

Nonthermal solid-solid phase transition in ferromagnetic iron

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We posit the existence of a nonthermal phase transition in iron, driven by a loss of ferromagnetic ordering on ultrafast timescales with increasing electron temperature. The transition corresponds to a solid-solid bcc to fcc phase transformation and takes place at an electron temperature of 0.62 eV while the ion lattice remains near room temperature. The bcc structure initially undergoes phonon softening during the magnetic transformation, followed by a solid-solid phase transition to the fcc structure, and a subsequent hardening of phonon modes. We present a detailed physical picture of the process, supported by finite-temperature density functional theory simulations of the phonon dispersion curves, electronic density of states, and thermodynamic free energy.

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I. INTRODUCTION

Short-pulse light sources such as femtosecond optical lasers and x-ray free electron lasers (XFEL) can produce non-thermal and nonequilibrium systems from solids by rapidly driving electrons to high temperatures. Electron excitations generated by ultrafast heating affect the electronic and magnetic structure of the system, its density of states, and lattice vibration spectra, but have also been seen to modify the ionic potential in surprising ways [1–9]. The resulting modified ionic forces can trigger nonequilibrium structural transitions in solids on picosecond timescales, even before any significant energy transfer between electrons and ions can occur [10–13].

To date, the study of nonthermal phase transitions following laser irradiation has predominantly focused on semiconductors. Ultrafast melting under laser excitation was observed by time-resolved reflectivity for GaAs [14] and time-resolved x-ray diffraction for InSb [5], Si [15], Ge [10], and Bi [16]. Ultrafast melting takes place in the surface layer of the material on a timescale of a few hundred fs, although results vary with laser fluence. Within the domain of solid-solid nonthermal phase transitions, there has been a focus on VO₂, a monoclinic insulator that transforms into a metallic rutile phase under laser irradiation. Although the insulator-metal transition has been shown to occur within 200 fs, the timescale of the structural phase transition remains controversial. This is due to uncertainties in the rate of nucleation and growth, and to the disputed nature of the phase transition, which could take place anywhere between 100 fs and 100 ps [17–19].

Laser-induced phase transformations in covalent bonded materials and semiconductors are predominantly modeled using first-principle methods and molecular-dynamics simulations [13,15,20–25]. Semiconductors such as Si show a large phonon softening and instability of the transverse acoustic mode in the whole Brillouin Zone (BZ) with increasing electronic temperature. In contrast, phonons of metals, such as Al and Au, are predicted to harden as the electronic temperature increases. However, the size of the effect strongly depends on the interplay between the lattice and the electronic structure. In Au, where the electronic DOS is dominated by the fully filled *d*-band which its upper edge barely cross the Fermi energy, increases in electron temperature can lead to a change in the electronic DOS near the Fermi level. This results in a strong electron-phonon coupling, which in turn leads to a more pronounced phonon hardening [1]. Conversely, in Al, the electronic DOS remains nearly constant with temperature due to its free-electron-like behavior, leading to weaker electron-phonon coupling and less pronounced phonon hardening. The potential hardening of phonon modes, which has also been suggested for other transition metals [1], stabilizes the metallic lattice and delays the solid-liquid phase transition [2]. In this work we argue that the metallic lattice stabilization also depends on the magnetic properties, and show that Fe, a partially filled *d*-band metal, can experience phonon softening, rather than hardening, due to demagnetization.

