Magnetic instabilities in PtFe$_3$ and in the fcc Ni-Fe system

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The self-consistent linear muffin-tin orbitals electronic structure calculations have been carried out for nonmagnetic and ferromagnetic phases of PtFe$_3$ and for a few ordered phases of the Ni-Fe alloy. The fixed-spin-moment scheme has been employed. The results reveal the existence of high-spin (HS) and low-spin (LS) branches of the magnetization curve for both systems and allow for a direct calculation of the energy differences between the HS, LS, and nonmagnetic phases. For the Ni-Fe alloy, the total energy and the state equations are calculated for a number of concentrations. It is shown that a vanishing energy difference between the HS and the LS states and the magnetic instability close to equilibrium are correlated. For PtFe$_3$ the pressure dependence of the total energy is discussed. It is shown that this information in conjunction with experimental values of the critical pressures at which the HS-LS transitions are observed allows for an independent estimation of the energy differences between these phases and that the estimate does not agree well with the results of local-density calculations. It is pointed out that this disagreement and the previously reported inability of the local-density approximation to account for observed high-field susceptibilities may be of common origin.

I. INTRODUCTION

PtFe$_3$ and Ni$_x$Fe$_{1-x}$ ($0.30 < x < 0.40$) alloys are the best known examples of Invar materials.[1] The Ni-Fe system is chemically disordered and displays INVAR anomalies, among them a very small thermal expansion coefficient is the most typical one, in a relatively broad range of concentrations. It has been shown[2,3] that in this range the system undergoes a transition from strong to weak ferromagnetism and that the other well-known anomalies as deviation of the lattice constant from the Vegard law and deviation of the average magnetic moment from the Slater-Pauling curve, often referred to in the INVAR context, are consequences[3] of the strong-to-weak ferromagnetism transition.

PtFe$_3$ displays INVAR anomalies in both ordered and disordered phases. It is believed to be a strong ferromagnet[4] and the detailed band-structure study[5] essentially confirms this assessment. The Pt-Fe system shows no deviations of the sort mentioned above for the Ni-Fe system.[4] This fact can also be easily explained[5] on the basis of the one-electron theory of itinerant magnetism. The electronic-structure calculations led Williams et al.[6] to the hypothesis that INVAR behavior is intimately connected with the existence of two energetically nearly degenerate states: a high-spin state at a large volume and a low-spin or nonmagnetic state at a smaller one. The energy difference between these states is supposed to be so small that the nonmagnetic (or, more general, low-spin) state should be attainable by thermal fluctuations.

It seems that the recent popularity of this concept[1] was greatly stimulated by a series of papers[7] in which the total energy calculations have been carried out for many transition metals. These studies employed the so-called "fixed-spin-moment" (FSM) method.[8] In contrast to the conventional spin-polarized band-structure calculations where the magnetic moment is one of the output parameters, in the FSM scheme it is an input parameter treated on the same footing as the atomic volume. As a result, one obtains a binding surface $E(V, M)$, i.e., total energy as a function of both atomic volume and magnetic moment. Taking the moment derivative of $E(V, M)$ one obtains a magnetic state equation $H(V, M)$ and a path in the M-V plane along which $H(V, M)$ vanishes is equivalent to the $M(V)$ curve. Using this technique, Moruzzi et al.[7] have shown that the $M(V)$ curve for fcc Fe is discontinuous and that at certain atomic volumes there are different (meta)stable magnetic states.

Until now, the FSM studies covered almost all bcc and fcc transition metals[7] and recently have been extended to hexagonal phases.[9] The results for fcc Fe seem to be of special significance for the INVAR problem. It has been tacitly assumed[10,11] that the HS and LS phases predicted theoretically for fcc Fe will be practically realized in INVAR materials. Kisker et al.[10] tried to prove existence of these phases using photoemission measurements for PtFe$_3$ below and above the Curie temperature. Recently, Abd-Elmeguid, Schlede, and Micklitz carried out a Mössbauer study of magnetic behavior of Ni$_x$Fe$_{1-x}(0.65 < x < 0.685)$[12] and PtFe$_3$ (Ref. 11) under pressure and demonstrated that the moment instabilities indeed occur in these systems

The hitherto reported FSM studies[7,9] for transition metals brought an abundance of new information on their metamagnetic behavior and, in particular, on the total energies of diverse magnetic phases. It has been recently shown by Wagner[13] that the energy difference between the ferro- and nonmagnetic phases and the difference of the respective atomic volumes specify, in a simplest ap-

proximation, the mechanism of coupled density and moment fluctuations. A proper description of such a mechanism is essential for any discussion of the INVAR behavior for $T \neq 0$.[14] The energy differences calculated within the FSM method are not directly measurable and their values have not yet been verified in any way. The well-known difficulties of the local density approximation (LDA) in a correct description of cohesive energies make such a verification even more desirable. We will show in the following how the results of the pressure experiments[11,12] in connection with our bulk modulus calculations give an independent estimate of this energy difference.

In this paper we report on the results of the self-consistent, spin-polarized, FSM electronic structure calculations carried out for Pt-Fe and Ni-Fe alloys. A special significance has been attached to the calculations for the ferromagnetic (FM) PtFe$_3$ phase. As mentioned before, the ordered phase of PtFe$_3$ exists and a body of experimental data is available for a direct comparison. As we have argued in Ref. 3, the disorder effects seem to influence significantly the properties of the Ni-Fe alloy and we suspect that the results of FSM calculations for the ordered phases of this system are of limited applicability. Besides, the FSM calculations for NiFe$_3$ have been very recently reported by Moruzzi[15] and by Mohn, Schwarz, and Wagner.[16] Therefore, we restrict our discussion of the FSM results for the Ni-Fe system to two problems: first, we investigate the nature of the magnetovolume instabilities and the existence of the high- and low-spin phases as a function of alloy composition, and, second, we calculate the total energy for a few supercells. We shall show that there are no coexistent HS and LS phases for the considered ordered phases of the Ni-Fe system and that the total energy difference between the HS and LS phases in the Invar region is relatively large.

