High-temperature anti-Invar behavior of γ-Fe precipitates in Fe_xCu_{100-x} solid solutions: Ferromagnetic phases

S. L. Palacios, R. Iglesias, D. Martínez-Blanco, P. Gorria, M. J. Pérez, and J. A. Blanco
Departamento de Física, Universidad de Oviedo, E–33007 Oviedo, Spain

A. Hernando
Instituto de Magnetismo Aplicado, UCM-RENFE, E-28230 Las Rozas, Madrid, Spain

K. Schwarz
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt, 9/165-Tc A-160 Vienna, Austria
(Received 19 January 2005; revised manuscript received 14 July 2005; published 1 November 2005)

High-temperature magnetization and neutron diffraction measurements on metastable Fe_xCu_{100-x} solid solutions have recently shown to imply that γ-Fe precipitates present ferromagnetic anti-Invar behavior. For this reason, we have studied the ferromagnetic phases of γ-Fe in moment-volume parameter space, using the general potential linearized-augmented plane-wave method and the fixed spin moment procedure in order to calculate the corresponding total energy. We find that only two ferromagnetic phases (one related to a low-spin state and the other to a high-spin state) can exist and even coexist in limited volume ranges (3.55-3.59 Å). Hence, our results provide a "revisited" version of the local spin density calculations used in the early article by Moruzzi *et al.* [Phys. Rev. B **34**, 1784 (1986)]. In addition, the fixed spin moment method—using an energy-moment-volume space representation—allows us to conclude that the high-spin state is the ground state of the γ-Fe precipitates, as the anti-Invar behavior is an intrinsic property of these states. This simple scenario seems to adequately describe the perplexing phenomenology recently observed on Fe_xCu_{100-x} solid solutions.

DOI: 10.1103/PhysRevB.72.172401 PACS number(s): 75.30.Kz, 75.50.Bb, 71.15.Ap

I. INTRODUCTION

Among transition metals (TM), iron has a special place,[1] not only for it remains to be one of the most used functional materials but because it also reveals new emerging phenomena where coexistence of superconductivity, ferromagnetism and spin glass has been found.[2] As is well known, at atmospheric pressure iron presents two different crystal structures, namely, the body centered cubic (bcc) and the face centered cubic (fcc). At room temperature (RT) only the ferromagnetic bcc (α-Fe) phase is stable, while at temperatures above the reversible martensite-austenite temperature T_{MA} $=1183$ K, α-Fe undergoes a discontinuous first-order phase transition into the fcc (γ-Fe) phase, which is stable up to 1665 K.

At temperatures lower than T_{MA} both the structural and magnetic properties of γ-Fe, pure or in form of Fe-TM alloys with the fcc structure such as Fe_xNi_{100-x} and Fe_xCu_{100-x}, are still far from being understood.[3,4] In particular, in these 3d fcc materials the magnetic moment can change discontinuously in the vicinity of a critical volume, thus exhibiting a moment-volume instability.[5] This feature is the key to understand the appearance of Invar and/or anti-Invar effects in these 3d fcc materials. Concerning the former effect, over a wide range of temperature these fcc materials possess an approximately invariant thermal expansion coefficient, while the latter one implies an enhancement of the thermal expansion at some system-dependent characteristic temperature.

II. BACKGROUND

A. Physical properties of anti-invar Fe-Cu

We have reported on the physical properties of ferromagnetic Fe_xCu_{100-x} mechanically alloyed solid solutions, combining both thermomagnetization and neutron diffraction experiments.[6,7] Invar and anti-Invar behaviors were observed for $x>15$. According to our results, a phase diagram was proposed. Very recently, Khmelevskyi and Mohn[8] have shown to imply that the origin of the Invar effect in these alloys is very much the same as in Fe-Pt and Fe-Pd, and it seems to be connected to the reduction of the Fe magnetic moment caused by thermally induced magnetic disorder. Furthermore, for low Fe amount ($x<10-15$ %) no percolation assures the existence of FM coupling between Fe ions. Since the ionic radius of Fe is lower than that of Cu, it could be expected that the lattice parameter of Fe_xCu_{100-x} in the paramagnetic phase would decrease with increasing Fe concentration. However, as this content increases above 15%, ferromagnetism is established, accompanied by important magnetovolume effects, whereby the equilibrium cell parameter $a=3.63$ Å is larger than that of pure Cu, namely, a $=3.61$ Å.[9,10] Hence, the appearance of ferromagnetism in fcc FeCu alloys entails an increase in the atomic volume and the existence of magnetovolume instabilities, as has been pointed out using both experimental[6] and theoretical[8] arguments.

