

Lattice dynamics and its effects on magnetocrystalline anisotropy energy of pristine and hole-doped YCo_5 from first principles

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We study the lattice dynamics effects on the phase stability and magnetocrystalline anisotropy (MCA) energy of CaCu_5 -type YCo_5 at finite temperatures using first-principles calculations based on density functional theory (DFT). Harmonic lattice dynamics (HLD) calculations indicate that YCo_5 with 56 full valence electrons is dynamically unstable and this instability can be cured by reducing the number of electrons (N_e). Crystal orbital Hamilton population analysis reveals that the observed phonon instability originates from the large population of antibonding states near the Fermi level, which is dominated by the Co atoms in the honeycomb layer. The antibonding state depopulates with decreasing N_e , resulting in stable phonons for hole-doped YCo_5 with $N_e \leq 55$. We then evaluate the temperature-dependent MCA energy using both HLD and *ab initio* molecular dynamics (AIMD) methods. For the pristine YCo_5 , we observe a very weak temperature decay of the MCA energy, indicating a small effect of lattice dynamics. Also, the MCA energies evaluated with AIMD at all target temperatures are larger than that of the static hexagonal lattice at 0 K, which is mainly attributed to the structural distortion driven by soft phonon modes. In the hole-doped YCo_5 , where the distortion is suppressed, a considerable temperature decay in MCA energy is obtained both in HLD and AIMD methods, showing that lattice dynamics effects on MCA energy are non-negligible.

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I. INTRODUCTION

The intermetallic compound CaCu_5 -type RECo_5 (RE = rare earth) has been extensively studied in the past, both experimentally and theoretically, due to its superior magnetic properties such as high Curie temperature, saturation magnetization, and strong coercivity [1–5]. One of the intrinsic magnetic properties associated with high coercivity is magnetocrystalline anisotropy (MCA) energy, which depends only on the crystal structures and chemical compositions. MCA energy is defined as the ground state energy difference between different directions of the magnetization with respect to the crystal axes. In the previous studies, it was found both experimentally and theoretically that RECo_5 (RE = Y, La, Ce, Sm) exhibits a uniaxial MCA energy that results in an energetically favored alignment of the magnetic moments along the crystallographic c axis [6–12]. In RECo_5 , the large MCA mainly arises from two aspects: the spin-orbit coupling of the itinerant $3d$ electrons at the Co sites, and the spin-orbit interaction of the localized $4f$ electrons at the RE site. Compared with $3d$ electrons, the MCA originating from $4f$ electrons shows a strong temperature dependence. The two contributions become comparable at finite temperatures. For example, Alameda *et al.* reported the MCA constant of YCo_5 was 7.4 MJ/m^3 at 4.2 K and slightly decreased to 5.8 MJ/m^3

at room temperature [6]. The corresponding values for the well-known SmCo_5 are 30 and 17 MJ/m^3 [12], respectively.

A theoretical study of the temperature effect on MCA energy is crucial since permanent magnets are usually used in a high-temperature environment. An important physical factor affecting MCA at finite temperature is the thermal fluctuation of the spin moment. This effect has approximately been included in density functional theory (DFT) calculations with disordered local moment (DLM) approach [13]. For example, Matsumoto *et al.* [14] investigated the temperature dependence of MCA energy and magnetization in hole-doped YCo_5 using the DLM approach. A DLM-based first-principles magnetization versus field (FPMVB) approach is introduced by Patrick *et al.* to study the temperature-dependent MCA energy of YCo_5 and GdCo_5 [15]. They found excellent agreement of temperature-dependent MCA energy curves in GdCo_5 between the FPMVB approach and experiments.

Lattice dynamics is another important factor that can affect the MCA energy at finite temperature [16,17]. At elevated temperatures, thermal excitation of phonons is expected to change the electronic structures, which then influences the MCA energy. For example, Urru *et al.* [17] has recently reported that the spin-reorientation transition of MnBi could be explained by considering the vibrational free energy contribution calculated within the harmonic approximation (HA). Thus it is intriguing to study lattice dynamics effects on the temperature-dependent MCA energy of permanent magnetic materials, particularly the CaCu_5 -type RECo_5 which displays the same hexagonal lattice as MnBi .

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In this work, we theoretically investigate the lattice dynamics and its effect on the MCA energy of YCo_{5-x} at finite temperature to study the MCA energy originating from the itinerant states. By performing phonon calculations of YCo_5 within the harmonic approximation, we show that the experimentally-reported CaCu_5 structure is dynamically unstable. This phonon instability originates from the presence of large antibonding states near the Fermi level, which can be removed by reducing the number of electrons (N_e). We find that at least one electron needs to be removed from the system to stabilize phonons of YCo_{5-x} . For the hole-doped YCo_{5-x} , we then evaluate the lattice dynamics effect on the MCA energy from the difference of the vibrational free energies computed with different spin orientations. In the high-temperature region, the phonon contribution to the MCA energy becomes significant and comparable to the MCA energy at 0 K obtained from DFT calculation. To evaluate the lattice dynamics effect in the undoped YCo_5 , we also perform *ab initio* molecular dynamics (AIMD) simulations and find that the MCA energy hardly changes with increasing temperature. We attribute this weak temperature dependence mainly to structural distortion.

The structure of this paper is organized as follows. In the next section, we describe our theoretical methods in detail. The MCA energy both at 0 K and finite temperatures, and computational details are described in Secs. II A, II B, and II C, respectively. In Sec. III, we show our main results. The dynamical instability of the CaCu_5 -type YCo_5 with 56 full valance electrons and the microscopic origin of stabilization by reducing N_e , or hole-doping, are discussed in Sec. III A. In Sec. III B, we evaluate the MCA energy both at 0 K and finite temperatures using different approaches and discuss the role of lattice dynamics in the temperature dependence of the MCA energy. Finally, we summarize this study in Sec. IV.

II. METHODS

A. MCA energy at 0 K from DFT calculation

We perform a noncollinear spin-orbit interaction calculation using the well-known force theorem [18] to obtain the MCA energy, K_u^{DFT} at 0 K, which is defined as

$$K_u^{\text{DFT}} = E_{\perp}^{\text{DFT}} - E_{\parallel}^{\text{DFT}}, \quad (1)$$

where E_{\perp}^{DFT} and $E_{\parallel}^{\text{DFT}}$ are the ground state total energies with the magnetic moment (\mathbf{m}) being aligned along the hard ([100] direction, $\mathbf{m} \perp \mathbf{c}$) and easy ([001] direction, $\mathbf{m} \parallel \mathbf{c}$) axes, respectively. The positive K_u^{DFT} indicates that the energetically favorable \mathbf{m} is parallel to the crystallographic c axis.