For PtFe$_3$ we present the first complete, *ab initio* calculation of the metamagnetic properties, magnetoelastic constants, magnetic and mechanical state equations, and total energy surface. We show how these results, together with the recent pressure experiments of Abd-Elmeguid and Micklitz,[11] can be used to estimate the error in the magnetic energy calculated within LDA. In this context, a mutual relationship between the magnetic energy, high-field susceptibility, and electron correlation effects is discussed. We argue that the calculated values of the spin susceptibility are probably not as much in error as commonly suspected and that the opposite holds for the experimental high-field susceptibility.

II. METHOD OF CALCULATIONS

The method of calculations has been essentially the same as that described in Ref. 9. Still, two comments are in order here.

(a) We have found that the combined correction terms (CCT) of the LMTO method[17,18] must be used if one wants to obtain credible results for the total energy difference between the FM and NM states of the Invar alloys. For the cases where this energy difference is large

(> 10 mRy/atom) the use of CCT is unimportant, but it becomes critical for the materials having small FM-NM energy separation. For PtFe$_3$, neglect of the CCT increases the calculated ΔE by more than factor of 2. A similar trend has been found for all Ni-Fe phases. Consequently, all the results presented in this paper has been obtained with CCT included.

(b) For alloys one has to examine anew applicability of the canonical scaling principle. The differential hybridization, neglected within this procedure, is much more important for alloys than for simple metals. For alloys, the neglect of different degrees of hybridization between the $3d$ orbitals of different atoms for varying magnetic moment amounts to the neglect of the *induced magnetic moments*. It is clear therefore that the scaling procedure will work well for simple metals and for compounds consisting of a single magnetic element and other hardly polarizable atoms (e.g., Fe$_2$P or magnetic semiconductors). For PtFe$_3$ the scaling procedure works fairly well but for the Ni-Fe alloy it must be used with great caution. In the present calculations we have assumed the following computational strategy: the fully self-consistent calculations have been carried out not only for the NM phase on a dense mesh along the V axis but also on a coarse mesh in the M-V plane. The results on the fine mesh in the M-V plane around the coarse mesh points have been obtained using the scaling procedure. The parameters of the two meshes have been chosen so as to maintain a predefined accuracy of the calculations. This trade-off between the requested accuracy and an acceptable computation time made it possible to obtain the FSM results for three different phases of the Ni-Fe systems and for PtFe$_3$ using very modest computational capability.

For all considered compounds the basis set included s, p, and d orbitals only. A relatively large number of $\mathbf{k}$ points was used (≥ 286) for all symmetries (cubic and tetragonal), so that the k-space integration was fully converged. Self-consistency has been assumed when the maximum relative error in the spin densities was smaller than 10^{-5}. The amplitude of the numerical noise in the calculated total energies was smaller than 0.1 mRy. This does not, of course, imply a comparable accuracy in absolute values of the total energy. In fact, use of the frozen core and muffin-tin approximations as well as neglect of the f orbitals prevent us from making any reliable estimate of its absolute value. Hence, all the total energy values are given with respect to the energy of the nonmagnetic state.

III. RESULTS AND DISCUSSION

A. Magnetic instabilities in the Ni-Fe system

The results of calculations are presented in Figs. 1 and 2. Figure 1 shows the combined magnetic field and pressure contour plots for the series of ordered phases of the Ni-Fe alloy: NiFe$_3$, Ni$_3$Fe$_5$, and Ni$_2$Fe$_2$. From the three phases considered, only NiFe$_3$ displays a magnetic instability close to the equilibrium. We observe a larger
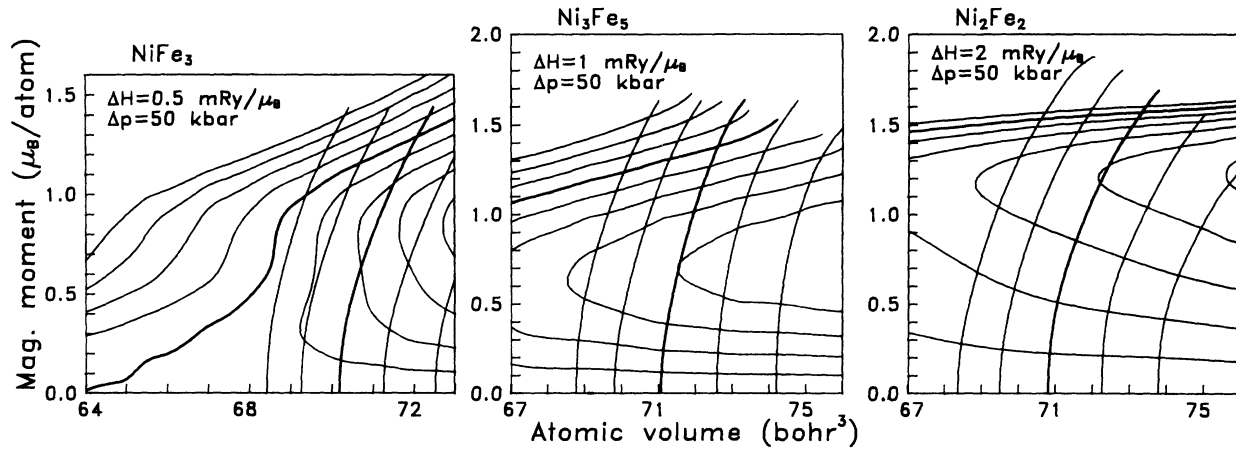
FIG. 1.   Magnetic field and pressure contours for ordered phases of the Ni-Fe system in the M-V plane. From left to right the plots for $NiFe_3$, Ni_3Fe_5, and Ni_2Fe_2 are displayed. Heavy lines indicate the $H = 0$ $[M(V)]$ and $p = 0$ contours. Contour distances are given on the plots.

sensitivity of the magnetic moment to volume changes for Ni_3Fe_5 as compared to Ni_2Fe_2 but we do *not* observe a magnetic instability for either phase in the considered volume range. For $NiFe_3$ we were not able to decide within the accuracy of computations whether the $M(V)$ curve is actually discontinuous. Anyhow, it displays two regions, separated by a shoulder, that could be called LS and HS phases. It is remarkable that the LS phase extends down to a volume of 64 a.u. ($r_{ws} \cong 2.48$ a.u.). The onset of magnetism is of the second order and the I-st type, i.e., there are no coexistent magnetic phases.

