First principles calculation of finite temperature magnetism in Fe and Fe₃C

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Density functional calculations have proven to be a useful tool in the study of ground state properties of many materials. The investigation of finite temperature magnetism, on the other hand, has to rely usually on the usage of empirical models that allow the large number of evaluations of the systems Hamiltonian that are required to obtain the phase space sampling needed to obtain the free energy, specific heat, magnetization, susceptibility, and other quantities as function of temperature. We have demonstrated a solution to this problem that harnesses the computational power of today's large massively parallel computers by combining a classical Wang–Landau Monte-Carlo calculation [F. Wang and D. P. Landau, Phys. Rev. Lett. **86**, 2050 (2001)] with our first principles multiple scattering electronic structure code [Y. Wang *et al.*, Phys. Rev. Lett. **75**, 2867 (1995)] that allows the energy calculation of constrained magnetic states [M. Eisenbach *et al.*, *Proceedings of the Conference on High Performance Computing, Networking, Storage and Analysis* (ACM, New York, 2009)]. We present our calculations of finite temperature properties of Fe and Fe₃C using this approach and we find the Curie temperatures to be 980 and 425K, respectively. © *2011 American Institute of Physics*. [doi:10.1063/1.3562218]

I. INTRODUCTION

Density functional-based first principles electronic structure calculations for condensed matter systems have reached a high level of maturity over the last few decades and are now a standard tool for the study of ground state material properties.[1] Although these methods have evolved to provide greater accuracy and deal with wider classes of materials, the field of finite temperature behavior has received less attention. The phase space usually is far too large to be dealt with directly. The usual methods of treating the thermodynamics of a physical system involve either the time evolution of an ensemble or the exploration of the most relevant parts of phase space by means of a Monte Carlo method. Both these approaches require a large number of evaluations of the underlying Hamiltonian that describes the system $[> O(10^5)]$, thus it is usually only feasible to treat severely simplified models that have to be designed to capture the essential physics, as opposed to a direct treatment of the density-functional Hamiltonian of the system.

To overcome this limitation we have developed the hybrid Wang–Landau/locally self-consistent multiple scattering (WL-LSMS) code. This code combines recent advances in computational statistical mechanics, namely the Wang–Landau (WL) method[2] with the locally self-consistent multiple scattering (LSMS) first principles method that has already demonstrated superb scalability on massively parallel machines.[3]

II. THE WANG–LANDAU METHOD

All thermodynamic potentials can be derived from the partition function $Z(T) = \int e^{-E(\mathbf{X})/(k_B T)} d\mathbf{X}$, where $E(\mathbf{X})$ is the internal energy of the system with the phase space described by the variable X in some high dimensional space consisting of all the microscopic degrees of freedom of the system (atomic positions, velocities, and/or magnetic moments).

The partition function can be rewritten in the form: $Z(T) = \int g(E)e^{-E/(k_B T)} dE$, where the density of states (DOS) is defined as $g(E) = \int \delta[E - E(\mathbf{X})] dX$ and $\delta(E)$ is the Dirac δ-function.

Flat histogram methods, such as the Wang–Landau algorithm, use the density of states, $g(E)$, for importance sampling, thus accepting the new configuration with probability,

$$\min[1, g(E_i)/g(E_{i+1})]. \tag{1}$$

This creates an equal probability of visiting each energy level in the system. The main obstacle of flat-histogram methods is that $g(E)$ is not known. Instead, an estimate of the density of states $\tilde{g}(E)$ must be constructed self-consistently as the Monte Carlo estimate is generated. The Wang–Landau algorithm accomplishes this by beginning with a prior estimate of the density of states, $\tilde{g}_0(E)$. Assuming that a Monte Carlo moves to a new configuration with energy E_{i+1} is accepted according to the criterion of Eq. (1), the density of states is updated with

$$\ln[\tilde{g}(E_{i+1})] \leftarrow \ln[\tilde{g}(E_{i+1})] + \ln f, \tag{2}$$

where f is the modification factor that is initially set to $\ln(f) = 1$. The modification factor is reduced in steps such that $\ln(f) \leftarrow \ln(f)/2$ and the density of states converges as $\ln(f) \rightarrow 0$. With this DOS the partition function that describes the thermodynamics of the system can be calculated for any temperature.

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A phase transition in the system can be identified by a jump in the internal energy U or a divergence the specific heat $c = \partial U / \partial T$.

III. THE LSMS ALGORITHM

For the energy evaluation, we employ the first principles framework of density functional theory (DFT) in the local spin density approximation (LSDA). To solve the Kohn–Sham equations arising in this context, we use a real space implementation of the multiple scattering formalism. The details of this method for calculating the Green function and the total ground state energy $E[n(\vec{r}), \vec{m}(\vec{r})]$ are described elsewhere.[4,5]

Most importantly for the application in the hybrid Wang–Landau first principles method, our LSMS method allows the possibility of noncollinear magnetism.[6] The orientation $\hat{e}^i$ of the magnetic moment for each site is determined by $\hat{e}^i = \int_{\Omega^i} d\vec{r}\,\vec{m}^i(\vec{r}) / \left| \int_{\Omega^i} d\vec{r}\,\vec{m}^i(\vec{r}) \right|$. As an arbitrary arrangement is not a DFT ground state we will have to deal with a constrained general state as presented by Stocks *et al.*[7,8] In the constrained local moment model the LSDA equations are solved subject to a constraint that ensures that the local magnetizations lie along the directions prescribed by $\{\vec{e}_i\}$. Thus, this method enables the calculation of the energies of arbitrary orientational states as generated by the Wang–Landau algoritm.

