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Prediction of the Curie temperature considering the dependence of the phonon free energy on magnetic states

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Prediction of the Curie temperature is of significant importance for the design of ferromagnetic materials. One of the most widely used methods to estimate the Curie temperature from first principles relies on a spin Hamiltonian, for example, the Heisenberg Hamiltonian, and exchange coupling parameters obtained by first-principles calculations at zero temperature. Even though there have been attempts to include the effects of magnetism on phonons, the influence of magnetism-dependent phonons on magnetism has been disregarded in the theoretical estimation of the Curie temperature. Here, we propose a first-principles thermodynamic approach to minimise the total free energy considering both the influences of magnetism on phonons and the feedback effect from phonons to magnetism. By applying our scheme to body-centered cubic Fe, we find a significant reduction of the Curie temperature due to the feedback effect. This result indicates the importance of the feedback effect for a quantitative description of finite-temperature magnetism. In addition, we point out that the reduction in the theoretical Curie temperature arises in a wide range of ferromagnetic materials that exhibit phonon softening due to magnetic disordering.

INTRODUCTION

The Curie temperature (T_C) is one of the essential properties of ferromagnetic (FM) materials because it characterises their applicability and performance[1,2]. The method of predicting T_C is, therefore, important not only for a fundamental understanding of FM materials but also for designing materials to work in specific temperature ranges. A typical technique for predicting T_C is a downfolding method from first-principles calculations to an effective lattice model as below: First, exchange coupling constants (J_{ij}) are derived by applying Green's function-based methods[3,4] or a frozen magnon approach[5,6]. Second, an effective lattice model, such as the Heisenberg model, is built, and J_{ij} is assigned to the model. Finally, the model is solved analytically or numerically, and T_C is estimated. This technique is applied to a broad range of materials, such as 3d transition metals[4,7–11] and rare-earth magnets[12–17]. Many studies have demonstrated that this prediction technique has some predictive accuracy.

Such a technique does not usually include temperature effects on magnetic interactions. Moreover, temperature-induced interactions between magnetism and other excitations, such as phonons, sometimes make an accurate prediction of T_C difficult. In a high-temperature range around T_C, there are two types of interactions between magnetism and phonons. One is the effect of thermal atomic displacements on J_{ij}[18–20]: Changes in J_{ij} obviously modify T_C. The other interaction is the effect of magnetic disordering on phonon frequencies. Early studies by Baltensperger and Helman[21] and Baltensperger[22] showed that the phonon frequencies of magnetic compounds depend on the spin order, and this type of interaction is still actively studied, mainly in the context of strongly correlated systems, in metallic oxides. Magnetism-dependent phonons were also found in relatively simple FM materials, such as body-centered cubic (bcc) Fe and Pd_3Fe[23–25]. These FM materials exhibit phonon softening phenomena at elevated temperatures near T_C, and several theoretical studies have revealed that this phonon softening is due to magnetic disordering[25–32]. Regarding the predictive accuracy for

T_C, magnetism-dependent phonons, including the phonon softening, do not apparently seem to be related to T_C. However, we recognise that this interaction is closely related to T_C from a thermodynamic viewpoint.

Thermal equilibrium states at finite temperatures correspond to the minimum of the total free energy at given conditions. This is usually called as the minimum principle for the free energy. A common procedure to study finite-temperature magnetism is constructing a magnetic Hamiltonian and deriving thermodynamic quantities, such as the magnetic energy and the magnetisation. This series of procedures agrees with the interpretation that equilibrium magnetic quantities are determined through the magnetic free energy only. This interpretation, however, collapses for systems that exhibit strong phonon softening due to magnetic disordering. The phonon frequencies are directly related to the phonon free energy. Thus, the phonon softening due to magnetic disordering means that magnetic states affect the phonon free energy as well as the magnetic free energy. As a result, equilibrium magnetic states should be determined not only based on the magnetic free energy but also on the phonon free energy, according to the minimum principle for the free energy. We call this effect of phonons on equilibrium magnetic states through the changes in the phonon free energy as a thermodynamic feedback effect. This feedback effect influences T_C as a consequence of the change in the equilibrium magnetic states. However, the significance of the feedback effect on T_C is unclear because the existence of this effect has been overlooked.