On the other hand, it is well known that FeCu solid solutions obtained by mechanical alloying are of metastable nature. Thus, heating above 500 K leads to a structural relaxation which produces a phase segregation. This segregation process gives rise to an fcc Cu, a γ-Fe, and an α–Fe crystalline phases, with different relative amounts depending on the initial composition of the sample.[11–14] As an example to illustrate this physical behavior, we have used a Cu-rich $Fe_{16}Cu_{84}$ compound.[7] When the as-milled sample is heated above 500 K, segregation begins and a predominant fcc Cu phase ($\approx 85\%$) together with an α-Fe phase ($\approx 15\%$) appear.

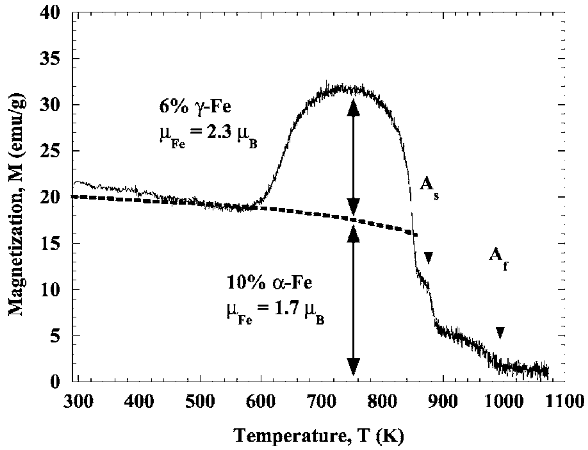

FIG. 1. Temperature dependence of the measured magnetization for $Fe_{16}Cu_{84}$. The dashed line corresponds to the contribution associated with α-Fe (Ref. 15). A_s and A_f represent the starting and final temperatures of the martensite-austenite transformation.

The segregation process finishes at about 780 K. However, further heating reveals an anomalous martensite-austenite transformation, beginning with a temperature much lower than for pure α-Fe and showing a large thermal hysteresis on heating-cooling cycles. Moreover, on cooling from high temperatures (1100 K) some Fe ions are retained under an fcc crystal structure, forming γ-Fe precipitates even at RT.[7] When the sample is heated again above 600 K, a large magnetization enhancement is observed, see Fig. 1, which has been associated with the γ-Fe precipitates. In addition to that, neutron diffraction measurements allow one to estimate the value of the linear thermal expansion coefficient α_T of the γ-Fe precipitates, which is larger than 20×10^{-6} K^{-1}. This value is in good agreement with those obtained from theoretical γ-Fe calculations.[1] Taking into account the relative percentages of α-Fe $(10\% \pm 1\%)$ and γ-Fe $(6\% \pm 1\%)$ obtained from neutron diffraction data, the magnetic moment μ_{Fe} at 750 K may be estimated for each phase (Fig. 1), resulting in $\mu_{Fe}(\alpha\text{-Fe}) \approx 1.7\ \mu_B$ and $\mu_{Fe}(\gamma\text{-Fe}) \approx 2.3\ \mu_B$, respectively. Extrapolation to $T=0$ K leads to the values $\mu_{Fe}(\alpha\text{-Fe}) \approx 2.1\ \mu_B \pm 0.2\ \mu_B$ and $\mu_{Fe}(\gamma\text{-Fe}) \approx 2.8\ \mu_B \pm 0.3\ \mu_B$.

