Metastability and compensation temperatures for a mixed Ising ferrimagnetic system

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(Received 7 March 2003; revised manuscript received 3 July 2003; published 10 December 2003)

In this paper we calculate the free energy of a mixed Ising ferrimagnetic system by a mean-field approach. The system consists of two interpenetrating square sublattices, one with spins $\pm 1,0$ and the other with spins $\pm 1/2$. We obtain the phase diagram of the system, identify the stable and metastable phases, calculate the temperature dependence of the magnetization, and give an estimate of the free-energy barrier between stable and metastable phases. By comparing our results with Monte Carlo simulations of the same model, we show that this approach gives an excellent estimate of the compensation temperatures and the magnetizations in a quite wide range of temperatures, up to quite close to the transition temperature, with a negligible computational effort. We found that when an external magnetic field is present, compensation temperatures only appear in the metastable phase, and that a system can have different compensation temperatures depending on how it is prepared. Some of these features have already been observed in experimental studies of molecular-based ferrimagnets. Our results suggest that the free-energy barrier becomes independent of the external field just at the compensation temperature.

DOI: 10.1103/PhysRevB.68.224411 PACS number(s): 05.50.+q, 75.10.Hk, 75.50.Gg

I. INTRODUCTION

In recent years ferrimagnetic materials have been intensely studied due to their importance in high-density magneto-optical recording. Novel materials based on molecular compounds have been synthesized in search for low-density, transparent magnets, with spontaneous moments at room temperature. Many of these materials have ferrimagnetic ordering.[1,2] In a ferrimagnet, the different temperature dependences of the sublattice magnetizations raise the possibility of the existence of compensation temperatures, temperatures below the critical point at which the magnetization vanishes.[3] Experimentally it has been shown that the coercivity of a material increases dramatically at the compensation temperature, a behavior that has important applications for thermomagnetic recording.[4] Mixed Ising models that include second-neighbors interactions have proven to be simple but interesting models to study several aspects of ferrimagnetism. They present compensation temperatures,[5,6] and recent results show that their coercivity increases at these temperatures.[7] In this work we apply a microcanonical approach to calculate the free energy of these systems. By minimizing the free energy we calculate the magnetizations and the compensation temperatures and identify the stable and metastable phases. The study of metastability and the time scales associated with escapes from metastable states is very relevant for applications in memory devices. It is desired to obtain rapid switching of magnetization under reversals of an external field, but no spontaneous reversals of the magnetizations. The magnetizations calculated with the approach described in this work are in agreement with Monte Carlo results in a wide range of temperatures, up to quite close to the critical temperature. We get excellent estimates of the compensation temperatures of the system, and their dependence on the external magnetic field, with a minimum computer effort. We found that compensation temperatures only appear in metastable states, and that systems can present different compensation temperatures depending on their preparation. Our model describes fairly well some general features of the thermal behavior of the magnetization of molecule-based ferrimagnets such as $[\mathrm{rad_2Ni_2Cu(opba)_3}]$ $(\mathrm{DMSO})_5\cdot 11\mathrm{H_2O}$, where opba stands for *ortho*-phenylenebys(oxamato) and rad for 2-(1-ethylpyridinium-4-yl)-4,4,5,5-tetra-methylimidazolin-1-oxyl-3-oxide.[2]

The rest of this paper is organized as follows: in Sec. II we define the model, in Secs. III and IV we describe the technique to calculate the free-energy and the phases of the system, the results for the magnetizations and compensation temperatures are given in Sec. V, and finally we present the conclusions in Sec. VI.

II. THE MIXED ISING FERRIMAGNETIC MODEL

The model consists of two interpenetrating square sublattices, one with spins $S=\pm 1,0$ and the other with spins $\sigma=\pm 1/2$. Each S spin has only σ spins as nearest neighbors (nn) and vice versa. Next nearest neighbors (nnn) are always of the same type.

The Hamiltonian has the form,

$$\mathcal{H}=-J_1\sum_{\langle nn\rangle}\sigma_i S_j-J_2\sum_{\langle nnn\rangle}S_j S_l-J_3\sum_{\langle nnn\rangle}\sigma_i\sigma_k -D\sum_j S_j^2-H\left(\sum_i \sigma_i+\sum_j S_j\right), \tag{1}$$

where J's are the exchange interaction parameters, D is the crystal field, and H is an external magnetic field, all in energy units. We choose $J_1=-1$, such that the coupling between nearest neighbors is antiferromagnetic.

