

Finite-temperature enhancement of magnetic interactions from first principles

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Density functional theory has demonstrated remarkable predictive power in calculating magnetic properties at zero temperature. At finite temperatures, thermally excited phonons affect magnetism. Efficient *ab initio* methods for calculating the temperature dependence of magnetic exchange interactions are still lacking despite the importance of room temperature magnetism for applications. Here we present a method to calculate the exchange interactions at finite temperatures from first principles using only two supercell calculations per temperature. Focusing on magnetic insulators, we find that magnetic exchange interactions decrease with temperature in NiO, while in Cr₂O₃ a substantial temperature-induced enhancement of 10% at $T = 300$ K is uncovered. The exchange constant is governed by an interplay between metal-ligand hybridization, Hubbard repulsion, and the band gap. They all depend on equilibrium interatomic distances and bond angles, themselves modified by thermal phonons.

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I. INTRODUCTION

Density functional theory and its extensions have been successful in describing magnetic properties of a wide range of material systems at zero temperature. At the same time, many materials of technological importance, such as halide perovskites, molecular magnets, and systems of reduced dimensionality (single and multilayer systems and twisted heterostructures) have strong thermal fluctuations at room temperature. Understanding how temperature affects magnetic interactions is therefore an intriguing challenge.

The majority of materials exhibit a decrease in magnetic interactions as temperature rises [1–3]. One scenario of such decrease is based on the linear thermal lattice expansion driving the ions apart, and thus reducing the orbital overlap [Fig. 1(a)]. Since exchange constants J are generally proportional to the overlap integral t squared, $J \propto t^2/U$, they should decrease with increasing temperature [4]. This is observed, e.g., in Cu₂OSeO₃ and Fe₃GeTe₂ [2,3,5]. However, other mechanisms, driven by phonons, could be at play, and this trend can even be reversed.

One scenario where the exchange may increase with temperature involves a structural transformation from a state of low symmetry to one of higher symmetry as temperature increases. For example, in transition metal–rare-earth perovskites ABX_3 , the tolerance factor of 1 indicates a perfect match between the sizes of the octahedra BX_6 and the A -site ion, resulting in the formation of an ideal cubic structure. A mismatch results in octahedral tilts at low temperatures, illustrated in Fig. 1(b) [6]. Such tilts reduce the metal–oxygen–metal bond angle from 180° , thus diminishing the exchange constant. At elevated temperatures, the tilts

disappear, and the bond angle returns to 180° , which must boost the magnetic exchange. This could lead to fascinating phenomena, such as reentrant magnetic ordering, where increasing T thermal fluctuations destroy the magnetic ordering, which reappears at a higher T due to increased exchange. On the other hand, if no octahedral tilts are present at $T = 0$ K, thermal displacements of the ions bend the bonds, thus lowering the exchange constants. We emphasize that the thermal expansion or octahedral tilt change shown in Fig. 1 are anharmonic effects: thermal phonon amplitudes oscillate around zero; thus, in the harmonic approximation, they would not alter the average octahedral tilt. Instead, in the harmonic approximation, the temperature dependence of the exchange is driven by its second derivatives with respect to the phonon amplitudes. These are the effects we consider in this work.

The increase in magnetic exchange due to thermally excited phonons has been found in CsO₂ [7]. As illustrated in Fig. 1(c), magnetism here is not derived from the conventional d or f electrons, but rather arises from the p orbitals of oxygen ions forming π^* molecular orbitals of O₂ dimers. The increase in exchange constants is thought to be driven by thermal librations of O₂ molecules, which cause enhanced orbital overlaps between the O- $p_{x,y}$ orbitals and the Cs- p_z orbitals [8]. Here we find a substantial temperature-induced enhancement of exchange interactions in Cr₂O₃: the dominant exchange increases by approximately 10%.

Incorporating thermally excited phonons in first-principles calculations requires large supercells and a significant number of configurations, on the order of $\sim 70\,000$, necessitating the generation of neural-network potentials [9]. Averaging over structures distorted by the presence of thermal phonons is a major computational challenge. In a recent advance, Mankovsky *et al.* calculated exchange constants at nonzero temperature, showing that 14 distorted structures are sufficient to converge the thermal average [1].

