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Pressure dependence of the Curie temperature in bcc iron studied by *ab initio* simulations

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The pressure dependence of the Curie temperature in bcc iron has been studied employing spin-density-functional theory in combination with the Heisenberg model. We show that the results correctly predict an essential independence of the Curie temperature of bcc iron on the external pressure, in agreement with the experimental findings. This behavior is explained as a result of a competition between the decrease in the local magnetic moments and the increase in the magnetic coupling as function of rising pressure.

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I. INTRODUCTION

For a tailored design of magnetic materials, a comprehensive understanding of their thermodynamic properties under different external conditions is decisive. Externally applied pressure is one of the parameters, which significantly affects magnetic properties of materials such as, e.g., diluted magnetic semiconductors,[1] shape memory alloys,[2] or magnetic alloys.[3] In particular, the pressure dependence of the ferromagnetic-paramagnetic transition [i.e., the Curie temperature $T_C(p)$] is of high importance due to its direct technological implications. In addition, critical temperatures are essential ingredients for semiphenomenological simulation tools such as CALPHAD,[4,5] a well-established approach for constructing phase diagrams of alloys at ambient pressure. In order to extend these simulation tools to a pressure-dependent domain, a reliable description of the pressure dependence of the input data is required. Since in many cases such experimental data is not available or difficult or expensive to measure, theoretical first-principles predictions and their incorporation into semiphenomenological simulation tools are desired.[6]

The *ab initio* predictions of the Curie temperature are typically obtained combining spin density-functional theory (DFT) calculations with model Hamiltonians that are solved either analytically or numerically. Despite the fact that many magnetic model Hamiltonians exist, e.g., a multiband Hubbard model[7] or spin-fluctuation theory,[8,9] the Heisenberg model[10,11] is most often used to simulate systems with strong localized magnetic-moments. The T_C of the Heisenberg model is conventionally obtained either within the Monte Carlo method (Refs. 3 and 12–14) or within many-body theory[13,15,16] and is known to be in reasonable agreement with experiment.[12,16]

Regarding the pressure dependence of T_C the Heisenberg model provides successful predictions for complex systems such as, e.g., diluted magnetic semiconductors,[1] Fe-Co-alloys,[3] or Heusler alloys.[2] Surprisingly, for such a key material as pure bcc iron, the experimental pressure dependence of the Curie temperature, $\partial T_C(p)/\partial p \approx 0$,[17] has not yet been well reproduced by first-principles calculations.[18] At the same time, in a recent study,[11] we have shown that the Heisenberg model is capable to capture the thermodynamics of bcc iron very accurately up to high temperatures. The reason for such selective failure of the computational method is, therefore, not clear. It can be due to the inapplicability of the model Hamiltonian itself (i.e., it does not capture the essential physics of the system under consideration), the approximations used to solve the model Hamiltonian, here the mean-field (MF) and the random-phase approximation (RPA), or due to the model Hamiltonian input which is derived from the DFT calculations.

In this work, we investigate the pressure dependence of the Curie temperature in bcc Fe employing the Heisenberg approach and show that it is capable to reproduce the correct $T_C(p)$ dependence. On that basis we propose a physical explanation for the experimentally observed essential insensitivity of T_C on the applied pressure p. In contrast to the absolute theoretical value of T_C, which is found to be rather sensitive with respect to the used form of the exchange-correlation (xc-)functional, and to the approximations used to solve the Heisenberg model Hamiltonian, the qualitative $T_C(p)$ dependence is nearly independent of the theoretical approach.

II. THEORY

The total energy of the Heisenberg spin system is given by

$$E = \sum_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j, \tag{1}$$

where the magnitudes of the local magnetic moments $|\mathbf{m}_i|$ and $|\mathbf{m}_j|$ at lattice sites (i,j) are included into the exchange coefficients J_{ij}, and the directions of the local moments are given by the unit vectors $\mathbf{e}_i$ and $\mathbf{e}_j$. We note that the conventional Heisenberg model neglects longitudinal fluctuations of the spin moments. However, for the system under consideration it has been recently shown in an extensive work by Ruban *et al.*[14] that these fluctuations have only a marginal effect on T_C. The exchange coefficients J_{ij} for the Heisenberg model can be extracted either in real space J_{ij} (see e.g., Ref. 16) or in the reciprocal space $J_{\mathbf{q}}$, where $\mathbf{q}$, the wave vector, characterizes the spin wave. Although both representations are complementary, the treatment of choice depends on the method used to solve the Heisenberg Hamiltonian and on the corresponding numerical efforts. The real-space coefficients J_{ij} are typically used when employing the Monte Carlo approach, while the Fourier transformed $J_{\mathbf{q}}$ is a convenient quantity when solving the Heisenberg model within many-