In this article, we propose a thermodynamic formulation for treating the feedback effect from phonons to magnetism. This formulation results in a simple optimisation problem for the total free energy. The ingredients to solve this problem are evaluated by first-principles phonon calculations and Monte Carlo simulations based on the Heisenberg model. By applying the formulation to bcc Fe, we demonstrate that T_C of bcc Fe significantly decreases by nearly 560 K. This result proves that the feedback effect is

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crucial for an accurate description of T_C. Thus, it is rather a correct tendency that the Heisenberg model with exchange couplings in the paramagnetic (PM) disordered local moment (DLM) state overestimates T_C significantly. In addition, we found that the significant decrease in T_C of bcc Fe contains an important message for the validation of the theory of finite-temperature magnetism: an accurate theory ignoring the thermodynamic feedback effect should rather overestimate the T_C of bcc Fe. Our insight and formulation will be foundations for a deeper quantitative understanding of finite-temperature magnetism from the viewpoint of spin–lattice couplings.

The remainder of this paper is organised as follows. First, we introduce a thermodynamic formulation for treating the thermodynamic feedback effect. Our formulation based on the minimum principle for the free energy is justified through the Legendre transformation and results in a simple optimisation problem. Next, we evaluate the magnetic entropy and the phonon free energy of bcc Fe as functions of the magnetic energy. These functions are needed to solve the optimisation problem. Finally, we evaluate the equilibrium magnetic energy around T_C by solving the optimisation problem. The shift in T_C of bcc Fe is estimated from the results of the equilibrium magnetic energy.

RESULTS

Thermodynamic formulation for magnetic materials

In conventional thermodynamic approaches for magnetic materials, the phonon and magnetic contributions are adiabatically decoupled. We start from this typical case for comparison with our formulation. The fundamental relation is written as

$$E_{\text{tot}}(S_{\text{ph}}, S_{\text{mag}}, V, M, N) \approx E_{\text{ph}}(S_{\text{ph}}, V, N) + E_{\text{mag}}(S_{\text{mag}}, V, M, N), \quad (1)$$

where E is the internal energy (hereafter referred to as simply "the energy"), S is the entropy, V is the volume, M is the total magnetic moment and N is the number of atoms. In multi-component systems, N is replaced with $\{N_1, N_2, \dots\}$. The subscripts tot, ph and mag represent total, phonon and magnetic, respectively. Here, we define the Gibbs free energy in an equilibrium state through the Legendre transformation as

$$G(T, p, H, N) = \min_{S,V,M}[E(S, V, M, N) - TS + pV - \mu_0 HM], \quad (2)$$

where T represents the temperature, p the pressure, H the external magnetic field and μ_0 the vacuum permeability. The mathematical notation $\min_x[f(x)]$ means finding the minimum value of the function $f(x)$ by changing the variable x. In the case of Eq. (2), the minimisation is performed to minimise the function in the square bracket with S, V and M as variables for given T, p and H. The total Gibbs free energy, G_{tot}, in the adiabatically decoupled system is derived by applying the Legendre transformation:

$$\begin{aligned} &G_{\text{tot}}(T, p, H, N) \\ &= \min_{S_{\text{ph}}, S_{\text{mag}}, V, M}[E_{\text{ph}}(S_{\text{ph}}, V, N) - TS_{\text{ph}} + E_{\text{mag}}(S_{\text{mag}}, V, M, N) - TS_{\text{mag}} + pV - \mu_0 HM], \end{aligned} \quad (3)$$

$$= \min_{E_{\text{ph}}, E_{\text{mag}}, V, M}[E_{\text{ph}} - TS_{\text{ph}}(E_{\text{ph}}, V, N) + E_{\text{mag}} - TS_{\text{mag}}(E_{\text{mag}}, V, M, N) + pV - \mu_0 HM], \quad (4)$$

$$= \min_{E_{\text{ph}}, E_{\text{mag}}, V}[E_{\text{ph}} - TS_{\text{ph}}(E_{\text{ph}}, V, N) + E_{\text{mag}} - TS_{\text{mag}}(E_{\text{mag}}, V, H, N) + pV - \mu_0 HM], \quad (5)$$

$$= \min_{E_{\text{ph}}, E_{\text{mag}}}[E_{\text{ph}} - TS_{\text{ph}}(E_{\text{ph}}, p, N) + E_{\text{mag}} - TS_{\text{mag}}(E_{\text{mag}}, p, H, N) + pV - \mu_0 HM]. \quad (6)$$

