Critical behavior of disordered fcc $Fe_{70}Pt_{30}$ alloy under high pressure

Sergii Khmelevskyi and Peter Mohn
Center for Computational Material Science, Vienna University of Technology, Vienna, Austria
(Received 21 July 2003; published 10 December 2003)

Employing the disordered local moment formalism in combination with a first-principles tight-binding linear muffin-tin orbital method we find that in disordered fcc $Fe_{70}Pt_{30}$ alloy the effective magnetic interaction changes from ferromagnetic to antiferromagnetic as the lattice constant is reduced from its equilibrium value at ambient pressure. This result explains recent experiments on this alloy that have claimed an appearance of the new magnetic spin-glass phase under high pressure. The value of the volume where the change in the magnetic interaction occurs is just slightly higher than the critical volume at which $Fe_{70}Pt_{30}$ becomes nonmagnetic, suggesting that under applied pressure the system exhibits two types of magnetic critical points. A comparison of our results with earlier theoretical studies of the fcc Fe-Ni Invar alloys reveals a similarity between the high-pressure magnetic state of $Fe_{70}Pt_{30}$ and the magnetic ground state of the Fe-Ni alloys at ambient pressure.

DOI: 10.1103/PhysRevB.68.214412 PACS number(s): 75.50.Bb, 71.20.Be, 71.23.−k, 75.30.−m

Face-centered-cubic (fcc) Fe-Ni and Fe-Pt alloys have attracted special interest in solid-state physics since they show anomalously low thermal expansion (Invar effect) in a certain range of chemical concentration.[1] This anomaly is associated with a large negative value of the spontaneous volume magnetostriction compensating the thermal expansion due to the anharmonicity of the lattice vibrations. Although both Fe-Pt and Fe-Ni alloys have very similar magnetovolume properties, they have many dissimilarities in their physical properties detected experimentally as well as theoretically. The Fe-Ni Invar alloys are weak unsaturated ferromagnets in contrast to Fe-Pt Invar alloys, which are strong ferromagnets.[1] In addition it has been found that at low temperature Fe-Ni Invar alloys show a transition into a spin-glass[2] state [reentrant spin glass (RSG)], which does not occur for Fe-Pt at ambient pressure. *Ab initio* supercell simulations of the $Fe_{65}Ni_{35}$ alloy[3] indeed show that the magnetic ground state in this alloy consists of noncollinear spin configurations. Later the existence of these noncollinear magnetic configurations with lower total energies and equilibrium volumes than the collinear ferromagnetic (FM) state was linked to the occurrence of the Invar effects in Fe-Ni.[4] The existence of the RSG state at low temperature as well as the stabilization of the noncollinear magnetic state in the supercell calculations is believed to be due to the strong competition between ferromagnetic and antiferromagnetic (AF) intersite interactions in disordered Fe-Ni alloys. An alternative way of looking at this phenomenon is to employ the disordered local moment (DLM) formalism as formulated in the framework of the density functional theory by Gyorffy *et al.*[5] Already earlier, Akai and Dederichs[6] have reported that for Fe-Ni, in the regime of Fe-rich Invar compositions, the DLM state has a lower total energy than the ferromagnetic state, suggesting that the ferromagnetic state is unstable at $T=0$ K with respect to the formation of magnetic disorder. Despite the fact that this approach ignores short-range order effects and possible noncollinear spin alignments, it however yields the same result as a supercell approach—namely, that the effective antiferromagnetic interaction leads to instability of the ferromagnetic state in Fe-Ni Invar alloys. An extensive discussion of the competing antiferromagnetic and ferromagnetic interactions in Fe-Ni alloys, also taking into the account possible effects of partial chemical ordering, can be found in a recent paper by Crisan *et al.*[7] In the case of a system with fairly localized moments like Gd the total energy difference between the FM and AF-DLM states allows us to analyze the resulting effective interaction in terms of a Heisenberg type Hamiltonian.[8] In the case of Fe-Pt the magnetic moments are far from being independent of the magnetic state so that such a detailed analysis becomes impractical. However, even in the present case the energy difference provides information about the effective average interaction between the magnetic moments at the different sites.

