

Magnetic properties and calculated electronic structure of iron-palladium alloys

C. A. Kuhnen

Departamento de Física, Universidade Federal de Santa Catarina (UFSC), 88 049 Florianópolis, Santa Catarina, Brazil

E. Z. da Silva

Instituto de Física Gleb Wathagin, Universidade Estadual de Campinas (UNICAMP), Campinas, São Paulo, Brazil

(Received 22 October 1991; revised manuscript received 29 May 1992)

The electronic structure of iron-palladium alloys are studied using the self-consistent linear muffin-tin orbital (LMTO) method. In particular, three compounds are analyzed, namely, Pd₃Fe, PdFe, and PdFe₃ and their stability investigated with respect to the iron concentration. Results are obtained from ferromagnetic calculations for each alloy. Our discussion on internal excess energy shows the PdFe₃ ordered structure to be at best metastable with respect to its disordered alloy, while Pd₃Fe and PdFe are stable compounds. Results for PdFe₃ show a collapse of its magnetic moment as a function of the lattice parameter.

I. INTRODUCTION

Alloys of Pd-Fe have been extensively studied both experimentally and theoretically by many authors. Recently theories of alloy phase stability, as well as first-principles calculations of phase diagrams, have been phrased in terms of the alloy's underlying electronic structure.¹⁻³ The present work may be considered as a test of these theories, since here we perform an *ab initio* band-structure calculation of Pd₃Fe, PdFe, and PdFe₃ in their ordered phases. Pd₃Fe has been the object of many experimental studies of magnetic⁴ and thermal⁵ properties, as well as of the effect of hydrogenation.⁶ Its electronic structure was investigated recently from a first-principle method, both in its ordered⁷ and disordered⁸ phase as well as its ordered hydride.⁹ In its ordered phase, Pd₃Fe has the Cu₃Au structure which corresponds to a fcc lattice, with Fe atoms located in the corners and Pd atoms at its face centers, and the experimental¹⁰ lattice parameter is $a = 3.849$ Å. The PdFe-ordered compound has the CuAuI superstructure, with Fe atoms located at the origin and Pd atoms at (0,0,0.5,0.5). PdFe is tetragonal¹¹⁻¹³ with $c/a = 0.966$, and therefore in this work it was modeled as having cubic structure taking the experimental lattice parameter $a = 7.0510$ a.u. For theoretical reasons¹⁴ we can suggest the existence of an ordered structure based on PdFe₃, and in the present work it is modeled in the ordered phase as having the Cu₃Au structure with Pd atoms located at the corners and Fe atoms at its face centers. This ordered compound rich in Fe has an electron per atom ratio $e/a = 8.5$. It has been known for decades that some Fe alloys with e/a in the range 8.4–8.7 show a very striking behavior known as the "Invar effect." This puts PdFe₃ in the class of magnetic alloys and compounds that show the Invar Effect. In the present work it is shown that this compound features a dramatic collapse of magnetic moment as a function of pressure.

In this work we have employed the spin-density-

functional theory for both von Barth-Hedin¹⁵ (vBH) and Vosko-Wilk-Nusair¹⁶ (VWN) approximations for the exchange-correlation energy of the electron gas. This was done to test the influence of different parametrizations for the exchange correlation in the ground-state properties of intermetallic compounds, such as magnetic and bulk properties as were previously done for iron¹⁷ in its bcc structure. We use the linear muffin-tin orbital (LMTO) method of Andersen¹⁸ to calculate the electronic structure of Pd₃Fe, PdFe, and PdFe₃. Since the LMTO method has been described in great detail in many publications,^{19,20} we confine ourselves to a description of particular details of the present LMTO calculation. The present calculation includes the combined correction terms but no spin-orbit interactions. The solutions of the Schrödinger equation used *s*, *p*, *d*, and *f* LMTO basis functions. The self-consistency cycles were carried out until energy convergence on a scale better than 1 mRy was achieved. The one-electron potentials were self-consistently obtained using reciprocal sums with 365k points. The density of states (DOS) were calculated as a sum of δ functions convoluted with Gaussian functions for a fixed number of energy mesh points for each case. Self-consistency was first achieved for the potential on 120k points and 500 energy points. Final DOS were calculated for 1500 energy points. Self-consistent field calculations within the local-density approximation (LDA) were performed for these three compounds in their ferromagnetic phase, for seven lattice parameters for each compound to obtain a clear understanding of the volume dependence of the ground-state properties. In the next sections we present a discussion of the results obtained for the compounds under study in this work.

II. RESULTS AND DISCUSSION

A. Bonding

Formation and stability of ordered phases can be studied by calculation of the excess internal energies. For iso-

structural $A_{1-x}B_x$ binary systems, the excess internal energy for a given state of order σ is given by^{21,22}

$$\Delta E = E(\sigma, V) - (N_A/N) \cdot E_A(V_A) - (N_B/N) \cdot E_B(V_B),$$

where N_A and N_B are the numbers of A and B atoms in the ordered $A_{M-N}B_N$ compound, whose state of order is σ . V is the volume and E_A and E_B are the total energy functions of the elemental A and B solids, respectively, at their V_A and V_B equilibrium volumes. The calculated total energies for the three compounds as well as the pure Fe and Pd solids in the fcc structure were obtained as functions of the lattice parameter using two approximations for the exchange correlation, giving their theoretical equilibrium volume.

Figure 1 shows the internal excess energy ΔE for the compounds as a function of the lattice parameter for the VWN exchange correlation. A comparison between these results with a calculation using the vBH approximation does not show a great deal of difference, but these two different approximations give equilibrium lattice parameters which differ slightly as well as differences in bulk modulus and internal excess energies at equilibrium. From Fig. 1 it is clear that Pd_3Fe and PdFe are stable compounds, whereas PdFe_3 is at best a metastable compound as its internal excess energy at the minimum (which corresponds to the equilibrium volume) is almost zero. The calculated minima data points in Fig. 1 correspond to the following lattice parameters: $a = 7.2759$, 7.1201 and 6.9904 a.u. for Pd_3Fe , PdFe , and PdFe_3 , respectively, which, as can be seen from Table I, do not differ appreciably from those obtained through an analytical fitting of the calculated total energies.