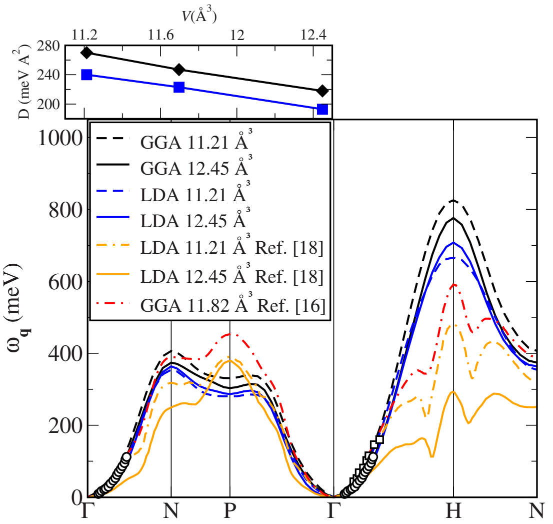

FIG. 1. (Color online) Calculated magnon spectra using planar spin spirals for two volumes, $V=11.21$ Å^3 (dashed lines) and $V=12.45$ Å^3 (solid lines), within GGA (black lines) and LDA (blue lines). For comparison the spectra obtained in Refs. 16 (red line) and 18 (orange lines) using TB-LMTO within GGA and TB-LMTO+ASA within LDA, respectively, are shown. Experiments: Ref. 29, measured at 10 K, open squares, and Ref. 30, Fe (12 at. % Si), measured at 300 K, open circles. Inset: Spin-wave stiffness D obtained by using a least square fit of the low $\overline{\Gamma H}$-energy branch up to $|\mathbf{q}|=0.4$ $(2\pi/a_0)$.

body theory. For an overview of the restrictions and difficulties of both methods we refer to Ref. 16.

In this work we apply the generalized Bloch's theorem to perform self-consistent spin-spiral calculations at different atomic volumes V and to obtain the exchange coefficients $J_{\mathbf{q}}(V)$. The spin-spiral state of the system for a single-atom unit cell corresponds to the magnetization that is given in the Cartesian coordinates by

$$\mathbf{m}_{\mathbf{q}}(\mathbf{R}) = m\begin{pmatrix}\cos \mathbf{qR} \sin \theta \\ \sin \mathbf{qR} \sin \theta \\ \cos \theta\end{pmatrix}, \tag{2}$$

where $\mathbf{R}$ is the lattice vector, m is the magnitude of the local magnetic moment, and θ is the cone angle of the spin wave. The energy differences of different spin spirals $\Delta E_{\mathbf{q},\theta}$ in a ferromagnet with a single-atom in the unit cell can be attributed to the magnon energies of the system[8]

$$\begin{aligned}\omega_{\mathbf{q}}(V) &= \frac{4}{m(V)}[J_0(V) - J_{\mathbf{q}}(V)] \\ &= \frac{4}{m(V)}\lim_{\theta\to 0}\frac{\Delta E_{\mathbf{q},\theta}(V)}{\sin^2\theta} \\ &\cong \frac{4}{m(V)}\Delta E_{\mathbf{q},\pi/2}(V),\end{aligned} \tag{3}$$

where $m(V)$ is the volume-dependent local magnetic moment. The latter relation is exact for a perfect Heisenberg system and, due to the stability of the local magnetic-moments versus the angle θ over a wide range of $\mathbf{q}$ vectors,[19] it is also known to provide a reasonable approximation in the case of bcc iron.[8,12] Equation (3) allows an estimate of the accuracy of the applied method by comparison of the calculated magnon spectrum with corresponding experimental data. To calculate the Curie temperature we use standard approximate analytic solutions of the Heisenberg model within many-body theory.[13,15,16] One obtains for the Curie temperature in mean-field approximation

