Invar effect in fcc-FeCu solid solutions

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Both Cu and Fe metals, with face-centered cubic (fcc) crystal structures, are nonmagnetic. However, the substitution of Cu atoms by Fe in the fcc-Cu lattice leads to the formation of a random solid solution and the appearance of ferromagnetic order, with a value of the magnetic moment per Fe atom in a fcc environment even above $2\mu_B$. This striking behavior is closely related to magnetovolume effects (Invar), which we have detected by means of lattice thermal expansion and magnetization measurements in FeCu alloys.

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I. INTRODUCTION

Recent reports on the magnetic properties of basic magnetic systems such as iron have revealed new phenomena, where coexistence of superconductivity and ferromagnetism[1,2] and spin-glass behavior has been observed.[3] These phenomena are only found by either using extreme conditions (such as high-pressure techniques[4]) or new synthesis routes [such as mechanical alloying (MA)]. As is well known, the stable state of Fe at room temperature and atmospheric pressure has a bcc crystal structure with a lattice parameter a of about 2.87 Å, the so-called α-Fe phase. In this state, Fe is ferromagnetic up to the Curie temperature $T_C = 1043$ K.[5] On heating to the reversible martensite-austensite transition temperature, 1183 K, a structural transition to a face-centered cubic fcc crystal structure takes place[5] to form γ-Fe, with $a \approx 3.54$ Å.

On the other hand, the understanding of the magnetic character of γ-Fe at low temperatures is one of the most interesting unresolved problems and has been the subject of discussion and controversy from both experimental and theoretical points of view.[6,7] However, the only straightforward way to stabilize the γ-Fe phase is the substitution or inclusion of Fe atoms in a stable monatomic fcc crystal lattice whose lattice parameter is similar to that of γ-Fe (around 3.5–3.6 Å). Two candidates fulfill this requirement, Ni ($a \approx 3.52$ Å) and Cu ($a \approx 3.61$ Å) but Ni is magnetic and therefore fcc-FeNi is not a suitable system for studying magnetism of Fe in a nonmagnetic fcc environment with γ-Fe characteristics. The other possibility, the fcc-Cu lattice, could provide the appropriate conditions because Cu is nonmagnetic. However, it has a significant drawback: the miscibility of Fe in Cu is extremely low, less than 1–2 at.% of Fe can be mixed with Cu by conventional alloying techniques. Other fcc lattices, such as Pt or Pd, present larger cell parameters ($\sim$3.9 Å), definitely higher than that of γ-Fe.

Nowadays, Fe-Cu alloys can be prepared across nearly the whole compositional range using the MA synthesis route,[8–11] displaying either a fcc or bcc structure depending on the relative starting amounts of each element. The fcc crystal structure is formed for $x \leqslant 70$, while a bcc structure forms for $x \geqslant 80$.[10] Moreover, an unexpected ferromagnetic behavior observed in these materials in the fcc region of the Fe-Cu phase diagram reignited the old controversy concerning the magnetism of γ-Fe and the evidence for obtaining this phase with ferromagnetic character. It is worth noting that fcc-FeCu phases are metastable in nature, because when samples are submitted to time-controlled heating, segregation of a bcc Fe-rich phase takes place at 500 K, while the fcc-FeCu decomposes completely into nearly pure fcc-Cu and bcc-Fe phases at temperatures above 1000 K.[12]

There are two open questions still under discussion. First, given that fcc-Cu and γ-Fe are nonmagnetic, why does fcc-FeCu show ferromagnetism? Second, it has been observed that the value of spontaneous magnetization, M_s measured at 5 K for the as-milled fcc-FeCu is greater than that of the heat-treated samples,[13] in which the measured M_s can come only from the segregated bcc-Fe; hence, is then the value of the magnetic moment of Fe in a fcc environment (FeCu) enhanced with respect to its value in the bcc state? There is no clear and convincing explanation to the first question; only a correlation between the Fe-Fe next-nearest (NN) neighbor distances and ferromagnetic or antiferromagnetic coupling due to changes induced in the Fe 3*d* band have been proposed.[12] The second question has been partially answered by suggesting two coexisting electronic states with different magnetic moments for fcc-Fe.[14,15] The aim of this work is to address these two issues properly.