The equilibrium lattice parameters, which are obtained by fitting the calculated total-energy data points to a third degree polynomial, the bulk modulus, and the energy formation for the compounds, are given in Table I. The results are shown for the vBH and VWN approximations to the LDA. We can observe that the lattice parameters differ slightly from one to the other approximation. The theoretical equilibrium volume for Pd_3Fe agrees very well with the experimental one, the deviation in the lattice parameter being less than 0.5%. The same is true for the PdFe -ordered compound in which the deviation in the lattice parameter is about 1%. The bulk

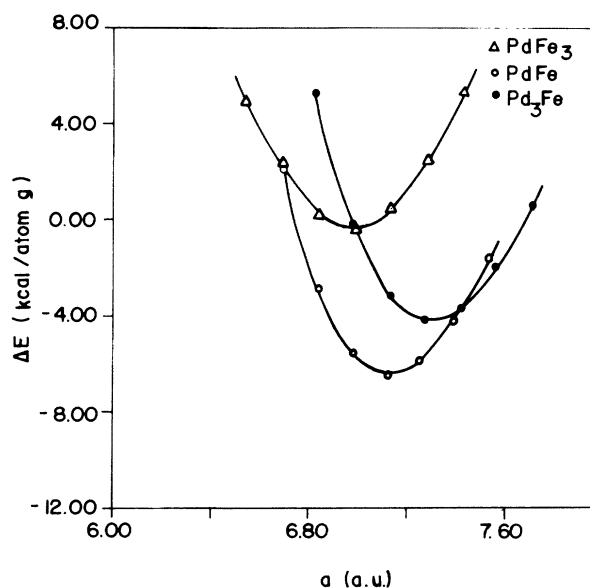


FIG. 1. Calculated internal excess energy, for seven lattice parameters, of Pd_3Fe , PdFe , and PdFe_3 ordered compounds.

modulus (B) shows a weak dependence on the type of approximation used for the exchange correlation. The values for the bulk modulus in Table I are obtained from a numerical five points differentiation of the calculated total energies. An analytical calculation by fitting the total energies with a third degree polynomial gives practically the same values for B . These results show differences which are much less pronounced than the results for pure elemental metals studied by Jansen, Hathaway, and Freeman¹⁷ (Table I). The internal excess energies, which are given in Table I for these compounds, show the stability of the Pd_3Fe and PdFe -ordered compounds and the metastability of the PdFe_3 compound. The results for ΔE in the case of PdFe_3 are close to zero and have a difference depending on the approximation used (vBH or VWN), which is of the order of their values, and therefore do not permit a clear cut statement on the stability of this compound. It can be said that it is either metastable or instable to the formation of its or-

TABLE I. Results for the three compounds Pd_3Fe , PdFe , PdFe_3 . Here, a is the equilibrium lattice parameter, B is the bulk modulus (in Giga Pascal) and ΔE is the internal excess energy. The results given are for two different approximations for the exchange correlation (von Barth-Hedin and Vosko-Wilk-Nusair).

	Pd_3Fe		PdFe		PdFe_3	
	BH	VWN	BH	VWN	BH	VWN
a (a.u.)	7.300	7.290	7.140	7.150	6.990	6.970
ΔE (kcal/at g)	-4.15	-4.00	-6.50	-6.20	-0.53	-0.16
B (GPa)	184	182	216	214	206	205
	Pd		Fe			
	BH	VWN	BH	VWN		
a (a.u.)	7.493	7.476	6.498	6.490		
B (GPa)	179	185	318	320		

dered structure since it is so near the instability ($\Delta E \sim 0$) value.

B. Results for Pd₃Fe

This section discusses results of a ferromagnetic self-consistent calculation for Pd₃Fe within the VWN approximation. The lattice parameter used here ($a = 7.2759$ a.u.) gives the minimum for ΔE (Fig. 1) and is the experimental value for this compound. The Wigner-Seitz spheres around the atoms are taken to be of equal size, with radii $s = 2.84343$ a.u. The results obtained are shown in Table II. The magnetic moment at Pd sites agrees very well with the experimental value which is 0.57 bohr magnetons.²³ On the other hand, at Fe sites, the theoretical value for the magnetic moment is smaller than in the experiment, which is $2.70\mu_B$.²³ In Fig. 2 we can see that the total magnetization for this compound is a smooth increasing function of its volume. This behavior is due to a continuous increase of the magnetic moment at Pd sites with the volume, since at Fe sites the magnetization practically does not vary. The relative lower value obtained for the magnetic moment at Fe sites is related to the degree of population of the spin-down d states. The main contribution for the DOS at the Fermi level (E_F) is due to d electrons, and at Fe sites the spin-down states give a higher value for the DOS at E_F . This leads to a greater value for the electronic specific-heat coefficient than the experimental² value 8.17 mJ/mol K^2 .

Charge transfer is very small (Table II) for the equilibrium lattice parameter, leaving 0.00168 electrons as excess charge at Fe sites. Charge transfer at iron sites as a function of the lattice parameter is displayed in Fig. 3. Charge transfer decreases with increasing volume; therefore the electron transfer from one site to the other has a strong dependence with the lattice spacing between Fe-Pd atoms. As electrons are transferred to Fe sites they occupy the empty states at these sites, which moves the Fermi energy to higher values, and as Fe atoms lose electrons those states remain empty, decreasing the Fermi

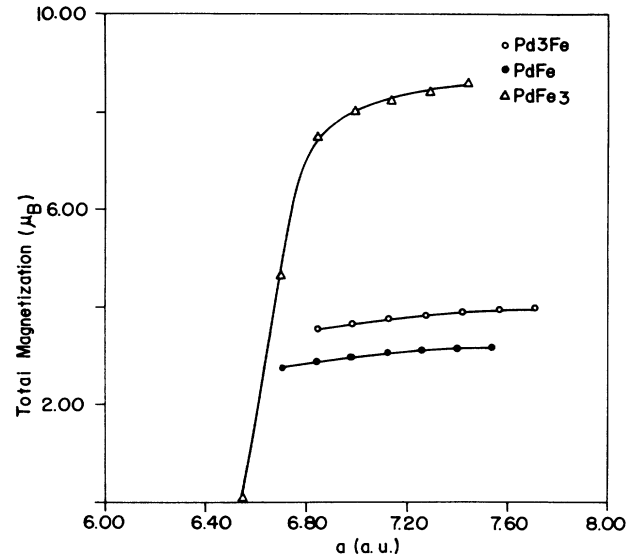


FIG. 2. Total magnetization (per unit formula) as function of lattice parameter, for the three ordered compounds.

level. This corresponds to a broadening of the d bandwidth in the first case (electron excess at Fe sites) and a narrowing of the bandwidth in the second case (electron deficiency at Fe sites), while the Fermi energy moves from one side of a valley in the DOS to another side of the valley. That is, the value of the DOS at E_F is increased in both cases (see below).

The density of states at Pd and Fe sites for both spin directions is shown in Figs. 4 and 5. The spin-up d electrons form a common d band [Figs. 4(a) and 5(a)]. At Fe sites, the spin-down electrons are almost excluded from these sites, which results in the formation of localized magnetic moments out of completely delocalized electrons. This fact was reported in a prior calculation⁷ on

TABLE II. Calculated parameter for ferromagnetic Pd₃Fe using the self-consistent potentials, with Vosko parametrization for exchange correlation.

