Volume dependence of phonon frequencies in paramagnetic bcc iron: a first-principles study

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Information on structural stability of crystals is essential in order to investigate their structural phase transitions. Phonon dispersions provide the information directly and hence are well investigated by both experimental and theoretical approaches. For magnetic crystals at finite temperatures, however, theoretical approaches face a complexity when they treat a paramagnetic (PM) state. Recently, Körmann et al. [1] proposed to use a special quasirandom structure (SQS) [2] for calculations of phonon dispersions of the PM state by the first principles calculations. In the present paper, we adopt the similar technique to investigate phonon dispersions for PM states in bcc iron with special interests on their volume dependence and pressure-induced phase transition.

Interatomic force constants for the PM state in bcc-Fe are obtained by the following procedure. First, a SQS for a binary system is constructed in order to represent a randomly disordered collinear magnetic configuration. The SQS-based configuration itself does not have the symmetry of bcc due to the disordered local moments and hence cannot be regarded as the ideal PM state of bcc-Fe. In order to recover the symmetry of bcc, all symmetry operations of bcc are applied to the SQS-based configuration. Then a set of configurations is obtained systematically. Force constants are computed by first-principles calculations for all these configurations. Finally, the averages of the force constants for all configurations are regarded as the force constants for the PM state, which have the symmetry of bcc.

A multi-purpose cluster expansion code, CLUPAN [3], is used for the SQS construction. Phonopy code [4] is used for the calculations of phonon dispersions. For the first-principles electronic structure calculations, the plane-wave basis projector augmented-wave method [5] is applied in the framework of density-functional theory within the generalized gradient approximation in the Perdew-Burke-Ernzerhof form [6] as implemented in the VASP code [7]. A plane-wave energy cutoff is set to 300 eV. The 3d and 4s electrons for Fe are treated as valence and the remaining electrons are kept frozen. A Γ-centered $16 \times 16 \times 16$ k-point mesh per conventional bcc unit cell is used for the Brillouin-zone integration of the supercell. The total energy is minimized until the energy convergence becomes less than 1×10^{-8} eV.

Before the calculations of phonon dispersions, the volumes for FM and PM states are optimized. The obtained values are 11.34 and 11.32 Å^3/atom for the FM and PM states, respectively. Next, phonon dispersions around the optimized volumes are investigated. Figure 1 shows calculated phonon dispersions of the FM and PM bcc iron. For the FM state, phonon frequencies in the whole region tend to increase as the volume decreases. On the other hand, it is found for the PM state that phonon modes with the lowest frequencies around the N point decrease their frequencies as the volume decreases; this is an unusual behavior. For the modes, imaginary frequencies are found at $V = 11.09$ Å^3/atom indicating the structural instability of the PM state under pressures. It is known that the soft mode at the N point is responsible for the martensitic bcc to hcp phase transition following the Burgers path. The present result clearly implies that the disorder of magnetic moments at finite temperatures influences the pressure-induced bcc-hcp transitions of iron.

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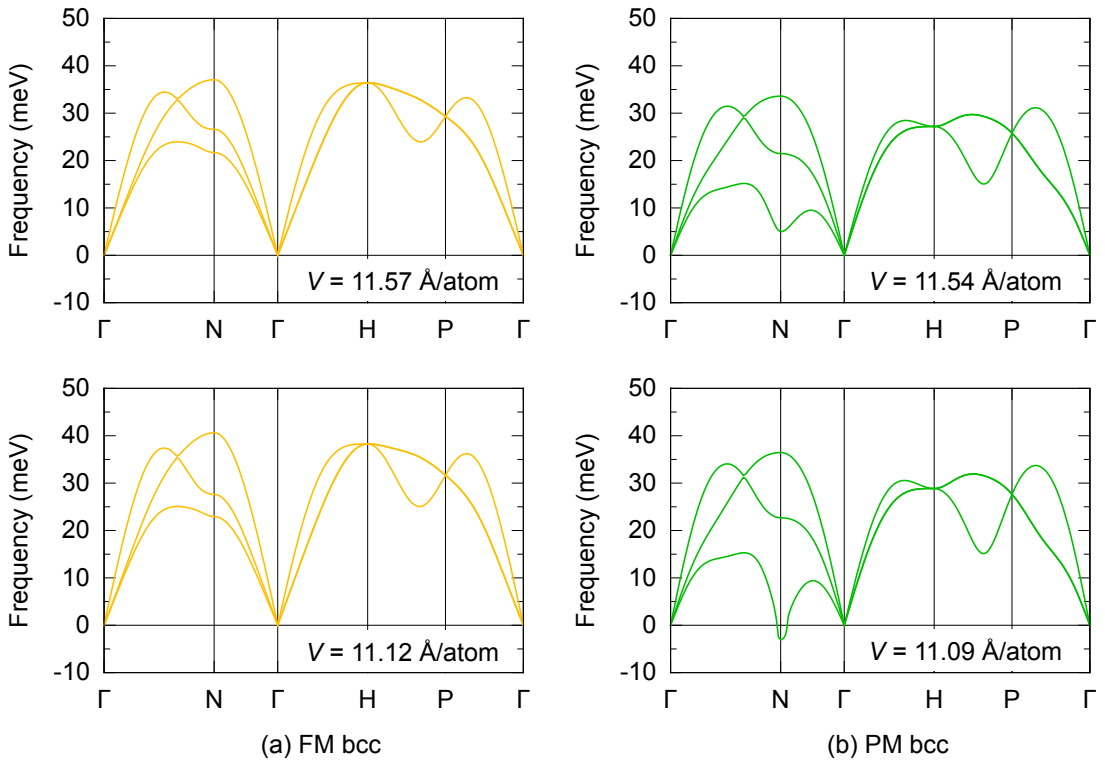

FIG. 1. Calculated phonon dispersions for the (a) FM and (b) PM bcc iron. Negative values for frequencies indicate imaginary modes.