IV. MAGNETIC TRANSITION TEMPERATURE FOR IRON AND CEMENTITE

Utilizing the methods and algorithm described earlier we calculated the Curie temperatures of bulk iron and cementite. For iron we consider a periodically repeated cell of 250 iron atoms and converge the Wang–Landau density of states $g(E)$ for changes in the magnetization direction on the individual iron sites. For the underlying LSMS calculation of these iron cells, the atoms were placed on a body-centered cubic lattice with a lattice parameter of 5.42 Bohr radius a_0, corresponding to the experimental room temperature value, and the local interaction zone has a radius of $11.5a_0$. The self-consistently converged potential for the ferromagnetic ground state was used for all the individual frozen-potential energy calculations in the combined WL-LSMS algorithm.

The calculation was performed by randomly choosing a site in the supercell and randomly picking a new moment direction. We chose as a convergence criterion for the Wang–Landau DOS the convergence of Curie temperature. Using 400 Wang–Landau walkers the calculation converged in 590 000 steps and required 4 885 720 central processing unit hours on the jaguar Cray XT5 system.

Additionally we also investigated cementite (Fe_3C) with the orthorhombic structure $D0_{11}$ with experimental lattice parameters. The periodically repeated cell contains 96 iron and 32 carbon atoms and the constrained local moment states considered include both the magnetic moments at the iron sites, as well as on the carbon sites.

The resulting densities of state are shown in Fig. 1. Although the computational resources needed for a system with several hundred atoms are considerable, the remaining
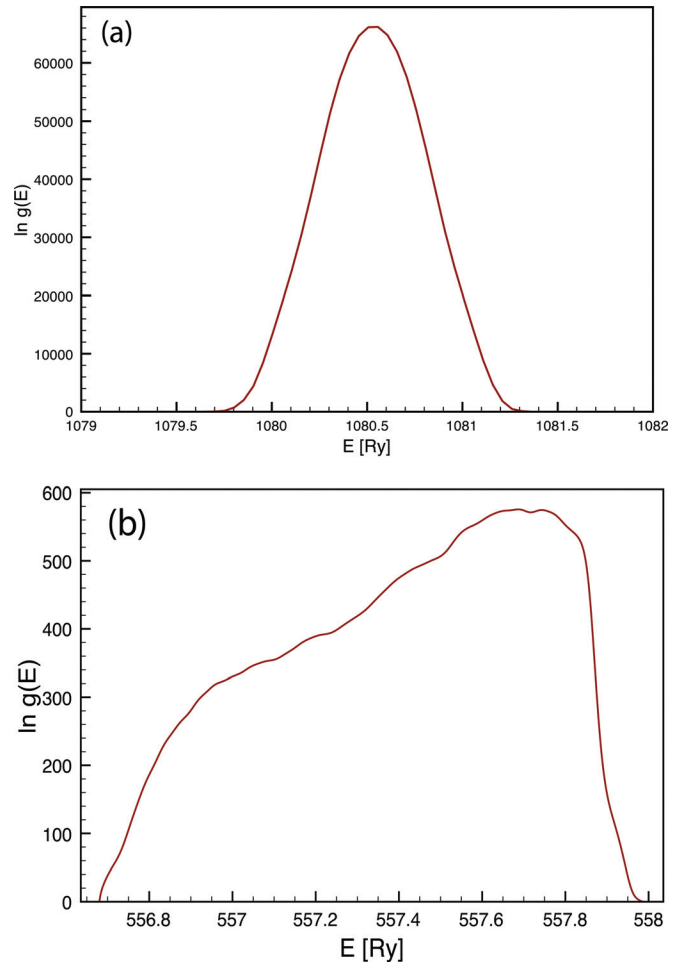

FIG. 1. (Color online) The unnormalized logarithmic Wang–Landau density of states $\ln g(E)$ for a periodic system of 250 iron atoms (a) and 128 atom cementite (b).