Our results are in a reasonable agreement with the results reported by Moruzzi,[15] although the calculated equilibrium magnetic moments and volumes differ a little. $NiFe_3$ seems to be a difficult case—the inclusion of CCT has changed the equilibrium moment value by almost 10%. Normally, the use of CCT has almost no effect on calculated ground-state properties.[18] In a recent paper Moroni and Jarlborg[19] report the value of equilibrium magnetic moments and equilibrium lattice constants that agree well with our FSM results. On the other hand, our floating moment calculations without CCT^3 and the cal-

culations of Moruzzi[15] give almost identical results that are however slightly different from our FSM and Moroni-Jarlborg results. The only conclusion from this observation is that for $NiFe_3$ a balance between volume and magnetism is particularly subtle and very small technical changes in calculations scheme may influence the results appreciably. For Ni_2Fe_2 such a sensitivity has not been observed.

Figure 1 shows that the pressure necessary to force $NiFe_3$ from the HS to the LS phase is roughly 120 kbar (Ref. 20). The experimental value of the pressure at which the HS component of the hyperfine field disappears for $Ni_{0.315}Fe_{0.685}$ is 58 kbar.[12] A possible source of this discrepancy will be discussed in the next subsection.

Figure 2 shows the total energy surfaces for all three phases. They illustrate the evolution of the magnetic properties of the Ni-Fe system with concentration. All surfaces have an FM minimum and an NM saddle point. The energy difference $\Delta E = E_{NM} - E_{FM}$ grows with Ni concentration and is equal to 0.8, 3.7, and 7.5 mRy for $NiFe_3$, Ni_3Fe_5, and Ni_2Fe_2, respectively. Moruzzi[15] found $\Delta E \cong 1$ mRy for $NiFe_3$ and Moroni and Jarlborg[19] re-
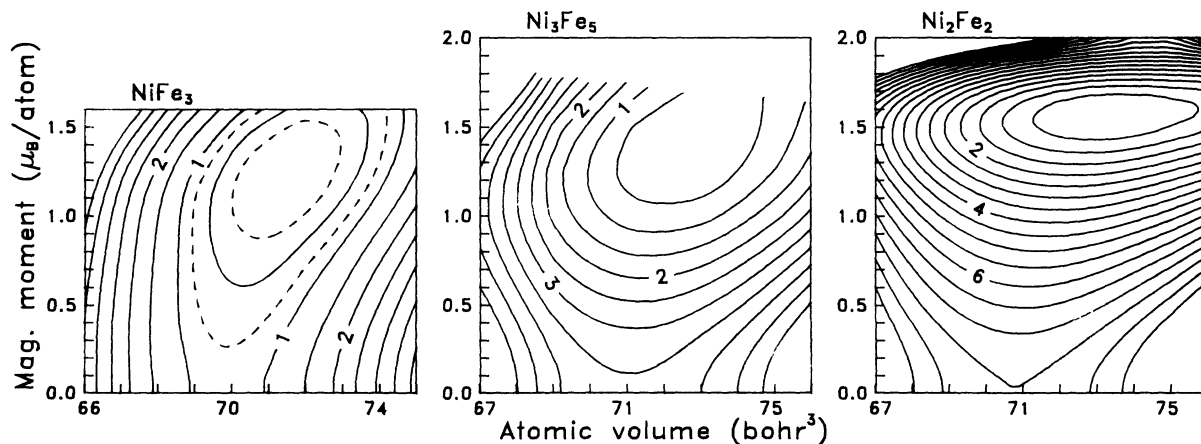

FIG. 2.   Binding surfaces for ordered phases of the Ni-Fe system in the M-V plane. From left to right the plots for $NiFe_3$, Ni_3Fe_5, and Ni_2Fe_2 are displayed. Energy contours are plotted every 0.5 mRy.

ported $\Delta E = 0.5$ mRy for NiFe$_3$ and $\Delta E = 7$ mRy for Ni$_2$Fe$_2$. There is, therefore, a close, encouraging correspondence of the results obtained independently with use of different calculational schemes. We note, however, that for ordered phases of the Ni-Fe alloy in the Invar region ΔE is *not* as small as expected.[1] A quadratic interpolation gives for the Invar region of the Ni$_{1-x}$Fe$_x$ alloy ($0.62 < x < 0.68$) the values of ΔE in the range of 3.7–2.2 mRy (or 580–370 K). Since the calculated ΔE's are somewhat larger than expected, the FSM results for the ordered phases of the Ni-Fe system seem not to exactly correspond to the picture of Invar set by Wassermann[1] and by Moruzzi.[15] Yet, the differences are quantitative rather than qualitative. The magnetovolume instabilities are predicted at too high Fe concentrations. Despite this quantitative disagreement, the FSM calculations for the Ni-Fe system allow for two general conclusions. First, the HS and LS phases exist for some alloy concentrations but a metamagnetic behavior has not been found. Hence, metamagnetism is probably not an essential ingredient of Invar phenomenon although it may be an associated feature, as we shall see in the next section. Second, Figs. 1 and 2 illustrate a direct correspondence between a small ΔE and a moment-volume instability *close to equilibrium*. Quantitatively we observe that the calculated LDA value of ΔE must not be larger than approximately 1.5 mRy to invoke a magnetic instability at experimentally relevant pressures.

There are two conceivable reasons for the quantitative discrepancy found for the Ni-Fe system: first, the LDA calculations are believed to overestimate a tendency toward the magnetic state. This point will be discussed in the next section. Second, disorder effects, neglected in the present calculations, may exert a non-negligible influence on magnetic instability of the Ni-Fe alloy.[3] Indeed, the very recent results of the self-consistent KKR-CPA total energy study for Ni$_{35}$Fe$_{65}$ (Ref. 21) have shown that the ΔE calculated for chemically disordered material amounts to less than 1 mRy, i.e., to one-third of our value. We tend to believe right now that the hypothetical *ordered* Ni-Fe alloy would display only weak Invar anomalies in the concentration region of 62–68 % Fe and that the chemical disorder enhances the Invar anomalies for concentrations close to the martensitic transformation for this particular material.