In contrast to Fe-Ni, in Fe-Pt Invar alloys a collinear ferromagnetic state is stable down to very low temperatures so that no experimental as well as theoretical evidence of any spin-glass or noncollinear (and antiferromagnetic) magnetic behavior at ambient pressure has been found. Moreover, we have shown recently[9] that for disordered Fe-Pt a fully quantitative account of the large spontaneous magnetostriction leading to the Invar effect and its dependence on the chemical concentration can be given on the basis of the conventional collinear DLM approach. It was found that in these alloys the DLM state has an energy well above the FM state and that the difference in their equilibrium volumes is in fair agreement with the experimental values of the spontaneous volume magnetostriction. Here we show that if the lattice constant decreases further towards the critical point where the Fe magnetic moment collapses, we find a region where the DLM state becomes more stable than the FM state, indicating that at these high pressures the situation in Fe-Pt alloys is very similar to that found in Fe-Ni (Ref. 6) at ambient pressure. Our present investigation is also stimulated by recent experiments,[10] which have reported a low-temperature magnetic phase in disordered $Fe_{70}Pt_{30}$ under high pressure (7 GPa). It has been claimed that this state is a RSG state similar to that in Fe-Ni alloys at low temperature. We find that our theoretical results confirm this observation. It is interest-

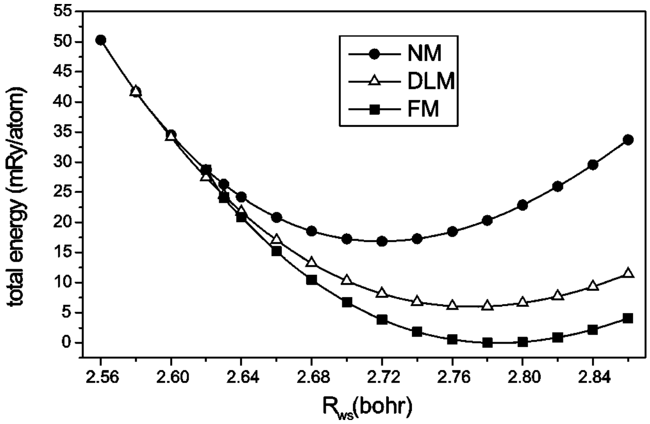

FIG. 1. Total energy as a function of the volume given in terms of the Wigner-Seitz radius. NM: nonmagnetic. FM: ferromagnetic. DLM: disordered local moment.

ing to note that our calculations show that close to the pressure-induced quantum critical point the behavior of disordered $Fe_{70}Pt_{30}$ follows a scenario theoretically predicted by Pinski *et al.*[11] for the pure γ-Fe. This scenario is rather different from those of usual weak ferromagnets since in $Fe_{70}Pt_{30}$ for a lattice constant larger than the critical one an antiferromagnetic state is stabilized with respect to ferromagnetic order. Chemical disorder and natural frustration of the fcc lattice lead to the formation of the spin-glass state at low temperatures. Thus $Fe_{70}Pt_{30}$ has essentially two critical points under applied pressure, marking the sequence of the transitions FM-AFM-NM (nonmagnetic state).

We base our investigations on application of the all-electron self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic-sphere approximation[12] (ASA) combined with the coherent potential approximation[13] (CPA). The effects of exchange and correlation are treated within the framework of the local-spin-density approximation using the parametrization by Vosko *et al.*[14] The integration in reciprocal space has been carried out using 770 k points in the irreducible wedge of the fcc Brillouin zone, which ensures an accuracy of the total energy better than 10^{-5}Ry. The idea of the DLM formalism[5] is to represent magnetic disorder within the CPA by treating a binary Fe_cPt_{1-c} alloy as a pseudoternary alloy $Fe_{c-x}{}^{+}Fe_x{}^{-}Pt_{1-c}$ where $c-x=n^{+}$ is the concentration of Fe atoms with up-spin Fe^{+} and $x=n^{-}$ of those with down-spin Fe^{-}. The case of $x=0$ describes a ferromagnetic solution, while $x=c/2$ represents an antiferromagnetic state (AF-DLM) with spin-up and spin-down local moments equipartitionally distributed on the Fe sites. The volumes of the Wigner-Seitz spheres are set to be equal for all atoms.

Figure 1 shows the calculated total energies as function of atomic Wigner-Seitz radius R_{ws} for FM, AF-DLM, and NM states of $Fe_{70}Pt_{30}$ ($V_{atom}=4\pi/3\,R_{ws}^{3}$). The ground state is ferromagnetic, and NM and AF-DLM states have much higher total energies than the FM state at the equilibrium value of $R_{ws}=2.786$ bohrs. As we have shown earlier,[8] a relatively large difference in volumes provided by the minima of the total energy curves for FM and AF-DLM states is related to a large spontaneous volume magnetostric-