For a square lattice of $N=L\times L$ sites, the sublattice magnetizations per site are defined as,

$$m_1=\frac{2}{N}\sum_i S_i,\quad m_2=\frac{2}{N}\sum_j \sigma_j, \tag{2}$$

so that the total magnetization per spin is

$$m=\tfrac{1}{2}(m_1+m_2). \tag{3}$$

Previous works[5,7] show that this model exhibits a compensation temperature T_{comp} defined as the temperature below the critical temperature, T_{c}, where the two sublattice magnetizations cancel each other, such that the total magnetization is zero,

$$|m_1(T_{\mathrm{comp}})|=|m_2(T_{\mathrm{comp}})| \tag{4}$$

and

$$\mathrm{sgn}[m_1(T_{\mathrm{comp}})]=-\mathrm{sgn}[m_2(T_{\mathrm{comp}})], \tag{5}$$

with $T_{\mathrm{comp}}<T_{\mathrm{c}}$.

Note that at both T_{comp} and T_{c} the total magnetization is zero, but at T_{comp} the sublattice magnetizations are not zero.

III. CALCULATION OF THE FREE ENERGY

The Helmholtz free energy of the system F is defined as[8]

$$F=E-T\mathcal{S}, \tag{6}$$

where $E=\langle\mathcal{H}\rangle$ is the internal energy and $\mathcal{S}$ is the entropy. For a system in thermal contact with a thermal reservoir the equilibrium state minimizes the Helmholtz free energy over the manifold of states of the constant (reservoir) temperature.

A. Internal Energy

To calculate the internal energy E of the ferrimagnetic model described above we will use a mean-field approach that assumes that each spin is in an effective field composed by the applied field and an average exchange field due to its neighbors.[9] In this approximation the Hamiltonian of the ferrimagnetic model can be written as

$$\mathcal{H}\approx\sum_i \langle K_1\rangle S_i-D\sum_i S_i^2+\sum_j \langle K_2\rangle\sigma_j, \tag{7}$$

where

$$\langle K_1\rangle=-\tfrac{1}{2}z(J_1m_2+J_2m_1)-H \tag{8}$$

and

$$\langle K_2\rangle=-\tfrac{1}{2}z(J_1m_1+J_3m_2)-H, \tag{9}$$

where z is the coordination number of the lattice, $z=2d$ for a hypercubic lattice of dimension d. The factor 1/2 assures the correct counting.

Within this mean-field approximation. The internal energy per site e is

$$e\equiv\frac{E}{N}=-\frac{1}{2}\left[zJ_1m_1m_2+\frac{1}{2}zJ_2(m_1)^2+\frac{1}{2}zJ_3m_2^2+Dm_1^*\right.$$
$$\left.+H(m_1+m_2)\right], \tag{10}$$

where m_1^* is the number of nonzero S spins per site, also called the quadrupole moment per spin of the S sublattice, $m_1^*=2\Sigma S_i^2/N$.

B. Entropy

In the statistical-mechanical formalism, entropy is defined as Boltzmann's constant (which is taken as 1 in this work) multiplied by the logarithm of the number of microstates consistent with the external constrains. In this section we calculate the entropy of each sublattice by counting the number of configurations compatible with a given magnetization and temperature. Within a mean-field approximation we can approximate the entropy of the system as the sum of the sublattice entropies, $\mathcal{S}\approx\mathcal{S}_1+\mathcal{S}_2$. In general the entropy of a interacting system is smaller that the sum of its parts.

The entropy of the σ sublattice $\mathcal{S}_2$ can be calculated exactly as

$$\mathcal{S}_2=\ln\frac{(N/2)!}{N_\uparrow!N_\downarrow!}, \tag{11}$$

where $N_\uparrow$ is the number of up σ spins and $N_\downarrow$ is the number of down σ spins. We have taken into account that each sublattice has $N/2$ spins and that $|\sigma|=1/2$. Then, for a particular

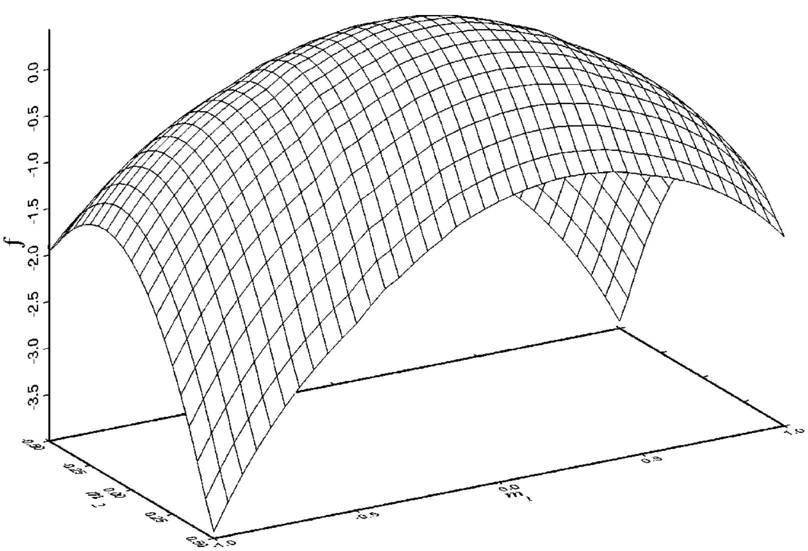

FIG. 1. Free-energy surface in the low-temperature region, $f(T=0.1,m_1,m_1^*=1.0,m_2)$. Four minima can be observed, two corresponding to degenerate metastable ferromagnetic phases and two corresponding to degenerate stable antiferromagnetic phases ($J_1=-1$, $J_2=2$, $J_3=6$, $D=-1$, $H=0$).