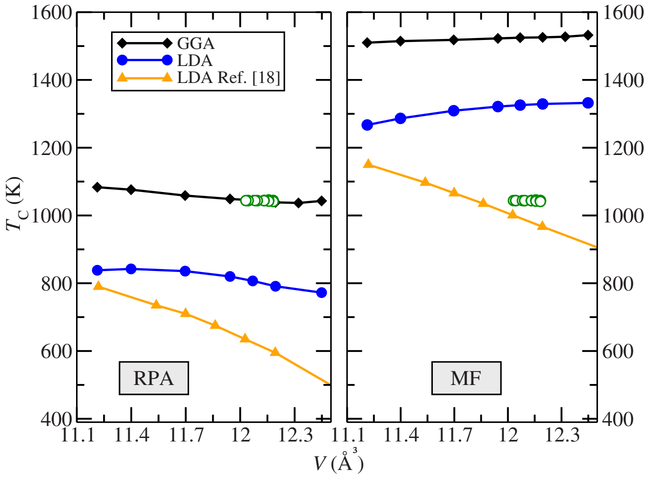

FIG. 2. (Color online) The Curie temperatures within the RPA (left panel) and the MF (right panel) approximation, for both LDA (blue lines) and GGA (black lines) xc-functionals. For comparison the results of Ref. 18 (LDA, orange curves), and the experimental Curie temperatures $T_C^{\mathrm{exp}}(V)$ for different volumes V (open green circles) are shown. The transformation of $T_C^{\mathrm{exp}}(p)$ (Ref. 17) to $T_C^{\mathrm{exp}}(V)$ is described in the text.

$$k_B T_C^{\mathrm{MF}}(V) = \frac{m(V)}{6}\sum_{\mathbf{q}}\omega_{\mathbf{q}}(V), \tag{4}$$

and in the random–phase approximation[20]

$$k_B T_C^{\mathrm{RPA}}(V) = \frac{m(V)}{6}\left(\sum_{\mathbf{q}}\frac{1}{\omega_{\mathbf{q}}(V)}\right)^{-1}. \tag{5}$$

It is well known that the MF solution typically overestimates critical quantities such as T_C, while the RPA solution provides more accurate predictions of the Curie temperature.[13,15,16] The pressure dependence of the Curie temperature $T_C(p)$ can be then obtained from the corresponding volume dependence $T_C(V)$ via $\partial T_C/\partial p = (\partial T_C/\partial V)(\partial V/\partial p)|_{V=V(T_C)}$, where $(\partial V/\partial p)|_{V=V(T_C)} = -[V/B_0(T_C)]$ is obtained by calculating[21] the temperature dependent bulk modulus B_0, as in detail described in Refs. 11 and 22. The backward transformation from the experimentally measured $T_C^{\mathrm{exp}}(p)$ to $T_C^{\mathrm{exp}}(V)$ was performed employing experimental data for $V^{\mathrm{exp}}(p,T=T_C)$.[23]

In this paper the DFT calculations are performed employing the VASP (Refs. 24 and 25) package using the projector augmented wave (PAW) method[26] within the local-density approximation (LDA) and the generalized gradient approximation (GGA) [Perdew-Burke-Ernzerhof (PBE) parametrization].[27] The following converged parameters have been used for both functionals: the density of the **k** points generated with the Monkhorst-Pack scheme is ≈ 5000 per atom, the plane-wave energy cutoff $E_{\mathrm{cut}}=450$ eV, and ≈ 3000 **q**-points for the magnetic integration in Eqs. (4) and (5). The total-energy differences are converged within less than 1 meV per atom which corresponds to uncertainties for the calculated T_C of less than 10 K. We calculate $T_C(V)$ starting from low volumes $V=11.21$ Å^3 up to higher $V=12.45$ Å^3, where the experimental volume at the Curie temperature under ambient pressure is around $V^{\mathrm{exp}}(T_C)\approx 12.1$ Å^3 and $T_C^{\mathrm{exp}}=1044$ K. The equilibrium volumes at $T=0$ K are given by $V_0^{\mathrm{GGA}}=11.39$ Å^3, $V_0^{\mathrm{LDA}}=10.31$ Å, and $V_0^{\mathrm{exp}}=11.69$ Å^3 for the experimental one, respectively. The contribution of phonon-magnon-coupling in this work is neglected since it is expected to be small.[28]

III. RESULTS

Based on Eq. (3), we have calculated the magnon spectrum $\omega_{\mathbf{q}}(V)$ of bcc iron at different volumes V for both LDA and GGA functionals. The results for two different volumes $V=11.21$ Å^3 and $V=12.45$ Å^3 are shown in Fig. 1 in comparison with experimental and previously published theoretical data from Refs. 16 and 18. The agreement between the experiment and our calculated frequencies is remarkable for LDA and GGA, indicating that both functionals provide a similarly accurate description of the magnetic excitations in the system. Within the region of experimentally accessible magnon energies there is also a fair agreement of the previously and presently calculated magnon spectra.

