

Direct observation of thermal spin depolarization in a type I_B half-metal NiCo₂O₄ by spin-resolved photoemission

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Half-metals (HMs), characterized by 100% spin polarization at the Fermi level (E_F), are ideal candidates for future spintronic memory devices. However, their spin polarization rapidly decreases with temperature, limiting their practical implementation. While this degradation has been theoretically attributed to nonquasi-particle (NQP) states—many-body electronic states arising from electron-magnon interactions that reduce spin polarization near E_F —experimental verification remains limited. Here, we report the temperature evolution of the electronic states in epitaxial NiCo₂O₄ (NCO) thin films, a predicted type I_B HM where the main spectral weight of NQP states lies below E_F . Using high-resolution bulk-sensitive laser-based spin-resolved photoemission spectroscopy, we reveal that at 20 K, a metallic Fermi edge is observed in the minority-spin states but is absent in the majority-spin states, providing spectroscopic evidence for the half-metallicity of NCO. As temperature increases, majority-spin spectral weight emerges at E_F , and spin polarization near E_F decreases—consistent with the emergence of NQP states. The onset of this behavior occurs around 100 K. Our results suggest that NCO provides a promising platform for investigating NQP-related many-body effects in type I_B HMs, guiding the design of spintronic materials with robust high-temperature spin polarization.

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I. INTRODUCTION

Magnetic memory devices have served as key nonvolatile memory elements since the dawn of computing [1]. More recently, spintronics—which exploits the spin polarization of conduction electrons for readout [2–4]—has led to significant technological advances, exemplified by the successful commercialization of hard disk drives. Furthermore, magnetic random-access memory (MRAM), a promising candidate for working memory applications, has already been subjected to large-scale statistical evaluation on 300 mm silicon wafers [5,6].

However, the tunneling magnetoresistance (TMR) ratio of the CoFeB/MgO/CoFeB magnetic tunnel junctions used in MRAM is approximately 230% at room temperature [7,8], which is insufficient to overcome device variability. As a

result, self-referenced readout is required [9,10], and the high-speed operation originally expected has not yet been realized.

To achieve higher-speed operation in MRAM, the development of materials with higher spin polarization is needed. Half-metals (HMs), in which only one spin channel is metallic near the Fermi level (E_F) [11–16], theoretically yield an infinite TMR ratio [17]. Nevertheless, HMs suffer a significant decrease in TMR ratio with increasing temperature [18–20]. One proposed origin of this degradation is a change in the electronic structure (ES) of the HM, attributed to many-body effects arising from electron-magnon interactions, which reduce the spin polarization only near E_F [21–27].

These many-body electronic states, referred to as nonquasi-particle (NQP) states, appear at different energies depending on the type of HM. HMs are classified as type I_A or type I_B depending on whether the majority- or minority-spin band crosses E_F [23,28], respectively, as shown in Fig. 1(a). In type I_A HMs, the main body of the NQP states exists above E_F and starts to leak below E_F at temperatures above a certain crossover temperature, T^* . This behavior has been directly observed in CrO₂ via bulk-sensitive spin-resolved photoemission spectroscopy (SRPES) [25,26]. On the other hand, dynamical mean-field theory (DMFT), which predicts the emergence of NQP states, also suggests

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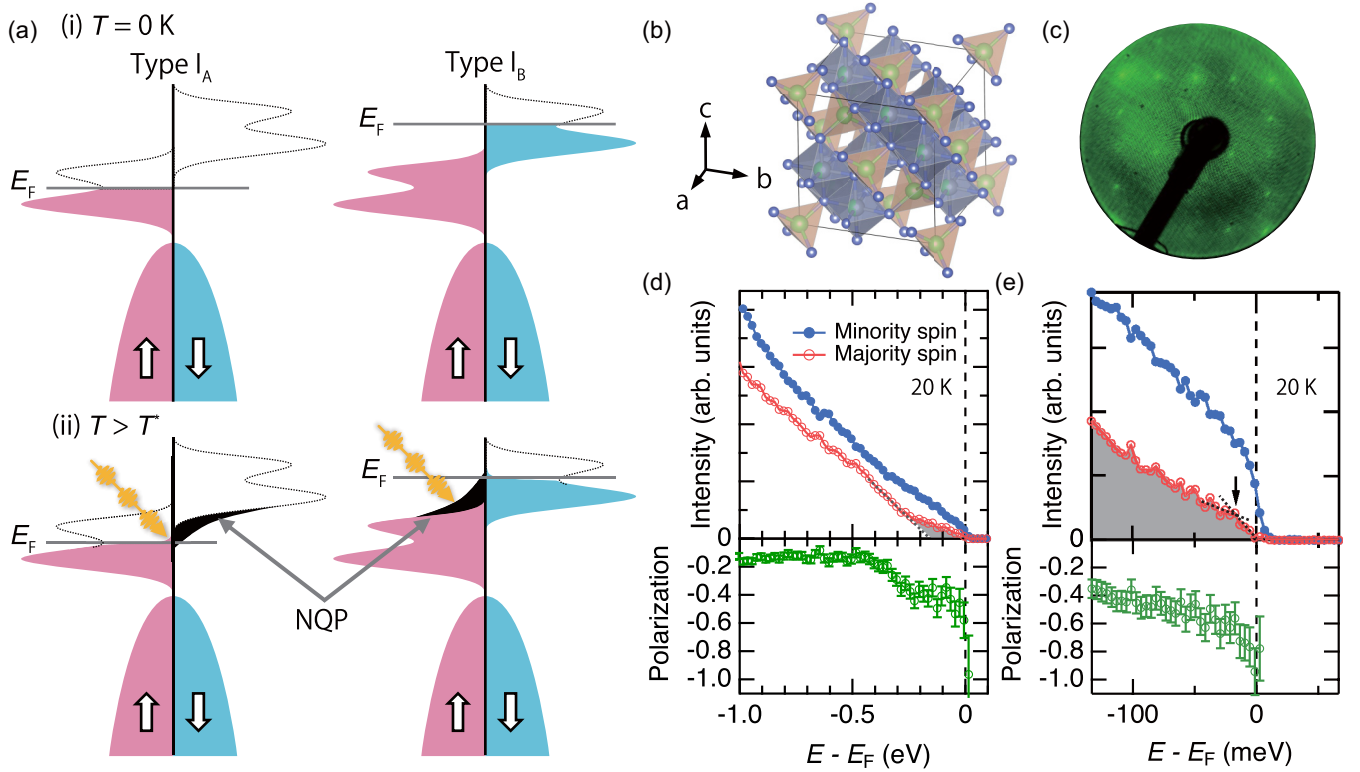