II. EXPERIMENTAL DETAILS

In order to achieve this purpose three Fe_xCu_{100-x} powder samples, with nominal compositions located at significant points of the fcc Fe-Cu phase diagram $(x=16,44,\text{and } 65)$, have been fabricated by MA. We have used *in situ* neutron thermodiffraction experiments to follow the temperature dependence of their crystal structures up to 1200 K (above the reversible α-γ transformation for Fe) and, together with low-temperature magnetometry up to 5.5 T, a detailed structural and magnetic characterization has been carried out. The diffraction patterns have been fitted using the Rietveld refinement method (FULLPROF package[16]).

III. RESULTS AND DISCUSSION

The most noticeable structural feature that we have observed by neutron thermodiffraction is the anomalous temperature dependence of the lattice parameter for the three fcc-FeCu samples. As we can see in Fig. 1 the lattice parameter presents a linear behavior for all of them. However, the slopes are very different as are consequently the estimated linear thermal expansion coefficients α_T. For the $Fe_{65}Cu_{35}$ sample [Fig. 1(a)] the calculated value for α_T is around $5\times10^{-6}\ K^{-1}$, lower than expected, taking into account the values for pure Fe $(\approx 13\times10^{-6}\ K^{-1})$ and pure Cu $(\approx 17\times10^{-6}\ K^{-1})$ in this temperature range. The same figure is observed in the case of the $Fe_{44}Cu_{56}$ sample [Fig. 1(b)] below 350 K, with $\alpha_T \approx 3\times10^{-6}\ K^{-1}$. A drastic change in the slope takes place above this temperature, leading to an increase in the value of α_T up to $16\times10^{-6}\ K^{-1}$. For the $Fe_{16}Cu_{84}$ sample [Fig. 1(c)] the calculated value for α_T is also around $15\times10^{-6}\ K^{-1}$, in between the values for pure Fe and Cu. Along the temperature range of the measurements, it has to be pointed out that the $Fe_{65}Cu_{35}$ sample is ferromagnetic, the $Fe_{16}Cu_{84}$ is paramagnetic, while $Fe_{44}Cu_{56}$ has its ferro-paramagnetic transition at around 350 K. It is worth noting that these extremely low values for α_T below the magnetic ordering temperature are typical for Fe Invar-like alloys.[17] We show in the inset in Fig. 1(b) the same trend in a conventional FeNi-Invar alloy that we have obtained by MA for comparison. The most striking feature of the Invar effect is that the temperature dependence of the volume magnetostriction compensates the thermal expansion, over certain ranges. The apparent zero or negative thermal expansion in the ferromagnetic regime, as shown in fcc-FeNi alloys, is caused by the opposite effects of anharmonic thermal expansion and the contraction associated with the decrease of the spontaneous magnetization. The observed thermal variation of the lattice parameter (Fig. 1) indicates clearly the presence

