodynamically stable or metastable) crystallographic structures of an alloy at fixed chemical composition can be prepared by epitaxial growth on some appropriate substrates, and their magnetic properties are very different.[10] Thus it is interesting to study theoretically the possible correlation between the structure and magnetism of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys at different compositions for both bcc and fcc structures.

There have been several theoretical investigations on the magnetism of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys using first-principles calculations. Galanakis *et al.* studied the $\mathrm{Fe}_{0.5}\mathrm{Pd}_{0.5}$ alloy using a relativistic full-potential linear muffin-tin orbital method (FP-LMTO) with both the local-spin-density approximation (LSDA) and the generalized gradient approximation (GGA).[11] Unfortunately, the Fe-rich and Pd-rich $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ cases were not investigated in that work, while they could be important in discussing the intermixing effect as mentioned above. On the other hand, Kuhnen and da Silva did investi-



(a) bcc structure (b) fcc structure

FIG. 1. Unit cells of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys in calculation: (a) bcc and (b) fcc structure.

TABLE I. Lattice constants (nm) used in calculation for both bcc and fcc phases.

	Fe	$Fe_{0.75}Pd_{0.25}$	$Fe_{0.50}Pd_{0.50}$	$Fe_{0.25}Pd_{0.75}$	Pd
fcc	0.361	0.368	0.375	0.382	0.389
bcc	0.287	0.293	0.298	0.304	0.309

gate Fe-rich $Fe_{0.75}Pd_{0.25}$ and Pd-rich $Fe_{0.25}Pd_{0.75}$ as well as the $Fe_{0.5}Pd_{0.5}$ alloy using the self-consistent LMTO method.[12] However, only the ferromagnetic spin configurations were considered in their calculation, while the ferrimagnetic or antiferromagnetic options were not taken into account.

In this work we have employed the first-principles linearized augmented plane-wave (LAPW) method with the LSDA to calculate the electronic structure and magnetism of $Fe_{1-x}Pd_x$ alloys at different chemical compositions for both body-centered-cubic and face-centered-cubic structures. Meanwhile, the ferromagnetic, antiferromagnetic, and ferrimagnetic spin configurations are all taken into account.

The crystallographic structures of $Fe_{1-x}Pd_x$ alloys are assumed to be chemically ordered. Because of the limitation of calculation capability, a unit cell containing only four atoms is considered, which means that only the $Fe_{1-x}Pd_x$ alloys with compositions of $x=0$, 1/4, 1/2, 3/4, and 1 are investigated. The unit cells for bcc and fcc structures are illustrated in Figs. 1(a) and 1(b), respectively. The four atoms labeled 1, 2, 3, and 4 in the figures can be either Fe or Pd atoms, representing $Fe_{1-x}Pd_x$ alloys with different compositions. The atomic magnetic moments at these sites can be different in magnitude as well as in direction, but only collinear configurations are considered. Fifty plane waves per atom and 45 k points in the first irreducible Brillouin zone (BZ) are used in the calculation. The self-consistency is better than $0.01\ \mathrm{me/a.u.}^3$ for charge density and spin density, and the stability is better than 0.1 mRy for the total energy per cell. The lattice constants of pure Fe and Pd are chosen from the experimental data of 0.361 and 0.287 nm for fcc and bcc Fe and of 0.389 nm for fcc Pd, respectively. Since there is no reported experimental value for bcc Pd so far, a value of 0.309 nm is used based on an assumption that it has the same atomic density as fcc Pd. With these four numbers fixed, the lattice constants for both bcc and fcc $Fe_{1-x}Pd_x$ alloys at different compositions are then obtained by linear interpolation, as listed in Table I. For the given lattice constants the total magnetic moments per unit cell as well as the individual atomic magnetic moments in each unit cell for both bcc and fcc $Fe_{1-x}Pd_x$ alloys are calculated. In the following we will discuss the results for the fcc and bcc cases separately.