To elucidate the sensitivity of the Heisenberg model with respect to the quality of the model input data, we compare the volume dependence of the Curie temperature employing three different DFT data sets. Specifically, we compare the qualitative behavior of $T_C(V)$ obtained on the basis of the DFT calculations (i) with the PAW basis set and LDA functional, (ii) with the PAW basis and the GGA xc-functional, and (iii) with the tight-binding linear-muffin-tin-orbital (TB-LMTO) basis set within the atomic sphere approximation (ASA) and LDA xc-functional to the experimental results (see Fig. 2). Comparison of the solutions (i) and (ii) allows to figure out the effect of the xc-functional, while comparison of solutions (i) and (iii) allows us to identify possible uncertainties related to the use of different DFT basis sets and methodologies for extracting the magnetic exchange constants (frozen-magnon vs frozen-magnon torque method[36]).

Figure 2 highlights that $T_C(V)$ of the Heisenberg model is, apart from a constant shift, very robust with respect to the choice of the xc-functionals for both RPA and MF solutions when the same basis set is used. We further find that the use of the basis sets in the DFT calculations seem to have a noticeable effect on the theoretical predictions for $T_C(V)$. The comparison with experiment reveals that all theoretical approaches evaluated in this work, i.e., GGA/LDA input with RPA/MF, are in good qualitative agreement with experiment showing a very weak dependence of the Curie temperature on the volume.

To analyze in the following the reason for the weak volume (pressure) dependence of the calculated Curie temperature, we consider first the corresponding changes of the magnon spectra, as shown in Fig. 1, and observe that the magnon branches become softer with increasing volume of the atomic cell, i.e., the energies of the corresponding magnons become smaller. This can be interpreted as a decrease in the magnetic coupling between the localized magnetic moments. To quantify this effect we show in the inset of Fig. 1 the volume-dependent spin-wave stiffness D, derived in the low wavelength limit $\omega_{\mathbf{q}\to 0}\approx D\mathbf{q}^2$. According to Eqs. (4) and (5) the decrease in the magnon energies leads to a decrease in the Curie temperature. For both functionals GGA as well as for LDA the decrease is apparently compensated by another mechanism since the Curie temperature remains essentially constant with pressure (see Table I).

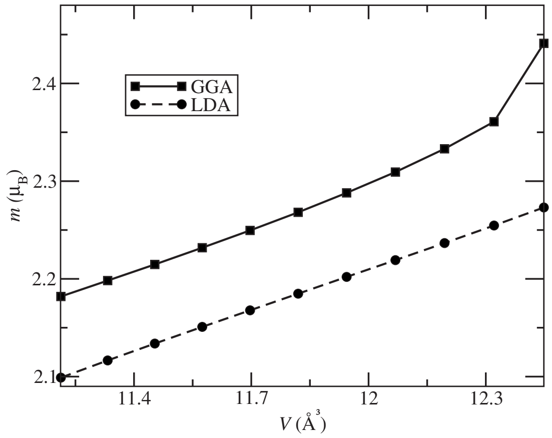

FIG. 3. The local magnetic spin moment of ferromagnetic bcc iron as function of the volume calculated within GGA (solid line) and LDA (dashed line) xc-functionals.

The reason for the stability of T_C versus the applied pressure can be understood recalling that the increase in the atomic volume does not only weaken the magnon excitation energies but also changes the magnitude of the local moments. We show the local magnetic spin moment $m(V)$ at different atomic volumes in Fig. 3 for both DFT functionals. At the theoretical groundstate volumes, i.e., V_0^{LDA} and V_0^{GGA}, LDA underestimates the local spin moment, while GGA slightly overestimates the experimental findings m^{exp} $(T=0\ \mathrm{K})=2.14\mu_B$.[31,32] In this work the small contribution to the local magnetic moment due to spin-orbit coupling $(<0.1\mu_B)$ is neglected. Both functionals show a smoothly increasing local magnetic spin moment with increase in the atomic volume, which is due to the increasing distance between the atoms and a consequent enhancement of the localization of the $3d$ electrons that form the local magnetic moments. According to Eqs. (4) and (5) the Curie temperature is directly proportional to the magnitude of the local magnetic moment $m(V)$, i.e., the increase in the local moments with increase in the volume should lead to a corresponding increase of the Curie temperature. Therefore, two coupled volume-dependent magnetic effects determine the behavior of the Curie temperature: The increase in the volume (decrease in the pressure) leads to a weakening of the spin-wave energy (reflecting the strength of the magnetic coupling) and simultaneously leads to an increase of the local magnetic moments. The sensitive interplay between these two effects

TABLE I. Derivatives of the Curie temperature T_C with respect to volume V and pressure p. $\partial T_C / \partial V$ is obtained by using a linear fit over the entire volume range from $V = 11.21$ Å^3 up to $V = 12.45$ Å^3. The values in brackets are obtained by the linear fit in a volume range from $V = 11.94$ Å^3 to $V = 12.19$ Å^3, which corresponds to the pressure range applied in experiment (≈ 20 kbar). The procedure of transforming $T_C(V)$ to $T_C(p)$ is described in the text.