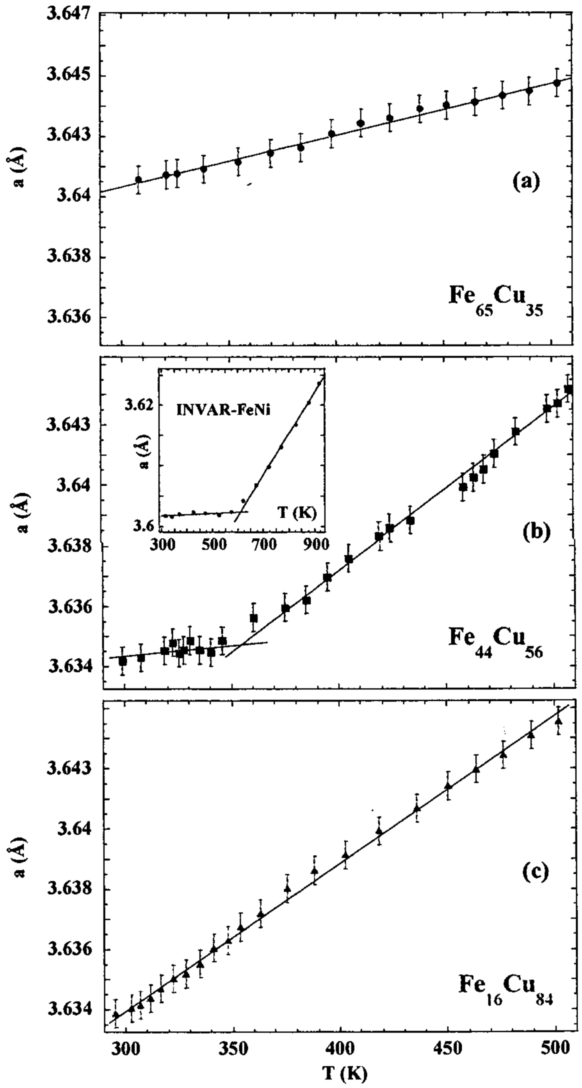

FIG. 1. (Color online) Temperature dependence of the lattice parameter for the (a) $Fe_{16}Cu_{84}$, (b) $Fe_{44}Cu_{56}$, and (c) $Fe_{65}Cu_{35}$ solid solutions. The corresponding dependence for a conventional FeNi-Invar alloy is shown in the inset for comparison. The full lines represent fits to obtain the value for each thermal expansion coefficient (see text for value).

of important magnetovolume effects in these fcc-FeCu materials.

Furthermore, previously reported magnetic moment results are commonly given in terms of magnetic moment per metal atom, giving rise to a linear dependence with respect to the nominal Fe content.[11] From our magnetization measurements we have estiamted a Fe magnetic moment μ_{Fe} of around 2 μ_B/Fe for Fe concentrations above 60 at.%, with a slight decrease of this value to 1.5 μ_B observed below 30 at.% Fe. The value of μ_{Fe} in fcc-FeCu alloys, extrapolated to 0 K, can be determined accurately from their magnetization curves, which were measured at 5 K and under high (5.5 T) applied magnetic fields (see Fig. 2). These curves present a clear slope at high fields, indicating that the samples are not saturated. Using a conventional approach to saturation law,[18] we have performed a fit to obtain the spon-

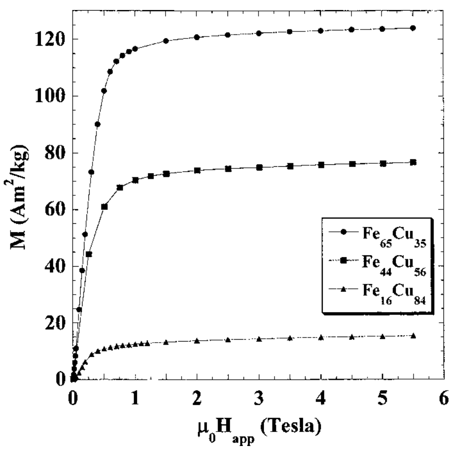

FIG. 2. (Color online) Magnetization curves obtained at 5 K and under applied magnetic fields ($\mu_0 H_{app}$) up to 5.5 T for the three FeCu samples. The solid lines are guides for the eyes.

taneous magnetization value at zero field. The observed large slope of the curves must be interpreted as a large value for the high-field susceptibility χ_{HF}. This fact suggests a strong influence of magnetovolume effects in the fcc-FeCu system, thus providing further evidence for the Invar character in these materials. The estimated values of $\chi_{HF}[\sim(3-8)\times 10^{-5}$ emu g^{-1} Oe^{-1}] are similar to those obtained in 31–40 at.% Ni-containing fcc-FeNi alloys [$\sim(1-6)\times 10^{-5}$ emu g^{-1} Oe^{-1}].[3,17] In Fig. 3 we present the compositional dependence of χ_{HF} and μ_{Fe} (inset) of the fcc-FeCu solid solutions at 5 K, with the values for bcc-Fe, fcc-Ni, and FeNi in the Invar region, also presented for comparison. We note that the correlation between χ_{HF} and μ shows the same trend as in well known FeNi-Invar alloys, that is, the value of χ_{HF} decreases as that for μ increases in both systems. The