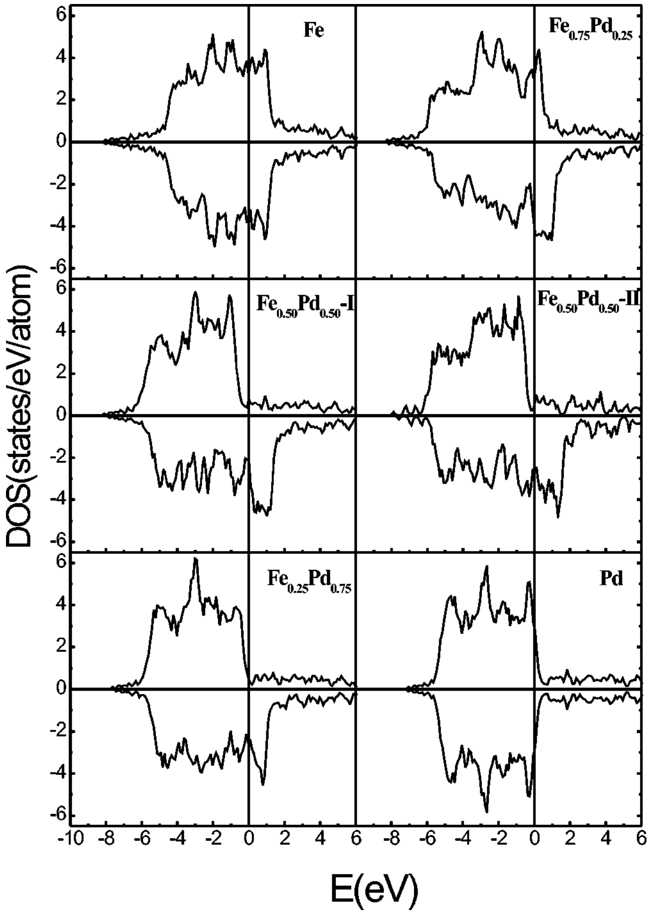


FIG. 2. Total density of states for majority and minority spins in the fcc phase.

fcc $Fe_{1-x}Pd_x$ *case*. The electronic structure and magnetism are calculated for fcc $Fe_{1-x}Pd_x$ at $x=0$, 0.25, 0.5, 0.75, and 1. The results are summarized in Table II.

Starting from the simplest case of pure fcc Pd, which is the thermodynamically stable phase of metallic Pd, the calculated result shows that it is paramagnetic, which certainly agrees to the known experimental result.

Adding 25% of Fe in the Pd matrix and forming a chemically ordered fcc $Fe_{1-x}Pd_x$ alloy with $x=0.75$, the calculated

TABLE II. Calculated atomic magnetic moments $m(i)$ (in unit μ_B for $i=1$, 2, 3, 4 as shown in Fig. 1) for fcc $Fe_{1-x}Pd_x$ alloys. m_{av} means the atomic moment averaged over the unit cell. The numbers with asterisks represent the values for Fe atoms, and the others are for Pd atoms.

	Fe	$Fe_{0.75}Pd_{0.25}$	$Fe_{0.50}Pd_{0.50}$-I	$Fe_{0.50}Pd_{0.50}$-II	$Fe_{0.25}Pd_{0.75}$	Pd
$m(1)$	1.86*	2.42*	2.81*	2.75*	0.31	0.00
$m(2)$	1.86*	0.23	0.34	0.26	3.11*	0.00
$m(3)$	-1.71*	2.42*	2.81*	0.26	0.31	0.00
$m(4)$	-1.71*	-1.51*	0.34	2.75*	0.24	0.00
m_{av}	0.07	0.89	1.57	1.51	0.99	0.00

TABLE III. Calculated atomic magnetic moments $m(i)$ (in unit μ_B for $i=1$, 2, 3, 4 as shown in Fig. 1) for bcc $Fe_{1-x}Pd_x$ alloys. m_{av} means the atomic moment averaged over the unit cell. The numbers with asterisks represent the values for Fe atoms, and the others are for Pd atoms.

	Fe	$Fe_{0.75}Pd_{0.25}$	$Fe_{0.50}Pd_{0.50}$-I	$Fe_{0.50}Pd_{0.50}$-II	$Fe_{0.25}Pd_{0.75}$	Pd
$m(1)$	2.32*	2.75*	2.92*	2.89*	0.28	0.00
$m(2)$	2.32*	0.40	0.35	0.27	3.13*	0.00
$m(3)$	2.32*	2.75*	2.92*	0.27	0.28	0.00
$m(4)$	2.32*	2.59*	0.35	2.89*	0.12	0.00
m_{av}	2.32	2.12	1.63	1.58	0.95	0.00