In order to understand the atomic site-dependent MCA energy, we carry out the second-order perturbation calculation. In the tight-binding regime, the Hamiltonian for spin-orbit coupling is given by the sum of the contributions from each atomic site, $H_{\text{SO}} = \sum_i \xi_i \mathbf{L}_i \cdot \mathbf{S}_i$, where $\mathbf{L}_i (\mathbf{S}_i)$ is the single-electron angular (spin) momentum operator, and ξ_i is the spin-orbit coupling constant of atom i . Compared with 3d bandwidth, ξ_i ($\xi_{\text{Co}} = 69.4$ meV) is relatively small, which can be treated as a perturbation term. The second-order

perturbation energy is expressed as

$$E^{(2)} = - \sum_k \sum_{n'\sigma'}^{\text{unocc}} \sum_{n\sigma}^{\text{occ}} \frac{|\langle \mathbf{k}n'\sigma' | H_{\text{SO}} | \mathbf{k}n\sigma \rangle|^2}{\epsilon_{\mathbf{k}n'\sigma'}^{(0)} - \epsilon_{\mathbf{k}n\sigma}^{(0)}}, \quad (2)$$

where $|\mathbf{k}n\sigma\rangle$ is the unperturbed state with energy $\epsilon_{\mathbf{k}n\sigma}^{(0)}$. \mathbf{k} , n , and σ represent the wave vector, band index, and spin, respectively. The index ‘‘occ’’ and ‘‘unocc’’ means the sum over the occupied and unoccupied states. $|\mathbf{k}n\sigma\rangle$ can be expanded as a sum of atomic orbitals, $|\mathbf{k}n\sigma\rangle = \sum_{i\mu} c_{i\mu\sigma}^{\mathbf{k}n} |i\mu\sigma\rangle$, where the atomic orbitals labeled as μ and the coefficient $c_{i\mu\sigma}^{\mathbf{k}n}$ can be obtained by DFT calculations. Therefore the site-dependent second-order contribution to the total energy with different spin processes and atomic orbitals can be calculated using first-principles calculations.

The MCA energy at 0 K, K_u^{PT} , within the second-order perturbation is defined as $K_u^{\text{PT}} = E_{\perp}^{(2)} - E_{\parallel}^{(2)}$, where $E_{\perp}^{(2)}$ ($E_{\parallel}^{(2)}$) are second-order perturbation energies calculated by Eq. (2) with the magnetization along hard (easy) axis of CaCu_5 -type YCo_5 . Then the decomposed part of K_u^{PT} at different atomic site with spin-transition process is written as

$$\begin{aligned} K_u^{\text{PT}} &= \sum_{i\sigma\sigma'} K_{\sigma\Rightarrow\sigma'}^i \\ &= \sum_i K_{\uparrow\Rightarrow\uparrow}^i + K_{\downarrow\Rightarrow\downarrow}^i + K_{\uparrow\Rightarrow\downarrow}^i + K_{\downarrow\Rightarrow\uparrow}^i. \end{aligned} \quad (3)$$

The first two terms in Eq. (3) are called spin-conserving terms and the rest are spin-flip terms, which originate from the spin scattering process between the occupied and unoccupied state near the Fermi level. The detailed formulation of $K_{\sigma\Rightarrow\sigma'}^i$ is given in Ref. [19].

B. Lattice dynamics contribution to MCA energy at finite temperatures

The MCA energy at finite temperatures, K_u , can be evaluated by the difference of Helmholtz free energies computed with two different spin orientations, which is defined as

$$K_u(V, T) = F_{\perp}(V, T) - F_{\parallel}(V, T), \quad (4)$$

where V is the volume of YCo_5 . According to adiabatic approximation, K_u is considered as the sum of the following terms:

$$\begin{aligned} K_u &\approx K_u^{\text{DFT}}(V_0) + K_u^{\text{el}}(V_0, T) + K_u^{\text{phon}}(V_0, T) \\ &\quad + K_u^{\text{mag}}(V_0, T) + K_u^{\text{TE}}(T), \end{aligned} \quad (5)$$

where $K_u^{\text{DFT}}(V_0)$ is the MCA energy obtained from the DFT calculation with the optimized volume V_0 , $K_u^{\text{el}}(V_0, T)$ and $K_u^{\text{phon}}(V_0, T)$ represent the electronic and vibrational contribution to K_u , respectively. $K_u^{\text{mag}}(V_0, T)$ is the magnon contribution, which is not considered in the current study. K_u^{el} for the present system is very small and thus can be ignored. We roughly evaluated the thermal expansion term, $K_u^{\text{TE}}(T) \approx K_u^{\text{DFT}}(V(T)) - K_u^{\text{DFT}}(V_0)$, using the measured temperature-dependent lattice constants of YCo_5 from Ref. [20]. Since the change in the lattice constant c is negligible, we only change the in-plane lattice constant a as $a(T) = kT + a_0$, where a_0 is the lattice constant optimized by DFT at $T = 0$ K,

and $k \sim 7 \times 10^{-5} \text{ \AA}^{-1}$ is the proportionality constant estimated from the experimental temperature dependence of the a value [20].

The vibrational MCA energy K_u^{phon} is computed from the difference between the vibrational free energies at different magnetic orientations. In the HA, it becomes [17]

$$K_u^{\text{phon}} = -\frac{1}{\beta} \ln \frac{Z_{0,\perp}}{Z_{0,\parallel}}, \quad (6)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature with k_B being the Boltzmann constant, and $Z_{0,m}$ is the partition function of the harmonic oscillator at the magnetic state m defined as

$$Z_{0,m} = \prod_{qv} \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega_{qv,m}}{2}\right)}, \quad (7)$$

with \hbar being the reduced Planck constant. $\omega_{qv,m}$ is the harmonic phonon frequency of the v th branch at crystal momentum q in the magnetic state m , which can be obtained by diagonalizing the dynamical matrix constructed from the second-order interatomic force constants (IFCs) calculated in the same magnetic state m . If the difference of $\Delta\omega_{qv} = \omega_{qv,\perp} - \omega_{qv,\parallel}$ is small, Eq. (6) can be approximated by a linear function of $\Delta\omega_{qv}$ as

$$K_u^{\text{phon}} \approx \frac{\hbar}{2} \sum_{qv} [1 + 2n(\omega_{qv,\parallel})] \Delta\omega_{qv}, \quad (8)$$

where $n(\omega) = (e^{\beta \hbar \omega} - 1)^{-1}$ is the Bose-Einstein distribution function. Since $\Delta\omega_{qv}$ is very small in many cases, Eq. (8) is a reasonable approximation to Eq. (6) and will be used for computing the modal contribution to K_u^{phon} in Sec. III B 2. In the classical limit ($\hbar \rightarrow 0$), Eq. (8) reduces to $K_u^{\text{phon}} \approx \beta^{-1} \sum_{qv} (\Delta\omega_{qv} / \omega_{qv,\parallel})$.

It is important to recall that the above harmonic lattice dynamics (HLD) method can be employed only when the structure is dynamically stable, namely, $\omega_{qv} \geq 0$ is satisfied for all phonon modes in the Brillouin zone. If the structure is dynamically unstable, which is the case for pristine YCo₅ as will be shown later, Eq. (7) becomes ill-defined and the HLD method breaks down. Hence, a beyond (quasi)harmonic approach is required for evaluating the vibrational contribution to the MCA energy of YCo₅. The limitation of the HLD method can be overcome by using anharmonic lattice dynamics methods, such as the self-consistent phonon theory [21–23] or temperature-dependent effective potential method [24], or *ab initio* molecular dynamics (AIMD) method. In this study, we employ AIMD and evaluate the finite-temperature MCA energy as

$$\langle K_u \rangle_{\text{MD}}(T) = \frac{1}{N} \sum_{s=1}^N K_u^{\text{DFT}}(\{\mathbf{R}_i\}_s), \quad (9)$$

where $K_u^{\text{DFT}}(\{\mathbf{R}_i\}_s)$ is the MCA energy computed at the s th structure snapshot $\{\mathbf{R}_i\}_s$ sampled from the AIMD trajectory at the target temperature T , and N is the number of structures sampled at each T . This approach can be used even for the systems where an unstable phonon mode ($\omega_{qv}^2 < 0$) exists. Besides, contributions from the anharmonic terms of the

potential energy surface and the effect of structural distortion are included automatically.