While the ultrafast demagnetization of ferromagnetic metals via electron excitations induced by femtosecond laser pulses has been studied for some time [26–32] our understanding of this process remains incomplete. This is mostly because the mechanisms behind laser-induced ultrafast demagnetization depend on the complex interaction of photons, electrons, spins, and the lattice, across a range of different timescales. The process can be simplified using a mean-field-like approach, within the following phenomenological three-temperature model. Initially, high-energy photons are absorbed, generating hot electrons that rapidly equilibrate to

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form an equilibrated electron liquid with a temperature of T_{el} . Then, electron-phonon coupling acts to equilibrate these hot electrons with the lattice, thermalizing the system to a new temperature of $T_{\text{el-ph}}$. Finally, the spin system which is characterized by an effective spin temperature of T_{spin} , interacts with the electrons and phonons. We thus expect the timescale of magnetization change to be determined by the equilibration processes of electron-electron, electron-phonon, and electron-spin interactions. Nevertheless, even within this simplified model, quantifying all the relevant physical processes remains a formidable computational task.

In this study, we investigate the relationship between the topology of the Fermi surface, demagnetization, and a solid-solid nonthermal phase transition in Fe, using finite-temperature density functional theory (DFT) [33,34] and density functional perturbation theory (DFPT) [35]. The phase diagram, spin dynamics, correlation effects, and electronic structure properties of iron have been widely studied using numerous theoretical methods and experimental techniques [36–43]. At ambient conditions, iron adopts the body-centered cubic (bcc) phase but transforms to a more thermodynamically stable face-centred cubic (fcc) phase called γ -Fe at a temperature of 1170 K. This α - γ phase transition has been extensively studied due to its practical applications and importance in material science [44]. At 1660 K, the fcc phase undergoes a reverse transformation to bcc, which eventually melts just above 1800 K [45]. It is known that the γ -Fe phase in the ground state has spin spiral noncollinear magnetic properties, with a spiral vector which strongly depends on the lattice parameter [46–48]. Here we do not consider noncollinear magnetism, and note that this assumption may have an impact on the detailed shape of the phase diagram for Fe. We aim to address features of this nature in future work.

II. COMPUTATIONAL DETAILS

To investigate the various Fe structures we use the QUANTUM ESPRESSO package [49], with the Perdew-Burke-Ernzerhof (PBE) parametrization [50] of the exchange-correlation (XC) functional with a spin-polarized generalized-gradient correction. We will consider bcc and fcc crystal structures of Fe at electronic temperatures up to 3 eV, using a kinetic-energy cutoff of the plane-wave basis set of 120 Ry and an augmentation charge energy cutoff of 960 Ry. The finite-temperature DFT and DFPT calculations were carried out using a (32, 32, 32) $\mathbf{k}$ grid and a (8, 8, 8) $\mathbf{q}$ grid, respectively. The projector augmented wave (PAW) pseudopotential [51,52] was generated using the scalar-relativistic calculation with 16 valence electrons. The electronic temperature is controlled by the standard Fermi-Dirac distribution function. The number of empty bands is increased by the electronic temperature.

III. RESULTS AND DISCUSSIONS

A. Demagnetization of radiated iron

We considered bcc and more close-packed fcc crystal structures of Fe over a range of electronic temperatures up to 3 eV. The spin-polarized electronic density of states (DOS)