Note that V and M in Eq. (6) are no longer parameters of the minimisation but thermodynamic state functions in equilibrium. In the transformation from Eqs. (3) to (4), we used the one-to-one correspondence between E and S by fixing the thermodynamic parameters, V, M and N. This correspondence is a property that

any thermodynamic system must satisfy. As an example, we can find a one-to-one correspondence between the magnetic energy and the magnetic entropy from Fig. 2b. By considering this correspondence, we can choose either E or S as a variable for the minimisation procedure. In this adiabatically decoupled system, the equilibrium magnetic energy ($E_{\text{mag}}^{\text{eq}}$) at T, p, H and N is determined as

$$E_{\text{mag}}^{\text{eq}}(T, p, H, N) = \underset{E_{\text{mag}}}{\text{argmin}}\left[G_{\text{mag}}^{\text{ad}}(T, E_{\text{mag}}, p, H, N)\right], \quad (7)$$

where $G_{\text{mag}}^{\text{ad}}$ denotes the adiabatically decoupled magnetic free energy defined as

$$G_{\text{mag}}^{\text{ad}}(T, E_{\text{mag}}, p, H, N) = E_{\text{mag}} - TS_{\text{mag}}(E_{\text{mag}}, p, H, N) + pV - \mu_0 HM, \quad (8)$$

and $\text{argmin}_x[f(x)]$ denotes the value of the variable x at which the function $f(x)$ is minimised. Although we also refer to the expression in Eq. (8) (and Eqs. (12) and (13) defined later) as (magnetic or phonon) free energy hereafter, note that this is just a shorthand notation: The usual definition of free energy refers to the one after the minimisation procedure in Eq. (6) has been performed. The blue part in Fig. 1 is an example of the procedure in Eq. (7) for $p = 0$ and $H = 0$ conditions.

Next, we incorporate the dependence of the phonon free energy on magnetic states. Körmann et al. treated the forces on each atom as a function of the magnetic energy. As a result, the phonon frequencies and, consequently, the phonon free energy have a dependence on the magnetic energy (see "Methods" section). Thermodynamically speaking, this treatment indicates that the phonon internal energy depends not only on the phonon entropy but also on the magnetic entropy and the total magnetic moment. The fundamental relation can thus be written as

$$E_{\text{tot}}(S_{\text{ph}}, S_{\text{mag}}, V, M, N) \approx E_{\text{ph}}(S_{\text{ph}}, S_{\text{mag}}, V, M, N) + E_{\text{mag}}(S_{\text{mag}}, V, M, N). \quad (9)$$

In principle, E_{mag} is also dependent on S_{ph}. This dependence can be regarded as an influence of thermal atomic displacements on magnetic quantities that determine finite-temperature properties.
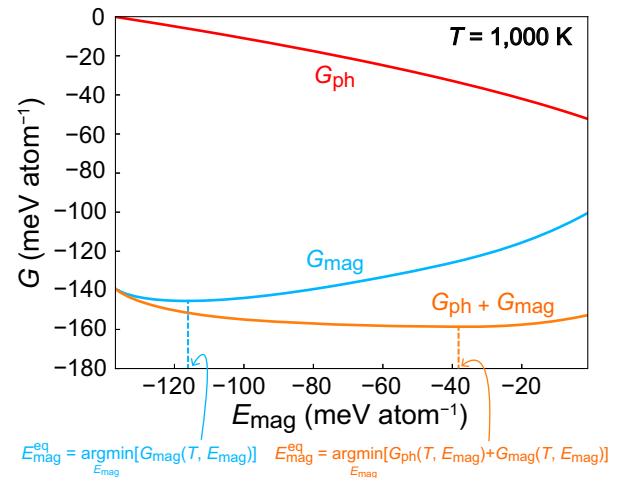

