

# Invar effect and noncollinear magnetism in FeCu alloys

Cite as: J. Appl. Phys. **105**, 07E509 (2009); <https://doi.org/10.1063/1.3063070>

Submitted: 17 September 2008 . Accepted: 29 October 2008 . Published Online: 10 March 2009

Markus Eisenbach, and G. Malcolm Stocks



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

[Invar effects of  \$\(\text{Fe}\_{71.2}\text{B}\_{24}\text{Y}\_{4.8}\)\_{96}\text{Nb}\_4\$  alloy in different structural states](#)

Applied Physics Letters **97**, 221907 (2010); <https://doi.org/10.1063/1.3524199>

[Giant negative thermal expansion in Ge-doped anti-perovskite manganese nitrides](#)

Applied Physics Letters **87**, 261902 (2005); <https://doi.org/10.1063/1.2147726>

[Nonferromagnetic Cr-Si-Mn Invar alloys](#)

AIP Conference Proceedings **24**, 384 (1975); <https://doi.org/10.1063/1.30144>

Lock-in Amplifiers

... and more, from DC to 600 MHz



## Invar effect and noncollinear magnetism in FeCu alloys

Markus Eisenbach<sup>1,a)</sup> and G. Malcolm Stocks<sup>2</sup>

<sup>1</sup>National Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

<sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

(Presented 11 November 2008; received 17 September 2008; accepted 29 October 2008; published online 10 March 2009)

The Invar effect has been observed in many Fe rich alloys, most famously Ni Invar. Generally the Invar behavior is associated with the strong coupling between the lattice and magnetic degrees of freedom, and therefore depends on the magnetic ordering in these alloys. Recent experimental works observed an Invar effect in fcc-FeCu solid solutions [Gorria *et al.*, Phys. Rev. B **69**, 214421 (2004)]. In the present paper the magnetic states of fcc-FeCu solid solutions for various concentrations are investigated. The first principles calculations employ the locally self-consistent multiple scattering real space method for solving the local-density approximation Kohn–Sham equation to investigate the noncollinear ordering of magnetic moments. The magnetic order for the low iron concentration is found to be noncollinear, spin glasslike, and the ferromagnetic order is not stable, whereas for the iron rich alloys for the ground state equilibrium lattice constants a magnetic order with parallel aligned Fe moments is stable. In this configuration the induced moments at the Cu sites order nontrivially on a cone with an opening of approximately 40° around the Fe moment direction. © 2009 American Institute of Physics. [DOI: [10.1063/1.3063070](https://doi.org/10.1063/1.3063070)]

### I. INTRODUCTION

A number of Iron rich fcc alloys show anomalous behavior of a number of physical properties, most notably an almost vanishing thermal expansion coefficient over a wide temperature range. Most importantly this effect had first been observed in the fcc Invar alloy (Fe<sub>65</sub>Ni<sub>35</sub>).<sup>1</sup> The Invar effect was early on recognized to be linked to the magnetism in these compounds and has been described as a transition from a low spin, low volume to a high spin, high volume state.<sup>2</sup> Also various authors explored both model electronic structure calculations for Ni and also Pt based Invar alloys.<sup>3–6</sup> This explanation was later refined to account for the shortcomings of the original explanation that was restricted to collinear spins by including noncollinear magnetic moments at the magnetic sites.<sup>7,8</sup> Despite this progress in understanding the Invar effect further, recent experimental<sup>9,10</sup> and theoretical<sup>11,12</sup> studies continue to deepen the understanding of this phenomenon.

Recent experimental work by Gorria *et al.*<sup>13</sup> observed an Invar effect in fcc-FeCu solid solutions. An initial theoretical investigation using coherent potential approximation was reported by Khmelevskyi and Mohn.<sup>14</sup> In the present paper we will investigate this new system at various concentrations and lattice constants using first principles calculations. This will give us the opportunity to investigate the interplay between the lattice, chemical concentration, and magnetism.