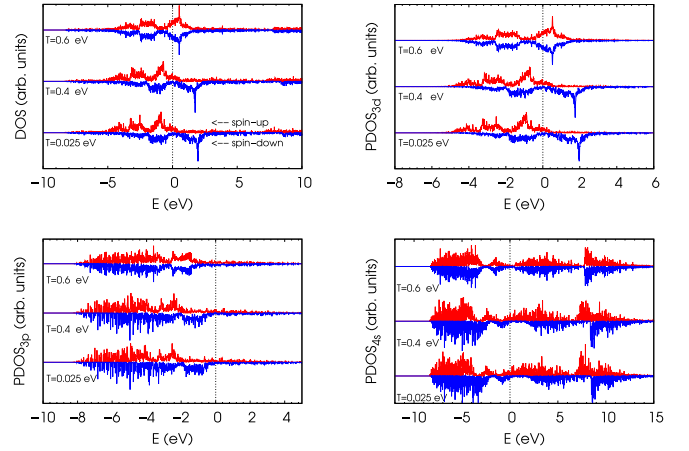


FIG. 1. Spin-polarized total electronic density of states (DOS) (top-left panel), 3d-orbital projected DOS (top-right panel), 3p-orbital projected DOS (bottom-left panel), and 4s-orbital projected DOS (bottom-right panel) of bcc Fe at electronic temperatures of $T_{\text{el}} = 0.025, 0.4, 0.6$ eV. The dotted vertical line is the Fermi energy at room temperature. The maximum values of PDOS_{3d} , PDOS_{3p} , and PDOS_{4s} are 4.1, 0.0045, 0.44 states/(eV cell), respectively. The density of states vicinity of the Fermi energy is dominated by 3d-band electrons at all temperatures. The demagnetization of bcc Fe at $T \sim 0.6$ eV is evident.

and the projected DOS (PDOS) of bcc Fe obtained at three different electronic temperatures of $T_{\text{el}} = 0.025, 0.4, 0.6$ eV are shown in Fig. 1. At low temperatures we see that the system is ferromagnetic: the majority of the spin-down channel sits above the Fermi energy, while the spin-up DOS sits below. The energy separation between spin-up and down electrons is mainly dominated by the d band, with maximum values of the 3d, 3p, and 4s PDOS of 4.1, 0.0045, and 0.44 states $\text{eV}^{-1} \text{cell}^{-1}$, respectively.

The projected density of states indicates that the DOS vicinity of the Fermi energy is dominated by the d band. The magnetic interaction at low temperatures causes spin splitting of the d bands in a way that the spin-up bands are almost filled, while in the spin-down bands the Fermi energy is located in the area of relatively low DOS. In these situations, the gain in the exchange energy compensates for enlarging the electron kinetic energy and consequently forces the ferromagnetic state to be stable compared with the paramagnetic state. We do not take into account the on-site Hubbard U interaction in our analysis; we consider the Stoner nature of ferromagnetism in this study. As the temperature increases, the energy separation between spin-up and spin-down electrons decreases, eventually destroying the ferromagnetic ordering at an electronic temperature of $T_c \simeq 0.62$ eV. We note that this value will be subject to some uncertainty since our simplified calculations neglect the true elementary excitations in the form of spin waves and are impacted by the choice of XC functional and the inaccuracy of DFT without Hubbard U parameter in describing the electronic and magnetic properties of strongly correlated transition metals.

Our calculations of the band structure of bcc Fe are shown in Fig. 2, which indicate that the almost filled spin-up d -band moves the Fermi energy upward, whereas the spin-down

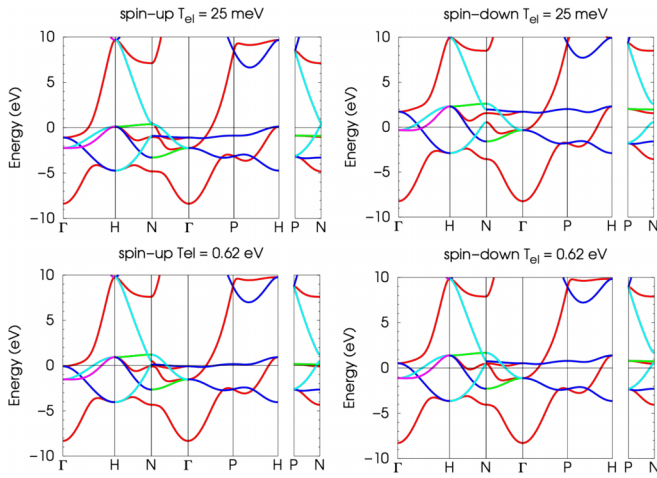


FIG. 2. Spin-dependent electronic band structure of bcc Fe at electronic temperatures $T_{el} = 0.025$ and 0.62 eV. Upshifting of spin-up and downshifting of spin-down bands near the Fermi energy can be observed by increasing the electronic temperature. The bands are colored based on their point groups.