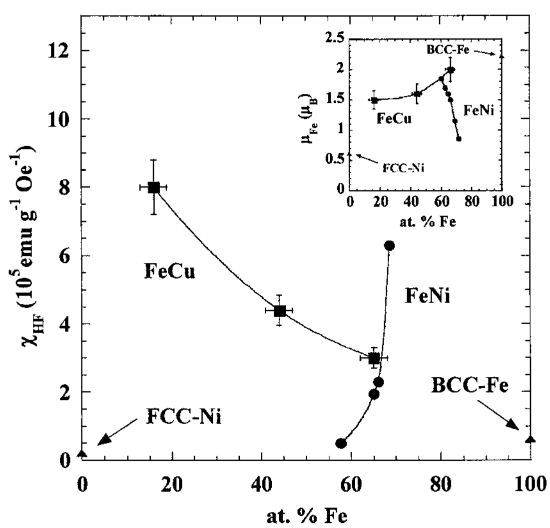

FIG. 3. (Color online) Compositional dependence of the high-field susceptibility χ_{HF} and magnetic moment μ_{Fe} (inset) for the three studied fcc-FeCu solid solutions (squares). Values of FeNi alloys taken from Ref. 5 (circles) in the Invar region and for bcc-Fe (triangles) and fcc-Ni (triangles) are also presented for comparison. The solid lines are guides for the eyes.

Invar character of fcc-FeCu alloys has been recently suggested,[19] but direct experimental evidence has not yet been reported.

To make further progress with these two main experimental results we must reexamine the basic aspects of the phase stability of fcc γ-Fe with respect to the Fe-Fe distances. A phenomenological model was proposed forty years ago by Weiss[20] to explain the ferromagnetism in fcc-FeNi Invar alloys, recently reinforced by theoretical approaches based upon band energy calculations for 3d elements.[21–23] This model considers two different states for fcc γ-Fe: one characterized by a low atomic volume ($\sim$11.09 Å^3) and ordered antiferromagnetically below 70 K with $\mu_{Fe}\approx 0.5\ \mu_B$, and another state with a high atomic volume ($\sim$12.06 Å^3) and a Fe ferromagnetic moment of $\mu_{Fe}\approx 2.8\ \mu_B$. In addition, the 3$d$ band structure of Fe in weakly ferromagnetic Fe alloys is very sensitive to slight variations in the atomic volume (or interatomic Fe-Fe distance).[21,24] Therefore, modifications of the Fe 3d band via increments in interatomic distances give rise to an increase in the density of states (DOS) at the Fermi level and thus an enhancement of Fe ferromagnetic character. Changes in the DOS are also provoked by modifications of the local symmetry, and/or the number of NN neighbors, and/or the distances between atoms. In our case, the former two are expected to be the same in the fcc-Fe_xCu_{100-x} solid solutions, but the distances between NN neighbors are changing through the solid solution composition (x=16, 44, and 65) owing to the different atomic sizes of Cu and Fe.