Motivated by recent modeling of optical absorption spectra using only one structure [10], here we explore the possibility

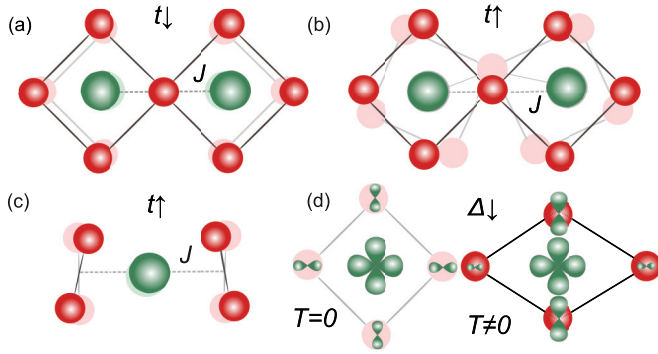


FIG. 1. Principal mechanisms driving temperature dependence of magnetic exchange constants: (a) linear thermal expansion elongates the bonds, resulting in the reduction of M - O - M hopping integrals t (here and in the following, $\uparrow, \downarrow$ indicate the increase/decrease of the quantity with increasing temperature) and the exchange constants; (b) reduction of octahedral tilts with temperature results in enhanced t_{MO} and stronger antiferromagnetic J ; (c) thermal librations of magnetic O_2 molecules in CsO_2 enhance t and J with increasing temperature. (d) Electron-phonon coupling mixes the top valence band and the bottom conduction band with higher conduction and lower valence bands, thus decreasing the gap (Δ). In real space this is manifested as increased metal-ligand hybridization, shown schematically. The corresponding energy decrease of the superexchange intermediate state drives the J increase with temperature.

of computing exchange constants at finite temperatures using a small number of first-principles supercell calculations, in the spirit of the special displacement method by Zacharias and Giustino (ZG) [10,11]. Our goal is to devise a method to accurately calculate magnetic interactions based on Density Functional Theory (DFT). In doing so, we aim to shed light on the remarkable interplay between temperature, associated ionic displacements, and magnetism. The paper is structured as follows: We start by introducing the special cell method for calculating magnetic exchange constants, benchmark it for NiO and Cr_2O_3 [Fig. 2(a) and 2(b)], discuss how the thermally

excited phonons modify the electronic structure (Fig. 3) and finish with the quantitative discussion of dominant mechanisms.

II. METHODOLOGY

Thermal phonons promote the changes in the electronic structure via electron-phonon coupling. This alters magnetism. Aiming to describe magnetic insulators with magnon frequencies lower than those of optical phonons, we neglect nonadiabatic effects and coherence between magnons and phonons. The case of resonance will be treated in the forthcoming paper. We aim to describe spins with the phonon-averaged Hamiltonian,

$$\mathcal{H} = \frac{1}{2} \sum_{ij} J_{ij}(T) \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where $J_{ij}(T)$ are the temperature-dependent exchange constants between spins $\mathbf{S}_i$ and $\mathbf{S}_j$, residing at sites i and j , respectively. In a frozen phonon approach, the interactions between electrons and phonons can be approximated by calculating the electronic structure in a supercell with frozen phonons (commensurate with the supercell) that mimic thermal atomic displacements. In the spirit of mean-field theory, the most probable phonon amplitudes are chosen so as to minimize the free energy at a given temperature [12], as in the ZG method. Thus, we aim to find a frozen-phonon structure, giving the value of $J_{ij}(T)$ which approximates a vibrational average $\langle J_{ij}(x_v) \rangle_T$. The approach obviates the need for explicit calculations of electron-phonon matrix elements.