d -band moves the Fermi level downward by increasing the temperature until they almost overlap at $T_{el} = 0.62$ eV, enlarging the DOS near the Fermi level. Hence, the energy ordering of spin-up and spin-down d bands with respect to the Fermi energy behaves differently as a function of T_{el} , which ultimately results in a ferromagnetic to a paramagnetic phase transition. The average bandwidth of spin-up bands crossing the Fermi energy is much larger than that for spin-down bands. Because of the smaller dispersion of the down bands, increasing the temperature affects the spin-down bands more than the spin-up bands.

Our analysis also shows that the effect of electronic temperature on the ordering of spin-polarized d bands significantly changes the Fermi surface topology and band degeneracies, which in turn affects the energy dispersion near band crossings and determines the nature of quasiparticles [53]. The Fermi surface (FS) of the two spin-down bands

crossing E_F is shown in Fig. 3 for electronic temperatures of 0.025 and 0.62 eV. The Fe bcc bands are plotted inside the first Brillouin zone (BZ). By increasing the temperature, the bandwidths of the spin-down bands are reduced, resulting in further localization of the spin-down bands near E_F and a modification of the topology of the FS near the BZ boundaries where the phonon dispersion anomaly occurs. The electronic excitations also modify the Fermi wave vector $\mathbf{k}_F$ and sharpen the Fermi surface, which can introduce a Kohn anomaly in the phonon spectra, which we discuss further in the following.

B. Phonon hardening and softening

To evaluate the dynamic stability of the two phases under electronic excitations, we calculate the phonon band structure as a function of electronic temperature. The fcc phase displays mechanical instability at low temperature (25 meV), which manifests through imaginary phonon frequencies along the Γ -K direction, as shown in Fig. 5. In contrast, we see in Fig. 4 that bcc Fe does not display imaginary phonons at the same temperature, indicating that Fe adopts the bcc structure at low temperatures. As the electronic temperature increases, the phonon dispersion curves of bcc Fe show the appearance of soft modes along the Γ -N lines. A softening of a branch in the whole BZ disorders the lattice, whereas a phonon softening along high-symmetry points in the BZ could be a sign of a nonthermal solid-solid phase transition.

The phonon dispersion curves of bcc Fe show the appearance of an anomalous dip in the lowest branch of the transverse-acoustic modes along the Γ -N direction at electronic temperatures between 0.62 and 1.0 eV. This anomaly results from a qualitative change in the electronic screening due to the modification of the electron-phonon coupling with electronic temperature. Importantly, we observe that bcc Fe undergoes phonon softening before demagnetizing and transitioning to the fcc phase. This is in contrast to the standard expectation for metals to exhibit phonon hardening under ultrafast laser radiation. For instance, Au was predicted to phonon harden with electron heating, leading to a sharp increase in its melting temperature [1,54]. For Fe, such behavior