C. Computational details

First-principle calculations in this study were performed by using the projector augmented wave (PAW) method [25], within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [26], as implemented in the Vienna *ab initio* simulation package (VASP) [27]. Lattice constants and atomic positions of CaCu₅-type YCo₅ were carefully optimized with a kinetic-energy cutoff of 400 eV for the plane-wave expansion, and the k -point mesh was generated automatically in such a way that the mesh density in the reciprocal space became larger than 450 \AA^{-3} . For the structural optimization and phonon calculations, we used the Methfessel-Paxton smearing method [28] with the width of 0.2 eV. On the other hand, the Methfessel-Paxton smearing method with a smaller width of 0.05 eV and tetrahedron method with the Blöchl correction [29] was used for calculating the MCA energy. Note that k mesh density of $\sim 6000 \text{ \AA}^{-3}$ was used to calculate K_u^{DFT} (K_u^{PT}) because the anisotropy energy is small, necessitating a denser mesh. To test the convergence of K_u^{DFT} with respect to k mesh density, we computed K_u^{DFT} with a denser mesh density of $\sim 11000 \text{ \AA}^{-3}$. The observed change in K_u^{DFT} was as small as 0.02 meV/f.u., showing that the adopted mesh density of $\sim 6000 \text{ \AA}^{-3}$ is dense enough. The initial local moments of $3 \mu_B$ and $-0.3 \mu_B$ were set for Co and Y atoms, respectively, for the collinear spin-polarized calculations, including phonon calculations.

The harmonic phonon calculations were conducted by using the finite-displacement method, as implemented in ALAMODE [22,30]. A $2 \times 2 \times 2$ supercell containing 48 atoms was adopted for the phonon calculation. To obtain K_u^{phon} using Eq. (6), we incorporated noncollinear spin-orbit interaction into the DFT calculation and estimated the second-order IFCs for two different spin orientations: $m \perp c$ and $m \parallel c$. We have confirmed that our implementation yields consistent results with the density-functional perturbation theory implementation [17] for MnBi. In addition, AIMD simulations were carried out to evaluate $\langle K_u \rangle_{\text{MD}}(T)$ using Eq. (9). At each temperature, we performed a collinear AIMD run for 5000 steps with a time-step of 2 fs and extracted 100 structural snapshots uniformly from the last 2500 steps. For each sampled snapshot, we then calculated the difference of the total energies between the two spin orientations. Finally, we estimated the average over the 100 snapshots using Eq. (9). We have confirmed that 100 structures were sufficient to obtain converged values of $\langle K_u \rangle_{\text{MD}}$.

III. RESULTS AND DISCUSSION

CaCu₅-type YCo₅ displays a layered hexagonal structure (space group: $P6/mmm$) shown in Fig. 1(a). The cobalt atoms are located either at the $2c$ or $3g$ Wyckoff sites, which respectively belong to the honeycomb and kagome layers. We label these inequivalent cobalt atoms as Co_{2c} or Co_{3g} . The symmetry of YCo₅ will be lowered with spin-orbit interaction when the magnetization is along the hard axis ([100] direction). The threefold Co_{3g} will be separated into two

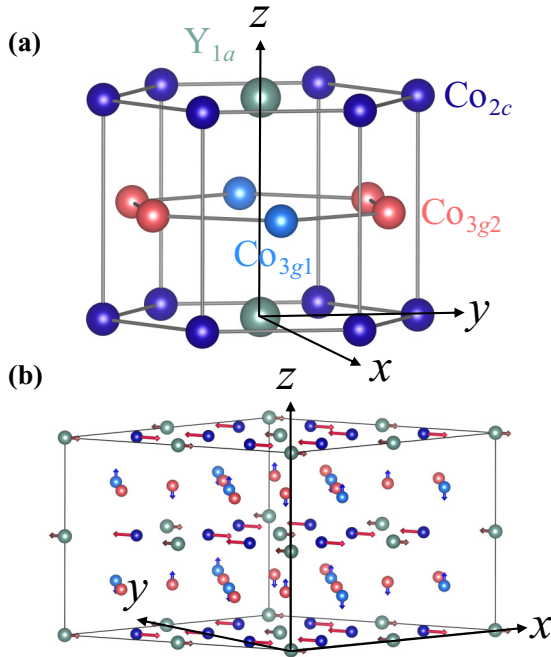


FIG. 1. (a) Crystal structure of CaCu₅-type YCo₅. The large spheres represent Y atoms, and the smaller ones are Co atoms. Wyckoff positions for different atoms are marked with the corresponding atom colors. (b) Crystal structure of YCo₅ with a $2 \times 2 \times 2$ supercell. The arrows indicate the displacement pattern of the lowest-energy soft phonon mode at L point [$\mathbf{q} = (\frac{1}{2}, 0, \frac{1}{2})$]. The length of the arrows represents the relative magnitude of displacements. Cartesian axes are labeled as x , y , and z , respectively.

inequivalent sites, which have the corresponding multiplicities of 1 (denoted as 3g1 hereafter) and 2 (denoted as 3g2 hereafter), respectively. The optimized lattice constants are $a = 4.907 \text{ \AA}$ and $c = 3.942 \text{ \AA}$, which agree reasonably well with the experimental values at 5 K ($a = 4.936 \text{ \AA}$, $c = 3.984 \text{ \AA}$, Ref. [20]) and at room temperature ($a = 4.950 \text{ \AA}$, $c = 3.986 \text{ \AA}$, Ref. [20]; $a = 4.921 \text{ \AA}$, $c = 3.994 \text{ \AA}$, Ref. [32]).

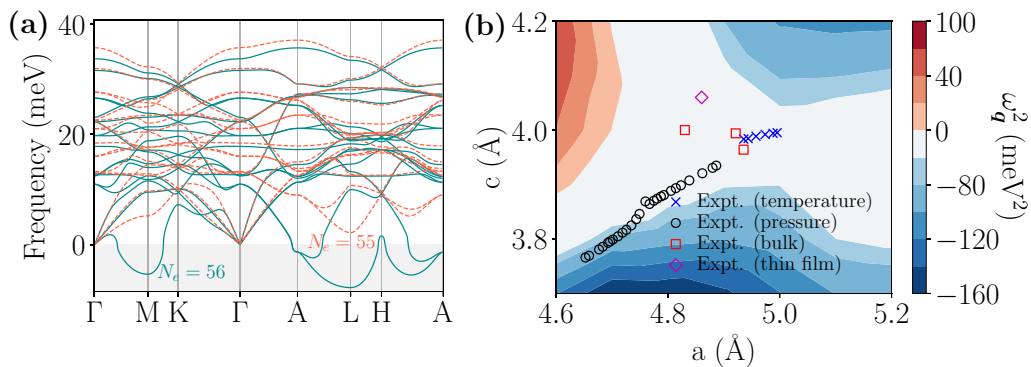


FIG. 2. Phonon frequencies of CaCu₅-type YCo₅ computed within harmonic approximation. (a) Phonon dispersion curves for the pristine YCo₅ ($N_e = 56$, solid line) and the hole-doped system ($N_e = 55$, dashed line). (b) Contour plot of the smallest $\omega_{\mathbf{q}}^2$ value for YCo₅ ($N_e = 56$) computed with various lattice parameters. The experimental lattice parameters are shown with open symbols. Crosses and circles are temperature- and hydrostatic pressure-dependence of lattice parameters from Refs. [20,31], respectively. Squares and diamonds are lattice parameters of bulk [32–34] and thin-film phases [35], respectively.