	Pd	m		Fe	m	
n (electrons/spin)	4.70	5.30	0.60	2.98	5.02	2.04
n_s (electrons/spin)	0.29	0.28	-0.01	0.32	0.33	0.01
n_p (electrons/spin)	0.31	0.30	-0.01	0.36	0.37	0.01
n_d (electrons/spin)	4.06	4.67	0.61	2.25	4.27	2.02
n_f (electrons/spin)	0.04	0.05	0.01	0.05	0.05	0.00
$N(E_F)$ (states/spin Ry)	9.29		3.65		43.37	1.47
$N_s(E_F)$ (states/spin Ry)	0.07	0.23		0.25		0.27
$N_p(E_F)$ (states/spin Ry)	0.41	0.35		0.37		0.35
$N_d(E_F)$ (states/spin Ry)	8.59	3.06		42.72		0.84
$N_f(E_F)$ (states/spin Ry)	0.22	0.01		0.03		0.01
$N(E_F)$ (states/atom Ry)	12.94			44.84		
$N(E_F)$ (states/unit cell Ry)			83.66			
γ (mJ/mol K ²)			14.42			
E_F (Ry)			0.600			
ΔQ (electrons)	-0.00056			0.00168		

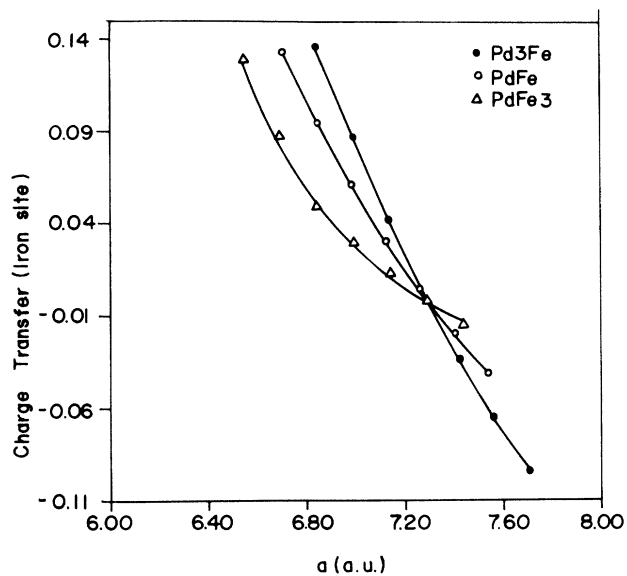


FIG. 3. Charge transfer (electrons) at iron sites for the compounds, calculated for seven lattice parameters.

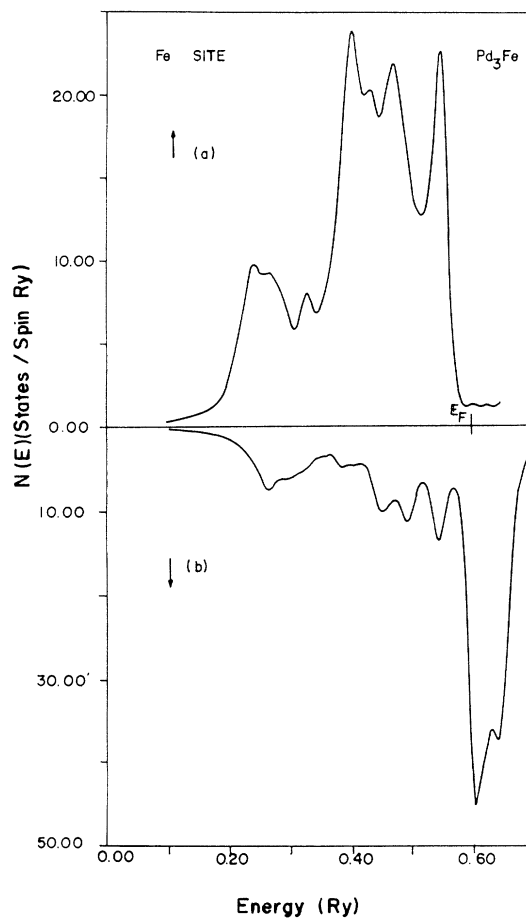


FIG. 5. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Fe site for Pd_3Fe .

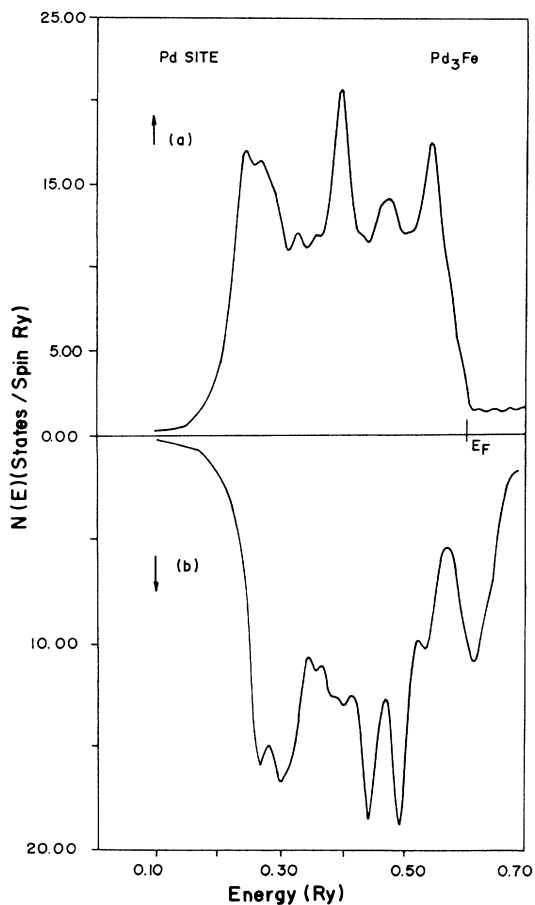


FIG. 4. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Pd site for Pd_3Fe .

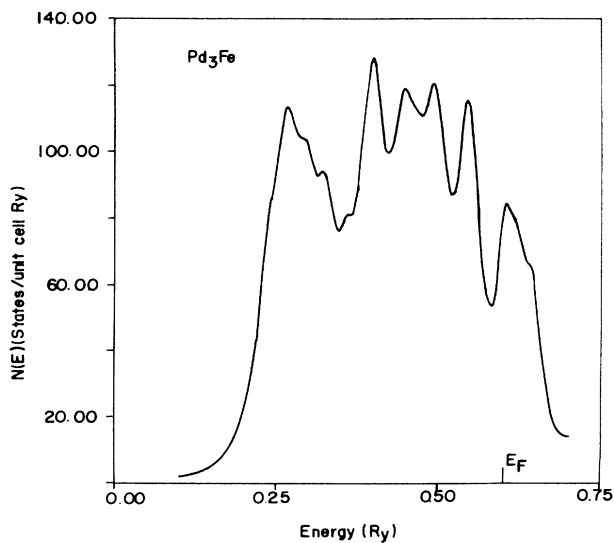


FIG. 6. Total density of states (in states/unit cell Ry) at equilibrium volume for the ordered ferromagnetic Pd_3Fe .

the ferromagnetic Pd₃Fe and by Kubler, Williams, and Sommers²⁴ for Heusler alloys. The projected densities of states [Figs. 4(a) and 5(a)] show that for up-spin states this contribution is very low at E_F . Spin polarization results in a splitting of up and down bands, putting the Fermi level in a valley between the DOS of up and down spins as shown in Fig. 6 for the total DOS for ordered Pd₃Fe. This reduces the density of states $N(E_F)$ tending to put it in agreement with the measured linear coefficient of the specific heat. Here our calculation gives a greater value for γ than in a previous calculation⁷ of the DOS. From the total DOS shown in Fig. 6 it is clear that the value of $N(E_F)$ is increased if the Fermi level moves in the direction of low or high energies, and this is exactly what happens when volume is increased or decreased. Clearly this is not only a simple rigid shift of the DOS; on the contrary, as the volume changes, the general features of the DOS are subtly altered, and since there is no drastic alterations we do not make more comments about this fact here. For PdFe₃ we analyze the behavior of the DOS as a function of the pressure.