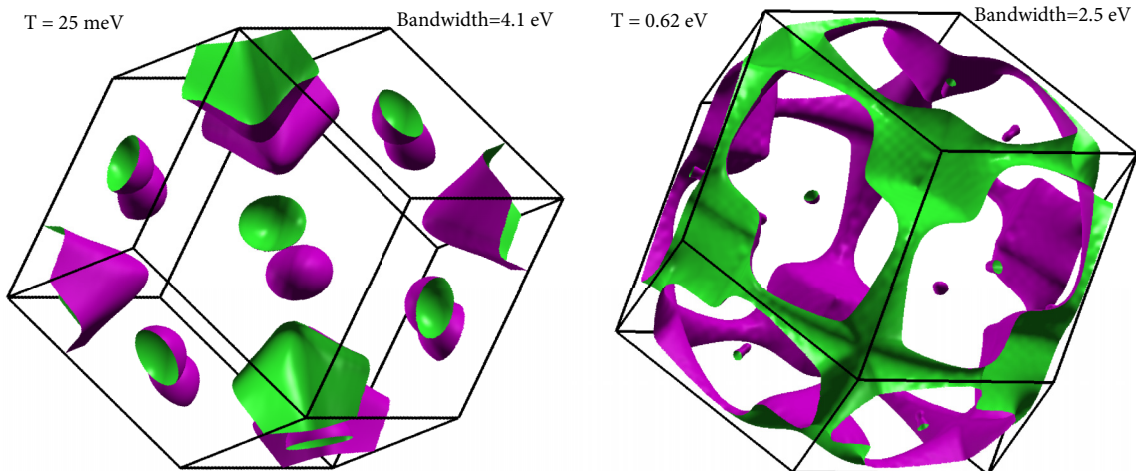


FIG. 3. Fermi surface of two spin-down bands at electronic temperatures 0.025 and 0.62 eV plotted inside the first BZ of the bcc structure. Increasing the electronic temperature reduces the bandwidth and localizes the band near the Fermi surface.

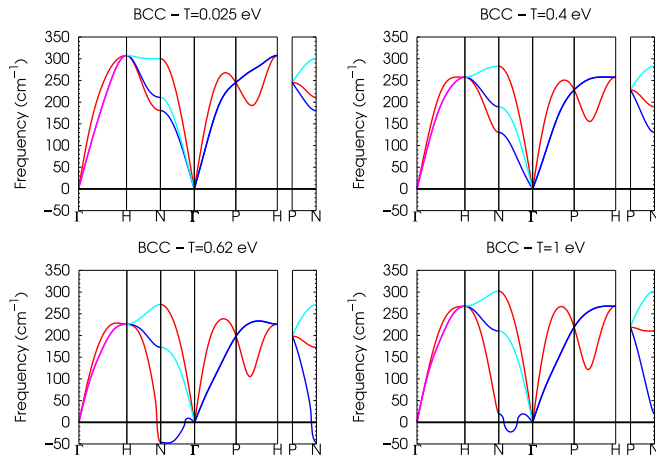


FIG. 4. Phonon dispersion curve of bcc Fe at $T_{el} = 0.025, 0.4, 0.62, 1.0$ eV. Phonon softening can be observed by increasing the temperature from 0.025 to 0.4 eV. Further raising the temperature from 0.4 to 0.62 eV, where the demagnetization takes place, causes the appearance of imaginary phonons. At temperature 1 eV, at which the system has already been demagnetized, imaginary phonons start disappearing and the phonon dispersion curve exhibits phonon hardening. The bands are colored based on their point groups.

can be seen in Fig. 5 for paramagnetic fcc Fe, where we calculate a rise in the Debye temperature and, consequently, an increase in the melting temperature. Our results indicate that the vibrational response of metals to ultrafast laser pulses depends not only on the electronic structure but also on the magnetic properties of the system. Interestingly, the two processes compete, and the demagnetisation of a partially d -band-filled ferromagnetic metal leads to a softening of modes and a lowering of the melting temperature. We speculate that the same scenario occurs for other partially d -band-filled ferromagnetic transition metals.