In the spirit of mean-field theory, root-mean-square amplitudes of all $3N - 3$ optical phonon modes $\sigma_v(T)$ commensurate with the supercell containing N atoms are chosen to minimize the free energy (three Γ -point acoustic modes do not modify magnetic exchange). This is achieved when $M_p \omega_v^2 \sigma_v^2 = \hbar \omega_v [n_{BE}(\hbar \omega_v / T) + \frac{1}{2}]$, resulting in $\sigma_{v,T} = [(2n_{v,T} + 1)\ell_v^2]^{1/2}$, where ω_v is the mode frequency, n_{BE} is the Bose-Einstein occupation of the v th mode, and $\ell_v = [\hbar / (2M_p \omega_v)]^{1/2}$ is the zero-point vibrational amplitude

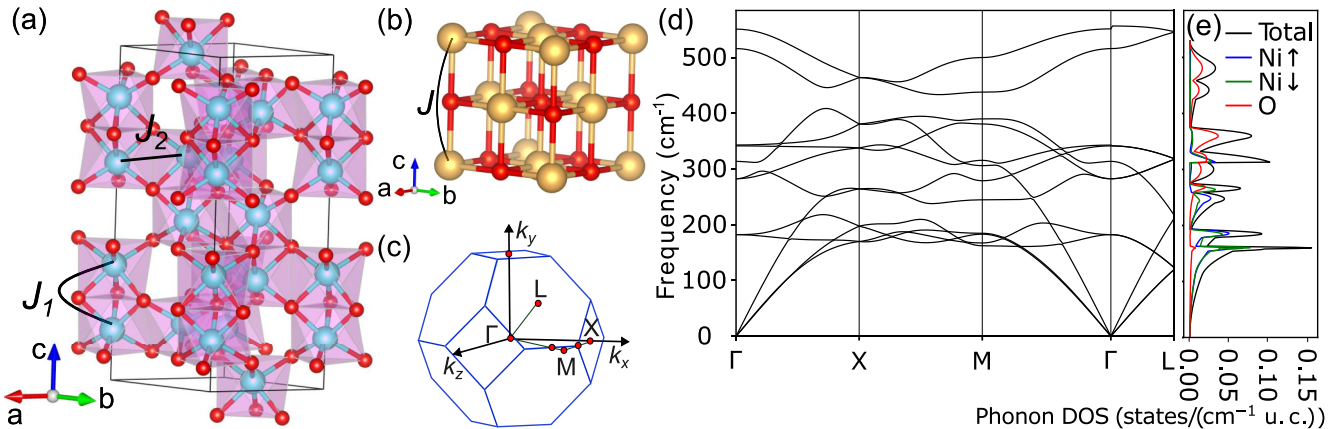


FIG. 2. (a) Crystal structure of Cr_2O_3 with Cr and oxygen atoms in blue and red, respectively. J_1 and J_2 are the two nearest-neighbor Heisenberg exchange constants. (b) Crystal structure of NiO. Ni ions are in yellow, while oxygens are in red. Heisenberg exchange J is on a 180° Ni-O-Ni bond. (c) Brillouin zone and a path along which the phonon dispersion is plotted. (d) Calculated phonon dispersion in NiO along the reciprocal space path shown in panel (c). (e) Phonon density of states in NiO.