result shows that its ground state is not paramagnetic any more but is ferromagnetic with an average magnetic moment of $0.99\mu_B$/atom. Individually, Fe atoms at position 2 have a magnetic moment of $3.11\mu_B$, Pd atoms at positions 1 and position 3 have the same magnetic moments of $0.31\mu_B$, and Pd atoms at position 4 have a magnetic moment of $0.24\mu_B$. There are several points to be noticed from these results. First, the magnetic moment of Fe atoms in fcc $Fe_{0.25}Pd_{0.75}$ ($3.11\mu_B$) is much higher than that in bulk Fe metal ($2.2\mu_B$). This phenomenon is similar to the well-established surface giant moment that Fe atoms on the surface show an increased atomic magnetic moment when the hybridization of their *d* orbitals with neighbor atoms is decreased. Second, it seem a little puzzling from first glance why Pd(1) and Pd(3) have the same magnetic moment ($0.31\mu_B$) but are different from that of Pd(4) ($0.24\mu_B$), while all of three Pd atoms have the same distance from the central Fe atoms. The reason behind is that they do have quite different coordination surroundings; Pd(1) or Pd(3) has four Fe atoms and eight Pd atoms as its first nearest neighbors, but Pd(4) has two Fe atoms and ten Pd atoms as its nearest neighbors. Pd(4) has a smaller magnetic moment than that of Pd(1) or Pd(3) because the former has fewer Fe atoms around, or in other words, it is less spin polarized by the Fe atoms. Finally, the results obtained here agree quite well with the neutron diffraction data where the magnetic moments of Fe and Pd were determined to be $2.98\mu_B$/atom and $0.34\mu_B$/atom, respectively.[13]

For fcc $Fe_{1-x}Pd_x$ at $x=0.5$, there are two distinct atomic arrangements in the alloy. Type I has the configuration of Fe(1), Fe(3), Pd(2), and Pd(4); Type II has the configuration of Fe(1), Pd(2), Pd(3), and Fe(4). The calculation indicates that $Fe_{0.5}Pd_{0.5}$ in both cases shows ferromagnetism. The only difference lies in their detailed values of the magnetic moments, as shown in Table II. From the total-energy calculation, it is found that type I has a lower energy of 17 mRy/cell than that of type II. Interestingly the experimental result of Cable *et al.* revealed that fcc $Fe_{1-x}Pd_x$ at $x=0.5$ is ferromagnetic and the magnetic moments measured by neutron diffraction were $2.85\mu_B$/atom for Fe and $0.35\mu_B$/atom for Pd, respectively,[13] which are also closer to those values of our type-I configuration.

Now for Fe-rich fcc $Fe_{1-x}Pd_x$ alloys at $x=0.25$, the calculated result shows that the Fe(1), Fe(2), and Pd(3) spins are parallel to each other but are antiparallel to the Fe(4) spins, leading to a ferrimagnetic ordering with an overall net magnetic moment of $0.89\mu_B$/atom in a unit cell. Similar to the foregoing discussion, the three Fe are not equal to each other because of the different coordination surroundings. However, the antiparallel alignment of Fe(4) spins with respect to the other Fe spins is presumably caused by the tendency of antiferromagnetism in pure fcc Fe.

fcc Fe is found to be antiferromagnetic with the Fe(1) and Fe(2) spins parallel to each other but antiparallel to the Fe(3) and Fe(4) spins, in agreement with the previous theoretical calculation.[14] However the small uncompensated net magnetic moment ($0.07\mu_B$ in Table II) here is presumably caused by the fact that the magnetic group operation (spin inversion plus translation between two sublattices) has not been explicitly included. Of course it could also be due to the numerical error from the finite number of *k* points in the BZ integration.