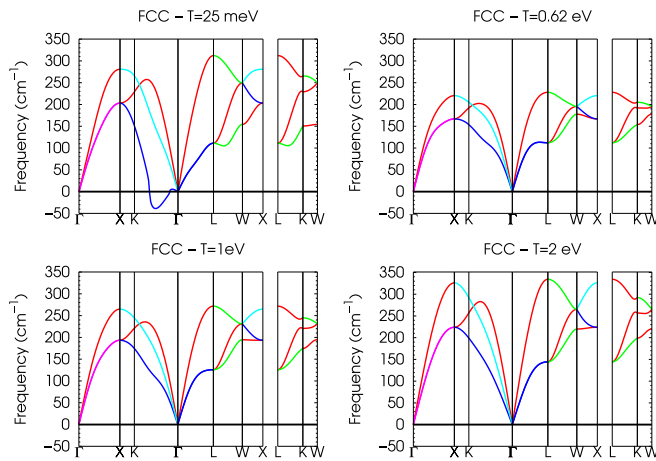


FIG. 5. Phonon dispersion curve of fcc Fe at $T_{el} = 0.025, 0.62, 1.0, 2.0$ eV. Imaginary phonons at $T = 0.025$ eV indicate that fcc is not a stable Fe crystal structure but bcc is. At $T = 0.62$ eV, where bcc Fe becomes unstable, and the absolute magnetization vanishes (Fig. 4), the fcc structure becomes stable with a large phonon softening. The phonon hardening can be observed by increasing the temperature to 1 and 2 eV. The bands are colored based on their point groups.

Analyzing the phonon spectra throughout the whole BZ of bcc Fe at temperatures above 0.6 eV exhibits that the imaginary frequencies introducing dynamical instabilities take place in a localized region in $\mathbf{q}$ -space. The localization nature of the anomaly in the reciprocal space originates from the electronic structure. According to the definition of Kohn anomalies, a screening introduced by the electronic state close to the Fermi energy in metals, which is involved in the electron-phonon coupling, can generate anomaly dips in the phonon band structure. The existence of these anomalies is affected by the Fermi surface and the $\mathbf{q}$ functionality of the electron-phonon coupling matrix. If the temperature-modified FS adopts a flat area with nesting vector $\mathbf{q}_{ano}$, there could be a large screening of the potential perturbation because of atomic displacements at $\mathbf{q}_{ano}$, which leads to a softening that is localized in reciprocal space. The size of the Kohn anomaly is sensitive to the electronic temperature, and increasing the electronic temperature can reduce the sharpness of the FS and weaken the anomaly. This effect can be observed from the phonon dispersions of Fe bcc at 0.62 and 1 eV in Fig. 4.

In contrast, we see in Fig. 5 that the phonon dispersion curves for paramagnetic fcc Fe at temperatures above T_c do not show any anomalies or imaginary phonons but instead exhibit phonon hardening. We calculated the elastic constants tensor and obtained bulk, Young, and shear moduli and the Debye temperature θ_D of fcc Fe at electronic temperatures of 0.62 and 3 eV. According to the Debye-Lindemann theory, the melting temperature T_m is related to θ_D as $T_m = C\theta_D^2$, where C depends on the atom's mass and density. Comparing the Debye temperatures at 0.62 and 3 eV reveals an increase in the melting temperature by a factor of 1.25. For Au, increasing the electronic temperature from 1 to 3 eV is predicted to increase the melting temperature by a factor of 1.44, which was attributed to the localization and large shift of the fully filled $5d$ bands to lower energies [1]. We observe a similar shift and localization in Fe with increasing electronic temperature, but these effects are less pronounced due to the partial filling of the $3d$ band.

C. Phase diagram

The absolute magnetization of bcc Fe as a function of electronic temperature (Fig. 6) shows that demagnetization occurs at $T_{el} = 0.62$ eV, nearly six times higher than the Curie temperature of Fe. Figure 6 shows the Helmholtz free energy of the fcc phase with respect to the bcc phase, including both electronic and lattice contributions. Importantly, note that the nonthermal solid-solid phase transition takes place at the same temperature as the demagnetization, from which we conclude that the bcc-fcc transition coincides with the ferromagnetic-paramagnetic phase transition.