In the remainder of this paper, we will describe the system to be studied, describe briefly our constrained moment direction, multiple scattering method that was used to perform the calculations, and finally present our results.

### II. METHOD

For our *ab initio* calculations, we employ density functional theory in the local spin density approximation. This results in a Kohn–Sham equation, which we solve by using the multiple scattering formalism. Since our interest here neglects relativistic effects, especially the coupling between electron spins and their orbital motion, we restrict ourselves to an ordinary Schrödinger equation with added magnetic interactions.

The details of the multiple scattering method for calculating the Green function and the total ground state energy  $E[n(\vec{r}), \vec{m}(\vec{r})]$  are described elsewhere.<sup>15</sup> Our locally self-consistent multiple scattering method allows the possibility for noncollinear magnetism.<sup>16,17</sup>

The new orientation  $\hat{e}^i$  of the magnetic moment for each site is determined by

$$\hat{e}^i = \frac{\int_{\Omega^i} d\vec{r} \vec{m}^i(\vec{r})}{\left| \int_{\Omega^i} d\vec{r} \vec{m}^i(\vec{r}) \right|}.$$

As the local-density approximation self-consistent field iterations proceed,  $\hat{e}^i$  will rotate in order to minimize the total energy. Thus we can find a noncollinear magnetic structure in which the orientations of the local moments vary from site to site. Since an arbitrary arrangement is not a discrete Fourier transform ground state we will have to deal with a constrained general state as presented by Stocks and co-workers.<sup>18,19</sup> In the constrained local moment (CLM) model the local spin density approximation (LSDA) equations are solved subject to a constraint

<sup>a)</sup>Electronic mail: eisenbachm@ornl.gov.