C. Results for PdFe

This section discusses the results of the calculation for the case of ordered PdFe. The lattice parameter used, $a = 7.1201$ a.u., gave the minimum data point in Fig. 1 (equal-size Wigner-Seitz spheres with radii $s = 2.7825$ a.u.) and produced the results displayed in Table III, where the VWN approximation was used for the exchange correlation. It shows an increase in the magnetic moments at Pd and Fe sites. The total magnetization for PdFe is a smooth increasing function of the volume, as seen in Fig. 2. Here, contrary to the Pd₃Fe compound, it shows a small variation of the magnetic moment at Fe sites (as a slightly increasing function), but again, the most important contribution for the behavior of the total magnetization is due to changes in the magnetic moment at Pd sites. This shows that the magnetization at Pd sites is most sensitive to lattice spacing variation (volume

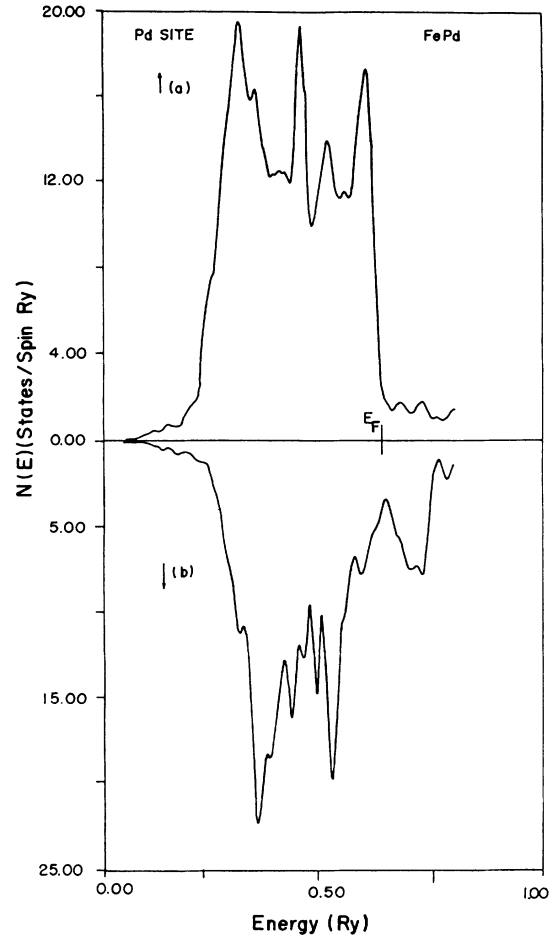


FIG. 7. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Pd site for PdFe.

effects). From Table III we note that the main contribution to $N(E_F)$ is due to d electrons for both sites. But now there is an abrupt decrease in $N(E_F)$ for spin-down d electrons at Fe sites; this fact is discussed below in

TABLE III. Calculated parameters for ferromagnetic PdFe (CuAu structure) using the self-consistent potentials, with Vosko parametrization for exchange correlation.

	Pd		m	Fe		m
n (electrons/spin)	4.59	5.38	0.79	2.89	5.14	2.25
n_s (electrons/spin)	0.29	0.29	0.00	0.34	0.33	-0.01
n_p (electrons/spin)	0.32	0.30	-0.01	0.37	0.38	0.01
n_d (electrons/spin)	3.95	4.75	0.80	2.14	4.38	2.24
n_f (electrons/spin)	0.03	0.04	0.01	0.04	0.05	0.01
$N(E_F)$ (states/spin Ry)	3.63	2.87		11.25	2.10	
$N_s(E_F)$ (states/spin Ry)	0.06	0.20		0.06	0.35	
$N_p(E_F)$ (states/spin Ry)	0.70	0.46		0.40	0.34	
$N_d(E_F)$ (states/spin Ry)	2.80	2.20		10.70	1.40	
$N_f(E_F)$ (states/spin Ry)	0.07	0.01		0.09	0.01	
$N(E_F)$ (states/atom Ry)	6.50			13.35		
$N(E_F)$ (states/unit cell Ry)			19.85			
γ (mJ/mol K ²)			3.44			
E_F (Ry)			0.639			
ΔQ (electrons)	-0.0301			+0.0301		

terms of the projected DOS. Therefore the calculated value of the linear coefficient of the specific heat (γ) for this compound is much smaller than the value obtained for Pd_3Fe . For this compound we obtain 0.030 electrons as the excess charge at Fe sites. Figure 3 shows that the electron transfer to Fe sites, as the volume is decreased, follows the same trend as Pd_3Fe . But here, due to the increasing iron concentration, Fe sites lose less electrons than in Pd_3Fe as the volume is increased from its equilibrium value, while Pd atoms lose many more electrons due to the strong Pd-Fe interactions as the lattice spacing between them is decreased, than in the ordered Pd_3Fe compound.

In Figs. 7 and 8 densities of states are displayed for up and down electrons at Pd and Fe sites, respectively. The main contribution for the DOS comes from d electrons and the formation of magnetic moments follows the same trends discussed^{25,26} for Pd_3Fe . Also, the DOS in the present case follows the same trends as in Pd_3Fe , with the exception that for spin-down electrons at Fe sites there is a larger population of down states, although the DOS resembles that of Fe sites in Pd_3Fe and the Fermi energy is located in a valley of the DOS.

Notice that with increasing iron concentration (e.g.,

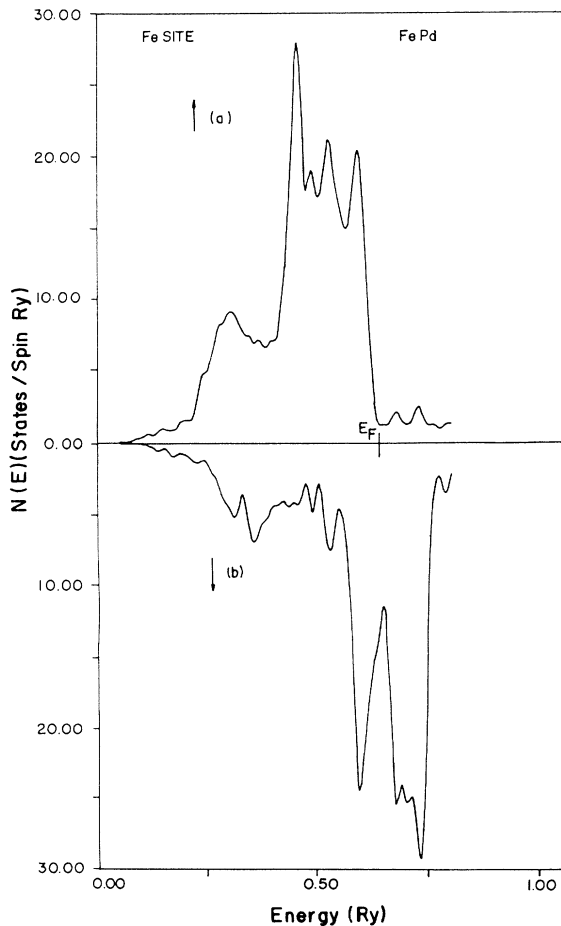


FIG. 8. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Fe site for PdFe.