B. Metamagnetic and magnetoelastic properties of PtFe$_3$

Figure 3 shows the $H(M)$ curves for PtFe$_3$ at a few atomic volumes[22,23] in the relevant range. The Fermi level for the NM phase of PtFe$_3$ is positioned at a local DOS maximum.[5] This is important not only for the existence of magnetic instability[5,7] but also for its character. With Fermi level positioned at a local DOS maximum, one expects the second-order magnetization onset for PtFe$_3$.[7] The slope of the $H(M)$ curves at $M = 0$ (Fig. 3) indicates ferromagnetic instability for all volumes shown. Curves 1, 2, and 3 indicate clearly an LS phase with $M < 0.4\mu_B$, and curves 2–6 an HS phase with $M > 1\mu_B$. Figure 4, where the contour of $H(r_{ws}, M)$ and $p(r_{ws}, M)$ are plotted, illustrates better this compli-
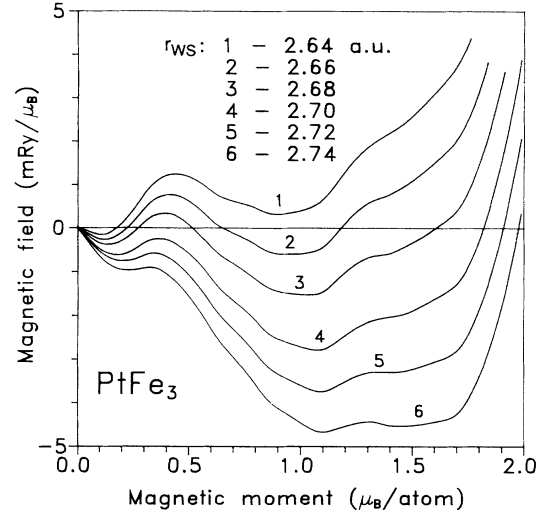

FIG. 3. Magnetic field as a function of the net magnetic moment for PtFe$_3$ at several lattice constants.

cated behavior and allows for a detailed analysis of the magnetic instability of PtFe$_3$. As expected, the onset of magnetism is of the second order. The NM phase is stable for $r_{ws} \leq 2.61$ a.u. [the Stoner criterion for PtFe$_3$ is fulfilled for $r_{ws} \geq 2.62$ a.u. (Ref. 5)]. The LS phase appears at this volume and the magnetic moment slowly increases up to $M \cong 0.37\mu_B$, where the LS phase ends abruptly at $r_{ws} \cong 2.69$ a.u. The HS phase appears at r_{ws} slightly below 2.65 a.u. with the magnetic moment of $\sim 1\mu_B$. In the range $2.65 < r_{ws} < 2.69$ a.u. PtFe$_3$ is *metamagnetic*, with two coexisting phases of a nonzero magnetic moment.

The overall magnetic transition is of the mixed second and first order and the III-rd type.[24] The $M(V)$ curve (the parts of the $H = 0$ contour plotted as a solid line)
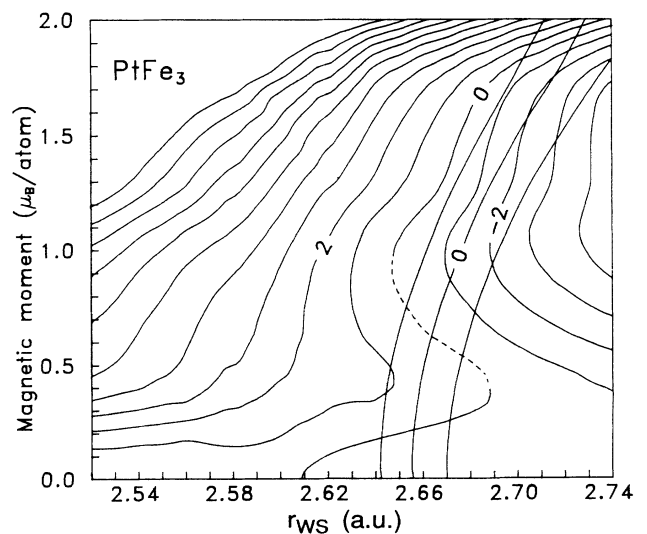

FIG. 4. Contour plot of the magnetic field in the r_{ws}-M plane for PtFe$_3$. Contours are plotted every 1 mRy/μ_B. Dashed line indicates the unphysical region of the $M(V)$ curve. Superimposed are the pressure contours for -50, 0, and 50 kbar.
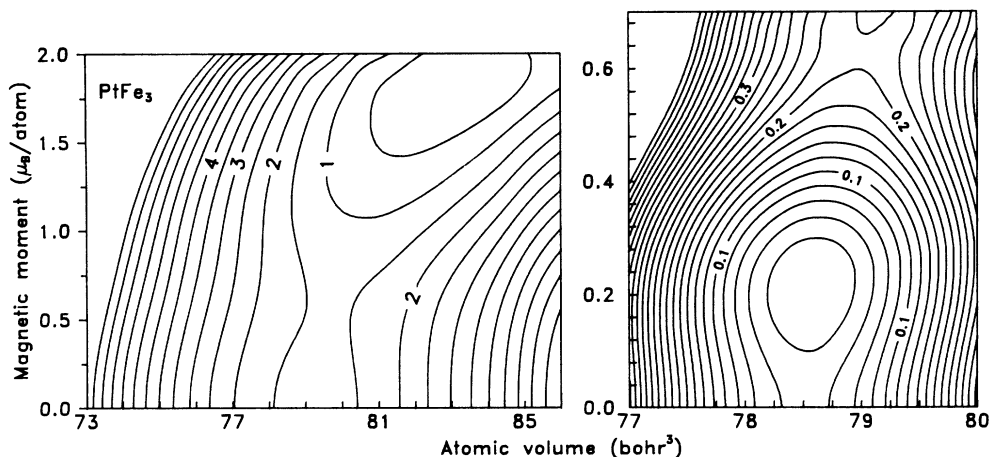
FIG. 5. Total energy surface for PtFe₃ in the V-M plane. Left panel shows the overall V-M area. Right panel shows the blow-up of the LS region.

is discontinuous. This reminds one of the complicated transition found for fcc Fe (Refs. 7 and 22) and is in contrast to the situation found for the ordered Ni-Fe phases. The case of PtFe₃ looks even more interesting when the pressure contours are superimposed onto the H contours (Fig. 4). The diagram indicates *two* local stability points $H = p = 0$: one on the HS branch of the $M(V)$ curve at $r_{ws} = 2.723$ a.u. and $M = 1.92\mu_B$ and second on the LS branch at $r_{ws} = 2.657$ a.u. and $M = 0.21\mu_B$, and two saddle points: one corresponding to the NM phase energy minimum at $r_{ws} = 2.655$ a.u. and second at the crossing point of the $p = 0$ contour with the unphysical part (dashed line) of the $H = 0$ contour at $M \cong 0.6\mu_B$. PtFe₃ is the first material for which such an exceptional situation has been theoretically found.