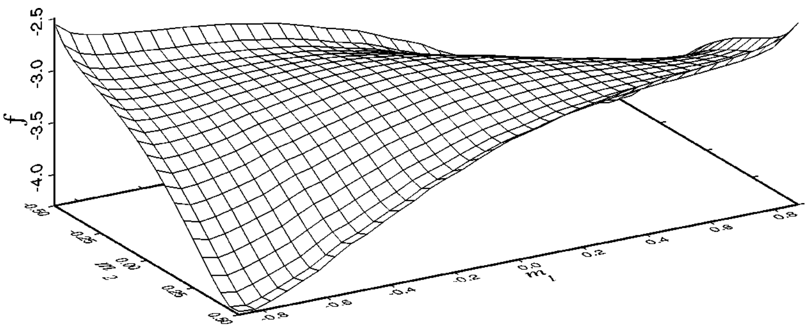

FIG. 2. Free-energy surface in the intermediate-temperature region, $f(T=4.1,m_1,m_1^*=0.875,m_2)$. The two minima correspond to degenerate antiferromagnetic phases ($J_1=-1$, $J_2=2$, $J_3=6$, $D=-1$, $H=0$).

value of m_2 we get that, in the limit of very large N, the entropy per spin of the σ sublattice, s_2, has the form

$$s_2(m_2)\equiv\frac{\mathcal{S}_2}{N/2}=\ln 2-\tfrac{1}{2}(1+2m_2)\ln(1+2m_2)-\tfrac{1}{2}(1-2m_2)\ln(1-2m_2). \quad (12)$$

To calculate the entropy of the S sublattice, $\mathcal{S}_1$, we take into account that the S spins can take values, $0,\pm 1$, then,

$$\mathcal{S}_1=\ln\frac{(N/2)!}{N_+!N_0!N_-!}, \quad (13)$$

where N_0, N_+, and N_- are the total number of S spins type, 0, 1, and -1, respectively. In the limit of very large N, the entropy per spin of the S sublattice, s_1, can be written as

$$s_1(m_1,m_1^*)\equiv\frac{\mathcal{S}_1}{N/2}=m_1^*\ln 2-(1-m_1^*)\ln(1-m_1^*)-\tfrac{1}{2}(m_1^*+m_1)\ln(m_1^*+m_1)-\tfrac{1}{2}(m_1^*-m_1)\ln(m_1^*-m_1). \quad (14)$$

Then the free energy per spin, in this mean-field approximation, takes the form

$$\begin{aligned}f(T,m_1,m_1^*,m_2)&=-\frac{1}{2}\left[J_1zm_1m_2+\frac{1}{2}J_2z(m_1)^2+\frac{1}{2}J_3zm_2^2+Dm_1^*+H(m_1+m_2)\right]+\frac{T}{4}[(m_1^*+m_1)\ln(m_1^*+m_1)\\&\quad+(m_1^*-m_1)\ln(m_1^*-m_1)+(1+2m_2)\ln(1+2m_2)\\&\quad+(1-2m_2)\ln(1-2m_2)+2(1-m_1^*)\ln(1-m_1^*)]\\&\quad-\frac{T}{2}(1+m_1^*)\ln 2. \end{aligned}\quad (15)$$

Note that, besides the temperature, the free energy is written in terms of three quantities, the order parameters of the system: the sublattice magnetizations m_1, m_2, and the average number of nonzero spins of the S sublattice, m_1^*.

In Figs. 1–4 we plot the free energy in terms of m_1 and m_2 for different values of temperature and magnetic field. For each point of coordinates T,m_1,m_2, the value of m_1^* is the one that minimizes the free energy.

IV. PHASES OF THE SYSTEM

The different magnetic phases of the ferrimagnetic model are given by the extremals of the free energy, i.e., by the solutions of the system of equations:

$$\frac{\partial f}{\partial \xi}=0, \quad \xi=m_1^*,m_1,m_2, \quad (16)$$

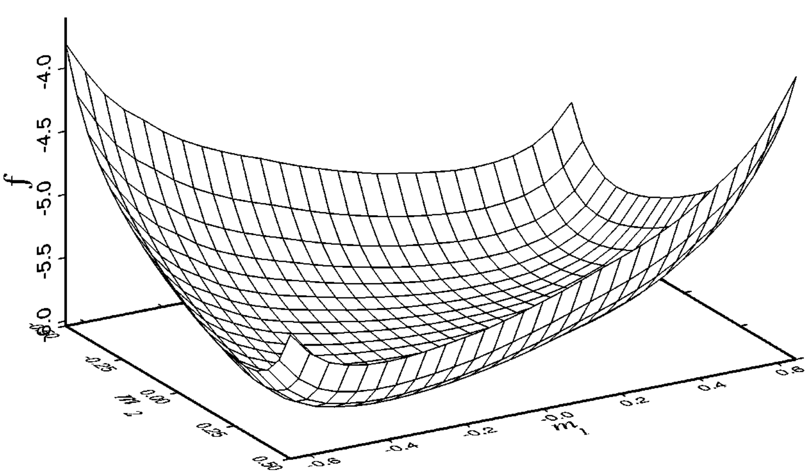

FIG. 3. Free-energy surface in the high-temperature region, $f(T=7.1,m_1,m_1^*=0.64,m_2)$. The only minimum corresponds to a paramagnetic phase ($J_1=-1$, $J_2=2$, $J_3=6$, $D=-1$, $H=0$).

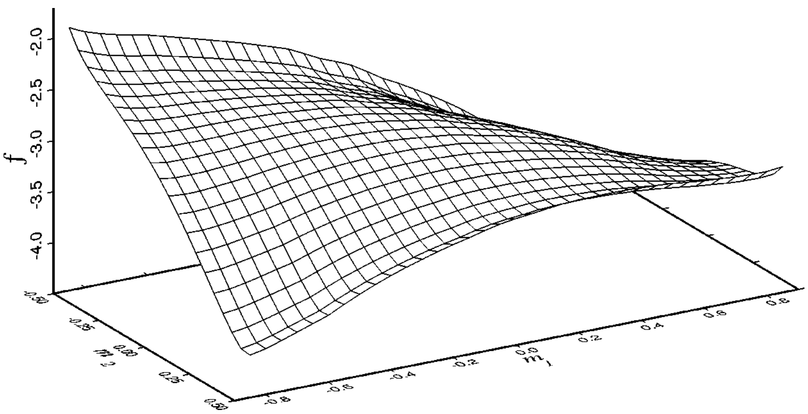

FIG. 4. Free-energy surface in the intermediate-temperature region when $H\neq 0$, $f(T=4.1,m_1,m_1^*=0.906,m_2)$. The degeneracies observed in Fig. 2 are eliminated, one phase is stable and the other metastable ($J_1=-1$, $J_2=2$, $J_3=6$, $D=-1$, $H=1$).

with the constrains $-1/2\leqslant m_2\leqslant 1/2$, $0\leqslant m_1^*\leqslant 1$, and $|m_1|\leqslant m_1^*$. The above system of equations is solved numerically by an optimization algorithm.

In order to understand the features of the free-energy landscapes and to get some insight in the rather complicated expression given by Eq. 15, we calculate its limit near the critical temperature, $T\rightarrow T_c$. In this limit, the sublattice magnetizations m_1 and m_2 go to zero, while m_1^* goes to a constant value different from zero, as can be seen in Fig 5. This limiting value of m_1^* depends on the parameters in the Hamiltonian. Then, near the critical temperature, the free energy can be further approximated as

$$f(T,m_1,m_1^*,m_2)\approx T_1 m_1 m_2+\frac{1}{4m_1^*}(T-T_2)m_1^2+(T-T_3)m_2^2 +\frac{T}{24(m_1^*)^3}m_1^4+\frac{2}{3}Tm_2^4-H(m_1+m_2) -Dm_1^*-\frac{T}{2}g(m_1^*), \tag{17}$$

where $T_1=-1/2zJ_1$, $T_2=m_1^* zJ_2$, $T_3=1/4zJ_3$ and

$$g(m_1^*)=(1+m_1^*)\ln 2-(1-m_1^*)\ln(1-m_1^*)-m_1^*\ln m_1^*. \tag{18}$$

In the absence of an external field $H=0$ as the temperature changes, we can distinguish three behaviors. In the low-temperature region, $T<T_2<T_3$, Eq. 17 exhibits four minima, two that correspond to degenerate metastable ferromagnetic phases, $m_1>0(<0)$, $m_2>0(<0)$, and the other two, to degenerate stable antiferromagnetic phases, $m_1<0$ (>0), $m_2>0(<0)$. These four minima can be clearly observed in Fig. 1.

In the intermediate-temperature region, $T_2<T<T_3$, the free energy exhibits only two minima corresponding to degenerate antiferromagnetic phases, as can be seen in Fig. 2.

At high temperatures, $T>T_3$, Eq. 17 has a minimum at $m_1=0$ and $m_2=0$ that obviously corresponds to a paramagnetic phase, $T_c=T_3$. Again this is observed in Fig. 3.