A. Dynamical stability

The harmonic phonon dispersion curves of the CaCu₅-type YCo₅ are shown in Fig. 2(a) by solid lines. While the previous experimental studies showed that the crystal structure of YCo₅ is the CaCu₅ type at and above room temperature, the harmonic phonon of the pristine YCo₅ turns out to be unstable. The largest phonon instability occurs at the L points of $\mathbf{q} = (\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The second-largest instability is observed at the M points of $\mathbf{q} = (\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, and $(\frac{1}{2}, \frac{1}{2}, 0)$. Since the calculated phonon frequency is rather sensitive to the lattice parameters, we also computed the phonon dispersion curves with various a and c values. The results are shown in Fig. S1 of the Supplemental Material (SM) [36]. As shown in Fig. 2(b), the smallest $\omega_{\mathbf{q}}^2$ value, which appears either at the L or M point, is negative in the wide region of the ac plane, including the area around the experimental (a , c) values reported in Refs. [20,31–35]. While the phonons can be dynamically stable in the upper left region ($a \lesssim 4.7 \text{ \AA}$, $c \gtrsim 3.9 \text{ \AA}$) of the figure, the experimental and theoretical lattice parameters are located away from that region. Thus the observed dynamical instability of YCo₅ cannot exclusively be attributed to the slight errors in the GGA-PBE lattice parameters.

The soft modes at the L and M points involve the in-plane displacements of Co_{2c} atoms accompanied by relatively small displacements of other atoms, as shown in Fig. 1(b). Once the atoms are slightly displaced along the polarization vector of the soft mode, the sixfold rotational symmetry in the honeycomb layer breaks, which decreases the total energy of the system. To understand the origin of the phonon instability, we investigated the bonding nature of the nearest-neighbor atomic pairs by computing the crystal orbital Hamilton populations (COHPs) [37] using the LOBSTER code [38]. The $-\text{COHP}$ values computed with collinear magnetism are shown in Fig. 3(a), where the dash and solid lines represent the results for the majority and minority spins, respectively. The most notable feature in Fig. 3(a) is the large negative peak of $-\text{COHP}$ for the nearest Co_{2c}-Co_{2c} bond at the Fermi level, representing its strong antibonding nature. The projected DOS in Fig. 3(b) shows that the antibonding state is formed by the d_{xy} and

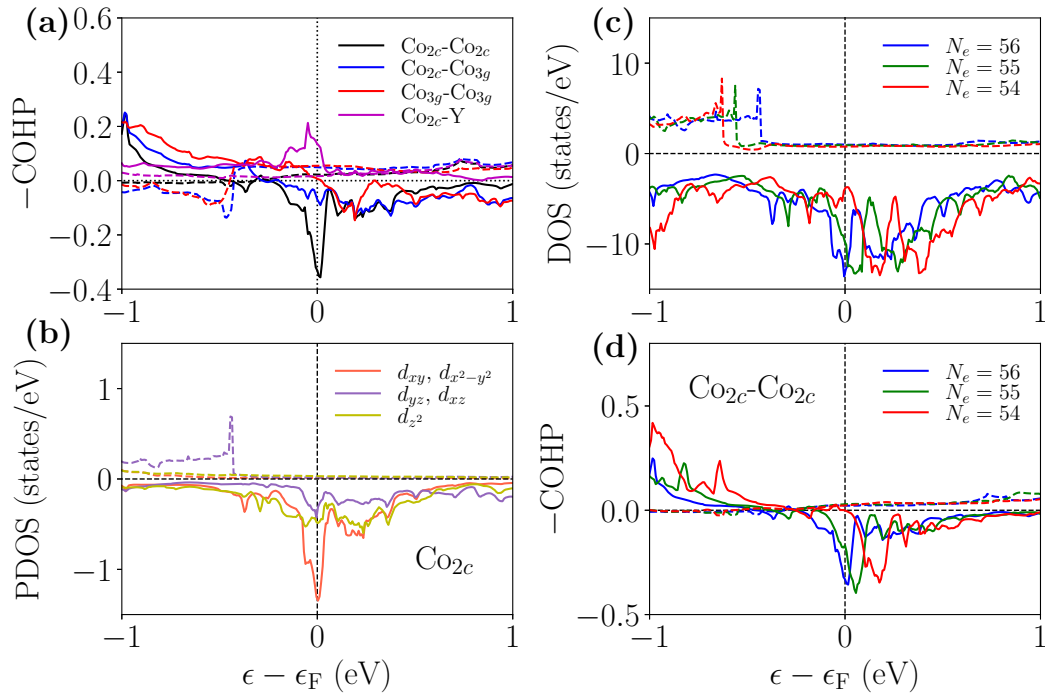


FIG. 3. (a) COHP calculation of different atomic bonds for YCo₅ with $N_e = 56$. (b) Projected density of states (PDOS) for $3d$ states at Co_{2c} site. (c) The total density of states (DOS) and (d) COHP calculation of Co_{2c}-Co_{2c} bonds for YCo₅ with $N_e = 56, 55$, and 54 respectively. The solid and dashed lines in all panels represent the results for minority and majority spin, respectively.

$d_{x^2-y^2}$ orbitals, while the contributions from the other orbitals both at Co_{2c} and Co_{3g} (see Fig. S2 in the SM [36]) sites are negligible around the Fermi level. The large antibonding contribution is energetically unfavorable. Hence, the system reacts in such a way that the population of the antibonding state decreases at the Fermi level, which can be achieved by distorting the structure and thereby lifting the orbital degeneracy.

The large antibonding population at the Fermi level may be reduced by hole doping, which is expected to improve the stability of the CaCu₅ structure. To see the effect of hole doping, we gradually reduced the number of valence electrons, N_e , from the original value of the pristine YCo₅ ($N_e = 56$) and computed the $-\text{COHP}$ values for the relevant Co_{2c}-Co_{2c} bond. As shown in Fig. 3(c), the Fermi level lowers with reducing N_e , and the peak position of the DOS in the minority spin state shifts to the higher energy. In addition, the population of the Co_{2c}-Co_{2c} antibonding state at the Fermi level decreases as decreasing N_e . Consequently, we observed that the phonons of the CaCu₅ structure became dynamically stable when $N_e \lesssim 55$ [see Fig. 2(a) for the $N_e = 55$ case] and the soft-mode frequency at the L point increased gradually with decreasing N_e , as tabulated in Table I.

On the basis of the above analyses, we now discuss possible scenarios explaining the inconsistency between our computational result and experiments about the stability of the CaCu₅-type YCo₅. First, since the detailed structure analyses using x-ray diffraction (XRD) measurement have been reported only at room temperature so far, there could be a lower-symmetry phase of pristine YCo₅ in the low-temperature region which is left to be discovered. Should

there be a structural phase transition, it would be second-order because no anomaly has been observed in the lattice parameters down to 5 K [20]. A lower-symmetry structure we found by distorting the structure following the imaginary mode at the L point [see Fig. 1(b)] is identified as *Imma*. After fully relaxing the structure, the total energy of the *Imma* structure is lower than that of experimentally reported hexagonal structure by 23.24 meV/f.u. The detailed structural information is tabulated in Table S1 of the SM [36]. The XRD patterns of the *P6/mmm* and *Imma* phases show noticeable difference, as shown in Fig. S3 of the SM [36]. Hence, the presence (or absence) of the lower-symmetry phase can be tested easily by XRD measurements conducted on pristine YCo₅ at low temperatures. The second scenario is the possible off-stoichiometry in the experimental samples. YCo₅ is the mother compound from which other Co-poor

TABLE I. Calculated N_e dependence of the MCA energies ($K_u^{\text{DFT}}, K_u^{\text{PT}}, K_u^{\text{VCA}}$) using different approaches (see the main text), anisotropy in the orbital moment (Δm_o), and the squared frequency of the soft mode at the L point (ω_L^2).