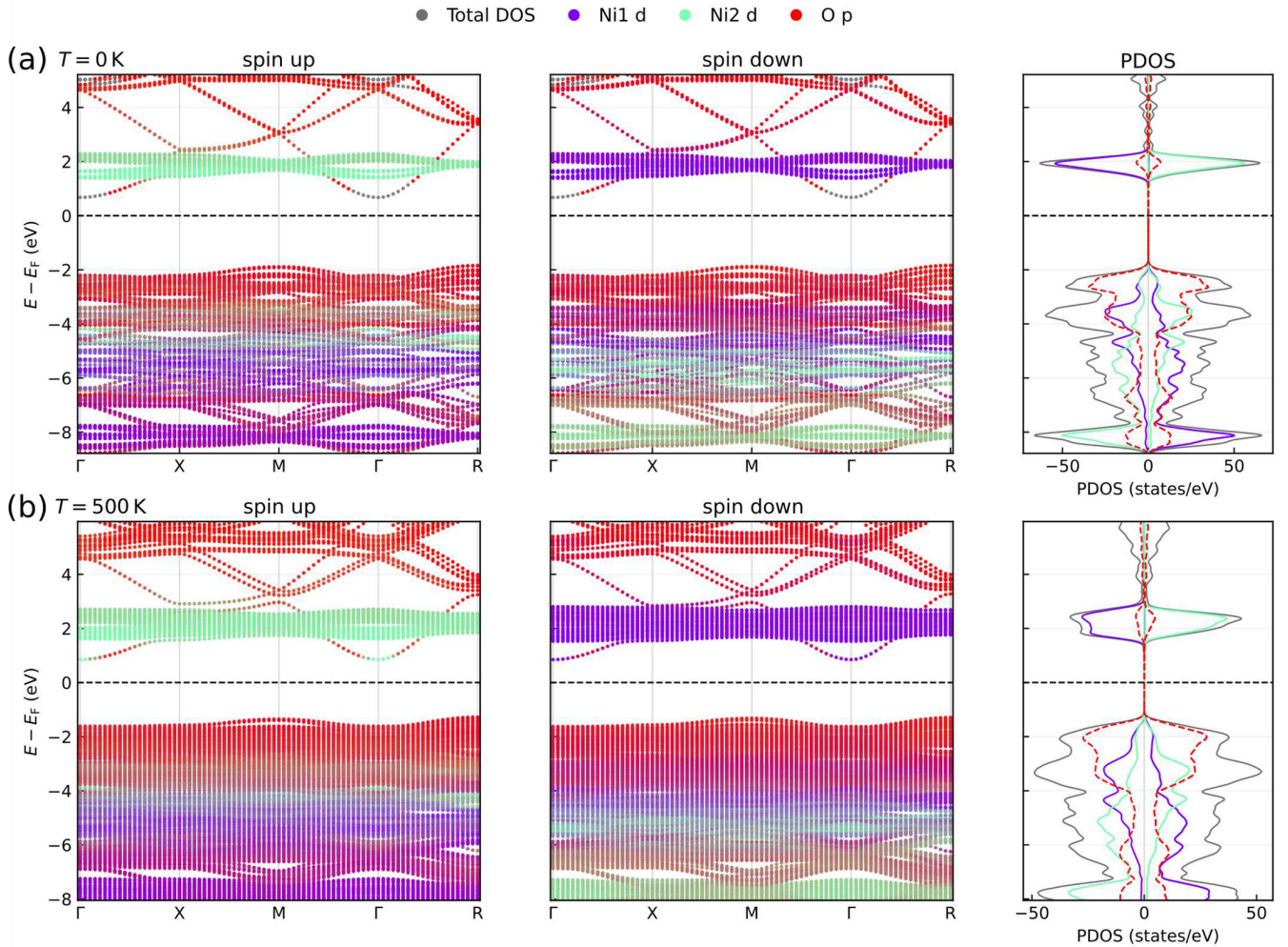


FIG. 3. Effect of thermal phonons on the band structure and orbitally resolved density of states (DOS) in NiO. (a) $T = 0$ K. The legend at the top indicates orbital characters encoded by the colors. (b) $T = 501$ K. DOS refers to the 32 f.u. supercell. The band gap reduction and band splitting at high-symmetry points are captured by the ZG method. The splitting within the conduction d bands is increased. The character change is evident at the bottom conduction band at a Γ point, indicating the increase in p - d hybridization with T . All these effects contribute to the temperature dependence of J .

expressed in terms of a reference mass M_p (conventionally the proton mass [11]); the atomic masses M_k enter through the factor $\sqrt{M_p/M_k}$ in the phonon eigenvector normalization, so that physical displacements are independent of the choice of M_p .