B. The ground state of γ-Fe

The first oversimplified phenomenological statistical explanation for these magnetovolume effects was given by Weiss more than forty years ago.[16] This model is based on the existence of two states γ_1 (upper level) and γ_2 (lower level). These two discrete states are known as the "low-spin–low-volume" state, (LS), with a lattice parameter around 3.54 Å , and the "high-spin–high-volume" state (HS), with a lattice parameter of 3.64 Å. The variation of population from the high–volume to the low-volume states with increasing temperature is claimed to cause the anomalously small thermal expansion. The resulting volume decrease approximately cancels the usual thermal expansion. The estimated value of the Fe magnetic moment in the $\gamma_1(\gamma_2)$ state is $0.5(2.8)\mu_B$. Nowadays, it has become clear that the two γ-state model does not explain satisfactorily the origin of the Invar effect in Fe-based alloys[17].

It is now well established from band structure calculations[18–21] that, while α-Fe is beyond all doubt a ferromagnet, the magnetic character of γ-Fe is on the whole rather complex, since it stands at the crossover between HS ferromagnetism and LS noncollinear antiferromagnetism (AF). The actual realization depends sensitively on both internal and external parameters. The transition from LS to HS states goes over a series of different AF states.[22] Aiming to understand the unusual high-temperature and high moment magnetic instability in γ-Fe observed in Fe_xCu_{100-x} mechanically alloyed solid solutions,[7] in which magnetovolume effects play an important role, our electronic structure calculations have been limited to the case in which a ferromagnetic constraint on the Fe magnetic moments is imposed in γ-Fe. Recently, Kong and Liu[23] have reported on the correlation of magnetic moment versus spacing distance in γ-Fe. These *ab initio* calculations, based on the projector augmented-wave pseudopotential method,[24] predict the existence of three distinct ferromagnetic orderings: two LS phases and an HS one. The third very LS phase, which has a lower energy and magnetic moment than the LS phase in Ref. 25, is also in qualitative agreement with the results found from an augmented-spherical-wave method using the FSM procedure.[26] However, some discrepancies concerning the volume range stability of the two LS phases can certainly be intensely debated. This puzzling situation raises the question: Has γ-Fe one or more LS ferromagnetic states? In an attempt to find an answer to this question, we now reexamine in detail the results of Moruzzi's paper[25] on the ferromagnetic phases of γ-Fe, using an efficient and accurate computer program that has the FSM method implemented.

III. RESULTS

We have used the full-potential linearized-augmented plane-wave method (FLAPW) implemented into the WIEN2k code by Blaha *et al.*[27] Our calculations were performed within density functional theory using the generalized gradient approximation (GGA) in the formula by Perdew *et al.*[28] for the exchange-correlation potential. In addition, we used −7.0 Ry as the energy to separate core from valence states in order to include low-lying (semicore) states, in our case the Fe-3*s*, into the valence region. Local orbitals were used with APW+lo for the Fe-3*d* orbital and LAPW+LO for the rest. The radius of the muffin-tin spheres R_{MT} was chosen to be 2.2 a.u. for all the lattice parameters analyzed, whereas for the interstitial region the number of plane waves was limited with $R_{MT}\times K_{max}=8.0$ and $G_{max}=14$. The *k*-mesh generated in the irreducible wedge of the Brillouin zone IBZ was formed by 165 *k* points [5000 in the whole Brillouin zone (BZ)]. The convergence in the total energy values was studied by finer *k* meshes up to 1059 *k* points in the IBZ (40 000 in the full first BZ). The differences in the converged energy-values were less than 1 mRy.

In order to check the reliability of the present calculations, we have first obtained the energy-volume dependence of α-Fe. The most relevant physical magnitudes were found to

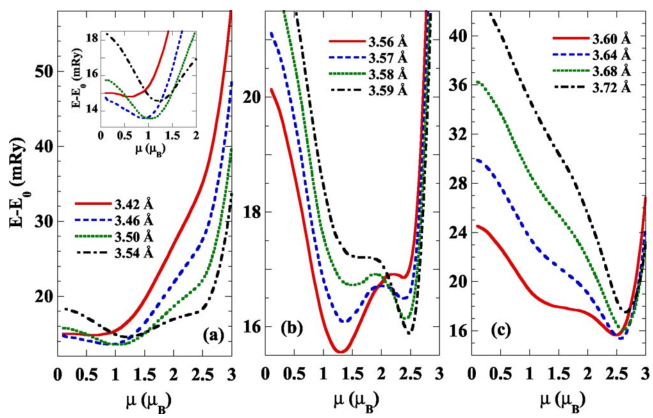

FIG. 2. (Color online) Magnetic moment dependence of the total energy $E-E_0$ for γ-Fe at several selected lattice parameters, showing the three distinct regimes. The inset in (a) shows the calculated values of $E-E_0$ around the minimum LS state.