When a magnetic field is switched on, $H\neq 0$, the degeneracies are lifted. For example, when $T_2<T<T_3$ and $H>0$, the phase with $m_1<0$ and $m_2>0$ now corresponds to a local minimum of the free energy, becoming the metastable phase, and the one with $m_1>0$ and $m_2<0$ corresponds to a global minimum becoming the stable phase. This can be seen in Fig. 4.

V. MAGNETIZATIONS AND COMPENSATION TEMPERATURES

Previous Monte Carlo results[5] indicate that the simplest model that gives compensation temperatures have $J_2=0$ and a $J_3\neq 0$ interaction that depends on the other parameters in the Hamiltonian. In this section we are principally interested in the behavior of the compensation temperatures, then we are going to simplify our model by choosing $J_2=0$. The equilibrium magnetization of the system is obtained by minimizing the free energy given by Eq. 15 by solving Eq. 16 with the given constrains. In Fig. 6 we compare, for a system in zero external field, the magnetizations calculated in this

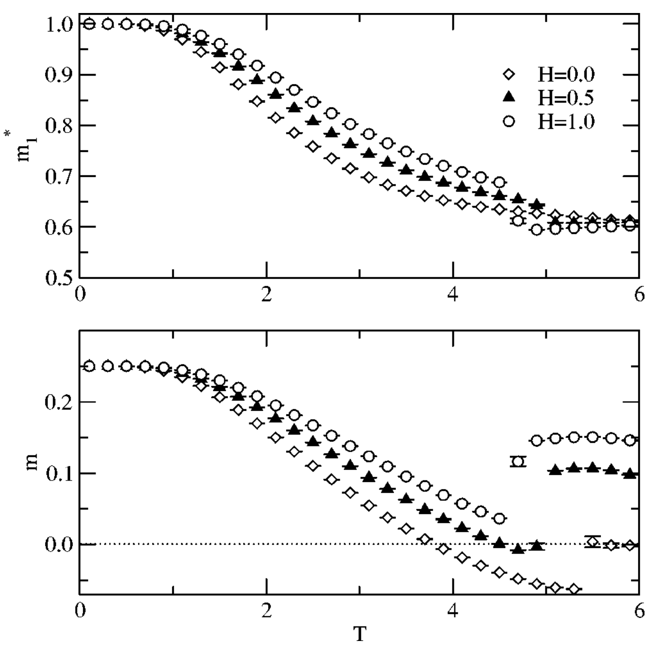

FIG. 5. Behavior of m_1^* and m vs temperature. Note that at the critical temperature m_1^* goes to a constant value that for our choice of parameters is approximately 0.6 ($J_1=-1$, $J_2=2$, $J_3=6$, $D=-1$).

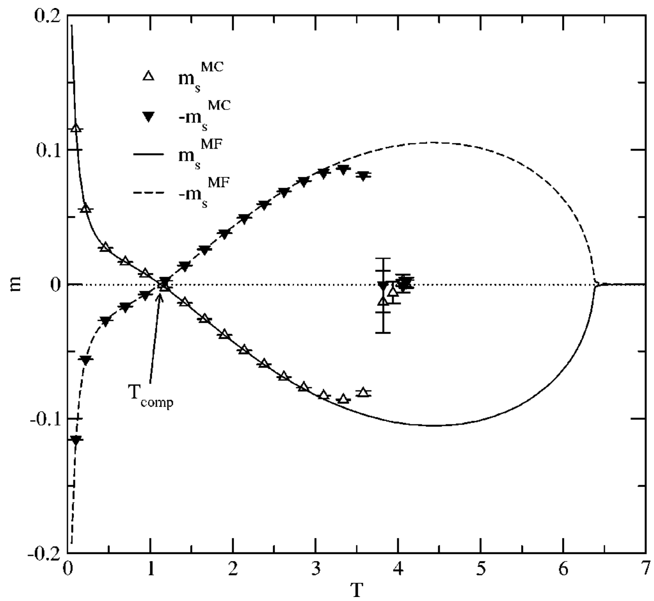

FIG. 6. Comparison between the magnetizations of the two stable degenerated phases, calculated by minimizing the free energies m_s^{MF} and $-m_s^{MF}$ and magnetizations calculated from Monte Carlo simulations that start from different configurations, m_s^{MC} and $-m_s^{MC}$, in absence of an external field ($J_1=-1$, $J_2=0$, $J_3=6$, $D=-1.9$, $H=0$).

way with the ones obtained by a standard Monte Carlo algorithm for a system of $N=100^2$ sites. It is worth noticing that our approach gives extremely good agreement with the Monte Carlo results for a surprisingly wide range of temperatures up to near the critical point, where obviously the mean-field approximation fails. In particular, we get an excellent estimate of the compensation temperature without requiring the considerable computational effort associated with a Monte Carlo simulation.