| N_e | MCA constant (meV/f.u.) | | | Δm_o (μ_B /f.u.) | ω_L^2 (meV ²) |
|-------|-------------------------|-------------------|--------------------|-------------------------------|----------------------------------|
| | K_u^{DFT} | K_u^{PT} | K_u^{VCA} | | |
| 56 | 0.383 | 0.177 | 0.383 | 0.074 | -61.1 |
| 55 | 2.947 | 2.451 | 2.757 | 0.206 | 4.7 |
| 54 | 1.797 | 1.442 | -0.611 | 0.153 | 79.3 |
| 53 | 0.356 | 0.426 | -1.407 | 0.074 | 130.1 |
| 52 | -0.643 | -0.384 | -1.553 | 0.028 | 156.3 |
| 51 | -1.069 | -0.833 | -1.331 | 0.001 | 156.1 |

and Co-rich phases, including YCo_3 , Y_2Co_7 , Y_5Co_{19} , and Y_2Co_{17} , are derived by partial substitution [40]. Since the formation energies of these derivatives are comparable to that of YCo_5 [41], the off-stoichiometry of YCo_{5+z} can occur rather easily in the samples prepared by a high-temperature treatment. Indeed, Pareti *et al.* [42] reported that YCo_{5+z} could be synthesized for the range of $-0.7 < z < 2.3$ by performing a quenching from high temperature. The Co-poor off-stoichiometry introduces excess holes to the system, which are expected to decrease the population of the antibonding state at the Fermi level and thereby improve the stability of the structure. Third, the phonon instability of YCo_5 might appear due to the limited accuracy of the present HLD calculation based on GGA-PBE. While we have also observed the same phonon instability with other semilocal functionals such as PBEsol, more accurate treatment of the electronic correlation, for example, by hybrid functionals or by the combination of the dynamical mean-field theory and the DFT (DFT + DMFT) may yield stable phonons. Moreover, the quantum fluctuation of atomic nuclei may help avoid the structural distortion to occur and stabilize the CaCu_5 -type YCo_5 , akin to the case of a superconducting hydride [43]. Answering which of these scenarios is the most plausible would be challenging as it requires additional experimental and theoretical investigations, which are left for a future study.

B. MCA energy of YCo_{5-x}

In the following, we will focus on the MCA energy of pristine YCo_5 ($N_e = 56$) as well as the hole-doped systems ($N_e < 56$) at 0 K and finite temperatures. In the case of results at 0 K, we compare the K_u^{DFT} with K_u^{PT} for various N_e values. In addition, we also calculated MCA energy K_u^{VCA} of the $\text{Y}(\text{Fe},\text{Co})_5$ alloy using virtual crystal approximation (VCA) [44,45] to compare with the experimental results. Note the volume of $\text{Y}(\text{Fe},\text{Co})_5$ alloy is fixed for the VCA calculation, similar to the case of manually reducing N_e . The corresponding total number of valance electrons for the VCA calculations, shown in the first column of Table I, is also labeled as N_e . In addition, the spin moment, namely $m_{\sigma,\text{Co}}$, at different Co sites and anisotropy in orbital moment, defined as $\Delta m_o = m_{\parallel}^o - m_{\perp}^o$, are also studied. As for the finite-temperature effects, we calculated the HLD contribution K_u^{phon} [Eq. (6)] for the dynamically stable cases and the ensemble average $\langle K_u \rangle_{\text{MD}}$ [Eq. (9)] for $N_e = 54, 55$, and 56 (pristine YCo_5).

1. MCA energy at zero kelvin

First, we discuss the N_e dependency of the MCA energy at 0 K obtained from the different approaches mentioned above. The present computational results are shown in Fig. 4 and Table I. We also show the N_e dependence of the spin magnetic moments in Appendix A. As shown in Fig. 4 and Table I, all approaches gave similar trends in that positive MCA energy first increases, then decreases, and finally changes the sign to negative as N_e decreases. This trend is qualitatively consistent with the MCA constants of $\text{Y}(\text{Fe}_x\text{Co}_{1-x})_5$ ($x = 0.00, 0.10, 0.16$, and 0.26) alloys measured by Rothwarf *et al.* [39]. Both K_u^{DFT} and K_u^{PT} values of the pristine YCo_5 ($N_e = 56$) are

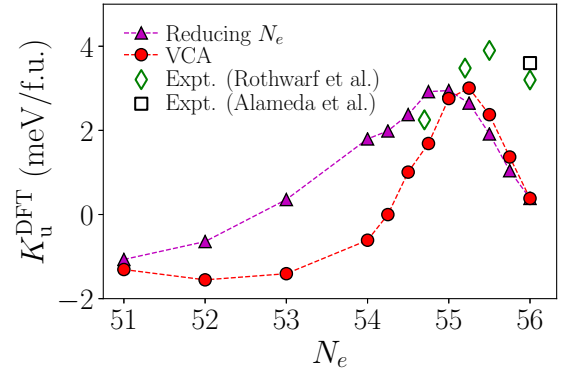


FIG. 4. Calculated MCA energy K_u^{DFT} as the function of valance electron number obtained by manually reducing N_e and VCA approaches, respectively. The computational results are compared with the experimental values reported by Rothwarf *et al.* [39] and Alameda *et al.* [6]. The dashed lines are shown to guide the eye.

smaller than the experimental values of ~ 3.6 meV/f.u. [6] and ~ 3.20 meV/f.u. [46]. Similar underestimation problems have also been observed in the previous LDA- or GGA-level calculations [7,47,48], which have successfully been resolved either by considering the orbital polarization contribution [47,49,50], by using DFT + U approach [7], or by DFT + DMFT [48]. Nonetheless, since the main subject of this work is to study the lattice dynamics effects on the MCA energy, and the GGA-PBE functional gives the reasonable results of the N_e dependency (Fig. 4), we still employ the GGA-PBE functional in the study.

From the results of the second-order perturbation calculation, we found that the significant enhancement of the MCA energy at $N_e = 55$ originates from the spin conservation term $K_{\downarrow\rightarrow\downarrow}^i$ at the Co sites. Moreover, we have calculated the anisotropy of orbital moments Δm_o (see Table I) and confirmed that the Bruno relation ($K_u^{\text{DFT}} \propto \Delta m_o$) [51,52] nicely holds for $N_e \geq 54$. More detailed discussion can be found in Appendix B.