FIG. 1. Low-temperature spin-resolved electronic structure of NCO epitaxial thin films. (a) Schematic diagrams illustrating the classification of HM: (i) the one-electron spin-resolved density of states (DOS) in the ground state and (ii) those including NQP states that emerge in each type above a crossover temperature T^* . In photoemission spectroscopy, only NQP states located below E_F are observable. (b) Crystal structure of NCO. Gray, green, and blue spheres represent Ni, Co, and O atoms, respectively. Sites shown as half gray and half green indicate 50% occupancy by Ni and Co atoms. (c) Low-energy electron diffraction (LEED) pattern of the NCO surface after SRPES measurements, showing well-defined diffraction spots and confirming surface crystallinity. (d) Spin-resolved energy distribution curves (EDCs) (top) and corresponding spin polarization (bottom) along the [001] axis measured over a wide energy range using a photon energy of $h\nu = 6.994$ eV. The black dashed line is a linear extrapolation from the shoulder feature in the majority-spin EDC near -0.5 eV. The gray-shaded region represents spectral weight not reproduced by first-principles calculations. (e) Magnified view of the spectra shown in panel (d), focusing on the near- E_F region. The black arrow indicates the onset of the majority-spin EDC depression.

a temperature-dependent shift of the entire valence band [23,24,29]. However, such a shift has not been observed experimentally by photoemission [30,31], implying that DMFT may not fully capture the temperature evolution of the electronic structure, and that further refinement of DMFT as well as more detailed experimental studies of NQP states is required.

In type I_B HMs, it has been predicted that the main part of the NQP states appears below E_F , and thus can be directly observed by SRPES even at temperatures below T^* [23]. NiCo_2O_4 (NCO) (001) epitaxial film with the inverse spinel structure [Fig. 1(b)] is a metallic ferrimagnet with perpendicular magnetic anisotropy [32–35], and has been predicted by first-principles calculations to be a type I_B HM [36–39]. A spin polarization of -74% at 35 K was reported from TMR measurements of NCO/ MgAl_2O_4 (MAO)/NCO tunnel junctions, supporting the potential of NCO as a promising type I_B HM [40].

In this study, we investigated the electronic states near E_F in NCO(001) epitaxial films using high-resolution bulk-sensitive laser-based SRPES. At low temperatures (20 K), the minority-spin states exhibited a clear Fermi edge, while the

majority-spin states lacked it, providing spectroscopic evidence for the half-metallic nature of NCO. Upon increasing the temperature above 100 K, we observed an increase in spectral weight at E_F in the majority-spin channel and a corresponding decrease in spin polarization near E_F . This behavior suggests a temperature-dependent evolution of NQP states, with the crossover temperature T^* estimated to be approximately 100 K.

II. RESULTS AND DISCUSSION

First, we measured the photoemission spectra over a wide energy range. Figure 1(c) shows a LEED pattern of the sample after SRPES measurements. A clear diffraction pattern was observed, confirming the absence of significant surface degradation due to the laser exposure during the SRPES measurements.

As shown in Fig. 1(d), the absolute value of spin polarization increases from $E - E_F = -0.4$ to -0.25 eV. This is attributed to a decrease in the intensity of the majority-spin component. This forms a shoulder structure in the spin-resolved EDC around -0.45 eV of the majority-spin channel.