However, free-energy minimization does not constrain the phonon phases S_v [12]. Without spin-orbit coupling, $S_v = \pm 1$. Each set of phases $\{S_v\}$ defines a thermal line [13], corresponding to specific amplitudes of supercell optical phonons:

$$\mathcal{T}_S = \{S_1\sigma_1(T), S_2\sigma_2(T), \dots, S_{3N-3}\sigma_{3N-3}(T)\}. \quad (2)$$

The thermally averaged J must be computed by averaging the exchange constant over thermal lines. The same can be achieved by considering a supercell calculation which is equivalent to freezing multiple thermal lines in a single primitive cell calculation. Hence a larger supercell corresponds to better averaging over thermal lines.

One can choose a particular set of phonon phases so that all phonons shift the first ion in the $+x$ direction. Adding the phonon displacements with such a phase choice makes

the first ion in the frozen phonon structure “fly away.” These configurations are inaccessible in reality, as they have high energy due to anharmonic terms, although such terms are difficult to include. Instead, in the ZG method, a choice of phases S_v is made to minimize the ionic displacements and thus the anharmonic energy. We do that by performing a Monte Carlo simulation over thermal lines $\mathcal{T}$. We start from a random set of S_v that includes an equal number of negative and positive signs. Then we iteratively reverse the sign of a randomly chosen phonon amplitude and accept the sign flip if it results in a decrease in the target function, the sum of squared ionic displacements in the supercell. We also impose the condition that after the sign update, the difference between negative and positive signs must not be greater than 2. We stop the Monte Carlo simulations when the $\{S_v\}$ is no longer changing within 500 steps. Tests show that convergence is reached in a few tens of steps, and the final value of the target function is insensitive to the initial state. That way, a representative configuration with appropriate energy is obtained. In computing exchange constants, the method relies only on a

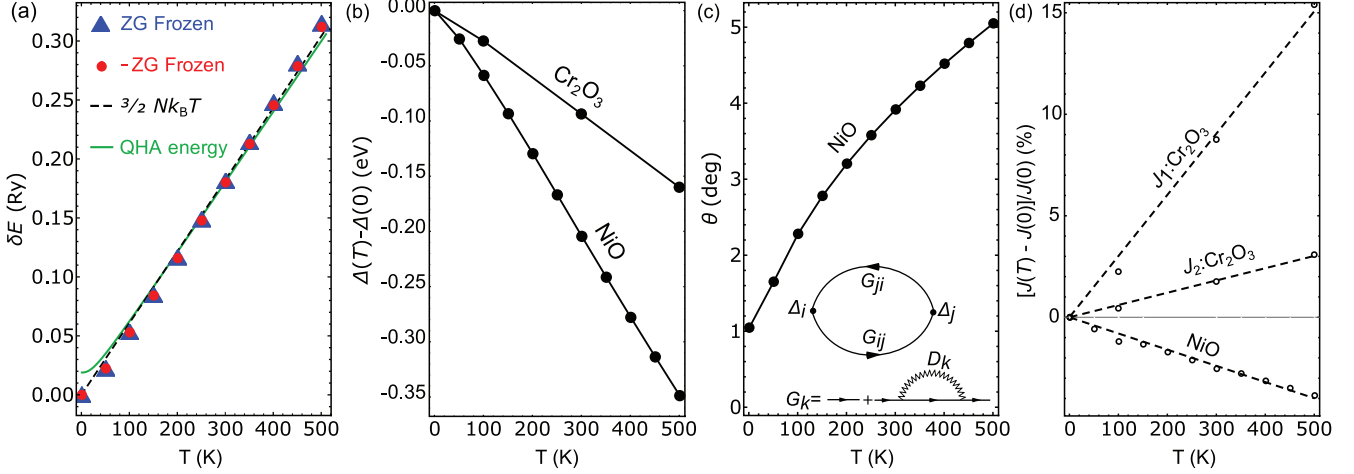


FIG. 4. (a) Increase of total energy with increasing temperature. Blue triangles and red dots show the total energy of +ZG and -ZG configurations. The dashed black line shows $\delta E = \frac{3}{2} N k_B T$, while the solid green indicates the energy increase in the quasi-harmonic approximation (QHA). (b) Temperature dependence of the band gap Δ . (c) Temperature dependence of θ , the deviation from 180° of the Ni-O-Ni bond angle in +ZG configuration in NiO. Note that in the -ZG configuration the bond bends in the opposite direction. Nonzero θ at $T = 0$ is due to zero-point fluctuations. The inset shows the Feynman diagram corresponding to the Katsnelson-Lichtenstein exchange constant J with thermal phonon correction. (d) Temperature dependence of magnetic exchange for NiO and Cr_2O_3 . At $T = 0$, $J_1 = 12$ meV, $J_2 = 10$ meV, $J = 20$ meV.