In this way, the occurrence of ferromagnetism in fcc-FeCu metastable alloys could be explained using the same arguments. The atomic volume for pure fcc-Cu at 0 K ($\sim$11.6 Å^3) is closer to the theoretical one for γ_2-Fe than that for γ_1-Fe, making the γ_2-Fe state more stable in the fcc-FeCu system with average atomic volumes around 11.95 Å^3. The same figure is also valid for FeNi alloys, but in this case the atomic volume for the fcc-FeNi phase has a maximum around 11.6 Å^3 (60 at.% in Fe), and then decreases with increasing Fe content. As a consequence of this, the value of μ_{Fe} is lower in the fcc-FeNi system than in the fcc-FeCu one (inset in Fig. 3) and deceases with atomic volume. For Fe concentrations above 70 at.% the atomic volume falls below the corresponding one for the γ_1-Fe state and an antiferromagnetic behavior is observed in FeNi alloys.[17] Moreover the energy difference between both γ-Fe states at 0 K is very small (around 25 meV), and hence $\gamma_2 \leftrightarrow \gamma_1$ transitions can be induced by increases in temperature, which will destroy the ferromagnetism in these systems. This fact is seen clearly by the low values for the T_C in fcc-FeCu solid solutions compared with the value for bcc-Fe. On the other hand, ferromagnetism cannot occur for compositions below 10 at.% Fe because the number of NN Fe neighbors of a given atom in a fcc structure is 12, and the probability of one Fe atom having a Fe NN neighbor decreases abruptly as shown in previously published results.[8] In this way, the substitution of Cu atoms by Fe atoms in a fcc crystal, above 10–15 at.% Fe, induces ferromagnetic order in Fe atoms. This ferromagnetic coupling counteracts, via a magnetovolume effect, the expected decrease in atomic volume associated with the lower values for the Fe ionic radius. Moreover, it gives rise to volume expansion up to values above 12 Å^3, near the

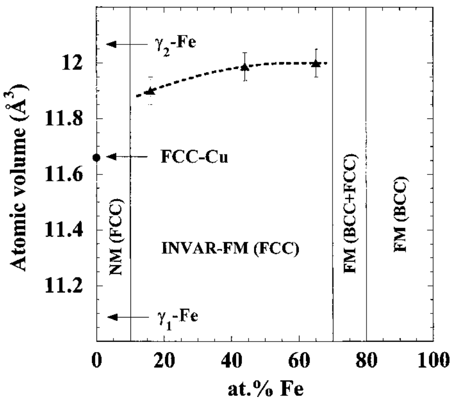

FIG. 4. (Color online) Fe_xCu_{100-x} magnetic phase diagram at 0 K; the atomic volume vs Fe concentration is shown. Atomic volumes for γ_1-Fe and γ_2-Fe together with that of pure fcc-Cu are marked with arrows. Red triangles correspond to our data, and a dashed line indicates the extrapolated compositional dependence for the atomic volume in the Invar-ferromagnetic region [ferromagnetic (FM); nonmagnetic (NM)].

corresponding volume for the γ_2-Fe state and with values of μ_{Fe} that could exceed 2 μ_B.

According to our results we propose the phase diagram of Fig. 4 for the fcc-FeCu Invar solid solutions. The high value for μ_{Fe} in the Fe-rich region (supersaturated solid solution) can be understood only with a lattice parameter close to the theoretical one for γ_2-Fe. When the amount of Fe is decreased, leading to a diluted solid solution, μ_{Fe} decreases, and hence the lattice parameter must decrease as has also been observed in fcc-FeNi alloys.[17] This diagram could be explained by considering that the introduction of Fe atoms into the Cu lattice has a two fold effect: (i) the lower Fe atomic radius produces a volume contraction of the lattice, and (ii) the ferromagnetic interaction between Fe atoms, ensured by the high atomic volume of the Cu lattice close to that for the γ_2-Fe state, leads to a lattice expansion. For low Fe dilution (below 10–15 at.%) the absence of Fe NN neighbors does not allow ferromagnetic coupling between Fe atoms; thus the atomic volume decreases. As the Fe content increases, the onset of ferromagnetism takes place, giving rise to an increase in the spontaneous magnetization and a lattice expansion due to the magnetovolume effect. However, this picture is only valid for intermediate regions, as pure fcc-Fe should not be ferromagnetic because the stable state is γ_1-Fe. Addition of a small amount of Cu is necessary to maintain the appropriate atomic volume and thus to stabilize the γ_2-Fe state.