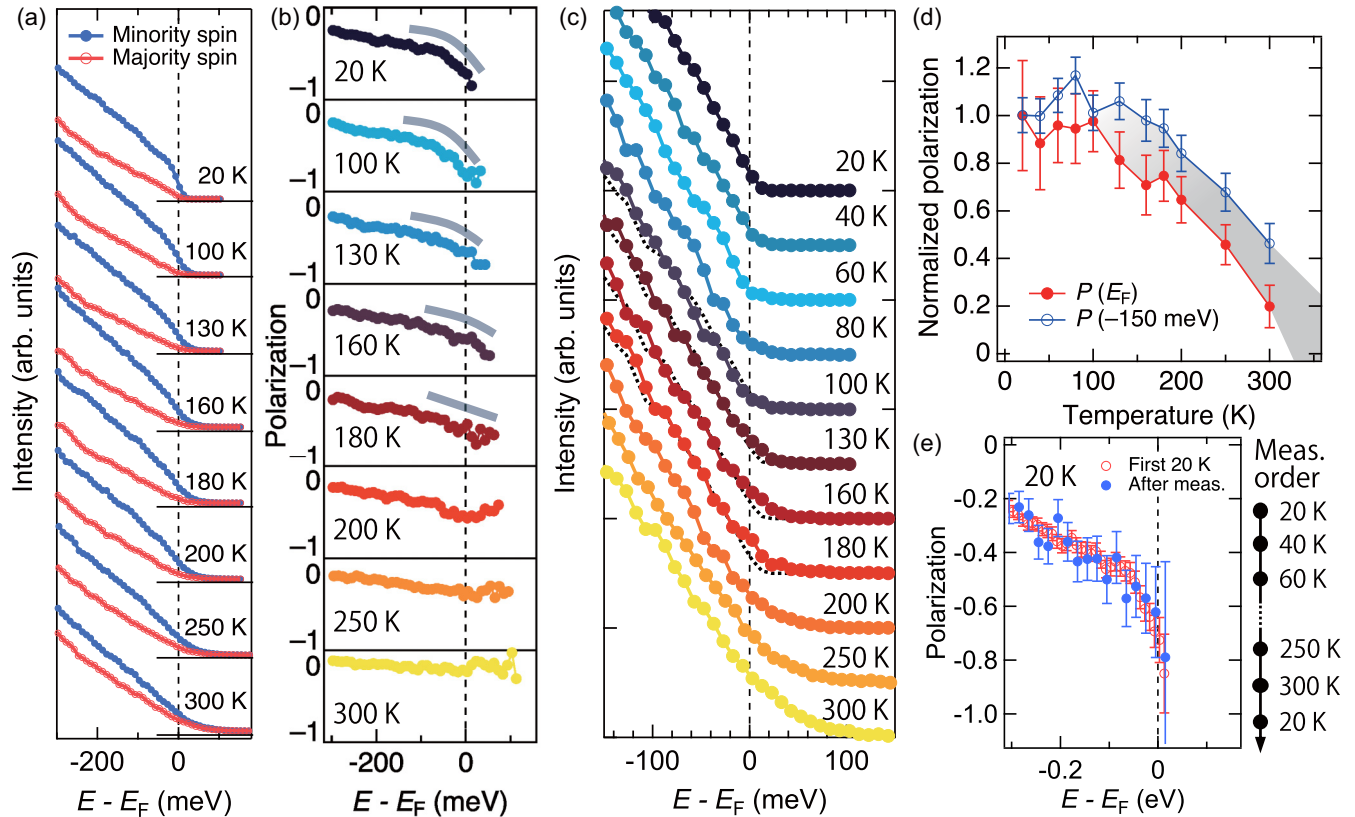


FIG. 2. Temperature dependence of the electronic states near the Fermi level. (a), (b) Spin-resolved EDCs and corresponding spin polarization, respectively. The gray curves are guides for the eye for the energy dependence of the spin polarization. (c) Temperature evolution of the majority-spin EDCs near E_F . The black dashed lines represent the normalized majority-spin EDC at 20 K. For each temperature, the intensity at -100 meV is normalized to that of the 20 K data to facilitate comparison. (d) Temperature dependence of the spin polarization at $E - E_F = 0$ eV [$P(E_F)$, red] and -150 meV [$P(-150$ meV), blue]. Each curve is normalized to its value at 20 K. Error bars represent the standard deviation within a 10 meV window used to calculate the average spin polarization. In the gray-shaded region, a pronounced deviation emerges between $P(E_F)$ and $P(-150$ meV), with $P(E_F)$ exhibiting more rapid spin depolarization. (e) Spin polarization acquired before and after the temperature-dependent measurement. The sample was heated from 20 to 300 K, and then cooled back to 20 K.

First-principles calculations indicate that this structure corresponds to the valence-band top for the majority spin [36–39]. While the calculations predict a gap of approximately 0.5 eV below E_F for the majority spin, EDC for the majority spin has a finite spectral weight extending up to E_F [gray shaded region in Fig. 1(d)]. This state does not appear within a single-particle picture and is thus possibly attributed to many-body effects.

We also examined the spin-resolved EDCs in the vicinity of E_F . As shown in Fig. 1(e), the majority-spin EDC drops sharply from $E - E_F = -18$ meV toward E_F , and the absolute value of spin polarization correspondingly increases to -80% . The fact that the spin polarization does not reach 100% is attributed to the finite energy resolution of the measurement. With an energy resolution of 10 meV, even if the majority-spin band just touches E_F , spectral broadening causes a reduction in the measured spin polarization at E_F . The absence of a Fermi edge in the majority-spin channel provides direct evidence that NCO exhibits a half-metallic electronic structure at 20 K.

In Fig. 1(d), we found that the spin polarization has a negative offset below -0.5 eV. According to first-principles calculations, the sign of the spin polarization is expected

to reverse at the energy corresponding to the valence-band maximum of the majority-spin channel; however, our experimental results do not exhibit such a sign reversal. This can be attributed to spin-polarized secondary electrons. It has been reported that secondary electron intensity increases when the spin channel has a high DOS near E_F [41]. For the case of NCO, only the minority-spin channel has a finite DOS at E_F , and the offset in spin polarization is negative, consistent with observing the spin-polarized secondary electrons.

Next, we investigated the temperature dependence of spin polarization [Figs. 2(a) and 2(b)]. The sharp increase in absolute value of spin polarization from -20 meV to E_F remained unchanged up to 100 K. However, above 130 K, the slope began to decrease, and at 180 K, the energy dependence of spin polarization became nearly linear. As shown in Fig. 2(c), this behavior is due to an increase in spectral weight at E_F at elevated temperatures compared to the 20 K spectrum.

Above 200 K, substantial spin depolarization occurred over the entire energy range. This can be attributed to spin-wave excitations, which project the minority-spin states onto the majority-spin channel [26,42]. Consequently, the majority-spin states around E_F exhibited temperature-dependent broadening consistent with the Fermi-Dirac distribution.

We now discuss the difference in steepness of the depolarization near E_F with respect to temperature, in comparison to the broader depolarization caused by spin-wave excitations. Figure 2(d) shows the temperature dependence of the spin polarization at $E - E_F = -150$ meV, $P(-150$ meV), and at E_F , $P(E_F)$, each normalized to their respective values at 20 K. Up to 100 K, both values exhibit nearly identical temperature dependence. However, above 130 K, $P(E_F)$ shows a significantly sharper decline compared to $P(-150$ meV).

If spin-wave excitations were the sole origin of spin depolarization, the temperature trends of $P(-150$ meV) and $P(E_F)$ would be identical; but these are not. Therefore, the growing gap between $P(E_F)$ and $P(-150$ meV) above 100 K indicates that an E_F -localized depolarization mechanism exists behind the gap between the P - T curves.

We also evaluated whether sample degradation contributes to the observed temperature dependence of spin polarization. Figure 2(e) shows the measurement sequence used for the temperature-dependent SRPES study, along with the spin polarization spectra obtained at 20 K both before and after the temperature cycling. Upon cooling back down to 20 K, the spin polarization fully recovered and completely reproduced the initial spectrum. This validates that the observed temperature dependence is intrinsic to the physical properties of NCO and not due to irreversible changes or degradation during measurement.

As a depolarization origin, we considered two possibilities: One is the presence of NQP states and the other is the broadening of the spin-resolved EDCs due to electron-phonon interactions.