single DFT calculation for this configuration, thereby enhancing our ability to investigate temperature effects efficiently. The exchange constants are computed using the Katsnelson-Lichtenstein formula [14,15] in the basis of Wannier functions [16,17].

The Heisenberg exchange constant for the ZG supercell has a form

$$J(T) = J_0 + \sum_v \frac{\partial J}{\partial x_v} \sigma_{v,T} + \frac{1}{2} \sum_v \frac{\partial^2 J}{\partial x_v^2} \sigma_{v,T}^2 + \frac{3}{3!} \sum_{\mu \neq v} \frac{\partial^3 J}{\partial x_\mu^2 \partial x_v} \sigma_{\mu,T}^2 \sigma_{v,T} + \frac{1}{3!} \sum_v \frac{\partial^3 J}{\partial x_v^3} \sigma_{v,T}^3. \quad (3)$$

Therefore, odd-order terms in the phonon amplitudes remain in the expression for J . In reality, however, since the phonon amplitudes oscillate on the timescale of slow magnetic dynamics, the first-order variation of J is averaged out. Hence, a single configuration, that contains the odd terms, is not suitable for estimating magnetic interactions. These odd contributions from the modes $k \neq 0$ cancel out when equivalent exchange constants are averaged over a large supercell, due to an oscillating $e^{ik \cdot R}$ but that does not hold for $k = 0$ modes. However, we note the latter cancel after averaging with the configuration with reversed phonon amplitudes (“-ZG”). Hence, to compute $J(T)$, we take average over the configurations ZG and -ZG:

$$J(T) = \frac{1}{2} (\langle J[\mathcal{T}_s] \rangle + \langle J[\mathcal{T}_{-s}] \rangle). \quad (4)$$

The odd terms in phonon amplitudes drop, and the corrections to the magnetic exchange constant $J(T)$ only contain terms even in phonon amplitudes [underlined in Eq. (3)], in the lowest order consistent with the Feynman diagram shown in the inset of Fig. 4(c). This is the essence of the proposed approach.

III. RESULTS AND DISCUSSION

We benchmark the method on NiO, a paradigmatic anti-ferromagnetic insulator, and Cr_2O_3 , a well-known magneto-electric antiferromagnet with a corundum structure [Fig. 2(a)]. NiO is known as a charge transfer insulator with a rocksalt (NaCl) crystal structure and 180° Ni-O-Ni bonds, as seen in Fig. 2(b).

All calculations were performed within the generalized gradient approximation to density functional theory [18] as implemented in the QUANTUM ESPRESSO code [19–21]. We used the optimal norm-conserving Vanderbilt (ONCV) pseudopotentials [22], generated by Schlipf and Gygi (SG15) [23] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [18]. The Kohn-Sham wave functions were expanded in plane-wave basis sets with the kinetic energy cutoff of 80 Ry. We used the simplified DFT + U method [24] for the calculation of electronic and magnetic properties to take into account strong Hubbard repulsion on d orbitals of Ni and Cr. For NiO, the rhombohedral magnetic unit cell consists of two Ni and two oxygen atoms. For Cr_2O_3 , the rhombohedral unit cell contains four Cr and six O ions. We relaxed the structure until the forces were reduced below 10^{-4} Ry/Bohr. The on-site Coulomb repulsion U is calculated in the basis of atomic d orbitals using the relaxed cell and a dense q grid of $4 \times 4 \times 4$ in the HPX code [25]. We obtain $U = 6.42$ eV on Ni d in NiO and $U = 5.25$ eV on Cr d in Cr_2O_3 . In DFT + U calculations with simplified rotationally invariant U [24], we used the calculated U and the intra-atomic Hund’s rule coupling was taken as $J_H = 0.9$ eV to produce $U_{\text{eff}} = U - J$ [26]. For NiO this gives a band gap of nearly 3.3 eV and a local magnetic moment of $1.72 \mu_B$. Phonon calculations used density functional perturbation theory for a rhombohedral cell with 2 formula units (f.u.) accommodating antiferromagnetic ordering and a q grid commensurate with a cubic cell