2. Lattice dynamics effects on the MCA energy at finite temperature

Next, we discuss the lattice dynamics effects on the MCA energy of the pristine and hole-doped YCo_5 . Figure 5(a) shows the temperature dependence of K_u^{phon} [Eq. (6)] calculated for the hole-doped YCo_5 ($N_e \leq 55$), for which the phonons are dynamically stable at 0 K. In the $N_e \geq 54$ region, the K_u^{phon} value gradually decreases as the temperature raises. As N_e decreases further, the temperature dependence becomes weaker, and the sign of the slope eventually changes at $N_e \simeq 53$. To understand the origin of this N_e dependence, we computed the mode- and energy-decomposed K_u^{phon} for $N_e = 55$ and 54, as shown in Figs. 5(b) and 5(c), respectively. Here, the mode-decomposed value was defined as $K_{u,qv}^{\text{phon}} = \frac{\hbar}{2} [1 + 2n(\omega_{qv,\parallel})] \Delta\omega_{qv}$, and the energy decomposition was performed by computing

$$\Delta F^{\pm}(\omega) = \frac{1}{N_q} \sum_{qv} K_{u,qv}^{\text{phon}} \delta(\omega - \omega_{qv,\parallel}) \theta(\pm \Delta\omega_{qv}), \quad (10)$$

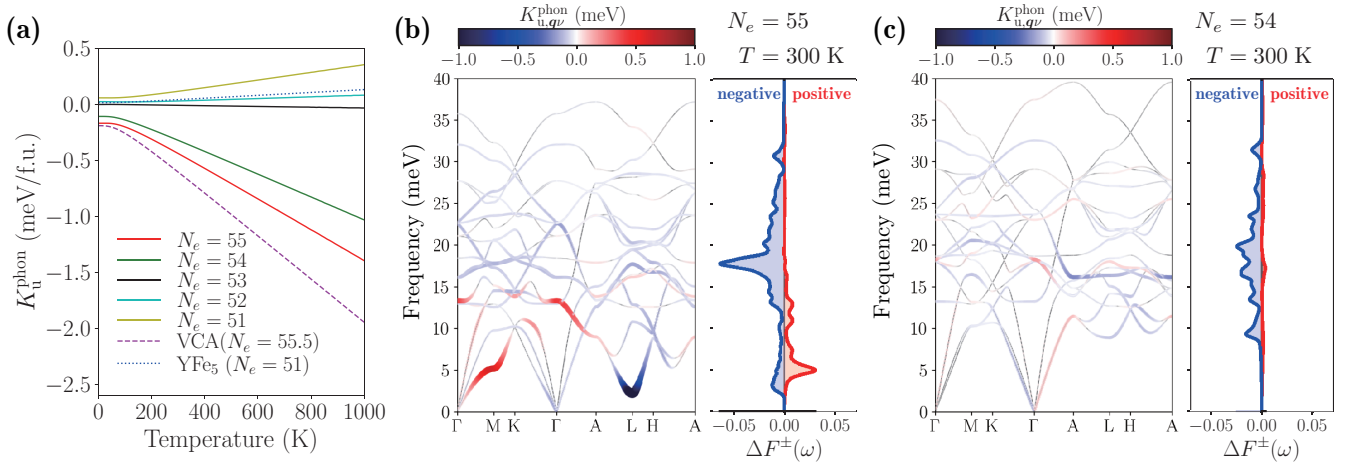


FIG. 5. (a) Calculated temperature dependence of K_u^{phon} . Solid lines represent K_u^{phon} of hole-doped YCo₅ obtained by manually reducing N_e , dashed line represents $K_{\text{VCA}}^{\text{phon}}$ of Y(Co,Fe)₅ obtained by VCA approach with $N_e = 55.5$, and dotted line is the K_u^{phon} value of YFe₅. (b) and (c) show the room-temperature (300 K) mode- and energy-decomposed K_u^{phon} of hole-doped YCo₅ with $N_e = 55$ and 54, respectively. In the mode-decomposed figures, the line color represents the sign of $K_{u,qv}^{\text{phon}}$, whose absolute value is represented by the linewidth.

where $\theta(x)$ is the step function which becomes $\theta(x) = 1$ when $x > 0$ and 0 otherwise. $\Delta F^+(\omega)$ ($\Delta F^-(\omega)$) includes the contributions from phonon modes that increase (decrease) K_u^{phon} . It is straightforward to show $\int_0^\infty d\omega [\Delta F^+(\omega) + \Delta F^-(\omega)] \approx K_u^{\text{phon}}$. It is remarkable in Fig. 5(b) that the soft phonon at the L point contributes negatively to the MCA energy at finite temperature. On the other hand, the lower transverse acoustic mode along the Γ -M line and the second-lowest optical mode around the Γ point have relatively large positive contributions. Moreover, $\Delta F^-(\omega)$ shows a large negative peak around $\omega \sim 18$ meV, which can be attributed to the weakly dispersive branches in this energy region. When one more electron is removed from the system, the antibonding nature further weakens, and consequently, the overall phonon frequency increases, as shown in Fig. 5(c). This hardening decreases $n(\omega_{qv,\parallel})$ in Eq. (8), which partially explains the disappearance of the clear structures in the mode- and energy-resolved K_u^{phon} . We also observed the same qualitative change in the VCA calculation, which is shown in Fig. S4 of the SM [36].

The zero-temperature MCA energy, shown in Fig. 4, takes the maximum value at around $N_e = 55$. By contrast, the lattice dynamics contribution tends to become more significant as increasing N_e from 54 to 56. Hence, the effect of the lattice dynamics on the MCA energy is expected to be larger in the large N_e region close to $N_e = 56$. Indeed, in the VCA calculation with $N_e = 55.5$, the K_u^{phon} value at 800 K is around -1.5 meV/f.u. [dashed line in Fig. 5(a)], whose absolute value is comparable to that of $K_u^{\text{DFT}} = 2.4$ meV/f.u. Accordingly, we may expect that the effect of the lattice dynamics would become even more significant for the pristine YCo₅ ($N_e = 56$). However, as N_e approaches 56, the phonon frequencies tend to soften, especially noticeable at the L point, and the effect of phonon anharmonicity would be greater. The phonon anharmonicity is expected to influence the phonon frequencies at finite temperatures and thereby the Bose-Einstein occupation function, which would affect the temperature-dependence of K_u^{phon} . Moreover, the (incipient)

distortion of the hexagonal structure, which is not considered in the HLD approach, may also influence temperature dependence.

To understand the effect of the phonon anharmonicity and the possible structural distortion on the MCA energy at finite temperature, we compare the calculated $\langle K_u \rangle_{\text{MD}}$ values with $K_u^{\text{tot}} = K_u^{\text{DFT}} + K_u^{\text{phon}}$ in Fig. 6(a). These two values should be similar in the high-temperature (classical) limit when phonon anharmonicity is weak. Besides, when there are no structural distortion, $\langle K_u \rangle_{\text{MD}} \approx K_u^{\text{DFT}}$ should hold in the $T \rightarrow 0$ limit because the present AIMD neglects the nuclear quantum effect, i.e., zero-point motion. Indeed, for $N_e = 54$

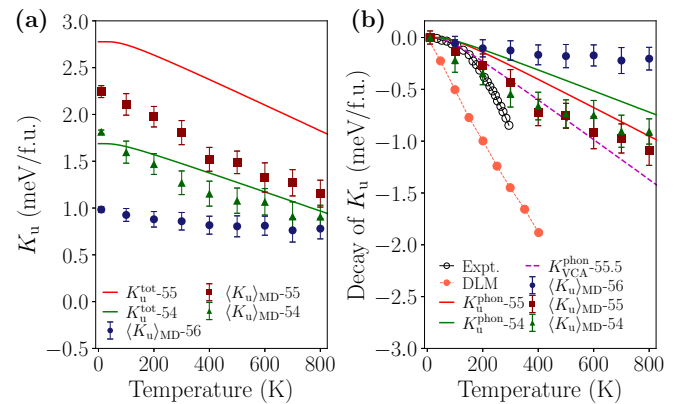


FIG. 6. Temperature dependence of MCA energy evaluated with different methods. (a) Filled symbols are $\langle K_u \rangle_{\text{MD}}$ values of YCo₅ evaluated from AIMD with $N_e = 56$, 55, and 54, respectively. Solid lines are K_u^{tot} (see text) of YCo₅ with $N_e = 55$ and 54, respectively. (b) Temperature decay of K_u for YCo₅ with $N_e = 56$, 55, 55.5, and 54, respectively. Dashed line is the $K_{\text{VCA}}^{\text{phon}}$ of Y(Co,Fe)₅ ($N_e = 55.5$) determined using VCA method. The experimental data (black open circles) and theoretical results (red solid circles) based on disordered local moment (DLM) method shown were taken from Refs. [6,15], respectively. The error bars are the calculated standard deviation obtained with the sampling structures.