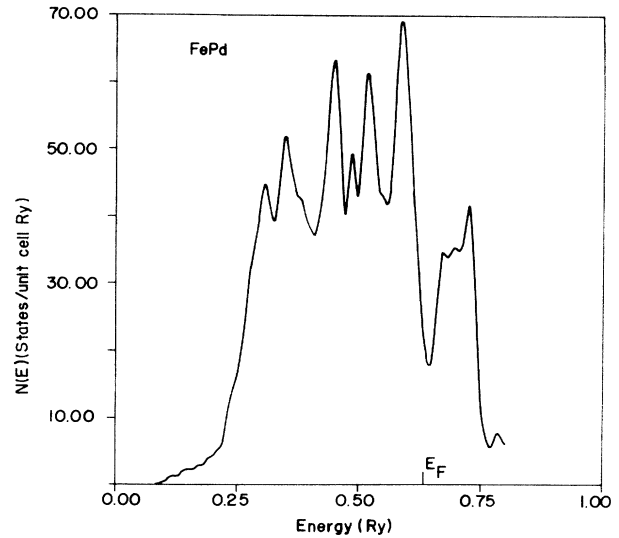


FIG. 9. Total density of states (in states/unit cell Ry) at equilibrium volume for the ordered ferromagnetic PdFe.

going from Pd_3Fe to PdFe) there is a great charge transfer to Fe sites which populates the spin-down states at these sites, hence with an abrupt decrease in the DOS at E_F . In Fig. 9 the total DOS for a PdFe-ordered compound (similarly to Pd_3Fe), shows the Fermi level located in a valley of the DOS, with a small value for $N(E_F)$ resulting in a low value for γ (see Table III).

D. Results for PdFe_3

It has been known for a long time that certain iron alloys with an electron per atom ratio (a/e) in the range 8.5–8.7 show the Invar effect. In this respect PdFe_3 is the most interesting of the three alloys studied in the present work since it has an $a/e = 8.5$, which should mean that it is at or near a magnetic instability. Indeed, it presents dramatic magnetoelastic effects with a collapse of its magnetic moment with pressure for modest pressures, an effect that can be followed and studied in terms of its electronic structure.

PdFe_3 was modeled as having the $L1_2$ (fcc structure with Pd atoms at the corners and Fe atoms at the face centers). The lattice parameter here is $a = 6.69904$ a.u., which gives the minimum data point in Fig. 1 (Wigner-Seitz spheres with the same radii $s = 2.7318$ a.u.). Table IV displays the calculated parameters for PdFe_3 with the VWN approximation for exchange correlation. At equilibrium volume the magnetic moments at Fe and Pd sites are greater than the magnetization for the other two compounds. But here its behavior with respect to the change in the volume is quite different (Fig. 2). As the lattice parameter is increased from its equilibrium value the magnetization increases smoothly, but more rapidly than in the other two compounds. For PdFe_3 the magnetic moment at iron sites is more sensitive to changes in volume, although for high volumes the most important contribution for the variation of the total magnetization

TABLE IV. Calculated parameters for ferromagnetic PdFe₃ using the self-consistent potentials, with Vosko parametrization for exchange correlation.

	Pd	<i>m</i>		Fe	<i>m</i>	
<i>n</i> (electrons/spin)	4.50	5.41	0.91	2.84	5.19	2.35
<i>n_s</i> (electrons/spin)	0.30	0.28	-0.02	0.33	0.32	-0.01
<i>n_p</i> (electrons/spin)	0.33	0.31	-0.02	0.38	0.39	0.01
<i>n_d</i> (electrons/spin)	3.85	4.78	0.93	2.10	4.44	2.34
<i>n_f</i> (electrons/spin)	0.02	0.04	0.02	0.03	0.04	0.01
<i>N</i> (<i>E_F</i>)(states/spin Ry)	6.65	3.37		15.77	2.71	
<i>N_s</i> (<i>E_F</i>)(states/spin Ry)	0.05	0.19		0.14	0.22	
<i>N_p</i> (<i>E_F</i>)(states/spin Ry)	1.34	0.33		0.99	0.37	
<i>N_d</i> (<i>E_F</i>)(states/spin Ry)	5.16	2.84		14.48	2.11	
<i>N_f</i> (<i>E_F</i>)(states/spin Ry)	0.10	0.01		0.16	0.01	
<i>N</i> (<i>E_F</i>)(states/atom Ry)	10.02			18.48		
<i>N</i> (<i>E_F</i>)(states/unit cell Ry)			65.46			
<i>γ</i> (mJ/mol K ²)			11.30			
<i>E_F</i> (Ry)			0.667			
<i>ΔQ</i> (electrons)	-0.0876			0.0292		

comes from Pd sites. For low volumes, the magnetization shows a drastic variation, going abruptly to near zero for a variation of 6% in the lattice parameter. This was already observed for fcc iron in a ferromagnetic cal-

ulation,²⁷⁻³¹ which was first described theoretically by Madsen and Andersen.³² Such behavior, the magnetic collapse or a breakdown of ferromagnetism which occurs at certain volume indicate particularly^{30,31,33} for fcc Fe

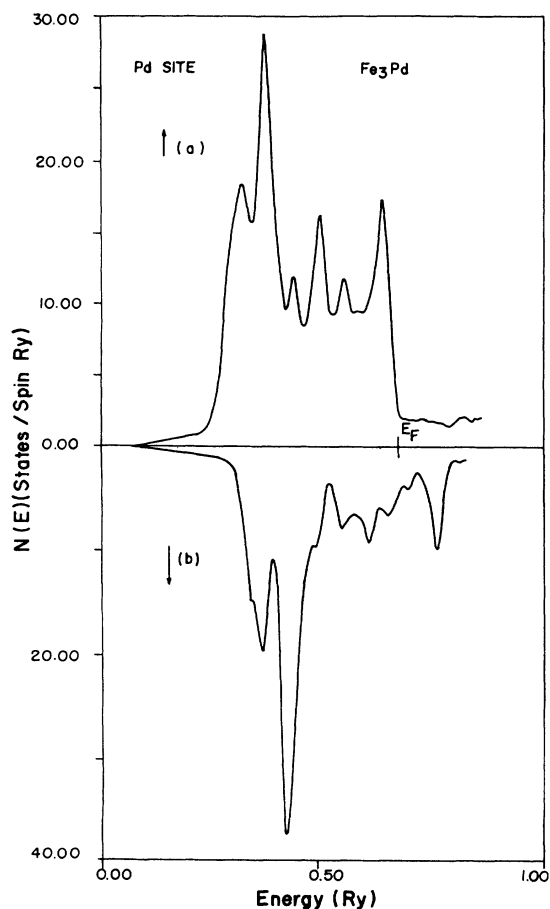


FIG. 10. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Pd site for PdFe₃.