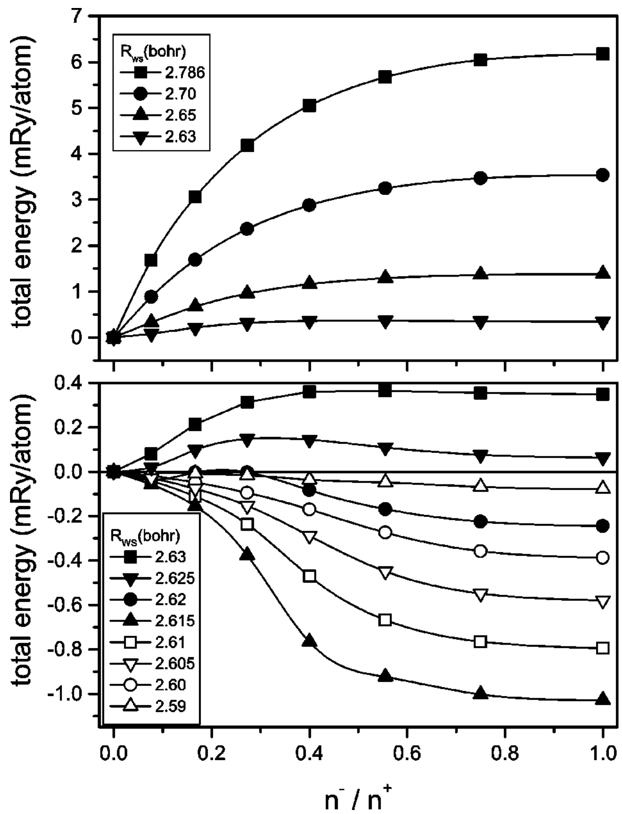

FIG. 2. Total energy differences with respect to the ferromagnetic state for various volumes as a function of n^{-}/n^{+} (for details see text).

tion and represents a prerequisite for the Invar anomaly in this alloy. The values of the energies of the partial (uncompensated AF) DLM states with $0<n^{-}/n^{+}<1$ (not shown in Fig. 1) are in between of those for the FM and AF-DLM states. It can be seen in upper panel of Fig. 2 where we plot the energy difference between DLM states and respective FM state for varying lattice constant, which as the lattice constant decreases the energy difference between the FM and AF-DLM states continuously vanishes (This is also true for the difference between the FM and NM states, as seen in Fig. 1). It is of course most interesting to examine what happens in the critical volume region $2.58R<R_{ws}<2.63$ bohrs (lower panel of Fig. 2) where these curves become energetically almost degenerate. It can be seen that character of the curves is changed with decreasing R_{ws}: at larger lattice constants the total energy monotonically increases with increasing degree of magnetic disorder, but at about $R_{ws}=2.63$ bohrs it shows a maximum at some partial DLM state. At the critical value $R_{ws}\approx 2.625$ bohrs the AF-DLM state becomes lower in energy than the FM state and the FM-AF transition at this point is of first order since the partial uncompensated DLM states are always higher in energy than the FM or AF-DLM states. Thus, in agreement with experiment,[9] our calculations predict stabilization of a new low-temperature magnetic phase in $Fe_{70}Pt_{30}$ under applied pressure. A further reduction of the volume leads to a further stabilization of the AF-DLM state with respect to ferromagnetic order up to $R_{ws}\approx 2.615$ bohrs where the nonmagnetic state becomes stable.

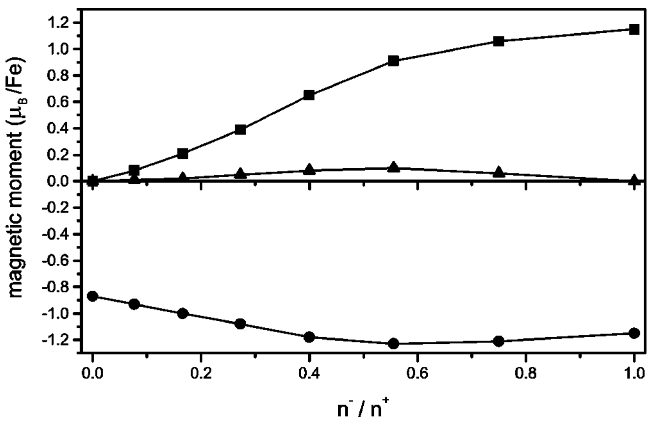

FIG. 3. Magnetic moment per Fe at $R_{ws}=2.605$ bohrs for various DLM states. Quantities shown: moment of Fe^+ (squares), moment of Fe^- (circles), and total moment (triangles).

This transition corresponds to the point where FM and NM total energy curves merge (Fig. 1). It is interesting to note that if we would not allow for the antiferromagnetic solutions the transition from the FM to the NM state would be of first order since Fe abruptly loses its moment of about 1.9 μ_B/atom, which has indeed been predicted by earlier fixed-spin-moment calculations for disordered[15] and ordered[16] Fe-Pt alloys where only ferromagnetic solutions have been considered. However, the ground state of the system is not FM anymore at this volume and it approaches a quantum critical point with increasing pressure with gradually decreasing magnetic moment in the AF-DLM state until just below $R_{ws}\approx 2.59$ bohrs it becomes nonmagnetic (lines with open symbols in Fig. 2). The transition from the AF-DLM to the NM state as the lattice constant decreases is of second order, since the AF-DLM state loses its magnetic moment continuously.