be lattice constant $a=2.83$ Å, magnetic moment per atom at 0 K, $\mu=2.2\mu_B$, and bulk modulus $B=223$ GPa, all in quite good agreement with the experimental results for α-Fe.[1]

FSM calculations allow us to carry out an analysis of the total energy in a rigid lattice for arbitrary values of the atomic moment and the lattice parameter. For α-Fe, the energy surface is characterized by a clear and well-defined ferromagnetic (FM) minimum at the values of μ and a quoted above. Furthermore, the curves $E(\mu)$ at a fixed lattice constant have only one minimum at finite μ throughout the whole range of lattice parameters studied ($a=2.65$ Å -2.95 Å). The results are very similar to those obtained by Moruzzi *et al.*[25]

In contrast, the binding energy surface for γ-Fe is quite different, as expected. Up to three distinct phases are found: a nonmagnetic, and two ferromagnetic LS and HS phases. These latter two correspond to the two clearly distinct and separate FM minima which can be seen in Fig. 2. However, the situation for intermediate a is more complex, since the two LS and HS minima can coexist in limited volume ranges (see below). From our calculations, no LS phase apart from that previously reported by Moruzzi was found, in contrast to Kong and Liu results.[23] The behavior of $E(\mu)$ curves at a fixed lattice parameter (Fig. 2) correctly describes the different phases and their coexistence. For low lattice parameters, $a<3.55$ Å, Fig. 2(a), only one FM-LS phase is observed with low values of the magnetic moment. It is worth noting [Fig. 2(a), inset] that the minimum is flatter and the value of μ decreases below $1.0\mu_B$ as the lattice parameter is lowered, indicating a loss of stability for this FM-LS phase when the lattice parameter of the system goes below 3.45Å, being the nonmagnetic phase stable thereafter. On the other hand, for high values of a [see Fig. 2(c) for $a\geqslant 3.60$ Å], only one and deep energy minimum is observed, thus confirming the existence of a very stable FM-HS phase with a high and nearly constant value of the magnetic moment $\mu=2.6\mu_B$. In the intermediate region, Fig. 2(b), between 3.55 and 3.59 Å, the two minima corresponding to LS and HS states may coexist, separated in energy by only one mRy or less. In fact, LS solutions are found at low volumes, while HS ones are found at high volumes.

IV. DISCUSSION

The appearance of anti-Invar features could be explained as follows: when a takes values close to 3.63Å, the ground state of the system is the HS, while for values of $a \approx 3.58$ Å, other LS ground states are expected to be present. In our case, the lattice parameter of the γ-Fe precipitates at RT is slightly below 3.6Å, whereas heating the sample above 600 K this value increases above 3.62Å,[7] and thus the HS state becomes energetically more favourable, giving rise to an enhanced volume expansion and the onset of ferromagnetism ($\approx$600 K, see Fig. 1). The anti-Invar effect of γ-Fe precipitates in FeCu alloys also involves a drastic rising in the value of the magnetic moment [$\mu_{Fe}(\gamma\text{-Fe})\approx 2.3\mu_B$ at 750 K, being zero at RT], caused by a slight increase in the lattice parameter. Other authors have reported on the absence of magnetic ordering in γ-Fe precipitates at RT from magnetic and Mössbauer spectroscopy measurements.[11–14] The high values of the magnetic moment and of the α_T coefficient for the γ-Fe precipitates, together with the change in the lattice parameter suggest that the ground state is the HS one. In other words, the observed high temperature magnetic instability is a consequence of the existence of strong magnetovolume effects. Thus, magnetization vs temperature measurements certainly offer the best experimental evidence of anti-Invar behavior.