IV. CONCLUSION

The origin of the ferromagnetism in Fe_xCu_{100-x} solid solutions with a fcc crystal structure is completely determined by the NN neighbor distance between Fe atoms and the weak ferromagnetic character of Fe. Hence, the emergence of ferromagnetism in the metastable fcc alloys induces magnetovolume effects, such as high-field susceptibility values and almost zero thermal expansion. In other words, fcc-FeCu constitutes a new family of Invar alloys. The discovery of new intermetallic compounds showing very low values for the thermal expansion above room temperature, such as FeCu or YbGaGe,[25] could open new perspectives in the design and development of new thermomechanical actuators that have to work under variable temperature conditions.

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[1] K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, and K. Amaya, Nature (London) **412**, 316 (2001).
[2] S. K. Bose, O. V. Dolgov, J. Kortus, O. Jepsen, and O. K. Andersen, Phys. Rev. B **67**, 214518 (2003).
[3] K. Fukamichi, in *Amorphous Metallic Alloys*, edited by F. E. Luborsky (Butterworth, London, 1983), Chap. 17, p. 317. For spin-glass behavior in nanocrystalline pure Fe see E. Bonetti *et al.*, Phys. Rev. Lett. **83**, 2829 (1999).
[4] L. Dubrovinsky, N. Dubrovinskaia, I. A. Abrikosov, M. Vennström, F. Westman, S. Carlson, M. van Schilfgaarde, and B. Johansson, Phys. Rev. Lett. **86**, 4851 (2001).
[5] *Magnetic Properties of Metals, d-elements, Alloys and Compounds*, edited by H. P. J. Wijn (Springer-Verlag, Berlin, 1991), p. 22.
[6] S. C. Abrahams, L. Guttman, and J. S. Kasper, Phys. Rev. **127**, 2052 (1962).
[7] L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).
[8] C. L. Chien, S. H. Liou, D. Kofalt, Wu Yu, T. Egami, and T. R. McGuire, Phys. Rev. B **33**, 3247 (1986).
[9] A. R. Yavari, P. J. Desré, and T. Benameur, Phys. Rev. Lett. **68**, 2235 (1992).
[10] J. Eckert, J. C. Holzer, and W. L. Johnson, J. Appl. Phys. **73**, 131 (1993).
[11] E. Ma, M. Atzmon, and F. E. Pinkerton, J. Appl. Phys. **74**, 955 (1993).
[12] P. Crespo, A. Hernando, R. Yavari, O. Drbohlav, A. García Escorial, J. M. Barandiarán, and I. Orúe, Phys. Rev. B **48**, 7134 (1993).
[13] A. Hernando, P. Crespo, A. García-Escorial, and J. M. Barandiarán, Phys. Rev. Lett. **70**, 3521 (1993).
[14] G. Mazzone and M. Vittori Antisari, Phys. Rev. B **54**, 441 (1996).
[15] L. E. Bove, C. Petrillo, F. Sacchetti, and G. Mazzone, Phys. Rev. B **61**, 9457 (2000).
[16] J. Rodríguez Carvajal, Physica B **192**, 55 (1993).
[17] E. F. Wassermann, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (North-Holland, Amsterdam,

1990), Vol. 5, Chap. 3, p. 237.
[18] S. Chikazumi, *Physics of Ferromagnetism* (Oxford University Press, Oxford, 1997).
[19] T. Mashimo, X. Huang, X. Fan, K. Koyama, and M. Motokawa, Phys. Rev. B **66**, 132407 (2002).
[20] R. J. Weiss, Proc. R. Soc. London, Ser. A **82**, 281 (1963).
[21] V. L. Moruzzi and P. M. Marcus, in *Ferromagnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 1993), Vol. 7, Chap. 2, p. 152.
[22] M. Van Schilfgaarde, I. A. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).
[23] S. Khmelevskyi, I. Turek, and P. Mohn, Phys. Rev. Lett. **91**, 037201 (2003).
[24] J. Kaspar and D. R. Salahub, Phys. Rev. Lett. **47**, 54 (1981).
[25] J. R. Salvador, F. Gu, T. Hogan, and M. G. Kanatzidis, Nature (London) **425**, 702 (2003).