When an external field is added, the degeneracies of the equilibrium states are removed. The state with the global minimum of energy is the stable state, and others, whose energies correspond to local minima, are metastable states. Figure 7 shows the magnetizations of metastable and stable states m_{ms}^{MF} and m_s^{MF}, respectively, obtained by minimizing the free energy as described above. In the same figure we plot the magnetizations calculated by a Monte Carlo algorithm from different starting configurations, m_1^{MC} and m_2^{MC}, that from comparison with the previous ones, can be identified as corresponding to the stable and the metastable magnetization, respectively. Again note the excellent agreement between both methods, except near the critical temperature. A remarkable fact, that cannot be deduced by looking only at the Monte Carlo results, is that for $H\neq 0$ only the metastable system exhibits a compensation temperature. When $H\neq 0$ the sublattice magnetizations of the stable and metastable states are interchanged at a temperature value that coincides with the value of the compensation temperature at $H=0$. At this point the system goes in a continuous way from the metastable to the stable phase, such that only one of the magnetizations m_1^{MC} exhibits a compensation temperature. It will be seen later that the free-energy barrier becomes zero at

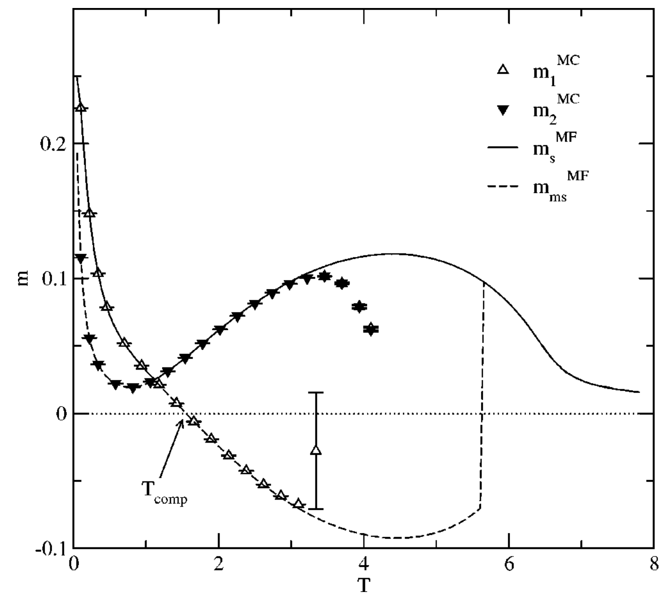

FIG. 7. Comparison between the magnetizations of the metastable and stable phase, m_{ms}^{MF} and m_s^{MF}, respectively, obtained by minimizing the free energy, and the magnetizations calculated by a Monte Carlo algorithm from different starting configurations m_1^{MC} and m_2^{MC} for $H\neq 0$. Note that the point where the stable and unstable magnetizations are interchanged occurs at the compensation temperature corresponding to $H=0$ ($J_1=-1$, $J_2=0$, $J_3=6$, $D=-1.9$, $H=0.2$).

this temperature. Reversal of magnetic poles at T_{comp} has been observed in molecular ferrimagnets.[2] When in a Monte Carlo simulation, the system is prepared in a paramagnetic phase ($T \gg T_c$) and then is cooled the magnetization would follow the path given by m_2^{MC}, which does not present a compensation point. This effect suggests that the existence of a compensation temperature in a material could depend on its preparation. Recent experimental results show that molecule-based ferrimagnets present different compensation temperatures depending on whether the magnetization is measured in cooling mode or in warming mode.[2]

Another interesting effect happens when we change the parameters D and H. Again, as Fig. 8 indicates when $H\neq 0$ only the metastable phase presents a compensation temperature, and the sublattice magnetizations are interchanged at the compensation temperature corresponding to $H=0$. But now the system exhibits two compensation temperatures. The magnetizations calculated from the Monte Carlo algorithm depend on the initial preparation (even after an extensive warm-up of the system) and each one exhibits an independent compensation point. If the system is cooled from a paramagnetic phase only one of the compensation temperatures will be reached. Materials with two compensation temperatures have already been reported in the literature.[10]

The dependence of the compensation temperature with the magnetic field can be seen in Fig. 9, where we plot the compensation temperatures calculated from the approach described in this paper and also by a Monte Carlo algorithm from different starting configurations, in terms of H. For small fields the compensation temperatures behave as

