High-temperature anti-Invar behavior of $\gamma$-Fe precipitates in $\text{Fe}_x\text{Cu}_{100-x}$ solid solutions: Ferromagnetic phases

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High-temperature magnetization and neutron diffraction measurements on metastable $\text{Fe}_x\text{Cu}_{100-x}$ solid solutions have recently shown to imply that $\gamma$-Fe precipitates present ferromagnetic anti-Invar behavior. For this reason, we have studied the ferromagnetic phases of $\gamma$-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 $\gamma$-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 $\text{Fe}_x\text{Cu}_{100-x}$ solid solutions.

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I. INTRODUCTION

Among transition metals (TM), iron has a special place,1 not only for its 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 ($\alpha$-Fe) phase is stable, while at temperatures above the reversible martensite-austenite temperature $T_{\text{MA}} = 1183 \text{ K}$, $\alpha$-Fe undergoes a discontinuous first-order phase transition into the fcc ($\gamma$-Fe) phase, which is stable up to 1665 K.

At temperatures lower than $T_{\text{MA}}$ both the structural and magnetic properties of $\gamma$-Fe, pure or in form of Fe-TM alloys with the fcc structure such as $\text{Fe}_{\text{Ni}}_{100-x}$ and $\text{Fe}_{\text{Cu}}_{100-x}$, 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$_x$Cu$_{100-x}$ 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 Mohn8 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$_x$Cu$_{100-x}$ 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 $a = 3.63 \text{ Å}$ is larger than that of pure Cu, namely, $a = 3.61 \text{ Å}$.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 experimental9 and theoretical8 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 $\gamma$-Fe, and an $\alpha$-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$_{19}$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 $\alpha$-Fe phase ($\approx 15\%$) appear.
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. 2 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%±1%) and γ-Fe (6%±1%) obtained from neutron diffraction data, the magnetic moment μ_{Fe} at 750 K may be estimated for each phase (Fig. 1), resulting in μ_{Fe}(α-Fe)≈1.7 μ_B and μ_{Fe}(γ-Fe)≈2.3 μ_B, respectively. Extrapolation to T=0 K leads to the values μ_{Fe}(α-Fe)≈2.1 μ_B±0.2 μ_B and μ_{Fe}(γ-Fe)≈2.8 μ_B±0.3 μ_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 γ_1 (γ_2) state is 0.5(2.8) μ_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 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, Cu_{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 planewave 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-3s, into the valence region. Local orbitals were used with APW+lo for the Fe-3d orbital and LAPW+LO for the rest. The radius of the muffin-tin spheres R_MTF 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_MTF×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
be lattice constant $a=2.83\ \text{Å}$, magnetic moment per atom at
0 K, $\mu=2.2\mu_B$, and bulk modulus $B=223\ \text{GPa}$, all in quite
good agreement with the experimental results for $\alpha$-Fe.\textsuperscript{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 $\alpha$-Fe, the en-
ergy surface is characterized by a clear and well-defined fer-
romagnetic (FM) minimum at the values of $\mu$ and $a$ quoted
above. Furthermore, the curves $E(\mu)$ at a fixed lattice con-
stant have only one minimum at finite $\mu$ throughout the
whole range of lattice parameters studied ($a=2.65\ \text{Å}$
$-2.95\ \text{Å}$). The results are very similar to those obtained by
Moruzzi et al.\textsuperscript{25}

In contrast, the binding energy surface for $\gamma$-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.\textsuperscript{23} The behavior of $E(\mu)$ curves at a
fixed lattice parameter (Fig. 2) correctly describes the differ-
ent phases and their coexistence. For low lattice parameters,
$a<3.55\ \text{Å}$, 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
$\mu$ 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 $3.45\ \text{Å}$, being the
nonmagnetic phase stable thereafter. On the other hand, for
high values of $a$ [see Fig. 2(c) for $a \geq 3.60\ \text{Å}$], only one and
deep energy minimum is observed, thus confirming the exis-
tence 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 $3.59\ \text{Å}$, 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 $3.63\ \text{Å}$, the ground
state of the system is the HS, while for values of $a$
$=3.58\ \text{Å}$, other LS ground states are expected to be present.
In our case, the lattice parameter of the $\gamma$-Fe precipitates at
RT is slightly below $3.6\ \text{Å}$, whereas heating the sample above
600 K this value increases above $3.62\ \text{Å}$, and thus the HS
state becomes energetically more favourable, giving rise to
an enhanced volume expansion and the onset of ferromag-
netism ($\approx 600\ \text{K}$, see Fig. 1). The anti-Invar effect of $\gamma$-Fe
precipitates in FeCu alloys also involves a drastic rising in
the value of the magnetic moment [$\mu(\gamma$-Fe) $=2.3\mu_B$ 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 $\gamma$-Fe precipitates at RT from magnetic
and Mössbauer spectroscopy measurements.\textsuperscript{11–14} The high
values of the magnetic moment and of the $\alpha_T$ coefficient for
the $\gamma$-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 insta-
Bility is a consequence of the existence of strong magneto-
volume effects. Thus, magnetization vs temperature mea-
surements certainly offer the best experimental evidence of
anti-Invar behavior.

V. CONCLUSION

In summary, first-principle band calculations for $\gamma$-Fe
confirm the existence of an unique LS ferromagnetic state
and a unique HS state between 3.40 and $3.75\ \text{Å}$, as obtained
from the FSM method. This HS state seems to be the ground
state of the $\gamma$-Fe precipitates present in ferromagnetic
Fe$_x$Cu$_{100-x}$ mechanically alloyed solid solutions, as found in
recent high-temperature magnetization and neutron diffrac-
tion experiments.\textsuperscript{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.

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