The phonon softening due to melting of the ferromagnetic order in elemental iron

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We study a fundamental question of the lattice dynamics of a metallic ferromagnet in the regime where the static long range magnetic order is replaced by the fluctuating local moments embedded in a metallic host. We use the ab initio Density Functional Theory(DFT)+embedded Dynamical Mean-Field Theory(eDMFT) functional approach, to address the dynamic stability of iron polymorphs and the phonon softening with increased temperature. We show that the non-harmonic and inhomogeneous phonon softening measured in iron is a result of the melting of the long range ferromagnetic order, and is unrelated to the first order structural transition from the BCC to the FCC phase, as is usually assumed. We predict that the BCC structure is dynamically stable at all temperatures at normal pressure, and is only thermodynamically unstable between the BCC-α and the BCC-δ phase of iron.

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The theoretical description of the interplay between structural, magnetic and electronic degrees of freedom in transition metals at finite temperatures is a central problem of condensed matter physics. The elemental iron is the archetypical system to study the coupling of the ferromagnetism and electronic degrees of freedom with the crystal structure, and its importance in both the geophysics at high temperatures and high pressures, and metallurgy at normal pressure but finite temperature, has made iron one of the most thoroughly studied materials. Its magnetic and mechanical properties undergo major changes through a series of structural phase transitions, but the clear understanding of the feedback effect of magnetism on the structural stability has been elusive.

Elemental iron cristalizes in four different polymorphs, among them are two body-centered cubic (BCC) phases and a face-centered-cubic (FCC) phase, all realized at normal pressure. The BCC-α phase is stable below 1185 K, the FCC-γ phase follows and is stable up to 1670 K, where it is transformed to the BCC-δ phase, which is stable up to the melting point around 1811 K. The α phase is ferromagnetic (FM) below the Curie temperature $T_c = 1043$ K.

Many theoretical methodologies to describe magnetism and energetics of different allotropes have been developed over the past few decades. The conventional Density Functional Theory (DFT), in its GGA approximation, predicts quite well the magnetic properties of the FM BCC structure with correct moment and good bulk modulus. However GGA severely underestimates the stability of the competing non-magnetic FCC phase, which is around 300meV higher in energy than FM BCC phase, and is dynamically unstable with many imaginary phonon branches [1]. Moreover the energetic along the path connecting the two phases does not capture the double-well potential, characteristic of the first order phase transition, but rather shows a single minimum. To circumvent these deficiencies, the combination of LDA and phenomenological Stoner model was adopted by Krasko and Olson [2] to capture the essence of competition between the BCC and FCC phase of iron. While this approach improves the energetics of the two phases, it does not predict the double-well potential for the first order phase transition, and still leaves paramagnetic BCC phase dynamically unstable, because it can not capture the essence of fluctuating local moments. Moreover, the finite temperature properties can not be simulated. The alternative approach adds the physics of local moments to the conventional DFT by supplementing DFT free energy by the free energy of the Heisenberg model, for which the exchange constants are determined by DFT [3]. Although this methodology can consider Heisenberg model at finite temperature and hence is able to describe some aspects of the finite-temperature magnetic properties of iron [4, 5], it is not physically convincing to treat the same electrons, which form wide metallic bands in DFT, by a fully localized spin model. Other single particle approaches, which try to mimics the presence of local moments by disordering static moments in real space were recently applied to iron [6, 7], and were able to reproduce experimentally determined softening of the phonons in paramagnetic phase, but their validity relies on the ergodicity of the quantum metallic system, which has not been established. In an alternative single particle method [8] the phonon-phonon interaction was taken into account to produce dynamically stable high temperature BCC structure of iron. But since the method still relies on DFT single-particle approximation, it mimics the local moments by simulation in a fictitious antiferromagnetic phase.

With the advent of the dynamical mean field theory (DMFT) and its combination with DFT, the nature of electrons which are partially itinerant, forming metallic bands in iron, and partly localized, giving rise to Curie-
Weiss susceptibility, could finally be simulated from ab-

\times \text{Curie temperature (close to the } \alpha \text{ transition in iron has been addressed by this method in Ref. 10, and was later extended to study lattice dynamics in the paramagnetic state of BCC and FCC structure [11], but the lattice dynamics of the ferromagnetic state has not been addressed by the DMFT method before. Moreover, the authors of Ref. 12 recently ascribe the previously ob-

The energy of BCC to FCC transition in iron has been addressed by this method in Ref. 10, and is the focus of this study. Moreover, previous DFT+DMFT calculations for iron [11, 12] were using non-stationary implementation of DFT+DMFT to-