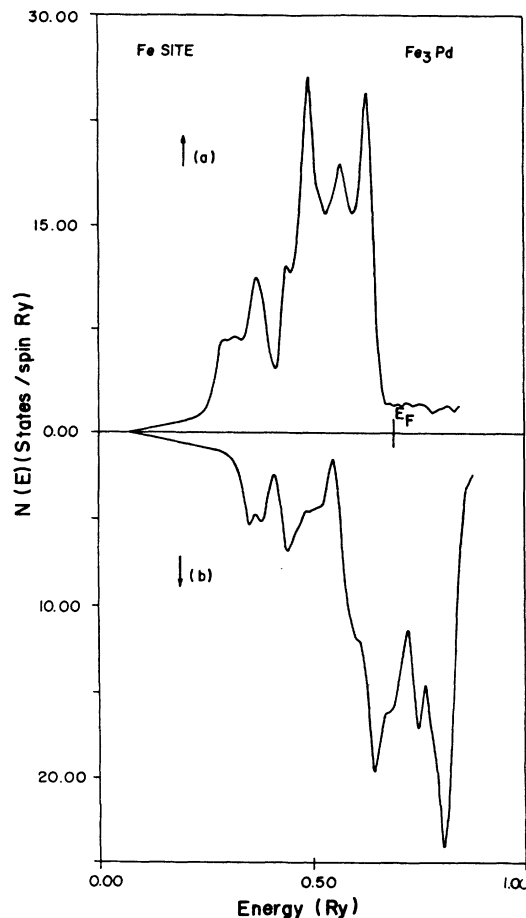


FIG. 11. Total density of states (in states/spin Ry) calculated at equilibrium volume: (a) spin-up and (b) spin-down electrons at the Fe site for PdFe₃.

the existence of more than one magnetic phase. Here we relate this behavior of the magnetization to specific features of the densities of states.

Table IV shows that the most important contribution to $N(E_F)$ comes from spin-down states at Fe sites. But a comparison with the Pd_3Fe compound shows that this contribution for $N(E_F)$ is smaller, due to the population of spin-down states at Fe sites with increasing iron concentration. The electron excess at Fe sites at equilibrium volume is $0.0292e$, which is almost equal to the value obtained for the PdFe compound (see Table II). On the other hand, here the Pd atoms lose many more electrons than in the other two compounds. In Fig. 3 we can see the charge transfer at Fe sites for various lattice parameters. For high volumes we see that less electrons are lost by Fe atoms compared with Pd_3Fe and PdFe . However, for low volumes the excess electrons at Fe sites follow the values obtained for the other two compounds. Therefore, for Pd-Fe systems the metal-metal interactions give charge transfer at Fe sites for low volumes that are approximately independent of the crystal structure and iron concentration, an atomic feature of these interactions. Metal-metal interactions seem to be most sensitive to the lattice environment and iron concentration for high volumes. From Fig. 3 we can see that, in the direction of high volumes, for Pd_3Fe the interaction between one Fe atom and three Pd atoms results in much more charge transfer than the interaction between three Fe atoms and one Pd atom in the PdFe_3 .

For the PdFe_3 -ordered compound, the density of states at Pd and Fe sites for each spin direction are shown in Figs. 10 and 11. Figures 10(a) and 11(a) show that spin-up electrons form a common d band as in the case of Pd_3Fe - and PdFe -ordered compounds. The main difference is that the peaks in the DOS move to low energies. On the other hand, if we compare Figs. 4(b), 7(b), and 10(b) for spin-down electrons at Pd sites, we observe that the DOS is much more altered, giving peaks for low

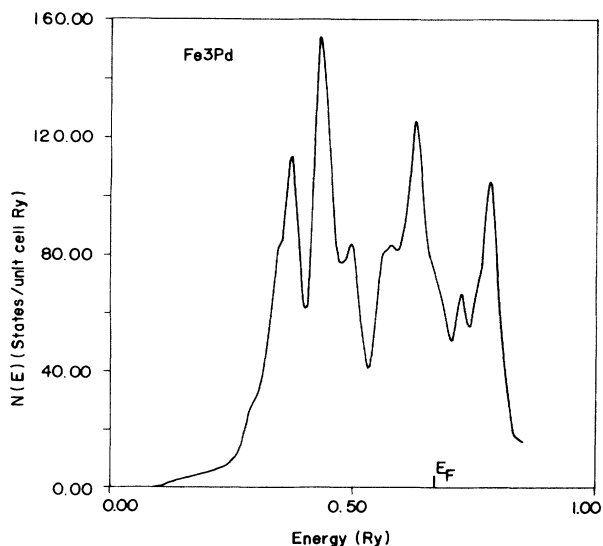


FIG. 12. Total density of states (in states/unit cell Ry) at equilibrium volume for the ordered ferromagnetic PdFe_3 .

energies and decreasing more and more rapidly in the direction of high energies as the Pd content in the compound is decreased. However, the contribution for $N(E_F)$ in the PdFe_3 from spin-down electrons at Pd sites is greater than PdFe , because here the Fermi level is not located in a depression of the DOS [as may be seen in Figs. 7(b) and 10(b)]. At Fe sites (Fig. 11), for spin-up electrons the general features of the DOS remain unaltered and for spin-down electrons the states are almost empty, thus excluding these electrons from Fe sites and giving the calculated magnetic moment (Table IV). We notice that for the three compounds, at Fe sites, the DOS for spin-down electrons around the Fermi energy has its peak broadened as the Fe content is increased, which may be seen by comparing Figs. 5(b), 8(b), and 11(b), showing that more and more spin-down electrons are excluded from those sites leading to high magnetic moments.

For PdFe_3 the contribution of Fe sites (spin-down) to the DOS at the Fermi level is higher than the PdFe , since here the Fermi level is not located in a depression of the spin-down DOS, which gives a high value for $N(E_F)$.

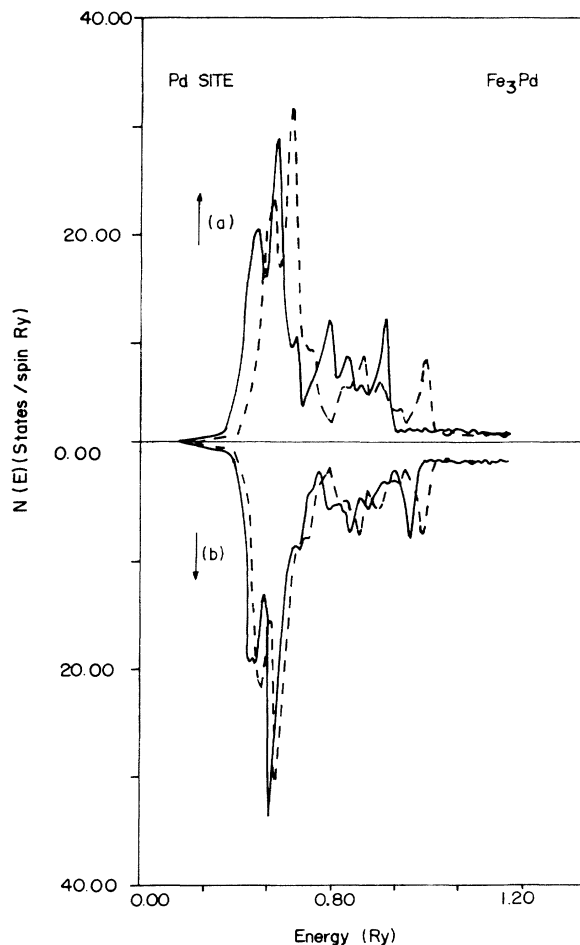


FIG. 13. Total density of states (in states/spin Ry) calculated for two lattice parameters near the collapse of magnetic moment: (a) spin-up and (b) spin-down electrons at the Pd site for PdFe_3 . Solid line $a = 6.6929$ a.u. Dashed line $a = 6.5442$ a.u.