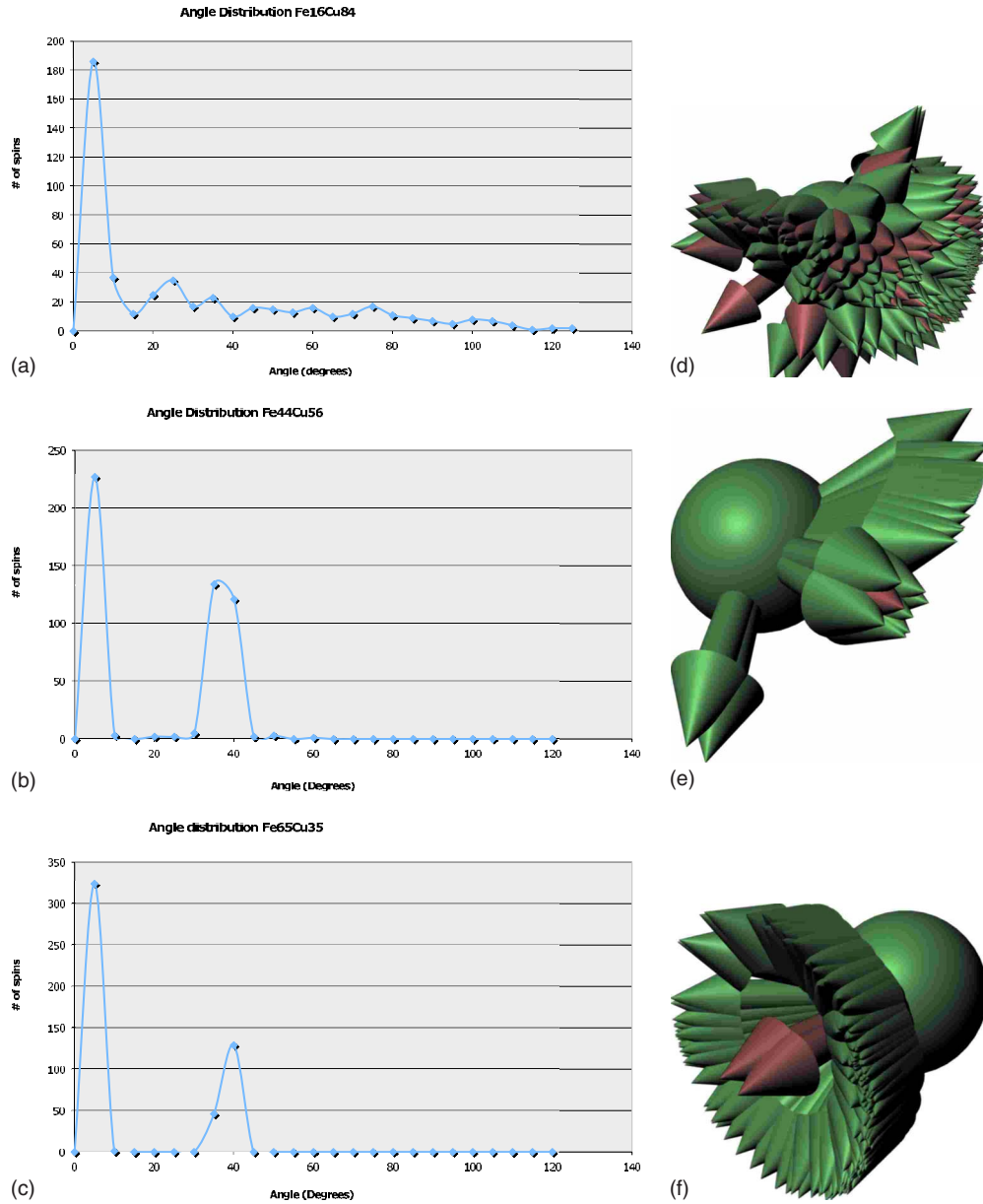


FIG. 1. (Color online) Directions of induced magnetic moments on the copper sites (green) and on the iron sites (red) for Fe<sub>16</sub>Cu<sub>84</sub> (top), Fe<sub>44</sub>Cu<sub>56</sub> (middle), and Fe<sub>65</sub>Cu<sub>35</sub> (bottom). All the moment directions have been drawn from a common origin. Additionally we show the histograms of the deviation of the moment directions from the total moment direction.

$$\int_{\Omega_i} \vec{m}_i(\vec{r}) \times \vec{e}_i d\vec{r} = 0 \quad (1)$$

that ensures that the local magnetizations lay along the directions prescribed by  $\{\vec{e}_i\}$ . The result is that in order to maintain the specific orientational configuration, a local transverse constraining field must be applied at each site. The constraining field is obtained from the condition

$$\frac{\delta E^{\text{con}}[\{\vec{e}_i\}, \{\vec{B}_i^{\text{con}}\}]}{\delta \vec{e}_i} = 0 \quad (2)$$

applied to all sites and where  $E$  is the generalized energy functional in the presence of the constraining field. To make use of the CLM model to find magnetic ground state configurations, we note that the internal effective field that rotates the spins is just the opposite of the constraining field,

i.e.,  $\mathbf{B}_i^{\text{eff}} = -\mathbf{B}_i^{\text{con}}$ . Using these effective fields, we can evolve the moment directions using a Landau–Lifshitz–Gilbert equation, where the damping constant can be adjusted to ensure rapid convergence to the ground state (or, at least, the nearest local minimum).

### III. IRON-COPPER INVARIANTS

Goria *et al.*<sup>13</sup> describe their observation of an Invar behavior in fcc-FeCu solid solution. They investigated three compositions: Fe<sub>65</sub>Cu<sub>35</sub>, Fe<sub>44</sub>Cu<sub>56</sub>, and Fe<sub>16</sub>Cu<sub>84</sub>. For the two higher Fe concentrations unexpectedly low linear thermal expansion coefficients of  $\alpha = 5 \times 10^{-6} \text{ K}^{-1}$  and  $\alpha = 3 \times 10^{-6} \text{ K}^{-1}$ , respectively, were reported, whereas the low Fe alloy showed a larger value of  $\alpha = 15 \times 10^{-6} \text{ K}^{-1}$ . Additionally they find the high Fe concentrations to be ferromagnetic and Fe<sub>16</sub>Cu<sub>84</sub> to be paramagnetic.