calculations to compute any desired temperature-dependent thermodynamic properties are marginal. Note that the iron density of states is symmetric around the paramagnetic energy, as could be expected from a system that is well described by a simple Heisenberg model. Cementite in contrast shows a broader and asymmetric density of states, this
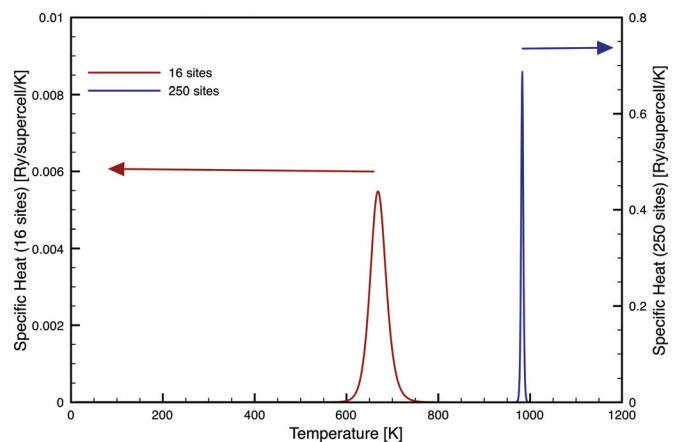

FIG. 2. (Color online) Specific heat c for periodic 16 and 250 iron atom systems calculated from the density of states $g(E)$ in atomic units. A respective transition temperature of 670 and 980 K can be read of these graphs.
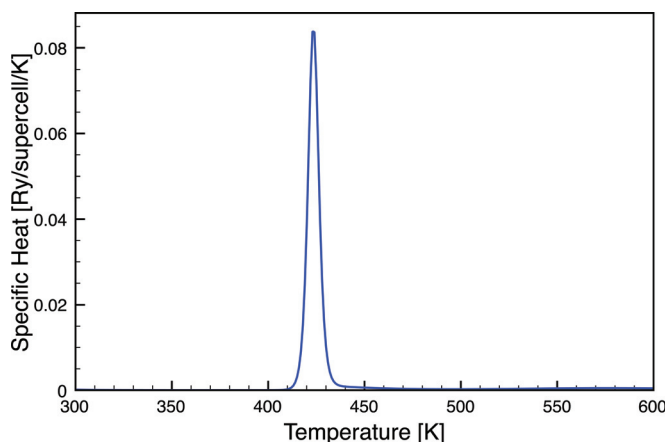
FIG. 3. (Color online) Specific heat *c* for periodic Fe$_3$C in atomic units. The peak in the specific heat corresponds to a magnetic transition temperature of 425 K.
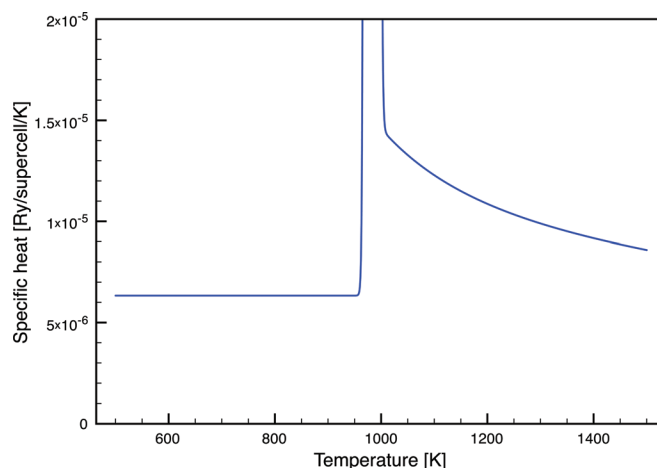

FIG. 4. (Color online) Specific heat for 250 Fe atoms around the Curie temperature. Note that the qualitative difference in the behavior below T_C, when compared with the experimental result and other calculations, results from the early termination of the Monte Carlo process that does not properly account for the low energy behavior of the Wang–Landau DOS.

might arise due to the change in the magnitude of the moments on the different iron and carbon sublattices for the disordered local moment states. Using the densities of state we can calculate the thermodynamic properties using the expressions provided in the Wang–Landau section. The pronounced peak in the specific heat, which we show for iron in Fig. 2 and for cementite in Fig. 3, readily allows us to identify the Curie temperature.

For bulk iron these calculations yield a transition temperature of 670 and 980 K, for the 16 atom and the 250 atom systems, respectively. The 16-site result is smaller, as finite size effects will lead to a reduction of the transition temperature. The result of the 250 atom calculation, however, is in remarkably good agreement with the experimentally known Curie temperature of bulk iron of 1050 K. In Fig. 4 we show the shape of the specific heat for the 250 atom system near the Curie temperature (T_C). Note that compared with both experimental and model results[9] the specific heat does not show the expected gradual rise below T_C but exhibits a sudden divergence, whereas the high temperature behavior has the qualitatively correct behavior. This peculiarity is an artifact of the convergence criterion we have chosen for the Wang–Landau DOS. The method will first discover the high DOS areas and gradually explore the lower lying regions. To limit the expense, the calculation was terminated when no further changes in T_C were observed. This will yield good values for the DOS at energies that correspond to the transition temperature and above. Conversely, for lower energies the DOS will be far from convergence, resulting in the wrong qualitative behavior of thermodynamic properties calculated below T_C. A full convergence of the DOS for lower energies would have required an order of magnitude more samples, which would have made this calculation impractical on the computer resources currently available. The Curie temperature obtained for Fe$_3$C is 425 K which again is in good agreement with the experimental value of 480 K. Further, our calculations yield a

ratio of the Curie temperatures of iron and cementite of 2.3 vs 2.2 for the experimental values.

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