The physical picture emerging from this state of the art computational technique is very different from previous DMFT reports: i) the first order phase transition from alpha to gamma phase is unrelated to observed phonon softening in iron. ii) The experimentally observed softening of phonons and their non-harmonic change is a consequence of the melting of the long range ferromagnetic order, and once the paramagnetic state is reached, the change of the phonons with temperature is reasonably well explained by the quasi-harmonic approximation. iii) The BCC state remains dynamically stable at all temperatures even though the FCC state is thermodynamically the stable phase between $\alpha$ and $\delta$ phase. Consequently the phonon-phonon interaction is not needed to make the high temperature BCC-$\delta$ phase dynamically stable, although the free energy of BCC and FCC phases at high temperature contain large contribution from the electronic, magnetic and vibrational entropy.

In this letter we use stationary version of DFT+DMFT method [18] which implements the stationary and charge self-consistent DFT+embedded DMFT functional [19, 20], and computes forces as a derivative of the free energy functional [17]. The continuous time quantum Monte Carlo in its rotationally invariant form is used as the impurity solver [21]. The screened value of the Coulomb interaction is determined by constrained LDA method resulting in $U = 5.5$ eV and Hund’s exchange interaction $J = 0.84$ eV [22], and we used the nominal double counting, which was shown to be very close to exact double-counting [23]. The DFT part is based on Wien2k package [24] and we use LDA functional which, when combined with DMFT, predicts better crystal structures. This is because in LDA functional both the electronic bandwith and equilibrium lattice constants consistently show signatures of overbinding, and can both be corrected by adding dynamic correlations, while in GGA the bandwidth shows similar overbinding tendency, while lattice constants many times shows underbinding tendency, hence they are harder to simultaneously correct by higher order theory. The phonon spectrum is calculated using direct approach implemented in the phonopy package [25].

In Fig. 1(a) we show the free energy versus volume curve at room temperature, which gives the equilibrium volume $11.9 \text{Å}^3$ and bulk modulus 181 GPa, which are in good agreement with experimental values of $11.69 \text{Å}^3$ [26] and 172 GPa [1]. Fig. 1(b) shows the magnetization versus temperature curve, which follows the mean field type of behaviour, and gives almost exact magnetic moment 2.2 $\mu_B$. The transition temperature in this direct calculation is overestimated, as expected for a method treating spatial correlations on a mean-field level, consequently the phase with a short range order is typically predicted to have stable long range order. We also show the same magnetization curve for the case when the Coulomb interaction is approximated with the density-density terms only (Ising approximation) to demonstrate that such approach, which was previously used in Refs. 10–12 leads to much higher transition temperature and somewhat larger magnetic moment. This effect was also noticed in Ref. 27 using Hirsch-Fye quantum Monte Carlo method, but was neglected in previous studies of lattice dynamics due to computational cost. In Fig. 1(c) we also show the electronic spectral function at 300K, which is in very good agreement with ARPES measurement of Ref. 28, in contrast to earlier DMFT calculations based on approximate impurity solvers [29]. We note that similar magnetization curve for iron was shown in Ref. 9 using
FIG. 1: (a) The electronic free energy as a function of volume \( V \) (the error bar represents Monte Carlo noise). (b) The temperature dependence of the ordered ferromagnetic moment of bcc iron using both the density-density (“Ising”) and the rotationally-invariant (“Full”) Coulomb interaction form. (c) The single-particle spectral function of the BCC-\( \alpha \) phase at 300 K (the majority and minority spectra are plotted in blue and red color, respectively).

In Fig. 2 we show the theoretical phonon spectra calculated in the three BCC phases of iron, in the ferromagnetic state at room temperature, in the paramagnetic \( \alpha \) state slightly above the Curie temperature (1.125 \( T_c \)), and in the paramagnetic \( \delta \) phase at high temperature, and we compare it to the measured spectra from Refs. 13, 14, 30. We notice reasonable agreement between the theory and experiment. Notice also that the paramagnetic (1.125 \( T_c \)) solution within the standard DFT has many unstable branches [11], which are here stabilized by proper description of the fluctuating moments existing above \( T_c \).