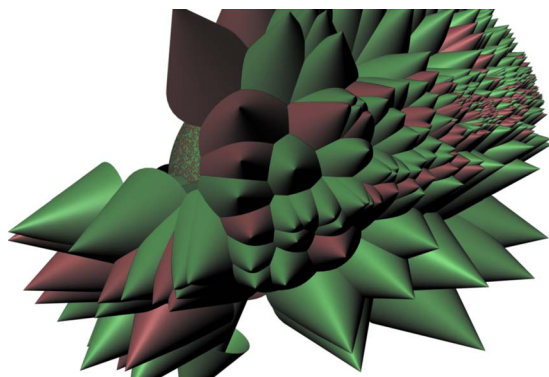


FIG. 2. (Color online) Moment distribution for  $\text{Fe}_{44}\text{Cu}_{56}$  that has been compressed to 0.95 in all linear dimensions or to 86% of its experimental ground state volume.

We model the systems for the three concentrations reported by Gorria *et al.*<sup>13</sup> by randomly distributing Fe and Cu atoms on a fcc lattice supercell of 500 sites at the zero temperature lattice constants of  $a_{\text{Fe}_{65}\text{Cu}_{35}} = 6.869a_0$ ,  $a_{\text{Fe}_{44}\text{Cu}_{56}} = 6.858a_0$ , and  $a_{\text{Fe}_{16}\text{Cu}_{84}} = 6.857a_0$ . Note that we perform only a calculation for a single disorder instance for each lattice constant. This can be compensated by increasing the size of the supercell, which, for sufficiently large cells, will be a realistic representation of an alloy system.

We first calculated a converged ferromagnetic solution with all moments aligned along the 100 directions in all three cases. Since these calculations did not include any spin-orbit effects, this provided a stable solution. To establish the existence of noncollinearity or the stability of ferromagnetic order all moment directions were randomly disturbed by less than  $5^\circ$  and the spin dynamics process described above was used to evolve the systems toward a stable solution. The resulting distribution of directions is shown in Fig. 1. Here we can clearly see a disordered arrangement of Fe moments for the low Fe alloy, outside the Invar regime, and an essentially ferromagnetic order of the Fe moments for the alloys where an Invar effect was observed. Also note that the direction of the induced Cu moments shows some alignments preferentially  $\approx 40^\circ$  to the iron moments. While this is a striking behavior, its discussion will be relegated to a later paper, since the specific of these induced moments might depend crucially on relativistic, i.e., spin-orbit, effects.

To investigate the interplay between lattice constant and magnetic order, we started from the ground state moment distribution obtained for  $\text{Fe}_{44}\text{Cu}_{56}$  and compressed it to 95% in linear dimensions, resulting in a volume compression of 86%. The relaxed magnetic moment directions for this compressed system are shown in Fig. 2. The results clearly show a change from an ordered magnetic arrangement to a disordered state. This is in agreement with the results obtained for

$\text{FeNi}$  Invar, thus the standard explanation for the Invar effect should also hold for the  $\text{FeCu}$  alloys investigated here.<sup>7,8,20</sup>

In conclusion, we find that the magnetic order behaves qualitatively different in the high and low Fe concentration alloys. The transition of the Fe moment directions from a disordered to a ferromagnetically ordered arrangement is in agreement with the standard explanation of the Invar effect in  $\text{FeNi}$  alloys. The induced moments of the Cu sites exhibit significantly different behaviors. It must be noted that the calculations presented here do not include relativistic spin-orbit coupling effects, which, as we have shown previously,<sup>17,21</sup> can have important influences on the magnetic properties of systems with induced moments.