Fig. 1 Dependence of the free energies on the magnetic energy for bcc Fe. The temperature is fixed at 1000 K. Within a common framework using the Heisenberg model, the equilibrium magnetic energy ($E_{\text{mag}}^{\text{eq}}$) corresponds to the minimum of the magnetic free energy, G_{mag} (blue line). In contrast, $E_{\text{mag}}^{\text{eq}}$ in our scheme corresponds to the minimum of the total free energy, $G_{\text{ph}} + G_{\text{mag}}$ (orange line). The origin of the phonon free energy (red line) is chosen to be the value at the ferromagnetic (left-side) limit. Note that the usual definition of free energy refers to the one after the minimisation procedure in Eq. (6) or (11).
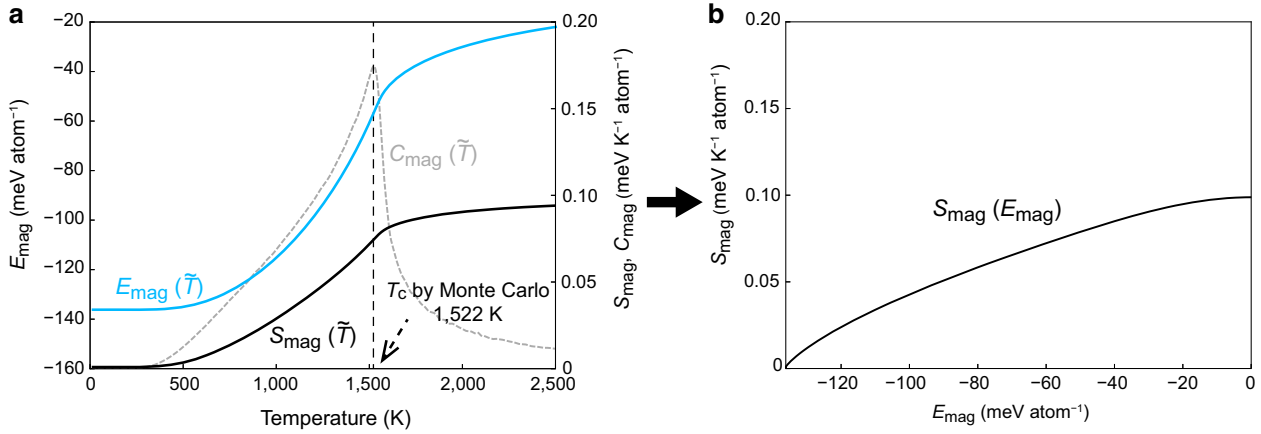
Fig. 2 Thermodynamic quantities of bcc Fe obtained by the rescaled Monte Carlo method. a Magnetic energy, entropy and specific heat vs. magnetic temperature in the spin–lattice model. The theoretical Curie temperature T_C was identified from the peak of the specific heat. **b** Magnetic entropy vs. magnetic energy.

If we want to incorporate this effect into the thermodynamic formulation, we have to express the magnitude of the effect in terms of a thermodynamic quantity, such as S_{ph}. However, the correspondence between the thermal displacements and S_{ph} is not obvious. Moreover, the magnitude of the effect of thermal atomic displacements on T_C is still under debate even in the case of bcc Fe[19,20,33]. Thus, we focus only on the dependence of E_{ph} on S_{mag}.

We apply the Legendre transformation as before:

$$G_{tot}(T, p, H, N) = \min_{S_{ph}, S_{mag}, V, M}[E_{ph}(S_{ph}, S_{mag}, V, M, N) - TS_{ph}$$
$$+ E_{mag}(S_{mag}, V, M, N) - TS_{mag} + pV - \mu_0 HM], \quad (10)$$

$$= \min_{E_{mag}}[G_{ph}(T, E_{mag}, p, H, N) + G_{mag}(T, E_{mag}, p, H, N)], \quad (11)$$

where

$$G_{mag}(T, E_{mag}, p, H, N) = E_{mag} - TS_{mag}(E_{mag}, p, H, N) - \mu_0 HM, \quad (12)$$

$$G_{ph}(T, E_{mag}, p, H, N) = \min_{E_{ph}}[E_{ph} - TS_{ph}(E_{ph}, E_{mag}, p, H, N) + pV]. \quad (13)$$

The details on the above derivation is described in Supplementary notes. Equation (11) is intuitive from a thermodynamic viewpoint: The equilibrium magnetic energy (E_{mag}^{eq}) is determined to minimise the total free energy as

$$E_{mag}^{eq}(T, p, H, N) = \underset{E_{mag}}{argmin}[G_{ph}(T, E_{mag}, p, H, N) + G_{mag}(T, E_{mag}, p, H, N)]. \quad (14)$$

As a microscopic description of Eq. (14) by statistical mechanics, an analytical formula for G_{ph} can be provided within the harmonic approximation, whereas G_{mag} expressed as Eq. (12) can be evaluated by the Heisenberg model. The details are explained in the next section. In the following sections, we apply this formalism to bcc Fe for $p = 0$, $H = 0$ and fixed N conditions. In this condition, G_{mag}^{ad} in Eq. (8) and G_{mag} in Eq. (12) are equivalent; thus, we will use the notation G_{mag} only. Accordingly, we omit the variables p, H and N in the thermodynamic formulations hereafter.

The magnetic entropy and the phonon free energy
As an example, we demonstrate the significance of the dependence of the phonon free energy on magnetic states for bcc Fe. As a starting point, we evaluate the magnetic entropy and

the phonon free energy depending on the magnetic energy ($S_{mag}(E_{mag})$ and $G_{ph}(T, E_{mag})$), in order to solve the minimisation problem in Eq. (14).