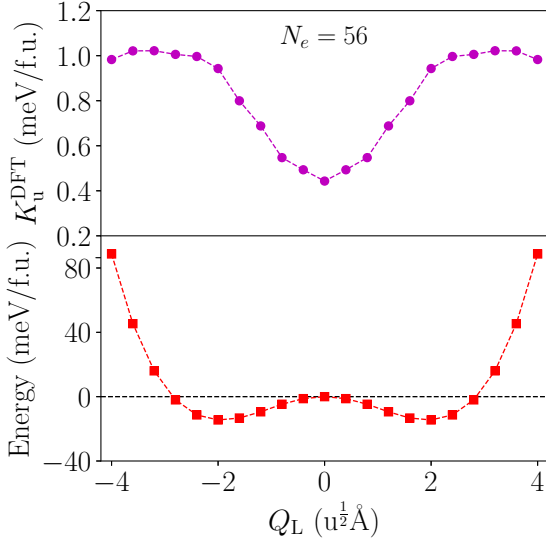


FIG. 7. Calculated MCA energy K_u^{DFT} (top) and total energy (bottom) as the function of normal coordinate amplitude Q_L of the L-point soft mode for the pristine YCo_5 . Note the total energy has been offset by the corresponding value at $Q_L = 0$. The dashed line is shown to guide the eye.

where the phonon frequencies are relatively higher than the $N_e = 55$ case, $\langle K_u \rangle_{\text{MD}}$ and K_u^{tot} agree reasonably well with each other. Also, the $\langle K_u \rangle_{\text{MD}}$ value at 10 K is 1.815 meV/f.u., which is in close agreement with $K_u^{\text{DFT}} = 1.797$ meV/f.u. (see Table I). By contrast, in the case of $N_e = 55$, the $\langle K_u \rangle_{\text{MD}}$ value at 10 K is ~ 2.24 meV/f.u., which is $\sim 24\%$ smaller than $K_u^{\text{DFT}} = 2.947$ meV/f.u. We also observed similar discrepancy between the canonical average of the orbital moment, $\langle \Delta m_o \rangle_{\text{MD}}$, at 10 K and the Δm_o value obtained for the perfect $P6/mmm$ structure shown in Table I (see Fig. S5 in the SM [36]). These discrepancies indicate that the hexagonal $P6/mmm$ structure transformed to another lower-energy structure in the present AIMD simulations at low temperatures even though the harmonic phonon was dynamically stable when $N_e = 55$ [Fig. 2(a)]. We have found that another structure possessing the $P6_3/mcm$ symmetry was slightly more stable than the $P6/mmm$ phase by ~ 0.25 meV/f.u., which explains the observed discrepancy. Nevertheless, except for the offset at $T = 0$ K, the temperature decay of $\langle K_u \rangle_{\text{MD}}$ is quite similar to that of K_u^{tot} in the wide temperature range. Hence, the effect of the anharmonicity on the MCA energy is insignificant for $N_e = 55$.

It is interesting to see that, in the case of $N_e = 56$, the $\langle K_u \rangle_{\text{MD}}$ values were larger than $K_u^{\text{DFT}} = 0.383$ meV/f.u. both in low- and high-temperature ranges. Also, the $\langle K_u \rangle_{\text{MD}}$ value is almost temperature independent. To obtain deeper insights into the mechanism behind them, we calculated the K_u^{DFT} value as a function of the normal coordinate amplitude Q_L of the L-point soft mode. As shown in Fig. 7, the sign of $\partial^2 K_u^{\text{DFT}} / \partial Q_L^2$ at $Q_L = 0$ is positive when $N_e = 56$. Since the L-point soft mode induces the structural distortion, it should affect the temperature dependence of $\langle K_u \rangle_{\text{MD}}$ most significantly. Hence, we can approximately write

$$\langle K_u \rangle_{\text{MD}} \approx \int_{-\infty}^{\infty} K_u^{\text{DFT}}(Q_L) P_T(Q_L) dQ_L, \quad (11)$$

where $P_T(Q_L)$ is the probability distribution of Q_L at temperature T . In the low-temperature region, $P_T(Q_L)$ has a peak around either side of the double-well minima, where $K_u^{\text{DFT}}(Q_L)$ becomes ~ 1.0 meV/f.u. This value is in good agreement with $\langle K_u \rangle_{\text{MD}}$ at 10 K. In the high-temperature limit, $P_T(Q_L)$ has a peak around $Q_L = 0$, i.e., $\langle Q_L \rangle \approx 0$, but the variance of the distribution $\langle Q_L^2 \rangle$ becomes large. Thus the $\langle K_u \rangle_{\text{MD}}$ value became larger than $K_u^{\text{DFT}}(0)$ because of $\partial^2 K_u^{\text{DFT}} / \partial Q_L^2 > 0$. We note that, for $N_e = 55$ and 54 , the sign of $\partial^2 K_u^{\text{DFT}} / \partial Q_L^2$ is negative (see Fig. S6 in the SM [36]), which is consistent with the negative sign of $K_{u,qv}^{\text{phon}}$ shown in Figs. 5(b) and 5(c).

We also show $\langle K_u \rangle_{\text{MD+TE}} = \langle K_u \rangle_{\text{MD}} + K_u^{\text{TE}}$ (see Fig. S7 in the SM [36]) which includes the effect of thermal expansion evaluated approximately as explained in Sec. II B. It is clear that the effect of thermal expansion is insignificant except for the $N_e = 54$ case at high temperatures, where the K_u^{TE} value amounts to -0.3 meV/f.u.

Figure 6(b) compares the predicted temperature decay of the MCA energy obtained from various computational methods, including the DLM result of Ref. [15], and that of the experimental result. Note that the data shown in Fig. 6(b) have been offset by the corresponding value at the lowest temperature: 10 K for $\langle K_u \rangle_{\text{MD}}$, and 0 K for the others. The present calculation based on GGA-PBE predicts that lattice dynamics hardly influences K_u for the pristine YCo_5 ($N_e = 56$) at finite temperatures mainly due to the presence of the structural distortion. Therefore it is reasonable to conclude that the lattice dynamics effect on the MCA energy is negligible for the pristine YCo_5 and the spin fluctuation remains the dominant effect for yielding the temperature decay of K_u . However, when the structural distortion is suppressed by hole-doping, the lattice dynamics effect becomes non-negligible in the $N_e \gtrsim 54$ region and therefore should be considered as well when comparing theoretical results with experimental ones.