## ACKNOWLEDGMENTS

The research was sponsored by DOE-OS, BES-DMSE, and OASCR-MICS under Contract No. DE-AC05-00OR22725 with UT-Battelle LLC. The calculations presented in this paper were performed at the Center for Computational Sciences (CCS) at ORNL and at the National Energy Research Scientific Computing Center (NERSC).

- <sup>1</sup>C. E. Guillaume, C. R. Acad. Sci. **125**, 235 (1897).
- <sup>2</sup>R. J. Weiss, *Proc. Phys. Soc.* **82**, 281 (1963).
- <sup>3</sup>J. Kaspar and D. R. Salahub, *Phys. Rev. Lett.* **47**, 54 (1981).
- <sup>4</sup>A. R. Williams, V. L. Moruzzi, C. D. Gelatt, J. Kübler, and K. Schwarz, *J. Appl. Phys.* **53**, 2019 (1982).
- <sup>5</sup>P. Entel, E. Hoffmann, P. Mohn, K. Schwarz, and V. L. Moruzzi, *Phys. Rev. B* **47**, 8706 (1993).
- <sup>6</sup>M. Uhl, L. M. Sandratskii, and J. Kübler, *Phys. Rev. B* **50**, 291 (1994).
- <sup>7</sup>Y. Wang, G. M. Stocks, D. M. Nicholson, W. A. Shelton, V. P. Antropov, and B. N. Harmon, *J. Appl. Phys.* **81**, 3873 (1997).
- <sup>8</sup>M. van Schilfgaarde, I. A. Abrikosov, and B. Johansson, *Nature (London)* **400**, 46 (1999).
- <sup>9</sup>M. Matsushita, Y. Miyoshi, S. Endo, and F. Ono, *Phys. Rev. B* **72**, 214404 (2005).
- <sup>10</sup>Y. Tsunoda, L. Hao, S. Shimomura, F. Ye, J. L. Robertson, and J. Fernandez-Baca, *Phys. Rev. B* **78**, 094105 (2008).
- <sup>11</sup>A. V. Ruban, M. I. Katsnelson, W. Olovsson, S. I. Simak, and I. A. Abrikosov, *Phys. Rev. B* **71**, 054402 (2005).
- <sup>12</sup>A. V. Ruban, S. Khmelevskiy, P. Mohn, and B. Johansson, *Phys. Rev. B* **76**, 014420 (2007).
- <sup>13</sup>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).
- <sup>14</sup>S. Khmelevskiy and P. Mohn, *Phys. Rev. B* **71**, 144423 (2005).
- <sup>15</sup>Y. Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek, and W. M. Temmerman, *Phys. Rev. Lett.* **75**, 2867 (1995).
- <sup>16</sup>G. M. Stocks, Y. Wang, D. M. C. Nicholson, W. A. Shelton, Z. Szotek, W. M. Temmerman, B. N. Harmon, and V. P. Antropov, *Mater. Res. Soc. Symp. Proc.* **408**, 157 (1996).
- <sup>17</sup>G. M. Stocks, M. Eisenbach, B. Újfalussy, B. Lazarovits, L. Szunyogh, and P. Weinberger, *Prog. Mater. Sci.* **52**, 371 (2007).
- <sup>18</sup>G. M. Stocks, B. Újfalussy, X. Wang, D. M. C. Nicholson, W. A. Shelton, Y. Wang, A. Canning, and B. L. Györfy, *Philos. Mag. B* **78**, 665 (1998).
- <sup>19</sup>B. Újfalussy, X. Wang, D. M. C. Nicholson, W. A. Shelton, G. M. Stocks, Y. Wang, and B. L. Györfy, *J. Appl. Phys.* **85**, 4824 (1999).
- <sup>20</sup>H. Akai and P. H. Dederichs, *Phys. Rev. B* **47**, 8739 (1993).
- <sup>21</sup>M. Eisenbach, B. L. Györfy, G. M. Stocks, and B. Újfalussy, *Phys. Rev. B* **65**, 144424 (2002).