To obtain $S_{mag}(E_{mag})$, we carried out calculations using a rescaled Monte Carlo method[34] based on the Heisenberg model. This method brings the thermodynamic quantities derived from classical Monte Carlo simulations closer to those of quantum Monte Carlo simulations. The exchange coupling constants (J_{ij}) in the Heisenberg model are derived from the PM DLM state[3,35] (see "Methods" section). The magnetic energy and entropy as functions of the lattice-model temperature $\tilde{T}$ are shown in Fig. 2a. The theoretical T_C (1522 K) is higher than the experimental value (1043 K). This overestimation has also been reported in the previous studies[3,20,36] using the DLM state. The overestimation has been recognised as a disadvantage of the DLM state and will be discussed later in conjunction with our results. As this magnetic system does not show a first-order phase transition, a one-to-one correspondence holds not only between E_{mag} and S_{mag} but between them and $\tilde{T}$,

$$E_{mag} \leftrightarrow \tilde{T} \leftrightarrow S_{mag}. \quad (15)$$

This correspondence in the magnetic system is justified by the monotonic behaviour of E_{mag} and S_{mag} with respect to $\tilde{T}$ (Fig. 2a). We constructed the function $S_{mag}(E_{mag})$ by using this correspondence (Fig. 2b).

Phonon frequencies depending on the magnetic energy ($G_{ph}(T, E_{mag})$) can be calculated using first-principles phonon calculations and Monte Carlo simulations, following previous research[29,37] (see "Methods" section). Phonon dispersions and the phonon density of states of bcc Fe dependent on the magnetic energy are shown in Fig. 3. The dependence of the frequencies on the magnetic energy is represented through the parameter a (see "Methods" section). The calculated phonon dispersions in the FM ($a = 1$) and PM DLM ($a = 0$) limits are consistent with the previous research[29]. Once the phonon frequencies at various magnetic energies (i.e. at various a) are calculated, the phonon free energy per atom for $p = 0$ and $H = 0$ can be evaluated from the analytical form[38],

$$G_{ph}(T, E_{mag}) = \frac{k_B T}{N_{\mathbf{q}}} \sum_{\mathbf{q}, j} \log\left[2 \sinh\left(\frac{\hbar \omega_{\mathbf{q}j}(E_{mag})}{2 k_B T}\right)\right], \quad (16)$$

where k_B represents the Boltzmann constant, $\omega_{\mathbf{q}j}(E_{mag})$ denotes the phonon frequency of the jth branch at a wavenumber of $\mathbf{q}$ as a function of E_{mag} and $N_{\mathbf{q}}$ is the total number of $\mathbf{q}$ points. Note that the more disordered the magnetic state, the lower the phonon frequencies (Fig. 3). This indicates that the phonon free energies of PM states are smaller than the value of the FM state
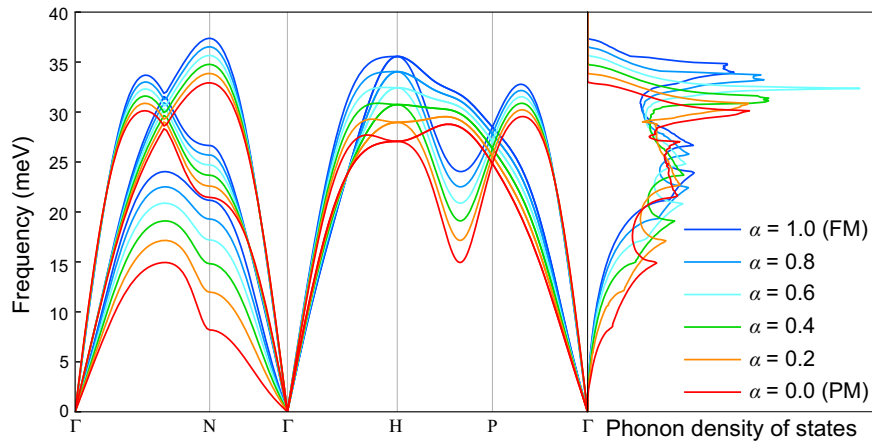
Fig. 3 The phonon dispersions and the phonon density of states of bcc Fe. The line colours represent the degree of magnetic order from the ferromagnetic limit (FM, $\alpha = 1$) to the paramagnetic state (PM, $\alpha = 0$) as shown on the right-hand side. For the definition of α, see the "Methods" section.

because of the monotonicity of the phonon free energy in Eq. (16) with respect to the phonon frequency. Consequently, PM states are thermodynamically stabilised by the phonon softening effect.