TABLE V. Calculated parameters for ferromagnetic Fe₃Pd for two lattice parameter near the collapse of magnetic moment (a) $a = 6.6929$ and (b) $a = 6.5442$.

(a)	Pd		m	Fe		m
n (electrons/spin)	4.706	5.026	0.32	3.326	4.762	1.436
n_s (electrons/spin)	0.291	0.281	-0.01	0.315	0.314	-0.001
n_p (electrons/spin)	0.345	0.332	-0.01	0.389	0.391	+0.002
n_d (electrons/spin)	4.042	4.370	+0.33	2.585	4.010	1.425
n_f (electrons/spin)	0.028	0.043	0.01	0.037	0.047	+0.010
$N(E_F)$ (states/spin Ry)	11.75	3.2		21.6	10.00	
$N(E_F)$ (states/unit cell Ry)				109.76		
E_F (Ry)				0.805		
ΔQ (electrons)		-0.264			0.088	
(b)	Pd		m	Fe		m
n (electrons/spin)	4.8075	4.8082	0.0007	4.0602	4.0673	0.007
n_s (electrons/spin)	0.2834	0.2833	-0.0001	0.3098	0.3098	0.0000
n_p (electrons/spin)	0.3444	0.3443	-0.0001	0.3891	0.3890	-0.0001
n_d (electrons/spin)	4.1428	4.1436	0.0008	3.3170	3.3242	0.0072
n_f (electrons/spin)	0.0369	0.0370	+0.0001	0.0443	0.0443	0.0000
$N(E_F)$ (states/spin Ry)	3.00	3.05		13.90	13.80	
$N(E_F)$ (states/unit cell Ry)			89.15			
E_F (Ry)			0.895			
ΔQ (electrons)		-0.383			0.128	

Figure 12 shows the total DOS for PdFe₃, and here again the Fermi level is located near a valley of the DOS, leading to a reduction in the value of $N(E_F)$ and giving γ near the value obtained for Pd₃Fe.

The breakdown of the magnetic moment as the lattice parameter is decreased (Fig. 2) can be understood in terms of the electronic distribution in the solid. To this end, results for PdFe₃ are given for two different volumes, whose lattice parameters are $a = 6.6929$ and 6.5442 a.u. (Table V). These values correspond to a deviation in the lattice parameter of -4% and -6% , respectively, from its equilibrium value (Wigner-Seitz spheres with the same radius in each case, that is, the radii are $s = 2.61559$ and 2.5574 a.u.). An inspection of Table V gives a clear idea of what happens with the electronic distribution when the interatomic spacing is diminished. For both sites, as volume is decreased there is an increasing number of spin-down d electrons accompanied by a decrease in the number of spin-up d electrons, which reduces their difference and hence gives small magnetic moments. This abrupt change in the magnetization can be viewed as a "population effect" of the spin-down d states at Fe sites. This can be clarified through Figs. 13 and 14, where the total DOS at Pd and Fe sites is shown for two different lattice parameters. At Pd sites [Figs. 13(a) and 13(b)] the general features of the DOS for spin-up states are drastically altered when compared with the DOS for equilibrium volume [Fig. 10(a)]. Now it resembles the structure of the spin-down DOS with a broadened peak around 0.35 Ry (0.32 Ry) below the Fermi energy, whose widths are 0.14 Ry for -4% and -6% of the deviation, respectively. These peaks are remnants of the peak in Fig. 10(a), which is centered about 0.29 Ry below the Fermi level and has a width of 0.14 Ry. Therefore, there is an increasing degree of localization of the majority-spin d electrons at the Pd sites, and this clearly shows that

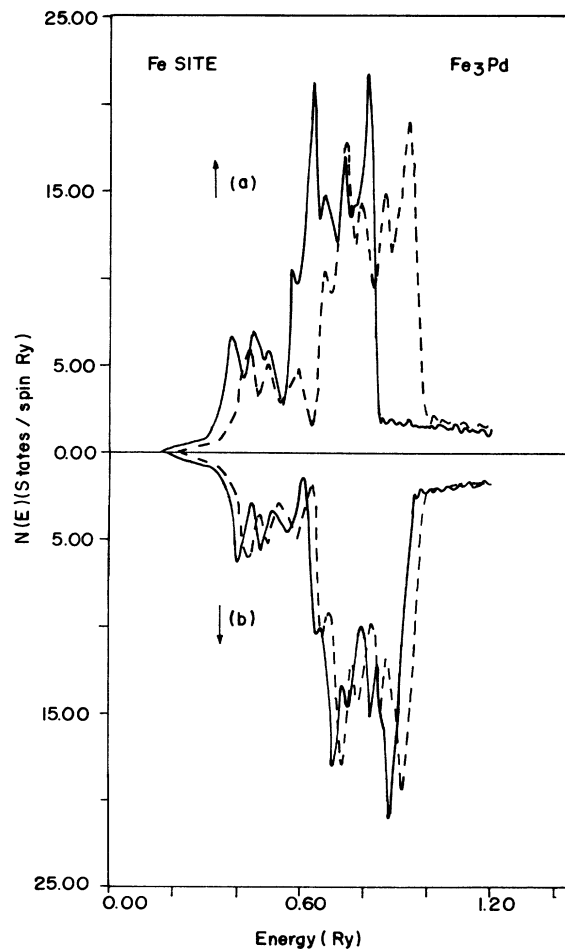


FIG. 14. Total density of states (in states/spin Ry) calculated for two lattice parameters near the collapse of magnetic moment: (a) spin-up and (b) spin-down electrons at the Fe site for PdFe₃. Solid line $a = 6.6929$ a.u. Dashed line $a = 6.5442$ a.u.

spin-up electrons are more affected than spin-down electrons as the interactions between atoms become more strong with reduction of lattice spacing. Further, these interactions affect spin-up electronic states included in a range from 0.30 Ry up to Fermi energy. From an inspection of Figs. 13 and 14 it is observed that, although there is an entire shift of the DOS, some alterations in these features occur, indicating the modification on the self-consistent potentials felt by the electrons. One remarkable aspect of these figures is that for both sites the structure of the DOS for up and down spins, as the volume is decreased, becomes equal, so the system is driven to the paramagnetic phase. At Fe sites (Fig. 14) it is more clear that, as the volume decreases, the spin-up DOS is shifted to higher energies, emptying up states and at the same time populating spin-down states as the Fermi energy moves to high energies. Therefore the magnetic breakdown comes from two factors; that is, the inversion of the spin-up into the spin-down population can be viewed as a shift in the DOS as well as the population of the spin-down states at Fe sites by the excess electrons yielded by Pd atoms.