We first discuss the effect of electron-phonon interactions. The spectral broadening due to electron-phonon coupling at temperature T , denoted as $G_{\text{el-ph}}^2(T)$, is given by the following expression:

$$G_{\text{el-ph}}^2(T) = G(0)^2 \left[1 + 8 \left(\frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \right], \quad (1)$$

where $G(0)$ is the Gaussian width from the phonon broadening at $T = 0$ K [43]. Θ_D is the Debye temperature. From Eq. (1), the spectral broadening due to electron-phonon interactions can be estimated by determining the parameters $G(0)$ and Θ_D .

We first estimate $G(0)$. The energy resolution in our measurements was set to 10 meV. Figure 3(a) shows the Fermi edge of the minority-spin EDC for NCO, along with a fitting curve generated by convoluting the Fermi-Dirac distribution function at $T = 20$ K with a Gaussian. From this fitting analysis, the full width of the Gaussian was estimated to be 11 meV. From these values, $G(0)$ was estimated to be on the order of ~ 4.6 meV.

Next, we determine Θ_D . Figure 3(b) shows the specific heat of NCO obtained from first-principles phonon calculations. By fitting the calculated heat capacity with the Debye model [44], we estimate the Debye temperature as $\Theta_D = 707$ K.

Using these parameters, we calculated the temperature-dependent electron-phonon broadening, $G_{\text{el-ph}}^2(T)$, as shown in Fig. 3(c). The resulting curve indicates that relative to $G(0)$, the broadening increased by $\sim 1\%$ at 100 K, $\sim 8\%$ at 200 K, and $\sim 20\%$ at 300 K. Given that $G(0)$ is approximately 4.6 meV, the absolute broadening width even at 300 K remains

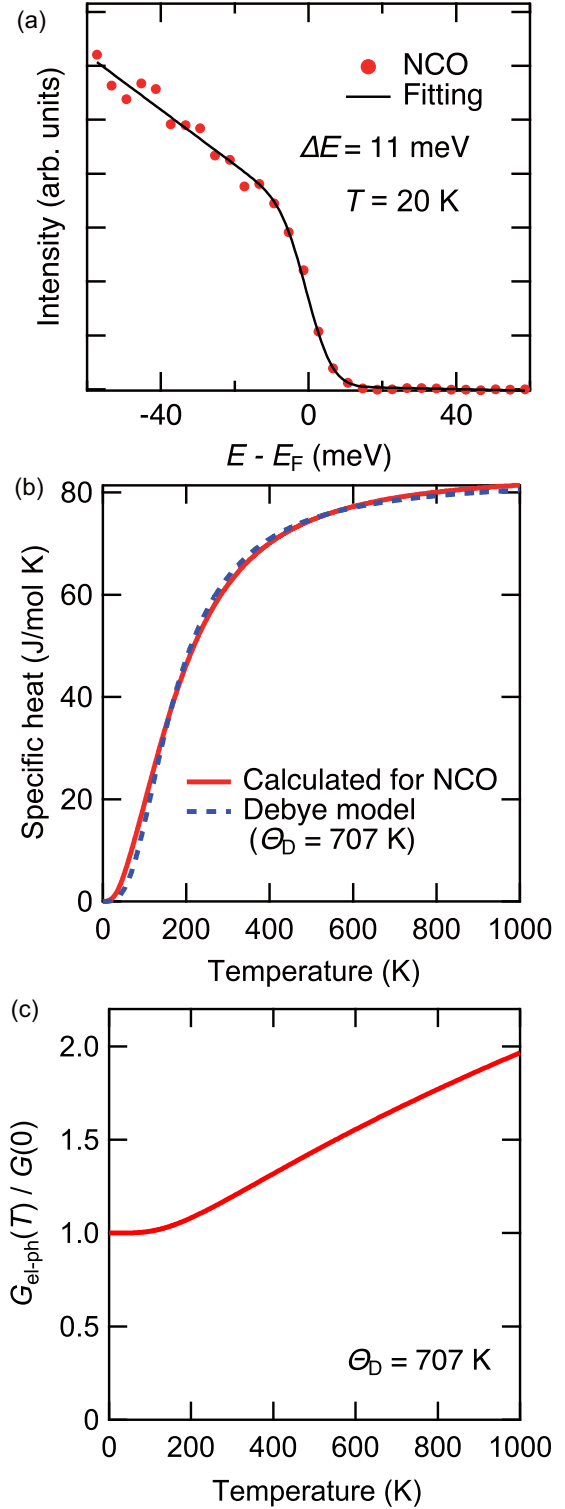


FIG. 3. Estimation of spectral broadening due to electron-phonon interaction. (a) Minority-spin EDC of NCO (red circles) and its fitted Fermi edge (black solid line). The fitting curve is obtained by convoluting the Fermi-Dirac distribution function at 20 K with a Gaussian of full width at half maximum of 11 meV. (b) Temperature dependence of the specific heat of NCO calculated from first-principles phonon calculations (red solid line), along with a fit using the Debye model (black dotted line). The Debye temperature extracted from the fitting is 707 K. (c) Calculated temperature dependence of normalized electron-phonon broadening, $G_{\text{el-ph}}(T)/G(0)$, using $\Theta_D = 707$ K.

limited to ~ 0.9 meV. In contrast, the disappearance of the kink structure in spin polarization shown in Fig. 2(b) occurs over an energy scale of ~ 20 meV, which clearly cannot be accounted for by electron-phonon broadening alone.

Electron-phonon coupling also should be considered as a possible origin [45]. Previous Raman spectroscopy [46] reports have identified four characteristic peaks at 187, 477, 527, and 670 cm^{-1} (assigned to $F_{2g}(1)$, E_g , $F_{2g}(2)$, and A_{1g} modes, respectively), which correspond to energies of 23, 59, 65, and 83 meV. Among these vibrational modes, the $F_{2g}(1)$ mode has the energy closest to the observed feature near E_F (~ 18 meV). However, its Raman intensity is nearly an order of magnitude lower than those of the other three modes, suggesting that $F_{2g}(1)$ is unlikely to be the dominant vibrational mode coupled to the electronic states.