In contrast to semiconductors, where optical irradiation causes a phonon softening resulting in nonthermal melting [5], the melting process in metals is a thermal process requiring energy transfer from excited electrons to the ions [25,55]. Femtosecond electron diffraction measurements [2] provided support for phonon hardening in Au and showed increasing lattice stability at high electronic temperatures, confirmed by first-principle simulations [1,54]. In contrast, ultrafast laser excitation measurements of Au

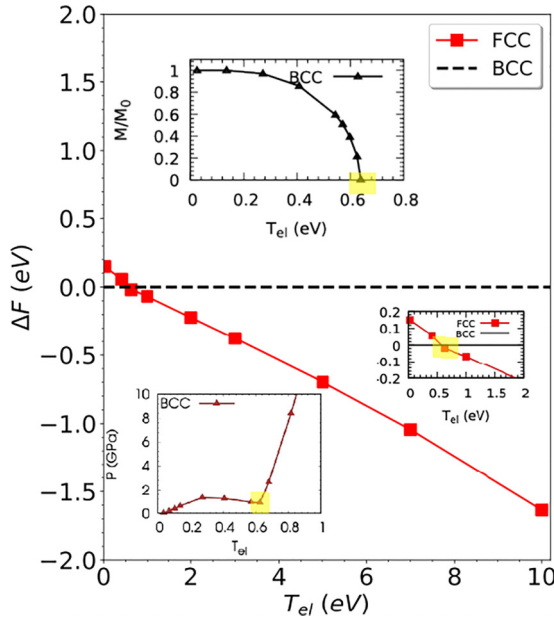


FIG. 6. The relative Helmholtz free energy ΔF as a function of electronic temperature T_{el} . The top inset shows the absolute magnetization (M) of bcc divided by its value at zero temperature (M_0) as a function of electronic temperature. The bottom-right inset shows the solid-solid bcc-fcc phase transition. The bottom-left inset shows the sudden jump in DFT-predicted pressure P for bcc as a function of electronic temperature. The bcc demagnetization, bcc-fcc phase transition, and the sharp rise of P all occur at $T_{el} \sim 0.62$ eV, highlighted by yellow color.

observed the heterogeneous coexistence of solid and liquid and evidenced a heterogeneous to homogeneous melting transition [55], which can be related to atomic bond softening.

Our results predict that phonon hardening or softening in magnetic transition metals under optical irradiation could be related to the compressive Coulomb stress caused by electronic entropy, the $-TS$ term in Helmholtz free energy. As illustrated in Fig. 6, the DFT predicted hot electron pressure P jumps at the demagnetization temperature, driving the structural transformation. The response of cold ions to this

rapid change in photoexcited electron pressure could be either phonon softening if a structural transition occurs, such as a bcc to fcc phase transition, or phonon hardening if the crystalline unit cell volume is confined and no structure is energetically available for the transition. The bcc and fcc structures have packing factors of 0.68 and 0.74, respectively. So the ratio of their packing factors ~ 0.92 is close to 1 and both have $c/a = 1$, where c and a are the lattice parameters in z and x - y directions, respectively. Hence, a relatively small change of 1.1 GPa in the internal pressure can cause a structural transition. The effect of hot electron pressure can also be explained using the homogeneous electron gas (HEG) model [56], which is widely used in developing exchange-correlation DFT functionals [57]. At zero temperature, there is a difference between the pressure of spin-unpolarized and spin-polarized HEG at the same density. Hence, losing the spin polarization due to electronic temperature introduces a gradient in electronic pressure. The response of cold ions to this gradient manifests itself either in the crystal transformation or in the phonon spectra.

IV. CONCLUSION

In summary, combining the Helmholtz free energy phase diagram, the absolute magnetization of bcc Fe as a function of temperature, and the phonon dispersion curves, we find that bcc Fe becomes dynamically unstable due to electronic excitations on ultrafast timescales. This instability leads to a decrease in its Debye temperature and in the absolute magnetization until the system transforms to the paramagnetic fcc phase. This phase, in contrast, experiences phonon hardening as the electron temperature is increased further. Our DFT simulations predict a nonthermal solid-solid phase transition takes place in Fe at an electron temperature of 0.62 eV, leading to an overall 25% increase in the melting temperature of Fe due to phonon hardening.

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