III. CONCLUSION

We have studied, by fully self-consistent band calculations within the LMTO method, the electronic structure of ferromagnetic Pd₃Fe-, PdFe-, and PdFe₃-ordered compounds. Through an analysis of the results obtained it was found that electronic and magnetic properties are sensitive to the iron content in iron-palladium alloys. On the one hand, we saw for these alloys a common behavior of the electronic states that explains in the same manner the formation of localized magnetic moments from an itinerant-electron point of view, similar to the case of Heusler alloys.²⁴ Some theoretical results agree well with experiment, and our calculated lattice parameters for Pd₃Fe and PdFe agree within 0.5% with respect to the experimental values for each type of approximation for the exchange correlation. Further, we have found no large differences between the values obtained from these

two calculations and the experiment. One possible way to improve the results is to attempt to go beyond LDA, as done by Manghi *et al.*³⁴ for GaAs and Si.

Concerning the stability of the compounds, the calculation for the internal excess energy show the stability of Pd₃Fe and PdFe with formation energies of -4.00 kcal/at.g. and -6.20 kcal/at.g., respectively. These values must be compared with -0.53 kcal/at.g. (vBH) or -0.16 kcal/at.g. (VWN) obtained for PdFe₃. On the basis of these results it can be said that PdFe₃ is at best a metastable compound since its formation energy is so close to zero. The electronic structure of these compounds was studied as a function of the lattice parameter with the aim of understanding the dependence of the ground-state properties (charge transfer, magnetization, etc.) with volume. As a consequence, the total magnetization for Pd₃Fe and PdFe are smooth increasing functions of the lattice parameter, the main contribution for this behavior arising from Pd sites, while for PdFe₃ a collapse of magnetic moments (at both sites) can be seen as the lattice parameter is decreased about 6%. This unusual behavior of the magnetization was analyzed in terms of the electronic redistribution of up and down states. These low and high moment states were discussed in terms of the general features of the DOS, as was done by Roy and Pettifor³⁴ for fcc iron. Remarkable changes were observed in the structure of the spin-up DOS at Pd sites, leading to an increasing degree of localization of the majority-spin electrons. The collapse of magnetic moments was explained by the subtle changes in the DOS, accompanied by the inversion of spin populations. To our knowledge, the study of magnetic moment breakdown in this intermetallic compound has not been reported previously.

ACKNOWLEDGMENTS

This work was partially supported by CNPq and FAEP(UNICAMP).

¹K. M. Rabe and J. D. Joannopoulos, Phys. Rev. Lett. **59**, (1987).

²K. Terakura, T. Oguchi, T. Mohri, and K. Watanabe, Phys. Rev. B **35**, 2169 (1987); S. Takizawa and K. Terakura, *ibid.* **39**, 5792 (1989).

³S.-H. Wei, A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. B **36**, 4163 (1987); A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Phys. Rev. Lett. **58**, 49 (1987); J. E. Bernard, L. G. Ferreira, S.-H. Wei, and A. Zunger, Phys. Rev. B **38**, 6338 (1988).

⁴A. Z. Man'sikov and V. A. Tsurin, Phys. of Metals and Metallurgy (USSR) **47**, 68 (1979); **45**, 82 (1978).

⁵C. A. Bechman, W. E. Wallace, and R. S. Craig, Philos. Mag. **27**, 1249 (1973).

⁶T. B. Flanagan, S. Majchrzak, and B. Baranowski, Philos. Mag. **25**, 257 (1972); M. H. P. Correa, W. H. Schreiner, J. E. Schmidt, P. J. Viccaro, and A. Vazquez, J. Phys. F **15**, 1779 (1985).

⁷C. A. Kuhnén and E. Z. da Silva, Phys. Rev. B **35**, 370 (1987).

⁸C. A. Kuhnén and E. Z. da Silva, J. Magn. Magn. Mater. **67**, 260 (1987).

⁹C. A. Kuhnén and E. Z. da Silva, Phys. Rev. B **36**, 452 (1987).

¹⁰M. Hansen *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958). Metallurgy and Metallurgical Engineering Series 2nd ed.

¹¹R. Hultgreen and C. A. Zapffe, Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. **99**, 509 (1938).

¹²G. Alavendov and S. Shavlo, Z. Tekh. Fiz. **9**, 211 (1939).

¹³W. Jellinghaus, Z. Tech. Physik. **17**, 33 (1936).

¹⁴N. V. Grum-Grzhimailo, Compt. rend. acad. Sci. URSS, **33**, 237 (1941).

¹⁵U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

¹⁶S. H. Vosko, K. Wilk, and M. Nusair, Car. J. Phys. **58**, 1200 (1980).

¹⁷H. J. Jansen, K. B. Hathaway, and A. J. Freeman, Phys. Rev. B **30**, 6177 (1984).

¹⁸O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

¹⁹O. K. Andersen and O. Jepsen, Physica (Utrecht) **91B**, 317

- (1977).
- ²⁰H. K. Skriver, *The LMTO Method: Muffin-tin Orbitals and Electronic Structure* (Springer, New York, 1984).
- ²¹L. G. Ferreira, S.-H. Wei, and A. Zuber, *Phys. Rev. B* **40**, 3197 (1989).
- ²²L. G. Ferreira, A. A. Mbaye, and A. Zunger, *Phys. Rev. B* **37**, 10 547 (1988); **35**, 6475 (1987).
- ²³A. J. Smith, W. G. Stirling, and T. M. Holden, *J. Phys. F* **7**, 2411 (1977).
- ²⁴J. Kubler, A. R. Williams, and C. B. Sommers, *Phys. Rev. B* **28**, 1745 (1983).
- ²⁵A. R. Williams, R. Zeller, V. L. Moruzzi, and C. D. Gellat, Jr., *J. Appl. Phys.* **52**, 3 (1981).
- ²⁶A. P. Malozemoff, A. R. Williams, and V. L. Moruzzi, *Phys. Rev. B* **29**, 1620 (1984).
- ²⁷U. K. Poulsen, J. Kollar, and O. K. Andersen, *J. Phys. F* **6**, L241 (1976).
- ²⁸O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, *Physica* **86-88B**, 249 (1977).
- ²⁹A. R. Williams, J. Kubler, and C. D. Gellat, Jr., *Phys. Rev. B* **19**, 6094 (1979).
- ³⁰J. Kubler, *Phys. Rev. Lett.* **81A**, 81 (1981).
- ³¹D. Bagayoko and J. Callaway, *Phys. Rev. B* **28**, 5419 (1983).
- ³²J. Madsen and O. K. Andersen, in *Magnetism and Magnetic Materials—1975 (Philadelphia)*, Proceedings of the 21st Annual Conference on Magnetism and Magnetic Materials, AIP Conf. Proc. No. 29 edited by J. J. Becker, G. H. Lauder, and J. J. Rhyne (AIP, New York, 1976), p. 327.
- ³³D. M. Roy and D. G. Pettifor, *J. Phys. F* **7**, L183 (1977).
- ³⁴F. Manghi, G. Riegler, C. M. Bertori, and G. B. Bachelet, *Phys. Rev. B* **31**, 3680 (1985).