Next, as another possible origin of the spin depolarization near E_F , we consider the temperature dependence of the exchange splitting. Within the Stoner model, where the exchange splitting Δ_{ex} is proportional to the magnetization M ($\Delta_{\text{ex}} \propto M$), the temperature-dependent magnetization of NCO [32] indicates a reduction of approximately 12% at 100 K relative to the ground state. Given that the exchange splitting in the ground state is approximately 0.8 eV [38], this corresponds to a reduction of ~ 0.1 eV at 100 K. Assuming a simple Stoner-like reduction of the exchange splitting and symmetric shifts of the two spin channels, the majority-spin one-electron band would be expected to shift by approximately 50 meV at 100 K. This energy scale is substantially larger than the ~ 18 meV near- E_F spectral feature observed experimentally. We emphasize, however, that the ~ 18 meV scale discussed here is not the one-electron majority-spin band edge, but rather the characteristic energy scale of the near- E_F intensity suppression that may be interpreted as the NQP cutoff. Therefore, the persistence of this feature alone does not rule out a temperature-dependent motion of the underlying one-electron bands. Instead, our data indicate that a simple rigid shift scenario is insufficient to reproduce the observed near- E_F spectral evolution.

We now compare these results with the s - d exchange model that predicts the emergence of NQP states. Type I_B HMs are theoretically treated using a negative s - d exchange parameter ($I < 0$) [23,47]. In this case, NQP states appear below E_F , and the total spin $S-1$ occupied states are quantum superpositions of the states $|S\rangle|\downarrow\rangle$ and $|S-1\rangle|\uparrow\rangle$. Assuming a free-electron-like DOS for the minority-spin channel, the NQP states—formed within the majority-spin gap—originate from the bottom of the minority-spin valence band. The DOS of the NQP states sharply decreases near E_F on the energy scale of the magnon maximum energy $\hbar\bar{\omega}$. This decrease in the DOS is consistent with the reduction in majority-spin EDC near E_F observed in Fig. 1(e). The onset of this intensity suppression occurs at $E - E_F = -20$ meV, which is comparable to the typical magnon maximum energy for well-known HMs such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [48] and Fe_3O_4 [49].

Based on this discussion, the cutoff in the majority-spin states near E_F can be attributed to the cutoff of the NQP states. Within this interpretation, the gray-shaded region shown in Fig. 1(d) corresponds to the main body of the NQP states. This suggests that NQP states are present even at low temperatures (~ 20 K) in type I_B HMs.

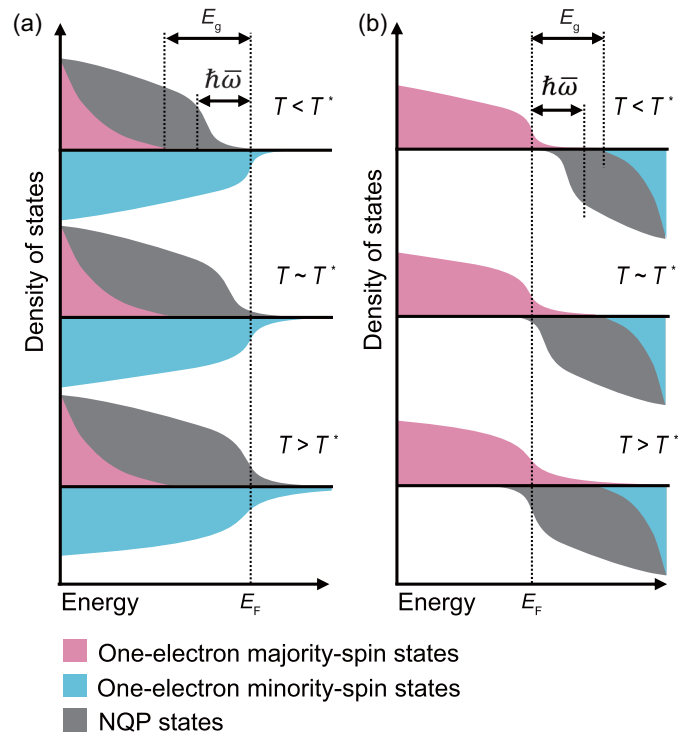


FIG. 4. Schematic NQP-based interpretation of the temperature-dependent electronic structure. (a) Schematic illustration of the temperature-dependent electronic structure of a type I_B HM. E_g denotes the gap of the one-electron states below E_F in the majority-spin channel. Near $T \sim T^*$, the NQP tail extends toward E_F , and at temperatures well above T^* , the gap is completely filled by thermally grown NQP states. (b) Same as panel (a), but for a type I_A HM. In this case, E_g represents the gap of one-electron states above E_F in the minority-spin channel.

By combining our experimental results with previous theoretical studies [23], we propose a model for the temperature-dependent electronic structure of type I_B HMs, as illustrated in Fig. 4(a). Even below the crossover temperature T^* , NQP states are present within the one-electron majority-spin gap, within the NQP interpretation. These states exhibit a cutoff in the DOS on the energy scale of $\hbar\bar{\omega}$, and their DOS vanishes exactly at E_F . Up to $T \sim T^*$, the NQP states do not show significant temperature dependence. Once the temperature reaches T^* , spectral weight of the NQP states begins to increase at E_F , and the sharp cutoff in the NQP DOS near E_F is progressively closed.

Assuming a similar temperature evolution occurs in type I_A HMs, the corresponding electronic structure would be illustrated as the schematic shown in Fig. 4(b). This picture is consistent with the temperature-dependent behavior of the occupied NQP states observed in CrO_2 [26]. These results support the interpretation that spin depolarization near E_F in type I_A HMs arises from NQP states.

However, it has been pointed out that in type I_A HMs, the temperature dependence of the valence-band EDCs observed by photoemission does not fully match the valence-band DOS obtained from DMFT calculations that account for NQP states [30,31]. This discrepancy suggests that improvements to the DMFT framework may be necessary to achieve a

comprehensive description of the electronic structure both near E_F and throughout the valence band.

The change in the majority-spin states near E_F observed here is expected to induce corresponding modifications in the minority-spin EDC. However, in this study, no clear temperature-dependent change beyond the thermal broadening described by the Fermi-Dirac distribution was observed in the minority-spin EDC. This indicates that any change in the metallic spin channel associated with the emergence of NQP states is too small to be detected within the energy resolution and statistical accuracy of the present experiment. Addressing this experimental limitation would enable a more definitive evaluation of the NQP scenario.