containing 32 f.u. Charge was calculated on a $4 \times 4 \times 4$ k grid. The interatomic force constants in the Born–von Kármán supercell were obtained by Fourier transforming the dynamical matrices [27]. The phonon dispersion and density of states for NiO are shown in Figs. 2(d) and 2(e). The highest optical phonons are at 70 meV. We selected the best thermal line (set of signs of phonon amplitudes) at 400 K by Monte Carlo minimization of rms ionic displacements over signs S_k . In all our trial runs we iterated until the displacement no longer decreased in 500 updates Supplemental Material [28]. We then followed this thermal line, by freezing the phonons into a cubic supercell with 32 f.u. for NiO (and a rhombohedral $2 \times 2 \times 2$ supercell for Cr_2O_3) and calculating exchange constants for temperatures between 1 and 501 K in steps of 50 K. Wannier-interpolation used transition metal- d and O- p orbitals for projections and windows extending between -8.5 and 7.5 eV for Cr_2O_3 and between -10.25 and 8.25 eV for NiO. The energies are given with respect to the Fermi level. Figure 4(a) shows the linear increase of total energy for frozen phonon structures with +ZG configuration indicated with blue triangles and -ZG with red points. We also compared the increment in energy with respect to an expected increase from quantum harmonic approximation (QHA), $\sum_{n,\omega} (n + \frac{1}{2}) \hbar \omega$, where ω are the calculated phonon frequencies Supplemental Material [28]. The $E = \frac{3}{2} N k_B T$ fit indicated with the black line in Fig. 4(a) coincides with the QHA curve, except at the lowest temperatures, $T < 50$ K.

The main exchange mechanism in NiO and Cr_2O_3 is superexchange via ligand p orbitals (and a direct d - d exchange between Cr in face-sharing octahedra [29]), so the Cr- d , Ni- d , and O- p orbitals were used for Wannier projections [30]. $J(T)$ was calculated for each individual temperature with averaging over symmetry-equivalent bonds using the Katsnelson-Lichtenstein formula as implemented in the in-house code [31]. The $6 \times 6 \times 6$ k grid was used for the Fourier transform of the Green's functions to the site representation, and the integration over ω was performed on a contour discretized into 4000 points.

In NiO, both for the +ZG and -ZG configurations, the magnetic moment decreases slightly, linearly with T , and at 500 K, the decrease is 0.25%. Figure 3 compares the band structure and orbitally resolved density of states between $T = 0$ K and $T = 500$ K frozen thermal phonon structures. As seen there and in Fig. 4(b), the band gap Δ decreases with temperature in both materials, $\partial \Delta / \partial T = -3 \times 10^{-4}$ eV/K and -7×10^{-4} eV/K in Cr_2O_3 and NiO, respectively. This behavior is typical for semiconductors [11], as the electron-phonon coupling mixes the top valence and bottom conduction bands with higher conduction and lower valence bands, respectively. This reduced gap implies energy lowering of the intermediate state, involved in the superexchange process, where the electron from one transition metal ion hops to the neighboring one. Therefore, the denominator in the superexchange formula is lowered, driving an increase of J . Furthermore, changes in hybridization could modify screening of Coulomb repulsion on correlated orbitals, i.e., the decrease of Hubbard U . We have computed U using density functional perturbation theory linear response approach [25] and found a slight increase with temperature, $U^{-1} \partial U / \partial T = 3 \times 10^{-5} \text{ K}^{-1}$ and $2.7 \times 10^{-4} \text{ K}^{-1}$ for Cr_2O_3 and NiO,