V. CONCLUSION

In summary, first-principle band calculations for γ-Fe confirm the existence of an unique LS ferromagnetic state and a unique HS state between 3.40 and 3.75Å, as obtained from the FSM method. This HS state seems to be the ground state of the γ-Fe precipitates present in ferromagnetic Fe_xCu_{100-x} mechanically alloyed solid solutions, as found in recent high-temperature magnetization and neutron diffraction experiments.[7] From our experimental results it follows that this HS state has an anti-Invar behavior. However, in order to establish a more complete picture of the origin of this anti-Invar behavior, additional efforts beyond the FSM calculations restricted to FM states will be needed. We hope that this interpretation will stimulate further research focused on these exciting FeCu alloys.

ACKNOWLEDGMENTS

We gratefully acknowledge the help of J. Luitz, who provided a script which permitted us to automatize our series of calculations. Financial support has been received from Spanish MEC Grant Nos. MAT2002-04178, MAT2002-11621-E, MAT2003-06942, and FICYT PB02-037. One of us (D.M.B.) thanks the Spanish MEC for a graduate grant.

[1] W. Pepperhoff and M. Acet, *Constitution and Magnetism of Iron and its Alloys* (Springer-Verlag, Berlin, 2001).
[2] S. S. Saxena and P. B. Littlewood, Nature (London) **412**, 290 (2001).
[3] J. M. Rojo, A. Hernando, M. El Ghannami, A. García-Escorial, M. A. González, R. García-Martínez, and L. Ricciarelli, Phys. Rev. Lett. **76**, 4833 (1996).
[4] R. H. Kodama, S. A. Makhlouf, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 1393 (1997).
[5] E. F. Wassermann, *Ferromagnetic Materials* (North-Holland, Amsterdam, 1990), Chap. 3, p. 238.
[6] P. Gorria, D. Martínez-Blanco, J. A. Blanco, A. Hernando, J. S. Garitaonandia, L. Fernández Barquín, J. Campo, and R. I. Smith, Phys. Rev. B **69**, 214421 (2004).
[7] P. Gorria, D. Martínez-Blanco, J. A. Blanco, M. J. Pérez, A. Hernando, L. Fernández Barquín, and R. I. Smith, Phys. Rev. B **72**, 014401 (2005).
[8] S. Khmelevskyi and P. Mohn, Phys. Rev. B **71**, 144423 (2005).
[9] J. Eckert, J. C. Holzer, and W. L. Johnson, J. Appl. Phys. **73**, 131 (1993).
[10] E. Ma, M. Atzmon, and F. E. Pinkerton, J. Appl. Phys. **74**, 955 (1993).
[11] P. Crespo, A. Hernando, R. Yavari, O. Drbohlav, A. García Escorial, J. M. Barandiarán, and I. Orue, Phys. Rev. B **48**, 7134 (1993).
[12] J. Z. Jiang, Q. A. Pankhurst, C. E. Johnson, C. Gente, and R. Bormann, J. Phys.: Condens. Matter **6**, L227 (1994).
[13] M. Eilon, J. Ding, and R. Street, J. Phys.: Condens. Matter **7**, 4921 (1995).
[14] G. Mazzone and M. Vittori Antisari, Phys. Rev. B **54**, 441 (1996).
[15] B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972), p. 617.
[16] R. J. Weiss, Proc. Phys. Soc. London **82**, 281 (1963).
[17] M. V. Schilfgaarde, I. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).
[18] L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).
[19] V. P. Antropov, M. I. Katsnelson, M. van Schilfgaarde, and B. N. Harmon, Phys. Rev. Lett. **75**, 729 (1995).
[20] Y. Kakehashi, O. Jepsen, and N. Kimura, Phys. Rev. B **65**, 134418 (2002).
[21] S. Khmelevskyi and P. Mohn, Phys. Rev. B **68**, 214412 (2003).
[22] P. James, O. Eriksson, B. Johansson, and I. A. Abrikosov, Phys. Rev. B **59**, 419 (1999).
[23] L. T. Kong and B. X. Liu, Appl. Phys. Lett. **84**, 3627 (2004).
[24] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[25] V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986).
[26] P. M. Marcus, S. L. Qiu, and V. L. Moruzzi, J. Phys.: Condens. Matter **11**, 5709 (1999).
[27] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties* (Technische Universität Wien, Austria, 2001).
[28] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).