This study reveals that the spin polarization near E_F begins to decrease around 100 K. This reduction in spin polarization poses a significant challenge for the practical application of NCO. Such behavior is a universal feature of half-metals [24–26]; thus, our observation of the temperature-dependent spin depolarization will contribute to suppressing the thermally induced degradation of spin polarization, facilitating the practical use of half-metallic materials.

III. CONCLUSION

We have demonstrated the half-metallicity of NCO using high-resolution SRPES and investigated the temperature evolution of the spin-resolved electronic structure within the majority-spin gap. At 20 K, the minority-spin states exhibit a well-defined metallic Fermi edge, while the majority-spin states show no Fermi edge, providing direct evidence for the half-metallicity of NCO. The majority-spin intensity decreases sharply within ~ 20 meV below E_F , consistent with the expected NQP DOS. Upon heating, thermal broadening of the minority-spin states leads to reduced spin polarization at E_F . A similar temperature-dependent behavior has also been observed in type I_A HMs, suggesting that spin depolarization due to NQP states is a universal feature of half-metallic systems. Our findings not only advance the understanding of itinerant magnetism, but also offer valuable insight into strategies for achieving higher spin polarization at room temperature, with potential implications for future spintronic applications.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: MATERIAL SYNTHESIS AND CHARACTERIZATION

Epitaxial thin films of NCO were grown on (001) MAO substrates by pulsed laser deposition [32,33]. Based on the lattice parameters of NCO ($a_{\text{NCO}} = 8.11$ Å) and MAO ($a_{\text{MAO}} = 8.08$ Å) in bulk, films experience the compressive strain of $\sim 0.4\%$ due to the lattice mismatch. The films were deposited by ablating a NiCo_2O_x ceramic target at 6 Hz with a KrF excimer laser ($\lambda = 248$ nm) with a laser spot density of 1.2 J/cm², at the fixed substrate temperature of 315 °C, and under the oxygen partial pressure of 100 mTorr. After the film growth, the films were cooled down to room temperature without changing the oxygen partial pressure.

Structural properties of the films were characterized by laboratory-source x-ray diffraction. The x-ray $2\theta/\theta$ diffraction measurements confirmed that the NCO layers were coherently grown on the substrates and the in-plane lattice constants of the NCO layers were identical to those of the substrates.

APPENDIX B: EXPERIMENTAL DETAILS

Spin-integrated and spin-resolved angle-resolved photoemission spectroscopy data were acquired by the laser-based spin- and angle-resolved photoemission spectroscopy apparatus at the Institute for Solid State Physics (ISSP) at the University of Tokyo [50]. The apparatus was equipped with highly efficient very-low-energy electron diffraction (VLEED) spin detectors, whose effective Sherman function S_{eff} was 0.25, and a hemispherical analyzer (SCIENTA-OMICRON DA30L). We used a vacuum ultraviolet laser ($h\nu = 6.994$ eV) with p -light polarization as an excitation light. During the measurement, the base pressure was kept below 1×10^{-8} Pa. The acceptance angle of the spin detector was set to 1° , which reliably corresponded to approximately 1% of the Brillouin zone in the LKWU plane centered at the L point. However, E - k maps obtained by angle-resolved photoemission spectroscopy do not show any clear angular dependence; therefore, our results are considered to be angle integrated. Calibration of E_F for the sample was achieved using a gold reference. We magnetized the NCO film along the magnetic easy axis ([001] direction) by a magnetic field of 0.4 T.

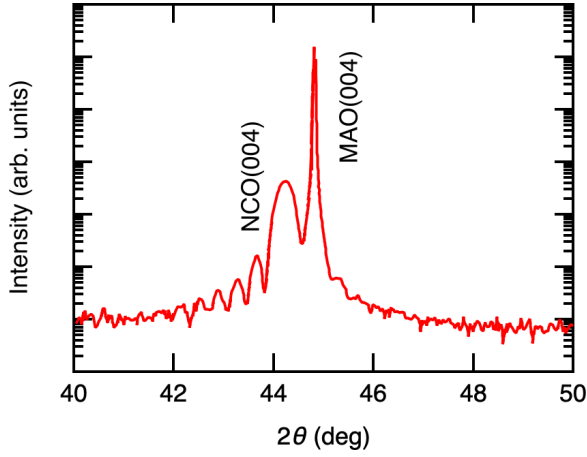


FIG. 5. 2θ - θ scan for the NCO sample on which we performed SRPES measurements.

To obtain absolute values of spin polarization using the VLEED detector, we used the equation $P = (1/S_{\text{eff}})(I^+ - I^-)/(I^+ + I^-)$, where $I^{+(-)}$ is the intensity of

the electrons reflected by the positively (negatively) magnetized target. Then we obtain the majority (I_+) and minority (I_-) spin spectra using $I_{\uparrow(\downarrow)} = [1 + (-)P](I_{\text{tot}}/2)$, where $I_{\text{tot}} = I^+ + I^-$ [51].

To estimate the characteristic energy at which the majority-spin EDC exhibits a sharp decrease [indicated by the black arrow in Fig. 1(e)], linear fittings were performed. The fitting ranges were set to -45 to -17 meV on the low-energy side and -17 to 0 meV on the high-energy side. From the intersection of these fitted lines, the characteristic energy of the majority-spin intensity suppression was estimated to be -18 meV.