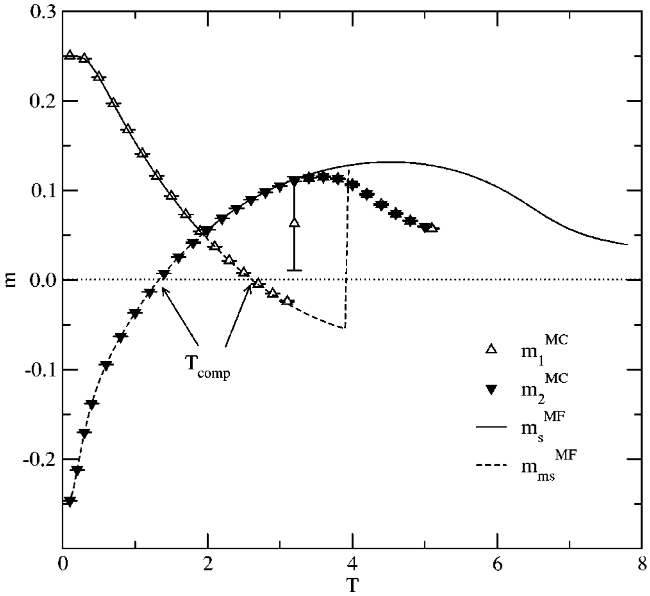

FIG. 8. Comparison between the magnetizations of the metastable and stable phase, m_{ms}^{MF} and m_{s}^{MF}, respectively, obtained by minimizing the free energy, and the magnetizations calculated by a Monte Carlo algorithm from different starting configurations, m_1^{MC} and m_2^{MC}, for $H\neq 0$ and a different value of D. The system presents different compensation points, depending on the starting configuration ($J_1=-1,\ J_2=0,\ J_3=6,\ D=-1,\ H=0.2$).

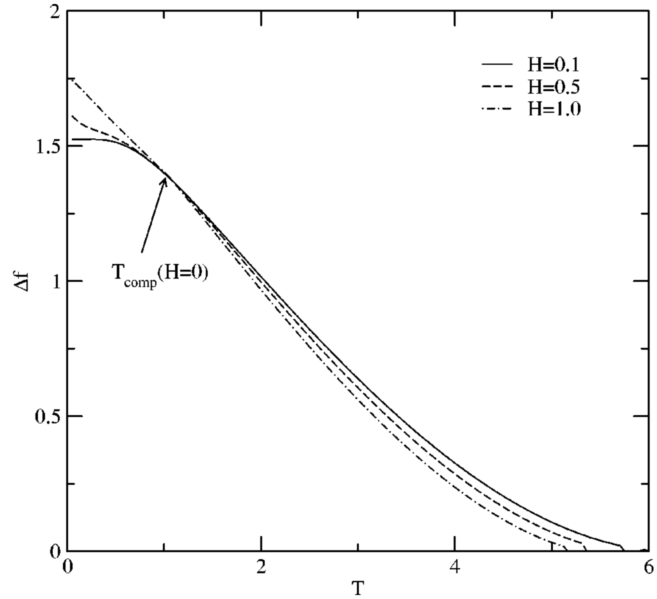

FIG. 10. Free-energy barrier between the stable and metastable phases vs temperature, calculated from Eq. 15, for different values of the external field H. The barrier becomes independent of H just at $T_{comp}(H=0)$ ($J_1=-1,\ J_2=0,\ J_3=6,\ D=-1.9$).

$T_{comp}(H)=T_{comp}(0)\pm\alpha H$, where α is a constant that depends on the parameters in the Hamiltonian. One shortcoming of using a mean-field approximation is that the system seems to have compensation temperatures in the region of high fields and high temperatures, however Monte Carlo results indicate that there is a maximum value of the field at which the system exhibits a compensation temperature, value that depends on the size of the system.

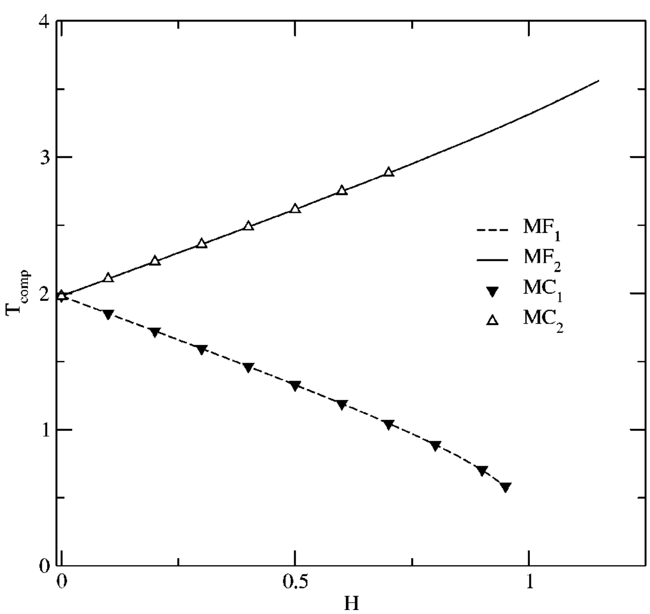

FIG. 9. Dependence of the compensation temperatures, obtained from the free-energy calculations MF_1,MF_2, and from Monte Carlo simulations MC_1,MC_2, with the magnetic field.