Next we show in Fig. 3(a) the temperature dependence of the theoretically obtained phonon spectra in BCC phase from low temperature through magnetic transition and up to the \( \alpha - \gamma \) transition. We notice very strong softening of lowest branch at the \( N \) point, which was shown to similarly soften experimentally in Refs. 13, 14, as well as substantial softening in the half-distance between \( H \) and \( P \) point. The arrows on the right mark the strong temperature variation of some phonon branches. All these trends are very consistent with experiments. In Fig. 3(b) we show phonon dispersion when the same cal-
FIG. 4: The change of the phonon frequencies for representative modes at different temperatures calculated with DFT+DMFT (red dots) compared to experimental data (green triangle) whenever available. The dashed blue lines denote the change predicted by the quasiharmonic model: \( \omega_{\text{qh}}(T) = \omega_{300K}(1 - \gamma_{\text{th}}) \frac{V_T}{V_{300K}} \), where \( \omega_{300K} \) is the calculated value of the phonon frequency at 300K, \( V_T \) is the experimental volume of the unit cell at temperature \( T \), and \( \gamma_{\text{th}} \) is the thermal Gr"uneisen parameter, approximated by a constant value of 1.81, as suggested in Ref. 14, 31.

calculation is done in metastable paramagnetic state below \( T_c \), where experimentally only the ferromagnetic state is stable, and also far above \( T_c \), in which FCC phase is thermodynamically more stable than the simulated BCC phase. In this paramagnetic calculation we fixed the volume to remove trivial quasi-harmonic effects on the phonon dispersion. We see that the phonon dispersion is barely changed at fixed volume in the paramagnetic state, and remains very similar up to very high temperature.

Fig. 4 shows the temperature dependence of selected phonon-branch frequencies and their comparison to quasi-harmonic approximation as well as to the experiment. The quasi-harmonic approximation (blue dashed line), which takes into account only the volume expansion, greatly underestimates the frequency change, while our simulation with melting of the long range order is in reasonable agreement with experiment from Ref. 14. The experimental change is somewhat less abrupt at \( T_c \) likely because the short range order persists in some limited region above \( T_c \) while the mean-field approach used here, can describe an infinite or zero correlation length in ferromagnetic and paramagnetic state, respectively.

On the basis of these results we can conclude that the phonon-softening, discovered experimentally many years ago [13], is mainly due to melting of the magnetic long range order, and hence has nothing to do with the proximity to the first order \( \alpha \) to \( \gamma \) phase transition, in contrast to what has often been assumed [13], and concluded in the previous DFT study [12]. In our view, both the paramagnetic BCC and the paramagnetic FCC phase are dynamically stable at all temperatures, and their relative stability has to be determined by comparing their respective free energies.

Since our results suggest that the phonon-softening mechanism in iron is unrelated to the \( \alpha \) - \( \gamma \) structural transition, we want to demonstrate that our theory correctly predicts thermodynamic competition of the BCC and FCC phases of iron. The martensitic \( \alpha \) - \( \gamma \) transformations is as usually modeled by a continuous crystallographic transition from initial to the final phase, and in case of BCC-FCC transition the Bain path [32] is most often picked, which consist of a continuous expansion of a bcc lattice along one of the cubic axes with a contraction along the two others. The path is described by a single parameter \( c/a \) with \( c/a = 1 \) for BCC and \( c/a = \sqrt{2} \) for FCC. In Fig. 5 we show the total energy along the Bain path, which clearly shows the double-well profile, characteristic of the first order phase transition, that does not require softening of phonons for the existence of the phase transition. At low temperatures (\( T = 300K, 1000K \)), the global minimum is at the BCC structure (\( c/a = 1 \)) and at high temperature (\( T = 1547K \)), it is at the FCC structure (\( c/a = \sqrt{2} \)). Along the path the ferromagnetic long range order disappears in our simulation, and at that value of \( c/a \) (yellow region) the double-well curve reaches a maximum. At high temperature (\( T = 1547K \)), where the ferromagnetic long range order disappears for all values of \( c/a \), the total energy still keeps the double-well shape with very small total energy difference between BCC and FCC phase (20meV), in contrast to the DFT
prediction, which has a single minimum with both the magnetic and non-magnetic functionals.

The importance of disordered localized magnetic moments in paramagnetic phases of iron was stressed early on in the pioneering work of Grimvall [33]. This physics now emerges from a quantitative first principles method, and its implications for many physical quantities has been elucidated. We predict that the softening of the phonons in BCC structure is not related to its first order $\alpha$ to $\gamma$ transition, but it is due to the melting of the long range magnetic order. Our prediction can be checked by measuring the phonon dispersion of the paramagnetic iron under applied magnetic field, to check that long range magnetic order in the field hardens the phonons at selected points in the Brillouin zone. We predict that the BCC structure is dynamically stable at all temperatures, and is only thermodynamically unstable due to lower free energy of the FCC-$\gamma$ phase at the intermediate temperatures between the $\alpha$ and the $\delta$ phase.

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