respectively Supplemental Material [28]. The different dependencies of Hubbard U and the gap are likely related to the charge-transfer character of NiO, with the gap separating O- p states and d states of the transition metal ions. If U were strongly dependent on T , it would be necessary to achieve self-consistency by recomputing the phonon frequencies with the new U value, and the resulting phonon frequency changes would drive further changes in U . Both variations of U and anharmonic phonon interactions modify phonon frequencies. To avoid repeated phonon calculations in a large supercell, a method was proposed to estimate the dynamical matrix of the forces on phonon modes in a distorted structure [32]. While in rigid NiO and Cr_2O_3 phonons are rather hard and we do not see a large variation of J in a full self-consistency, in softer materials like NiI_2 and CrI_3 that could lead to major effects.

Neglecting the weak temperature dependence of U in both materials, we compute $J(T)$ shown in Fig. 4(d). In NiO the bonds at $T = 0$ are straight, which maximizes J . With increasing temperature, the Ni-O-Ni bond angles deviate from 180° , as illustrated in Figs. 1(b) and 4(c), thus resulting in a reduced orbital overlap and a decrease in the exchange constant J . We note that the bond bending angle is zero on average in our harmonic approximation, and whether the exchange grows or decreases with T due to a contribution from a specific phonon is determined by the curvature of the J surface as a function of the phonon amplitude. Remarkably, in Cr_2O_3 , where the M -O- M bonds are not straight and therefore the exchange is not guaranteed to decrease with bending, we find an opposite behavior of $J(T)$. Direct d - d exchange dominated J_1 grows by 15% at 500 K (12% is linear expansion is included).

IV. MAGNETIC TRANSITION TEMPERATURE

We now estimate the magnetic transition temperature. In the mean-field approximation, $k_B T_c = \frac{z}{3} S(S+1)J$, where z is the lattice coordination number ($z = 6$ and $S = 1$ for NiO). If J strongly varies with T , one must determine T_c self-consistently from the exchange at T_c . That gives the equation $J(T) = \frac{3k_B T}{zS(S+1)}$, satisfied for $T_c = 440$ K. If we neglect the temperature dependence in $J(T)$, we obtain $T_c = 456$ K instead. Both values are in reasonable agreement with the experimentally measured $T_N = 523$ K [33,34] (we have neglected a weaker ferromagnetic exchange on 90° bonds with $z = 12$). Approximations beyond the mean field may further increase the precision of the T_c estimate [35].

V. CONCLUSIONS

We have studied how the leading phonon renormalization modifies spin interactions in solids. A computationally affordable approach based on the special displacement method and the Katsnelson-Lichtenstein formula is devised. The approach is easy to implement on top of any electronic structure code.

In NiO, the bending the Ni-O-Ni bond with temperature results in a decrease of J . Notably, in Cr_2O_3 , where bond angles are far from 180° , we find a substantial temperature-induced enhancement of the dominant exchange interaction, reaching approximately 10% at room temperature. While a temperature-induced increase in exchange

has been observed experimentally in the molecular magnet CsO_2 , our results provide a demonstration of this effect from first principles and show that it extends to conventional transition metal oxides. The speedup provided by the method opens the path to high-throughput computation of magnetic exchange constants at finite T . In the future it would be important to address the regime beyond the harmonic approximation—thermal expansion and bond bending can add further temperature dependence of magnetic exchange constants—and consider nonadiabaticity associated with close proximity between phonon and magnon frequencies in many magnets. Thermal expansion can be estimated by optimizing the cell vectors of the thermal supercell and gives a further 2% decrease of J in NiO (and 3% decrease of J_1 in Cr_2O_3). The results motivate theoretical studies of

anharmonic effects in magnets and experimental investigations of temperature effects in soft halide-based magnets, organic-inorganic hybrids, and layered magnetic materials, where thermal effects may be important.

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DATA AVAILABILITY

All the data, including the simulation input files are available on request to the authors.

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