APPENDIX C: FIRST-PRINCIPLES PHONON CALCULATION

First-principles phonon calculations were performed using the supercell finite-displacement method, as implemented in ALAMODE [52]. A $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing 56 atoms was used. To identify the most stable inverse spinel structure, the total energies of various configurations of Co and Ni atoms at the octahedral sites were computed using

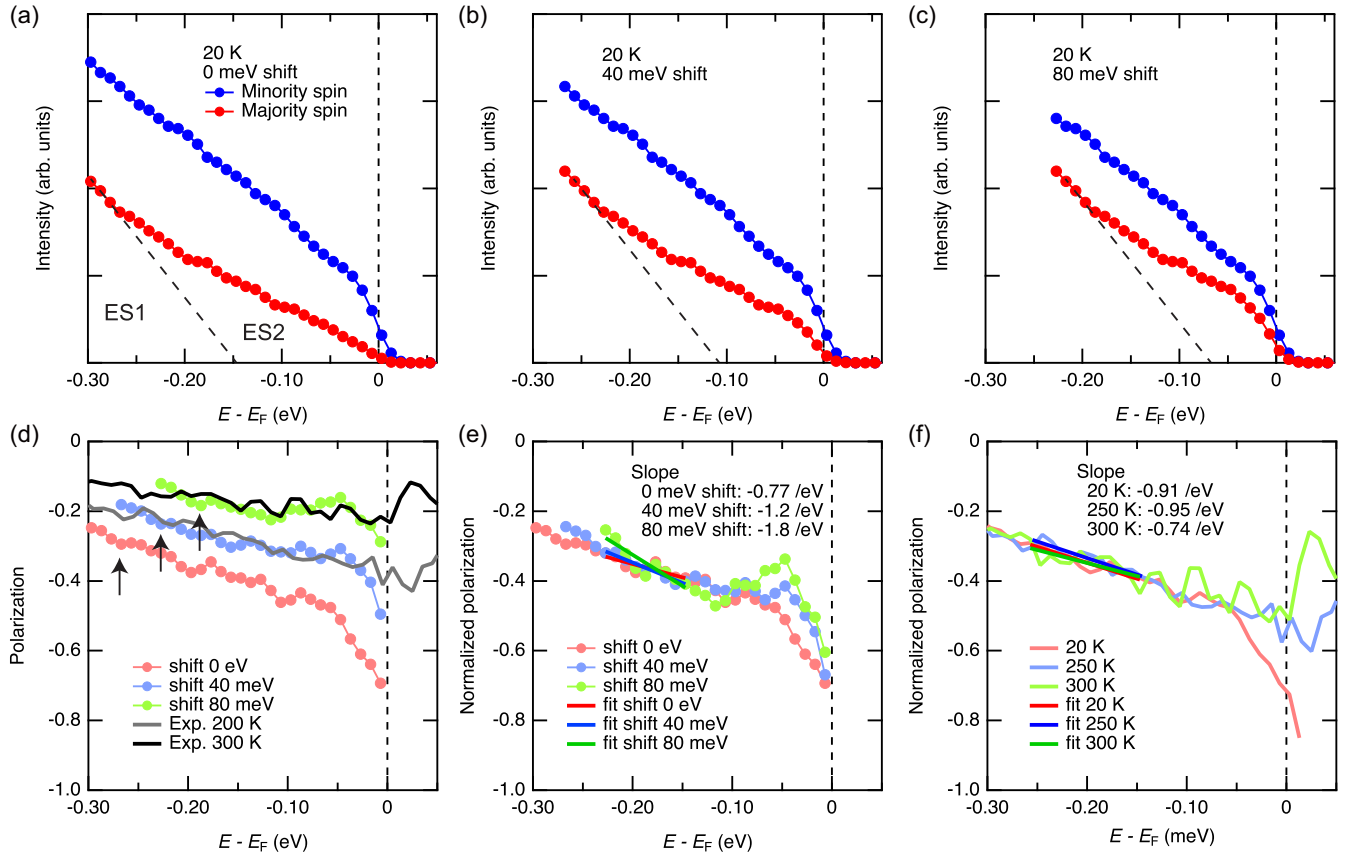


FIG. 6. Analysis based on shifted spin-resolved EDCs measured at 20 K. (a) Spin-resolved EDCs without shifting the majority-spin component. ES1 and ES2 correspond to the majority-spin valence-band maximum of the one-electron state and the NQP state discussed in the main text, respectively. (b) Same as panel (a), but with the majority-spin EDC shifted by 40 meV toward higher energy and multiplied by a Fermi-Dirac function convoluted with the experimental resolution. (c) Same as panel (b), but with an 80 meV shift. (d) Spin polarization calculated from the EDCs in panels (a)–(c), overlaid with experimental data at 200 and 300 K. Black arrows indicate the energy where the slope of the spin polarization changes due to the variation in the relative contributions of ES1 and ES2. (e) Spin polarization normalized at $E - E_F = -0.18$ eV, together with linear fits in the range from -0.22 to -0.15 eV. (f) Experimentally obtained spin polarization at 20, 250, and 300 K, normalized at $E - E_F = -0.18$ eV, with linear fits in the range from -0.25 to -0.15 eV.

density functional theory (DFT). Based on the most stable structure identified (space group: $P4_122$), we calculated phonon dispersion and phonon heat capacity within the harmonic approximation. The heat capacity was evaluated using the phonon frequencies at $40 \times 40 \times 30$ q points sampled in the first Brillouin zone. The DFT calculations were conducted using the Vienna *Ab Initio* Simulation Package [53], which implements the projector augmented-wave method [54]. A kinetic energy cutoff of 520 eV was used, along with a $5 \times 5 \times 5$ Monkhorst-Pack grid for the Brillouin zone sampling and a convergence criterion of 10^{-7} eV for the self-consistent-field iteration. The Perdew-Burke-Ernzerhof functional optimized for solids [55] was used for the exchange-correlation term.

APPENDIX D: CHARACTERIZATION OF NCO EPITAXIAL FILM

We characterized the film by x-ray diffraction (XRD) as shown in Fig. 5. We observed a sharp diffraction peak at 44.8° corresponding to the (004) reflection, accompanied by clear thickness fringes, which is consistent with an epitaxial NCO film (lattice constant $a = 0.811$ nm) on an MAO substrate. For rock-salt NiO ($a = 0.418$ nm) and CoO ($a = 0.426$ nm), the (200) diffraction peaks with Cu $K\alpha$ radiation would appear at 43.25° and 42.40° , respectively; no such peaks are observed in our XRD pattern.

Co_3O_4 has a slightly smaller lattice constant ($a = 0.808$ nm) than NCO, and we do not observe diffraction peaks attributable to Co_3O_4 either. In addition, compositional analysis by resonant x-ray scattering on NCO films grown under the same conditions indicates that the Ni/Co ratio at the octahedral sites is approximately unity [33]. This further suggests that a Ni-deficient Co_3O_4 phase, if present at all, is negligible.