Total free energy minimisation

We are now able to proceed to the total free energy minimisation in Eq. (14) using the functions $G_{ph}(T, E_{mag})$ and $S_{mag}(E_{mag})$. Minimisation procedures are simple. First, we fix the temperature at T. Second, we calculate the total free energy ($G_{ph}(T, E_{mag}) + E_{mag} - TS_{mag}(E_{mag})$) with E_{mag} as a variable. The variable range of E_{mag} is between the FM limit and the PM limit. Third, we find E_{mag} that corresponds to the minimum point of the total free energy (E_{mag}^{eq}). The orange part in Fig. 1 is an example of these steps at 1000 K. Finally, these steps are repeated for a temperature range around T_C. From Fig. 1, we also understand that the decrease in the phonon free energy and the increase in the magnetic free energy due to magnetic disordering are of the same order. The equilibrium magnetic state is determined by the competition between them and, consequently, the equilibrium magnetic energy will also be different from the results when considering only G_{mag} (Fig. 2a).

The equilibrium magnetic energies of bcc Fe obtained by two different methods are shown in Fig. 4. One is the minimisation of the total free energy, as expressed in Eq. (14); the other is the minimisation of the magnetic free energy only, as expressed in Eq. (7). Note that the latter method is equivalent to the Monte Carlo simulation based on the Heisenberg model, that is, the blue lines in Figs. 2a and 4 are the same. The equilibrium magnetic energies obtained by the minimisation of the total free energy are larger than those when considering only G_{mag}. This is, as mentioned before, due to the stabilisation of PM states by the phonon softening effect. The magnitude of the stabilisation indicates that the phonon contribution is not negligible at all in the determination of equilibrium magnetic states around T_C.

The stabilisation of PM states leads to a decrease in T_C. As shown in Fig. 4, as a result of the minimisation of the total free energy, T_C is lowered to 959 K when compared to the estimation using G_{mag} only (1522 K). This represents a decrease of nearly 560 K. Notably, T_C when considering both G_{mag} and G_{ph} is much closer to the experimental value (1043 K) than when considering only G_{mag}, that is, T_C in the Heisenberg model. Although $T_C = 959$ K is lower than the experimental value, the anharmonicity of phonons probably compensates for the deviation. Heine et al.[31] investigated the phonon softening phenomenon in bcc Fe by including the anharmonic effects. They showed that at 1043 K, a temperature at which the anharmonicity is effective, the
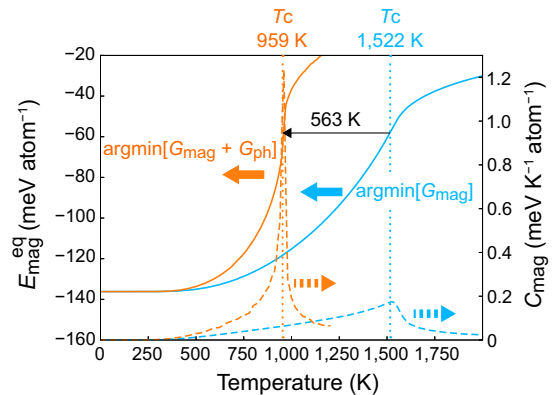

Fig. 4 Temperature dependence of equilibrium magnetic energy and magnetic specific heat. The equilibrium magnetic energy and the specific heat are represented by solid and dashed lines, respectively. The orange (blue) lines represent the results obtained by the minimisation of the total free energy (the magnetic free energy only). The results shown in the blue lines are the same as in Fig. 2.

differences between the frequencies of the FM and PM states are reduced compared with those at 300 K. Thus, the difference in the phonon free energies between the two magnetic states is also reduced. This consequently makes the degree of the decrease in T_C smaller than the one found in our study. The underestimation seen in our result is, therefore, qualitatively correct.

Our thermodynamic formulation as the minimisation of the total free energy indicates that T_C of bcc Fe decreases by the stabilisation of PM states due to the phonon softening irrespective of the microscopic description of magnetism. Therefore, an accurate theory of finite-temperature magnetism that ignores the thermodynamic feedback effect should overestimate T_C of bcc Fe. Note that this general statement is not limited to the Heisenberg model. In this sense, it is appropriate that the PM DLM state overestimates T_C significantly[3,20,36]. There are typically two representative reference magnetic states in the derivation of J_{ij}, the FM state and the PM DLM state. Even though the FM state provides T_C much closer to the experimental value[4-6,8,11,39,40] than the DLM state does, the agreement with T_C when the thermodynamic feedback effect is included implies that the PM DLM state is better than the FM state for the derivation of J_{ij}. It should be noted, however, that the magnetic state at T_C is characterised by the absence of long-range order and the presence of short-range

Table 1. Calculated exchange coupling constants (J_{ij}) of bcc Fe for the paramagnetic DLM state.