The total energy surface is plotted in Fig. 5. The energy contours, plotted every 0.5 mRy [Fig. 5(a)], indicate the global minimum for the HS solution and a saddle point for the NM solution, with the energy difference of less than 1.5 mRy. It is therefore a ferromagnetic binding surface with a very small magnetic binding energy. Since the structure around the LS phase is not resolved in the scale of Fig. 5(a), Fig. 5(b) shows a blow-up of the relevant part of the V-M plane. The energy contours are plotted every 0.02 mRy with respect to the LS energy minimum. The LS minimum as well as both saddle points at $M = 0$ and $M \cong 0.6\mu$ are now clearly visible. The total energy calculated along the $M(V)$ branches is shown in Fig. 6. As expected, the global minimum is found along the HS branch. The NM and LS total energies differ very little as one could expect from the low-magnetic moment of the LS phase. The difference does not exceed 0.05 mRy, but it should be noted that the NM and LS phases are (meta)stable in the nonoverlapping V regions, so that the one or the other can be realized. From Fig. 6 we find that actual $\Delta E = E_{NM} - E_{HS} = 1.32$ mRy. We see therefore that the calculated energy difference between the NM and HS states of PtFe₃ is of the order of 200 K. The LS minimum is positioned at $M = 0.21\mu_B$ and $r_{ws} = 2.656$ a.u. and its energy is 0.03 mRy lower than that of the NM saddle point (these and other numerical data are collected in Table I).

The FSM approach is the most general method of calculation of the magnetoelastic constants. To exploit these virtues we have calculated all magnetoelastic functions of PtFe₃. The following quantities have been calculated: magnetic spin susceptibility at constant volume $\chi_V = \left(\frac{\partial H}{\partial M} \right)^{-1}$, bulk modulus at constant magnetic moment $B_M = V\frac{\partial P}{\partial V}$, magnetovolume coupling $g = \frac{\partial H}{\partial V} = -\frac{\partial P}{\partial M}$, magnetovolume enhancement factor $\eta = (1 - Vg^2\chi_V/B_M)^{-1}$, magnetic spin susceptibility at constant pressure $\chi_P = \eta\chi_V$, bulk modulus at constant magnetic field $B_H = B_M/\eta$, forced volume magnetostriction $h = \frac{1}{V}\left(\frac{\partial V}{\partial H} \right)_P = -\eta g\chi_V/B_M$, and logarithmic pressure derivative of the magnetic moment $d = \frac{1}{M}\left(\frac{\partial M}{\partial P} \right)_H = -\frac{V}{M}h$.

The numerical results for the HS, LS, and NM phases and the available experimental data are collected in Table I. We note that the results of the approximate FSM procedure are in good agreement with the conventional floating-moment calculations (Ref. 5, Table VI), the differences resulting mostly from the fitting procedure used to find the analytic description of the binding surface.
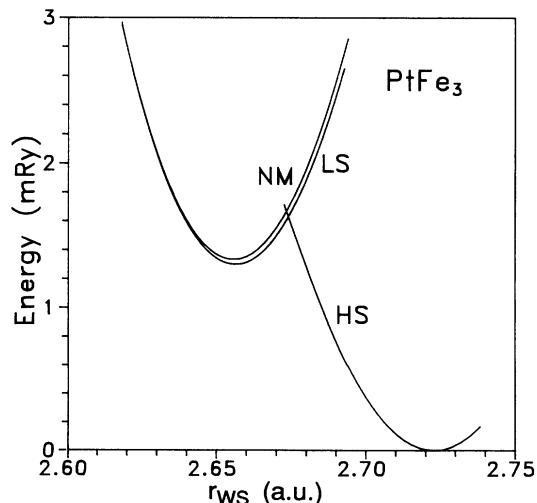

FIG. 6. Total energy calculated along the HS and LS branches of the $M(V)$ curve and for the nonmagnetic phase.

TABLE I. Ground-state properties of $PtFe_3$ calculated from the FSM procedure. For description of symbols see text. The experimental data marked with an asterisk have been calculated using the reported values of the measurable parameters.

	HS phase	Expt.	LS phase	NM phase
r_{ws} (a.u.)	2.723	2.75[a]	2.656	2.655
M (μ_B)	1.92	2.16[b]	0.21	0.0
E (mRy)	0.0		1.20	1.32
η	1.21	1.07*	1.02	1.0
g (10^7 Oe mol/cm)	−2.34	−0.52*	−0.36	0.0
B_M (Mbar)	2.47	2.11*	3.21	3.20
B_H (Mbar)	2.04	1.95 ∓ .05[c]	3.16	3.20
χ_P (10^{-4} emu/mol)	1.22	8.0[b]	4.88	−8.18
χ_V (10^{-4} emu/mol)	1.01	6.5*[d]	4.81	−8.18
h (10^{-9} Oe $^{-1}$)	1.2	1.8[b]	0.6	0.0
d (10^{-4} kbar $^{-1}$)	−8.3	−7.0[e],−12.0[b]	−36.0	0.0

[a]Reference 36.
[b]Reference 26.
[c]Reference 37.
[d]Orbital susceptibility of 1×10^{-4} emu/mol reported by Takahashi and Shimizu (Ref. 38) for Fe has been subtracted.
[e]Reference 25.

This proves convincingly a suitability of the approximate approach.