IV. SUMMARY

To summarize, we theoretically studied the structural stability and lattice dynamics effects on the MCA energy for pristine and hole-doped YCo_5 using first-principles methods based on DFT. The CaCu₅-type ($P6/mmm$) structure of pristine YCo_5 is predicted to be dynamically unstable at 0 K, and the soft phonon modes appear at L and M points. This phonon instability originates from the large population of antibonding states near the Fermi level which is formed by the nearest Co atoms in the honeycomb layer. We demonstrated that the phonon instability can be removed by hole doping, which depopulates the antibonding states. We also evaluated the effect of lattice dynamics on the MCA energy based on harmonic lattice dynamics and AIMD methods by computing K_u^{phon} and $\langle K_u \rangle_{\text{MD}}$, respectively. For the pristine YCo_5 , we found that lattice dynamics hardly influence the MCA energy at finite temperature. Also, the ensemble average $\langle K_u \rangle_{\text{MD}}$ at finite temperature turned out to be larger than the K_u^{DFT} computed with the static $P6/mmm$ lattice. We attributed these unique features to the dynamical distortion of the structure, which is induced by the soft phonon modes. By contrast, in the hole-doped YCo_5 where the dynamical distortion is suppressed, a much larger temperature decay was observed

TABLE II. Calculated N_e -dependent total spin magnetic moments in YCo_5 and site-dependent spin magnetic moments for different Co ($m_{\sigma,\text{Co}}$). The spin magnetic moments of previous works (experimental or theoretical) are obtained from Refs. [7,32,47,54–56]

| N_e | m_{tot} ($\mu_B/\text{f.u.}$) | $m_{\sigma,\text{Co}}$ (μ_B) | | | |
|-------|--|------------------------------------|------------------|-------------------------------------|-------------------------------------|
| | | This study | | Previous work | |
| | | Co_{2c} | Co_{3g} | Co_{2c} | Co_{3g} |
| 56 | 7.026 | 1.498 | 1.525 | 1.44 ^a 1.62 ^b | 1.31 ^a 1.64 ^b |
| | | | | 1.61 ^c 1.46 ^d | 1.68 ^c 1.51 ^d |
| 55 | 7.859 | 1.685 | 1.668 | | |
| 54 | 8.625 | 1.833 | 1.810 | | |
| 53 | 9.342 | 1.950 | 1.953 | | |
| 52 | 10.073 | 2.061 | 2.100 | | |
| 51 | 10.803 | 2.170 | 2.231 | 2.05 ^e | 2.00 ^e |

^aExperimental results, Refs. [54,55].

^bDLM, Ref. [32].

^cGGA + U , Ref. [7].

^dFLAPW, Ref. [47].

^eYFe₅,GGA, Ref. [56].

both in K_u^{phon} and $\langle K_u \rangle_{\text{MD}}$. While the lattice dynamic effect on the finite-temperature MCA energy is not as significant as that of the spin fluctuation, its effect should not be neglected when making a quantitative comparison between theory and experiments, particularly for the hole-doped YCo_5 .

ACKNOWLEDGMENTS

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APPENDIX A: MAGNETIC MOMENT

Saturation magnetization is an important factor for realizing high-performance permanent magnets. The N_e -dependent total spin magnetic moments, m_{tot} , and site-dependent moments, $m_{\sigma,\text{Co}}$, are listed in Table II. For $N_e = 56$, the calculated spin moment of 1.498 μ_B (1.525 μ_B) for Co_{2c} (Co_{3g}) is slightly larger than the experimental value of 1.44 μ_B (1.31 μ_B) [54,55]. By contrast, the calculated total spin moment of 7.03 $\mu_B/\text{f.u.}$ is smaller than the experimental saturation magnetization with the value of ~ 8.4 $\mu_B/\text{f.u.}$ [32], which can partly be attributed to the contribution from orbital moments that is neglected in the collinear spin-polarized calculation. To compare with previous theoretical results, a selection of results based on different methods is summarized in Table II. These values are spin moments obtained by DLM method [32], GGA + U method [7], and full potential linearized augmented plane wave (FLAPW) method [47]. Our results match well with the FLAPW values but differ slightly

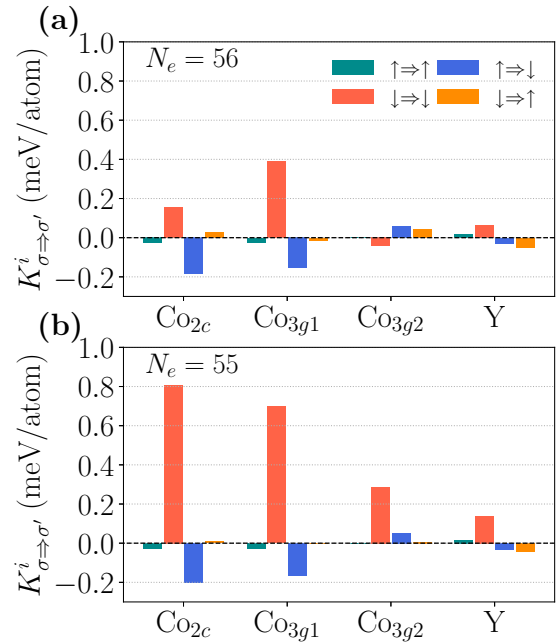


FIG. 8. Decomposed atomic sites dependence of MCA energy, $K_{\sigma \Rightarrow \sigma'}^i$, obtained from second-order perturbation analysis in YCo_5 with $N_e = 56$ (a) and 55 (b), respectively.

from the GGA + U and DLM results. The spin moments of both Co sites increase with decreasing N_e , which can be explained by the DOS shown in Fig. S8(a), and (b) of the SM [36]. When N_e is decreased, the minority spin states shift to the higher energy, increasing spin splitting. Since the majority spin states are fully occupied, the decrease of minority spin states will lead to an increase of the net single spin states, then a larger spin magnetic moment. Note that the spin magnetic moments for $N_e = 51$ is slightly larger than that of YFe₅ with the values of 2.082, and 2.033 μ_B for Fe_{2c} and Fe_{3g} according to our calculations, which may be attributed to the not fully occupied 3d majority spin states (see Fig. S8(d) in the SM [36]) in YFe₅ ($N_e = 51$). As shown in Figs. S8(c) and S8(d) of the SM [36], the majority spin states of Y(Fe,Co)₅ evaluated by the VCA approach will become partially occupied when $N_e \leq 52$, which is different from the DOS determined by reducing N_e approach.

APPENDIX B: VALIDITY OF THE BRUNO RELATION

According to the Bruno relation, the MCA energy is proportional to the anisotropy in the orbital moment ($K_u^{\text{DFT}} \propto \Delta m_o$). To understand the validity of the Bruno relation with N_e , the atomic site dependence of $K_{\sigma \Rightarrow \sigma'}^i$ with different spin-transition processes are shown in Fig. 8 and Fig. S9 of the SM [36], respectively. The maximum K_u^{PT} for $N_e = 55$ originates mainly from the enhancement of positive spin conservation term $K_{\downarrow \Rightarrow \downarrow}^i$ both at Co_{2c} , Co_{3g1} , and Co_{3g2} sites. However, positive $K_{\downarrow \Rightarrow \downarrow}^i$ decrease dramatically as NE decreases (see Fig. S9 in the SM [36]). The negative spin-flip term $K_{\uparrow \Rightarrow \downarrow}^i$ of Co_{2c} and Co_{3g1} mainly contributes to K_u^{PT} when $N_e \leq 52$, resulting in a negative K_u^{PT} . Since the spin-flip term is absent in the orbital magnetic moment, the Bruno relation holds for $N_e \geq 53$ and not for $N_e \leq 52$. Although we

find a qualitatively similar K_u^{PT} for YCo_5 with $N_e = 51$ and YFe_5 with the corresponding values of -0.833 meV/f.u., and -0.919 meV/f.u., respectively, the mechanism is different for these two systems. The negative $K_{\uparrow\Rightarrow\downarrow}^i$ (see Fig. S9(d) in the

SM [36]) at Co_{2c} and Co_{3g1} makes a main contribution to K_u^{PT} for YCo_5 with $N_e = 51$, while negative $K_{\downarrow\Rightarrow\uparrow}^i$ (see Fig. S10 in the SM [36]) at Fe_{2c} and Fe_{3g1} sites also makes a considerable contribution besides $K_{\uparrow\Rightarrow\downarrow}^i$ in YFe_5 .

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