Nearest neighbour	J_{ij} (meV)
First	27.18
Second	2.62
Third	1.33
Fourth	0.21
Fifth	−1.37

order at the same time, making a contrast with the PM and FM limits.

We would like to emphasise the generality of the decrease in the theoretical T_C. The PM DLM state consists of randomly oriented magnetic moments; thereby, the splitting of electronic energy levels occurs due to the randomness in the ligand field considering the exchange potential, that is, the exchange ligand field[41]. The impact of the electronic energy splitting in the DLM state is significant for highly symmetric (e.g. cubic) materials that exhibit high degeneracy. This change in the electronic structure by the magnetic disordering modifies phonon frequencies as well. Therefore, a decrease in the theoretical T_C due to the phonon softening is likely to arise not only in bcc Fe but also in other FM materials with high crystal symmetry.

Our thermodynamic formulation becomes complete if we incorporate the dependence of E_{mag} on S_{ph}. However, to our knowledge, a consensus is yet to be reached regarding the degree of its impact on finite-temperature magnetism and theoretical framework for treating the effect. For example, a study combining J_{ij} calculations and molecular dynamics showed that T_C of bcc Fe decreased ~400 K due to thermal atomic displacements[20]. In contrast, the decrease in T_C of bcc Fe within the dynamical spin-fluctuation theory incorporating the lattice vibration[33] was one-third of that obtained by the former approach. Thus, further progress will be necessary to formulate the dependence of E_{mag} on S_{ph}.

DISCUSSION

We have quantitatively evaluated the thermodynamic feedback effect from phonons to magnetism on T_C for bcc Fe. The phonon softening due to magnetic disordering leads to the stabilisation of the PM DLM states. As a result, T_C of bcc Fe decreased by nearly 560 K from the value reached when ignoring the feedback effect, that is, the value for the Heisenberg model. This implies that overestimation of T_C within the Heisenberg model with J_{ij} in the PM DLM state is a correct tendency. The large decrease in T_C for bcc Fe indicates the importance of the concept of the stabilisation of PM states by the phonon softening. This concept holds not only within the Heisenberg model but also for any theoretical framework of finite-temperature magnetism. Therefore, we suggest that an accurate theory ignoring the thermodynamic feedback effect should overestimate T_C for bcc Fe.

Finally, we mention the applicability of our thermodynamic formulation. We focused on bcc Fe in this study, but our formulation is not restricted to it: It is intriguing to apply the formulation to other magnetic materials that exhibit magnetism-dependent phonons. In addition, the core concept of the formulation can be applied to not only the interaction between phonons and magnetism but also other interacting excitation phenomena. If a contribution (X) affects another contribution (Y) and changes the free energy of Y, the thermal equilibrium state of X is also affected through the minimum principle for the free energy. In our study, X refers to magnetic states, and Y denotes phonons. Therefore, the concept of our thermodynamic

formulation can be applied to other interacting excitations if appropriate treatments using thermodynamic variables are established to describe the interaction. The formulation will be helpful for a quantitative description of the finite-temperature properties of materials.

METHODS

First-principles phonon calculations

All phonon calculations were carried out within the harmonic approximation. To evaluate the phonon frequencies for an intermediate magnetic ordering, we employed a force-averaging method[29,37]. In this method, the atomic forces for an intermediate magnetic ordering are determined by mixing the forces of the FM and PM DLM states. Following refs [29,37], the force constants of an intermediate magnetic ordering can be written as

$$\boldsymbol{\Phi}_{i-j} \approx a\boldsymbol{\Phi}_{i-j}^{FM} + (1-a)\boldsymbol{\Phi}_{i-j}^{PM}, \tag{17}$$

where $\boldsymbol{\Phi}_{i-j}$ is the force constants between the pair of ith and jth atoms and a is a mixing parameter. A solid expression of a using the magnetic energy (E_{mag}) can be written as[29]