A comparison of the calculated and experimental values is somewhat difficult because the experimental data quoted in the table seem inconsistent. First, the experimental d values are controversial: the values reported by Hayashi and Mori[25] and by Shimizu[26] are −7 and −12 × 10^{-4} kbar $^{-1}$, respectively, while Abd-Elmeguid and Micklitz[11] report almost complete insensitivity of the Fe magnetic moment on pressure ($d \cong 0$) close to equilibrium. Next, we note that the h and d values are related by the simple formula $d(V, M) = -\frac{V}{M}h(V,M)$. The reported value of h (Ref. 26) is only consistent with the value of $d = -12 \times 10^{-4}$ kbar^{-1}. From the magnetoelastic constants listed in the table, χ_P, B_H, h, and d are measurable quantities. Using their values one can calculate the magnetovolume enhancement factor η and the magnetovolume coupling g

$$\eta = (1 - Vh^2 B_H/\chi_P)^{-1} \qquad (1)$$

and

$$g = -\eta h B_H/\chi_P, \qquad (2)$$

and, subsequently, B_M and χ_V. The calculated values, marked by an asterisk, are also listed in Table I. We see that the estimated value of η is surprisingly small. For Invar alloys one expects in general a large η.[26] The η calculated with use of the FSM value of χ_P (1.22 × 10^{-4} emu/mol) would be 1.65. This estimate represents the upper limit for η in $PtFe_3$. The value estimated from other experimental parameters according to Eq. (1) is smaller than the calculated one and even smaller than the value reported by Takahashi and Shimizu[27] for bcc Fe. This results from a very large experimental value of the high-field susceptibility χ_P. However, as noted by Wassermann,[1] the χ_P is a notoriously ill-defined experimental quantity. The calculated value is too small, and we shall try to estimate its error below when discussing

credibility of the calculated total energies. The agreement of the calculated and experimental bulk modulus is very good, and h and d are some 30% too small. As it is clear from the relations between the magnetoelastic constants, this disagreement must be attributed to the same source as the disagreement of the calculated and experimental susceptibility.

Despite the discussed uncertainties, it is useful to discuss briefly a general behavior of the magnetoelastic constants for a material with such complicated metamagnetic properties as $PtFe_3$. Figure 7 shows the magnetoelastic functions calculated along the $M(V)$ branches. We note singularity of the χ_{NM} at the onset of the LS phase and singularities of the ferromagnetic susceptibilities at the terminating points of the LS and HS phases. The magnetovolume enhancement factor η is also singular close to these points. This is a direct consequence of the singular behavior of χ_V: while g and B_M behave regularly at the terminating points, increase of χ_V causes the denominator of the expression for η [Eq. (1)] to vanish at some point close to the terminating point. Singularity of η causes the (measurable) bulk modulus B_H to vanish, and the high-field spin susceptibility χ_P to attain very high values. In contrast, the bulk moduli at constant magnetization B_M increase almost linearly with decreasing lattice constant and are insensitive to the singular behavior of the $M(V)$ curve. It is also interesting to observe a mutual relationship of the different bulk moduli: we note, for instance, that for a given lattice constant $B_M^{HS} > B^{NM} > B_H^{HS}$. Finally, we note the correlated behavior of h and d. These functions also become singular at the $M(V)$ singular points.

The total energy surface for $PtFe_3$ has been used in connection with the spin-fluctuation theory for calculation of the thermal evolution of the magnetoelastic properties of this alloy. The results of these calculations have been presented elsewhere.[28]
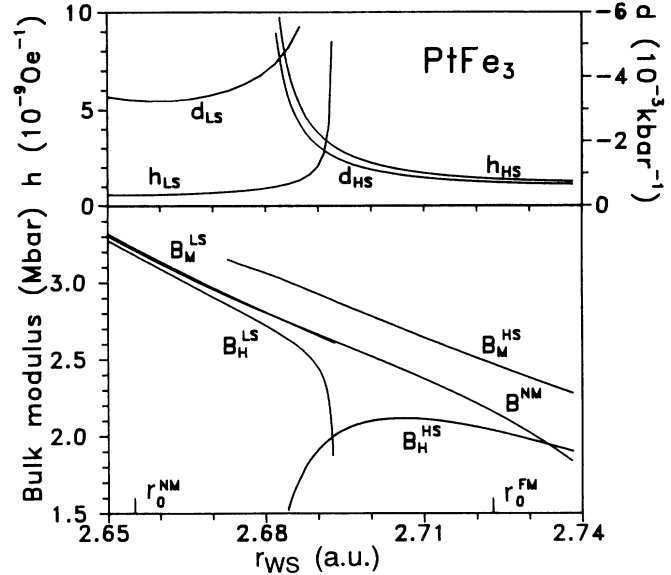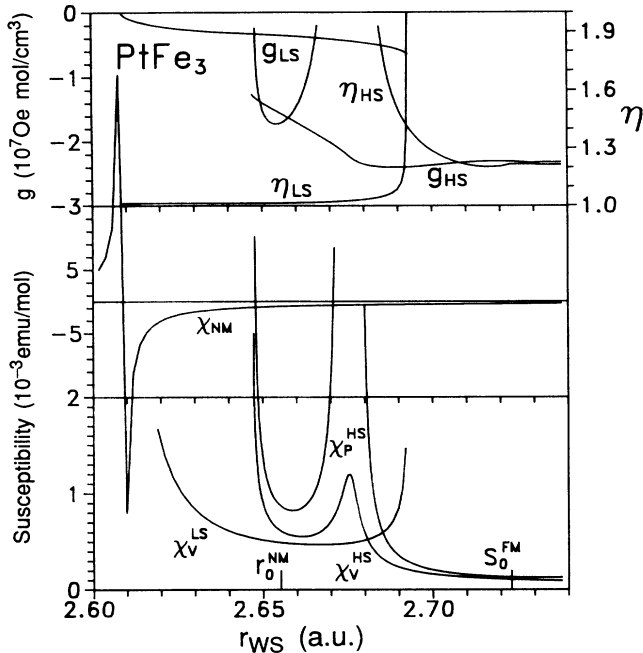
FIG. 7. Magnetoelastic constants calculated along the branches of the $M(V)$ curve and for the nonmagnetic phase. The functions g (magnetovolume coupling), η (magnetovolume enhancement factor), h (forced volume magnetostriction), and d (logarithmic pressure derivative of the magnetic moment) are defined in the text.