At the equilibrium lattice constant $Fe_{70}Pt_{30}$ is a strong ferromagnet with a calculated local moment on Fe of 2.7 μ_B. As the lattice constant decreases under applied pressure, the Fe moment decreases to about 1.9 μ_B for $R_{ws}\approx 2.615$ bohrs where it suddenly drops to zero. In the AF-DLM state the Fe moment decreases gradually from 2.4 μ_B at equilibrium volume and becomes zero at $R_{ws}\approx 2.59$ bohrs. In Fig. 3 we plot the calculated Fe moments for $R_{ws}\approx 2.605$ bohrs, which is in the middle of the critical region. The moment in the AF-DLM state, which has the lowest total energy at this volume (see Fig. 2), is 1.1 μ_B. In the uncompensated AF (partial) DLM states the large asymmetry in the Fe moments with spin up and spin down can be seen. This asymmetry is clearly due to the antiferromagnetic character of the intersite magnetic interactions, which lead to a distribution of moments such that the total magnetization tends to vanish. It is interesting to see what happens when we approach the pure FM state ($n^-/n^+=0$). In the FM state there is no stable moment on the Fe sites. However, if we allow for few Fe atoms to have opposite spin direction, the system decreases the total energy by creating a moment of the order 0.8 μ_B on these few sites but compensating it by small antiparallel moments on all other sites. It can be thus be concluded that the existence of two separate metastable minima of the total energy as predicted by fixed-spin-moment calculations[15,16] for Fe-Pt alloys, which has been believed to be the reason for the Invar anomaly in these systems, is just an artifact of the ferromagnetic constraint imposed on the system during the calculations. Removing this spin symmetry constraint revealed that this increase in parameter space transforms one of the total energy minima into a saddle point.

In conclusion we note that the DLM approach predicts a stabilization of the AF magnetic interaction in disordered $Fe_{70}Pt_{30}$ alloys at applied pressure. Due to chemical disorder and magnetic frustration of the fcc lattice, it is likely that this mechanism will lead to the formation of a spin-glass phase at low temperature in agreement with recent high pressure experiments.[9] To understand the physical nature of this spin-glass phase an application of methods which consider short-range order effects may be important. In particular, it can be expected that calculations similar to those of van Schilfgaarde *et al.*[4] can detect a stabilization of the noncollinear magnetic ground state at volumes much lower than equilibrium. However, in Fe-Pt it is unlikely that stabilization of the AF interaction and a possible noncollinearity of the magnetic structure under high pressure can be linked to the Invar anomaly in these systems, since these critical volumes are not accessible for the system under ambient pressure where the Invar anomaly occurs.

This work was supported by the Austrian Ministry of Science (Grant No. GZ 650.758/1-VI/2a/2002).

[1] M. Shiga, in *Material Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH Verlagsgesellschaft, Weinheim, 1994), Vol. 3b, pp. 159–210.
[2] T. Miyazaki, Y. Ando, and M. Takahashi, J. Appl. Phys. **57**, 3456 (1985).
[3] Yang Wang, G. M. Stocks, D. M. C. Nicholson, W. A. Shelton, V. P. Antropov, and B. N. Harmon, J. Appl. Phys. **81**, 3873 (1997).
[4] M. van Schilfgaarde, I. A. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).
[5] B. L. Gyorffy, A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. **15**, 1337 (1985).
[6] H. Akai and P. H. Dederichs, Phys. Rev. B **47**, 8739 (1993).
[7] V. Crisan, P. Entel, H. Ebert, H. Akai, D. D. Johnson, and J. B. Staunton, Phys. Rev. B **66**, 014416 (2002).
[8] I. Turek, J. Kudrnovský, G. Bihlmayer, and S. Blügel, J. Phys.: Condens. Matter **15**, 2771 (2003).
[9] S. Khmelevskyi, I. Turek, and P. Mohn, Phys. Rev. Lett. **91**, 037201 (2003).
[10] M. Matsushita, S. Endo, K. Miura, and F. Ono, J. Magn. Magn. Mater. **260**, 371 (2003).
[11] F. J. Pinski, J. Staunton, B. L. Gyorffy, D. D. Johnson, and G. M. Stocks, Phys. Rev. Lett. **56**, 2096 (1986).

[12] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[13] I. Turek, V. Drchal, J. Kudrnovský, M. Šob, and P. Weinberger, *Electronic Structure of Disordered Alloys, Surfaces and Interfaces* (Kluwer Academic, Boston, 1997).
[14] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[15] R. Hayn and V. Drchal, Phys. Rev. B **58**, 4341 (1998).
[16] M. Podgorny, Phys. Rev. B **46**, 6293 (1992).