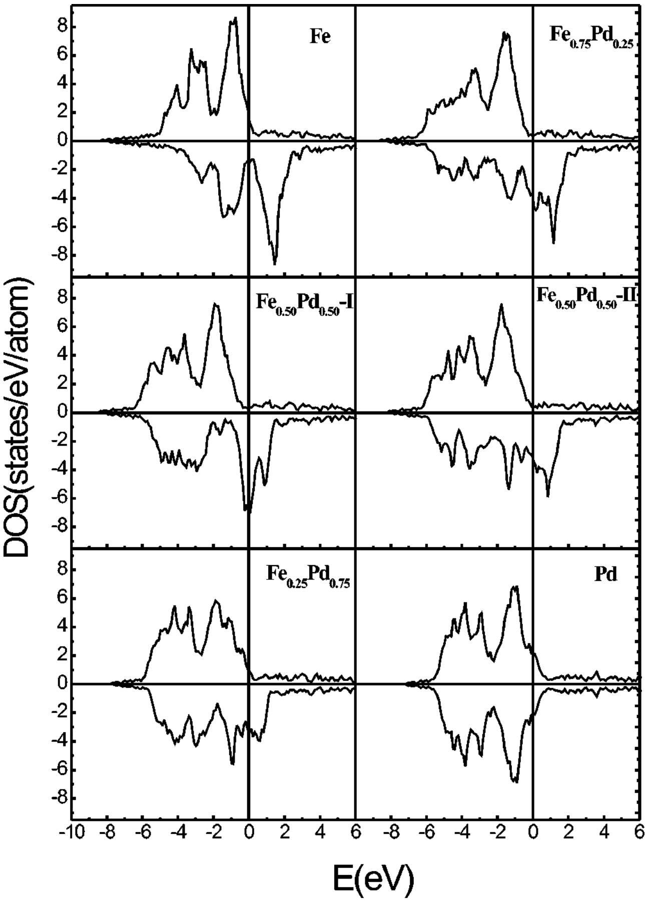


FIG. 3. Total density of states for majority and minority spins in the bcc phase.

In addition, as shown in Fig. 2, it might be useful to provide here the calculated density of states near the Fermi energy for the $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys with different compositions, in order to be verified with photoemission in the future.

bcc $Fe_{1-x}Pd_x$ case. The calculated results for bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ at different compositions are much simpler comparing to the fcc case and they are listed in Table III. The magnetic orderings of bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ are all ferromagnetic, except for pure bcc Pd, which is paramagnetic as expected. Starting from pure bcc Pd, the average magnetic moment per unit cell increases monotonically with Fe concentration. This strong tendency of ferromagnetism is certainly very different from that in the former fcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ cases. A clear difference is observed between fcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ and bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ at $x=0.25$. The former is ferrimagnetic with an average moment $0.89\mu_B$/atom while the latter is ferromagnetic with an average moment $2.12\mu_B$/atom. It is wished that such a difference can be observed in experiments in the future. Similar to the foregoing fcc case, bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ at $x=0.5$ has two configurations too. However the total-energy calculation indicates that the type-I configuration is much more stable with an energy difference of 94 mRy/cell lower than that of type-II configuration. Again we show in Fig. 3 the calculated density of states near the Fermi energy for bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys, waiting for future experimental verification.

In summary, it is shown in this work that the magnetism of $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloys depends strongly on their structures as well as the chemical compositions. A ferrimagnetic ordering is predicted for the fcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ alloy at $x=0.25$, while the ferromagnetic ordering is obtained for both fcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ at $x=0.5$ and 0.75 and bcc $\mathrm{Fe}_{1-x}\mathrm{Pd}_x$ at all compositions.

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[1] J. Kubler, in *Theory of Itinerant Electron Magnetism* (Clarendon Press, Oxford, 2000).

[2] E.P. Wohlfarth, Proc. Leeds Philos. Lit. Soc., Sci. Sect. **5**, 89 (1949).

[3] D.H. Parkinson, Rep. Prog. Phys. **21**, 226 (1958).

[4] C. Liu and S.D. Bader, J. Appl. Phys. **67**, 5758 (1990).

[5] O. Rader, E. Vescovo, J. Redinger, S. Blugel, C. Carbone, W. Eberhardt, and W. Gudat, Phys. Rev. Lett. **72**, 2247 (1994).

[6] H.J. Choi, R.K. Kawakami, E.J. Escorcia-Aparcio, and Z.Q. Qiu, Phys. Rev. Lett. **82**, 1947 (1999).

[7] X.F. Jin, J. Barthel, J. Shen, S.S. Manoharan, and J. Kirschner, Phys. Rev. B **60**, 11 809 (1999).

[8] D.Q. Li, R. Cuenya, J. Person, and S.D. Bader, Phys. Rev. B **64**, 144410 (2001).

[9] X.F. Jin *et al.* (unpublished).

[10] D. Wu, G.L. Liu, C. Jing, Y.Z. Wu, D. Loison, G.S. Dong, X.F. Jin, and D.S. Wang, Phys. Rev. B **63**, 214403 (2001).

[11] I. Galanakis, S. Ostanin, M. Alouani, H. Dreysse, and L.M. Wills, Phys. Rev. B **61**, 599 (2000).

[12] C.A. Kuhnen, and E.Z. da Silva, Phys. Rev. B **46**, 8915 (1992).

[13] J.W. Cable, E.O. Wollan, and W.C. Koehler, Phys. Rev. **138**, A755 (1965).

[14] Yumei Zhou, Wenqing Zhang, Lieping Zhong, Xiliang Nie, and Ding-sheng Wang, J. Magn. Magn. Mater. **167**, 136 (1997).