IV. DISCUSSION

In Ref. 5 we have suggested that one can use the value of the critical pressure for the HS-LS transition and the calculated non- and magnetic state equations to find the energy difference $\Delta E = E_{NM} - E_{FM}$ for PtFe₃. In the present study we have calculated directly the value of ΔE. Figure 8 shows the total energies, calculated for the NM, LS, and HS phases, plotted as functions of the external pressure. We hoped to obtain in this way a
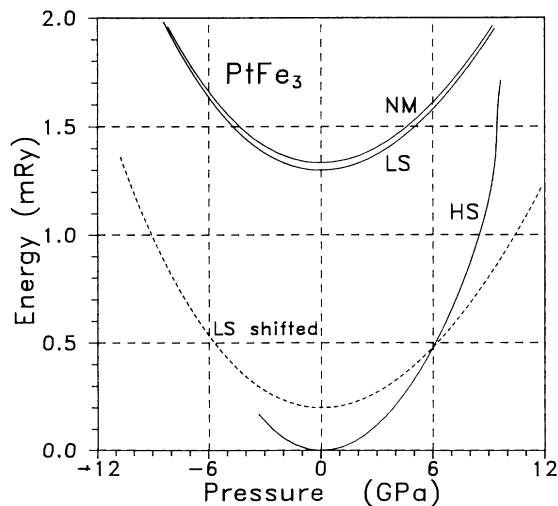

FIG. 8. The total energies for the NM, LS, and HS phases of PtFe₃ calculated as functions of the external pressure. Solid lines—LDA calculated energies, dashed line—the ferromagnetic energy shifted downward so as to provide the correct value of the critical pressure.

theoretical value of the critical pressure p_c for the HS-LS transition. Although in the figure the relevant total energies do not cross, an extrapolation gives a value of $p_c \cong 10$ GPa $= 100$ kbar. While this value does not seem to differ dramatically from the measured $p_c = 60$ kbar,[11] the consequences for the total energy difference are dramatic. To obtain the p_c value that agrees with experiment it would be necessary to shift the LS curve downward so that the value of ΔE would be equal to ~ 0.2 mRy, in agreement with the value we have reported already in Ref. 5. Very similar results have been obtained for the Ni-Fe system. Therefore, the results of the high-pressure Mössbauer experiment carried out by Abd-Elmeguid and Micklitz[11] give us a unique opportunity to test an important aspect of the LDA scheme, namely, its ability to calculate the energy difference ΔE between a magnetic and a nonmagnetic state of a material.

This energy has been by now calculated for many metals. The well-known difficulties[29] the LDA method has had with a correct description of the ground state of Fe show that it is a complex and sensitive problem. It is intimately connected with a basic question of how large and important are LDA errors due to neglect of the electron and spin correlations and how these errors depend on the magnetic state of a material. This is a large field in itself and we cannot and intend not to go into more detail here. On general grounds one expects that LDA overestimates a tendency toward magnetism. A basic physics is readily understood: LDA, in contrast to the Hartree-Fock approximation, accounts for some electron correlations, but by far not for all. Correlations keep the electrons apart whereby the exchange interactions, responsible for the first Hund rule, are reduced. Thus

neglect of any electron correlations enhances magnetism. Stollhoff, Oleś, and Heine (SOH)[30] have shown recently using a model Hamiltonian that inclusion of electron correlations decreases the magnetic energy (i.e., the energy gain due to magnetization). They proposed that the LDA magnetic energy for Fe may be reduced by even a factor of 2–3 by correlations. The total energy difference ΔE can be formally written as

$$\Delta E = E_{\text{FM}} - E_{\text{NM}} = \Delta E_p + \Delta E_H, \qquad (3)$$

where ΔE_p is the energy necessary to expand the lattice from V_{NM} to V_{FM} and ΔE_H is the magnetic energy resulting from magnetization of a material at V_{FM}. The latter energy can be in turn written as a sum of the kinetic and exchange-correlation energies:

$$\Delta E_H = \Delta E_H^{\text{kin}} + \Delta E_H^{xc}. \qquad (4)$$

ΔE_p is always positive whereas ΔE_H may be of any sign. To our understanding, the energy difference considered by SOH is the magnetic energy ΔE_H. In the case of PtFe$_3$, the calculated LDA values of ΔE_p and ΔE_H are equal to 5 and −6.3 mRy, respectively. It is important to note that, at least for Invar materials, ΔE is algebraically much smaller than both terms ΔE_p and ΔE_H. These terms are almost equal but of opposite sign. It implies that even a very large relative change of ΔE requires only a moderate change of ΔE_H. In the particular case of PtFe$_3$, to change ΔE from the LDA value of −1.3 mRy to the (presumably) correlated value of −0.2 mRy (Fig. 8), ΔE_H should change from −6.3 to −5.2 mRy, i.e., by some 18%. We see therefore that the estimated change of the magnetic energy is much smaller than that proposed by SOH. We note that for Invar alloys a change of the magnetic energy ΔE_H of the proposed magnitude would render the alloys nonmagnetic. It seems that, unless the ΔE_p term can be shown to be also strongly affected by volume-dependent electronic correlations, the quantitative prediction of SOH cannot apply to Invar materials. As it is clear from our analysis, the character of the magnetic state equation $H(M)$ and the value of ΔE_H depend critically on volume. We suspect that the rigid-band model used in Ref. 30 to generate LDA state densities might not be accurate enough to cope with this complexity. We think that it would be very useful to repeat the calculations discussed by SOH for realistic, volume dependent, hybridized DOS functions for simple metals, and to carry out such a calculation for PtFe$_3$. A marginal stability of Invar materials should help in estimating the relative importance of the correlation effects for the total energy calculations of a magnetic state.

Although we have reason to believe that the relative weight of the correlation effects is overestimated by SOH, their qualitative conclusions are doubtlessly correct. The total energy difference ΔE as given by LDA seems to be too large. This shortcoming must be added to the list of the LDA drawbacks, including already overestimation of the cohesive energies, underestimation of the equilibrium lattice constants, and inability to calculate a correct energy gap for insulators and semiconductors. Whereas it is clear by now that any repair of the last deficiency is impossible within strictly one-electron theory, attempts

to improve the description of the ground-state properties are legitimate. New, nonlocal exchange-correlation functionals have been proposed recently by Langreth, Mehl, and Hu (LMH)[31] and by Perdew and Wang (PW).[32] Very recently, Bagno, Jepsen, and Gunnarsson[33] applied them for calculation of the lattice constants and total and cohesive energies of a few third-row elements. The results for the equilibrium lattice constants and cohesive energies were encouraging. For most considered elements a discrepancy between the experimental and theoretical values was substantially reduced.[33] However, both LMH and PW functionals increased the calculated value of $\Delta E = E_{\text{NM}} - E_{\text{FM}}$ by ca. 70 and 100%, respectively. This is in an obvious disagreement with arguments of SOH and with our suggestions. The LMH and PW nonlocal XC functionals give results closer to the Hartree-Fock results than to correlated ones. This failure has not been discussed by Bagno, Jepsen, and Gunnarsson.[33] If their results are correct, the LMH and PW XC energy functionals cannot be recommended for studies of the magnetic state of solids.