	GGA		LDA		
	$\partial T_C / \partial V$ (K/10^{-1} Å^3)	$\partial T_C / \partial p$ (K/kbar)	$\partial T_C / \partial V$ (K/10^{-1} Å^3)	$\partial T_C / \partial p$ (K/kbar)	Ref.
MF	1.63(1.25)	−0.14(−0.11)	5.35(3.04)	−0.60(−0.34)	This work
RPA	−3.81(−3.30)	0.32(0.28)	−5.60(−11.51)	0.61(1.26)	This work
Experiment	0.0 ± 0.04	0.0 ± 0.03	0.0 ± 0.04	0.0 ± 0.03	17 and 33

determines the actual dependence of the Curie temperature on the volume (pressure) for a particular material.

All calculated volume and pressure dependencies are summarized in Table I. The volume dependence is obtained by using a linear fit over the entire atomic volume range from $V = 11.21$ Å^3 up to $V = 12.45$ Å^3. Since the pressure applied in experiment (17.5 kbar) corresponds to a smaller change of the volume, i.e., ≈ 0.25 Å^3 (see Refs. 33 and 34), we also fit the volume dependence of T_C in a volume range starting from $V = 11.94$ Å^3 to $V = 12.19$ Å^3. The corresponding results are also shown in Table I (shown in brackets).[35] Using the smaller fit-range, the volume and pressure dependencies are only slightly changed, except for the combination of LDA-RPA where the volume dependence is more pronounced. Except for the latter case, the calculated changes of the Curie temperature in the experimental range of applied pressures is less than 10 K. Regarding the quantitative agreement between theory and experiment, GGA appears to be closer to experiment with respect for the Curie temperature. The constant shift between LDA and GGA is a direct consequence of the higher calculated magnetic moment since the calculated magnon spectra within both GGA and LDA are almost similar. In overall the Curie temperatures calculated with both functionals do not significantly depend on the volume (see Table I), and we get within GGA $(\partial T_C^{\mathrm{RPA}} / \partial V) \approx 3.8$ K/10^{-1} Å^3. This corresponds to a change of the Curie temperature of $\Delta T_C \approx 5$ K for the pressure range investigated in the experiment[17] (up to 17.5 kbar).

IV. SUMMARY AND CONCLUSIONS

In this work we have calculated the pressure dependence of the Curie temperature T_C of bcc iron employing the conventional analytical solutions for the Heisenberg model, namely, the mean field and the random-phase approximation. The magnetic exchange constants of the underlying Heisenberg Hamiltonian J_{ij} are extracted from DFT calculations using the generalized Bloch's theorem for both LDA and GGA (PBE) xc-functionals. It is shown that both functionals yield good agreement for the magnon spectra and describe the correct pressure dependence of T_C within both MF and RPA. It is also shown that although the MF solution allows us to get a qualitatively correct dependence of $T_C(p)$, it significantly overestimates the magnitude of the Curie temperature. Our results confirm that considered solutions of the Heisenberg model (MF or RPA) in combination with DFT GGA as well as LDA calculations allow to qualitatively correctly reproduce the pressure dependence of the Curie temperature (GGA even quantitatively). In agreement with experiment, our theoretical calculations reproduce an extremely weak dependence of the Curie temperature on the pressures up to ≈ 20 kbar. The observed behavior can be understood as a result of the interplay between two competing pressure-dependent mechanisms, namely, the increase in the magnetic coupling between the localized magnetic moments in the system, and the simultaneous decrease in the magnitude of the local magnetic moments under the increase in the external pressure. While the first mechanism tends to increase the Curie temperature, the second mechanism acts against it. In the particular case of bcc iron, they nearly completely compensate each other, leading to $\delta T_C^{\mathrm{RPA}} \approx 0.3$ K/kbar. We expect that such a nearly perfect compensation of the two competing effects for bcc iron is not specific for all ferromagnetic materials, but is, likely, an exception. Nevertheless, the proposed picture of two competing magnetic mechanisms can be used for an intuitive interpretation of the physical reasoning underlying different behavior of the pressure-dependent Curie temperature in other ferromagnetic materials.

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