$$a = \frac{E_{mag} - E_{mag}^{PM}}{E_{mag}^{FM} - E_{mag}^{PM}}, \tag{18}$$

where E_{mag}^{PM} (E_{mag}^{FM}) is the magnetic energy in the high (low) temperature limit in the Heisenberg model. In the original paper[29], the temperature dependence of E_{mag} is determined by Monte Carlo results only. Therefore, a was treated as a function of the magnetic temperature in the spin–lattice model ($a = a(\widetilde{T})$). This is equivalent to the equilibrium magnetic energy at a temperature being determined to minimise the magnetic free energy, not the total free energy. In contrast, in our study, a is not regarded as a function of temperature but is interpreted as a function of the magnetic energy ($a = a(E_{mag})$). This interpretation allows for the phonon free energy to be regarded as a function of the magnetic energy ($G_{ph} = G_{ph}(T, E_{mag})$). The temperature dependence of E_{mag} is determined after the minimisation of the total free energy in Eq. (14). This interpretation is the key for solving the minimisation problem in the minimum principle for the free energy. We also mention that the difference in the evaluation method for the magnetic energy between the previous work[29] and this study. The magnetic energy in Eq. (18) was evaluated using quantum Monte Carlo simulations in the previous work. In contrast, we employed the rescaled Monte Carlo approach, which is a post-process method of classical Monte Carlo simulations to reproduce the thermodynamic quantities of quantum Monte Carlo simulations. A common point between both methods is that they lead to the thermodynamic quantities reflecting the quantum effect.

The PM DLM state in the phonon calculations was mimicked by a special quasirandom structure (SQS)[42] on the spin configuration (up and down)[26,43] as obtained from the ATAT package[44]. The force constants were calculated by the finite-displacement approach[45] with random displacements of 0.01 Å to all atoms. The use of the SQS for phonon calculations is based on the approximation that the atoms in the PM DLM state feel an averaged potential in various spin configurations. An SQS on the spin configuration contains various local spin configurations. Therefore, the force constants of the averaged potential can be realised by the force constants determined by sampled displacement and force data sets from the SQS. We used a $3 \times 3 \times 3$ cubic supercell (54 atoms) for the force calculations for both FM and PM conditions. The employed lattice constant $a = 2.86$ Å was derived by combining the relaxed lattice constant and experimental lattice expansion ratio at $T = 1043$ K[46]. Although this determination procedure of lattice constants probably gives some pressure even in the framework of the quasiharmonic approximation, we assume its effect is minor, and so we fixed the volume. First-principles calculations were based on density functional theory within the projector augmented-wave method[47], as implemented in the VASP code[48,49]. For the exchange-correlation functional, the generalised gradient approximation parametrised by Perdew, Burke and Ernzerhof[50] was used. The cutoff energy of 360 eV and a $6 \times 6 \times 6$ k-point grid were used for the supercell for the force calculations. The derivation of the force constants and the calculations of the phonon free energy were performed by using the ALAMODE code[51].

Calculations of exchange coupling constants

Exchange coupling constants, J_{ij}, in the Monte Carlo simulations were derived with the magnetic force theorem[4] and the Korringa–Kohn–Rostoker (KKR) Green's function method along with the coherent potential approximation (CPA)[52,53], implemented in the AkaiKKR code (http://kkr.issp.u-tokyo.ac.jp/jp/)[53]. The exchange-correlation functional was treated within the local density approximation[54]. The lattice constant was set to be the same as in the phonon calculations. PM DLM state[3,35] was employed as a reference magnetic state in the derivation of J_{ij}. The calculated J_{ij} values are listed in Table 1.

Monte Carlo simulations

To evaluate the magnetic entropy as a function of the magnetic energy, we employed the rescaled Monte Carlo method[34] that reproduces the quantum specific heat from the classical specific heat. The specific heat to be rescaled is obtained by classical Monte Carlo simulations for the Heisenberg model,

$$H = -2 \sum_{(i,j)} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j, \tag{19}$$

where J_{ij} denotes the exchange coupling constant and $\mathbf{e}_i$ is the unit vector on site i. We included up to the third nearest-neighbour pairs as interacting shells. Classical Monte Carlo simulations were performed using the ALPS code[55]. The magnetic energy and entropy were derived by integrating the specific heat. The spin quantum number $s = 1.07$ for the DLM condition as calculated by KKR-CPA was used in the rescaled Monte Carlo method. The Monte Carlo simulations were carried out using $16 \times 16 \times 16$ sites and involve 300,000 steps for equilibration and 2,700,000 steps for averaging. The temperature grid of 0.1 mRy was used in the range near T_C; otherwise, we used the grid of 0.2 mRy. Note that the entropy in the rescaled Monte Carlo method does not go to zero at $T \to 0$. Thus, this method is not suitable for describing thermodynamic quantities in a low-temperature range. Our thermodynamic formulation, however, needs only the result at a temperature range around T_C. Thus, the shortcoming does not matter in this study.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CODE AVAILABILITY

The calculation codes used in this paper are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

The formulation was established by T.T. and Y.G. All of the calculations were conducted by T.T. The project was supervised by Y.G. All authors discussed the results and contributed to writing the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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