A realistic calculation of the free-energy barrier between stable and metastable phases must include, among other terms, interphase boundaries, not taken into account in mean-field approximations. However, we can obtain an estimate of this barrier by calculating the difference between the local minimum and the saddle point of the free-energy surface Δf in the understanding that this result comes mostly from the bulk contribution to the barrier. It is commonly believed that in many processes, the average lifetime of the metastable phase, τ, has an exponential dependence on the height of the free-energy barrier between the stable and metastable phases,[11–14] $\tau\sim\exp(\Delta f)$. Figure 10 shows the dependence of the free-energy barrier on the external field. As expected the barrier disappears at high temperatures where the system exhibits only one phase. Note that the barrier becomes independent of H just at the compensation temperature of the system at $H=0$.

VI. CONCLUSIONS

We calculate the free energy of a mixed ferrimagnetic model by a mean-field approximation. We plot the free-energy surfaces and determine the phase diagram of the system identifying its stable and metastable phases. A direct comparison between the magnetizations obtained from this technique and the ones calculated by standard Monte Carlo simulations shows excellent agreement in a quite broad range of temperatures, except close to and above the critical temperature where, as expected, the mean-field approximation fails. This approach allows the calculation of the compensation temperature and its dependence on the magnetic field with a minimum computational effort, compared with Monte Carlo simulations. We find that when an external field is present, compensation temperatures occur only in the metastable phase of the system. We also show that, depending on its initial configuration, the system can present two different compensation temperatures, both strongly dependent on the external field. These results suggest that the existence of compensation temperatures and even their values depend on the preparation of the system. A similar effect has already been observed experimentally.[2]

Within this mean-field approach we also estimate the free-energy barrier that separates the metastable and the stable phases, and find that it is independent of the external field just at the compensation temperature corresponding to $H=0$, maybe suggesting that magnetization reversal of the spins at this temperature is very difficult.

ACKNOWLEDGMENTS

We thank Per Rikvold and Mark Novotny for many useful discussions.

[1] Y. Rem, T.T.T. Palastra, D.I. Khomskii, E. Pellegrin, A.A. Nugroho, A.A. Menovosky, and G.A. Sawatzky, Nature (London) **396**, 441 (1998); M.M. Turnbull, C.P. Landee, T.C. Soesbe, and R.W. Willet, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **233**, 269 (1993); C.J. Nuttall and P. Day, Chem. Mater. **10**, 3050 (1998).

[2] O. Cador, M.G.F. Vaz, H.O. Stumpf, and C. Mathoniere, J. Magn. Magn. Mater. **234**, 6 (2001).

[3] L. Néel, Ann. Phys. (Paris) **3**, 137 (1948).

[4] C. Mathoniere, C.J. Nuttall, S.G. Carling, and P. Day, Inorg. Chem. **35**, 1201 (1996); A. Hernando and T. Kulik, Phys. Rev. B **49**, 7064 (1994); M. Alex, K. Shono, S. Kuroda, N. Koshino, and S. Ogawa, J. Appl. Phys. **67**, 4432 (1990).

[5] G.M. Buendía and M.A. Novotny, J. Phys.: Condens. Matter **9**, 5951 (1997); G.M. Buendía and R. Cardona, Phys. Rev. B **59**, 6784 (1999); G.M. Buendía and N. Hurtado, Phys. Status Solidi B **220**, 959 (2000).

[6] A. Bobak and M. Jascur, Phys. Rev. B **51**, 11 533 (1995); A. Bobak and D. Horvath, Phys. Status Solidi B **203**, 449 (1999).

[7] G.M. Buendía and E. Machado, Phys. Rev. B **61**, 14 686 (2000).

[8] H.B. Callen, *Thermodynamics and Introduction to Thermostatistics* (Wiley, New York, 1985); C. Garrod, *Statistical Mechanics and Thermodynamics* (Oxford University Press, Oxford, 1995).

[9] P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1997), Chap. 4, p. 144.

[10] S.I. Ohkoshi, Y. Abe, A. Fujishima, and K. Hashimoto, Phys. Rev. Lett. **82**, 1285 (1999).

[11] P.A. Rikvold and B.M. Gorman, *Annual Reviews of Computational Physics I*, edited by D. Stauffer (World Scientific, Singapore, 1995).

[12] J.D. Gunton and M. Droz, *Introduction to the Theory of Metastable and Unstable States*, Lecture Notes in Physics Vol. 183 (Springer-Verlag, Berlin 1983).

[13] J.D. Gunton, M. San Miguel, and P.S. Sahni, in *The Dynamics of First Order Phase Transitions*, edited by C. Domb and M.S. Green, Phase Transitions and Critical Phenomena Vol. 8 (Academic Press, New York, 1983), p. 269.

[14] J.S. Langer, Ann. Phys. (N.Y.) **41**, 108 (1967); Phys. Rev. Lett. **21**, 973 (1968); Ann. Phys. (N.Y.) **54**, 258 (1969).