The total energy considerations may be used to estimate the LDA error in the calculated spin susceptibility. As we have argued above, a change of ΔE_H [Eq. (4)] by some 20% would bring the calculated and experimentally estimated values of ΔE [Eq. (3)] into agreement. Since ΔE_H may be expressed as $\int H(M')dM'$, it is obvious that it is proportional to the amplitude of $H(M)$ and thereby to the inverse susceptibility $\frac{\partial H}{\partial M}$. This estimate assumes that the electron correlation effects do not depend strongly on magnetization. Indeed, this dependence, as estimated by SOH, does not cause more than a 25% difference of the Stoner parameters $I(0)$ and $I(M_0)$. It is therefore justified to expect that the LDA error of the calculated χ_P is not larger than 50%. This very rough and rather conservative estimate sets the upper limit for $\chi_P(V_{\text{FM}})$ to $\sim 2 \times 10^{-4}$ emu/mol, as compared to the experimental value of 8×10^{-4} emu/mol. This argument, together with the previously discussed inconsistencies of the experimental data, make us suspect that the experimental value of the spin susceptibility is much more in error than the theoretical one.
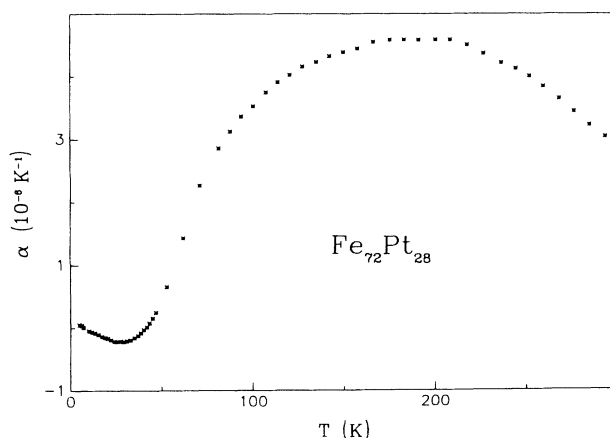

FIG. 9. Thermal expansion coeffiecient α as a function of temperature for the ordered phase of Pt$_{28}$Fe$_{72}$ (from Ref. 34).
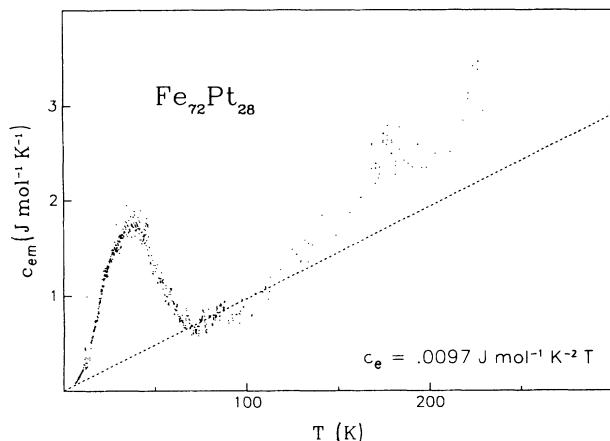
FIG. 10. Specific heat as a function of temperature for the ordered phase of $Pt_{28}Fe_{72}$ (from Ref. 35).

It remains a question whether the estimated value of $\Delta E = 0.2$ mRy ($\sim$32 K) for PtFe₃ makes sense. In absence of a rigorous thermodynamical theory of Invar behavior at $T > 0$ the question is difficult to answer. It is known that Invar anomalies are observed for temperatures up to T_C ($\sim$500 K), so the "as calculated" ΔE value of ca. 200 K seems to fit better into an intuitive picture. Yet, an even cursory inspection of the recent, very precise measurements of the thermal expansion coefficient α (Ref. 34) and the specific heat[35] reveals very distinct anomalies of both observables at just 30 K (Figs. 9 and 10). These new data, the pressure experiment of Abd-Elmeguid and Micklitz,[11] and our analysis make a picture that is too consistent to be accidental. Yet, this notion adds to the complexity of the Invar problem rather than explaining anything. At once questions arise concerning the high value of the critical temperature T_C or the nature of the high-temperature Invar anomalies. We recently attempted to address this problem carrying out the FSM calculations for the antiferromagnetic INVAR alloy MnFe.[39] In this paper we have shown that the total energy change correlated with spin flip may be an order of magnitude larger than the energy change necessary to quench the magnetic moment. This observation offers a clue how to reconcile the apparently contradictory observations. Still, much more work is necessary to achieve a thorough understanding of microscopic mechanisms leading to INVAR behavior.

V. SUMMARY

In this paper we reported on the FSM study of the moment-volume instabilities in the Ni-Fe and Pt-Fe systems. The calculations for a sequence of ordered phases of the Ni-Fe alloy have shown that a small energy difference ΔE between the HS and LS phases and a moment-volume instability near equilibrium are closely correlated. This supports the recently emerging picture of Invar as a phenomenon having its origin in moment-volume instabilities. The quantitative results for the Ni-Fe alloy suggest that the influence of the chemical disorder and resulting magnetic inhomogeneity may be non-negligible, as proposed already in Ref. 3. For PtFe₃, the first ab initio calculation of the binding surface and magnetoelastic constants has been presented. PtFe₃ has been shown to have a small ΔE and to display complicated metamagnetic properties with NM, LS, and HS phases. The magnetoelastic properties have been calculated and their comparison with experimental data discussed. The analysis of the experimental and theoretical data led us to the conclusion that the actual ΔE in PtFe₃ may be as small as 0.2 mRy/atom, the difference of the calculated and estimated value having its origin in electron correlations. We have proposed that the calculated and measured properties of PtFe₃ may be used to estimate the relative importance of the electron correlation effects in magnetic solids. Furthermore, we have suggested that the well-known discrepancy between the calculated and measured spin susceptibility is caused not as much by inaccurate calculations as by unsuitable measurements.

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