APPENDIX E: SPECTRAL SHIFT ANALYSIS

In ferromagnets, the temperature evolution of the electronic structure exhibits a reduction of the exchange splitting with increasing temperature due to Stoner damping [56]. To examine whether the spin depolarization near E_F observed in this study can be explained by Stoner damping, we performed an analysis in which the majority-spin EDC obtained at 20 K was artificially shifted (Fig. 6).

Figures 6(a)–6(c) show the spin-resolved EDCs constructed by shifting the majority-spin EDC by 0 (no shift), 40, and 80 meV toward higher energy, respectively, followed by multiplication with a Fermi-Dirac distribution function convoluted with the experimental energy resolution. From these spin-resolved EDCs, the spin polarization defined as $P = (I_{\text{majority}} - I_{\text{minority}}) / (I_{\text{majority}} + I_{\text{minority}})$ was calculated, and the results are shown in Fig. 6(d). For comparison, experimentally obtained spin polarizations at 250 and 300 K are also plotted.

As indicated by the black arrows, a pronounced change in the slope of the spin polarization is observed at the energy where the relative contributions of ES1 and ES2 are interchanged. As shown in Fig. 6(e), linear fitting of the normalized spin polarization reveals that the slope of the fitted line increases with increasing shift magnitude. This behavior originates from the shift of the bending point in the spin polarization curve.

In contrast, as shown in Fig. 6(f), the slope of the experimentally obtained spin polarization does not exhibit any systematic change with increasing temperature. This result indicates that a simple band shift due to Stoner damping cannot account for the temperature dependence of the spin polarization observed in the experiment. Therefore, we conclude that the spin depolarization near E_F originates not from Stoner damping, but from the temperature evolution of the NQP states.

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- [1] B. Bhushan, Historical evolution of magnetic data storage devices and related conferences, *Microsyst. Technol.* **24**, 4423 (2018).
 - [2] I. Žutić, J. Fabian, and S. D. Sarma, Spintronics: Fundamentals and applications, *Rev. Mod. Phys.* **76**, 323 (2004).
 - [3] S. Bhatti, R. Sbiaa, A. Hirohata, H. Ohno, S. Fukami, and S. N. Piramanayagam, Spintronics based random access memory: A review, *Mater. Today* **20**, 530 (2017).
 - [4] S. S. P. Parkin, M. Hayashi, and L. Thomas, Magnetic domain-wall racetrack memory, *Science* **320**, 190 (2008).
 - [5] F. Yasin *et al.*, Extremely scaled perpendicular SOT-MRAM array integration on 300 mm wafer, in *2024 IEEE Symposium on VLSI Technology and Circuits, Honolulu, HI, USA* (IEEE, Piscataway, NJ, 2024), pp. 1–2.
 - [6] S. Ikegawa, F. B. Mancoff, and S. Aggarwal, Commercialization of MRAM—Historical and future perspective, in *2021 IEEE International Interconnect Technology Conference, Kyoto, Japan* (IEEE, Piscataway, NJ, 2021), pp. 1–3.
 - [7] D. D. Djayaprawira, K. Tsunekawa, M. Nagai, H. Maehara, S. Yamagata, N. Watanabe, S. Yuasa, Y. Suzuki, and K. Ando, 230% room-temperature magnetoresistance in CoFeB/MgO/CoFeB magnetic tunnel junctions, *Appl. Phys. Lett.* **86**, 092502 (2005).
 - [8] S. Ikeda, K. Miura, H. Yamamoto, K. Mizunuma, H. D. Gan, M. Endo, S. Kanai, J. Hayakawa, F. Matsukura, and H. Ohno, A perpendicular-anisotropy CoFeB–MgO magnetic tunnel junction, *Nat. Mat.* **9**, 721 (2010).
 - [9] G. Jeong *et al.*, A 0.24- μm 2.0-V 1T1MTTJ 16-kb nonvolatile magnetoresistance RAM with self-reference sensing scheme, *IEEE J. Solid-State Circuits* **38**, 1906 (2003).
 - [10] T. Na, S. H. Kang, and S.-O. Jung, STT-MRAM sensing: A review, *IEEE Trans. Circuits Syst. II Exp. Briefs* **68**, 12 (2021).
 - [11] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, New class of materials: Half-metallic ferromagnets, *Phys. Rev. Lett.* **50**, 2024 (1983).
 - [12] H. Y. Hwang and S.-W. Cheong, Enhanced intergrain tunneling magnetoresistance in half-metallic CrO_2 films, *Science* **278**, 1607 (1997).
 - [13] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Direct evidence for a half-metallic ferromagnet, *Nature (London)* **392**, 794 (1998).

- [14] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure, *Nature (London)* **395**, 677 (1998).
- [15] M. Jourdan, J. Minár, J. Braun, A. Kronenberg, S. Chadov, B. Balke, A. Gloskovskii, M. Kolbe, H. J. Elmers, G. Schönhense, H. Ebert, C. Felser, and M. Kläui, Direct observation of half-metallicity in the Heusler compound Co_2MnSi , *Nat. Commun.* **5**, 3974 (2014).
- [16] H. Fujiwara, M. Sunagawa, K. Terashima, T. Kittaka, T. Wakita, Y. Muraoka, and T. Yokoya, Intrinsic spin polarized electronic structure of CrO_2 epitaxial film revealed by bulk-sensitive spin-resolved photoemission spectroscopy, *Appl. Phys. Lett.* **106**, 202404 (2015).
- [17] A. M. Haghiri-Gosnet, T. Arnal, R. Soulimane, M. Koubaa, and J. P. Renard, Spintronics: Perspectives for the half-metallic oxides, *Phys. Status Solidi* **201**, 1392 (2004).
- [18] M. Oogane and S. Mizukami, Tunnel magnetoresistance effect and magnetic damping in half-metallic Heusler alloys, *Philos. Trans. R. Soc. A* **369**, 3037 (2011).
- [19] S. Majumdar and H. S. Majumdar, On the origin of decay of spin current with temperature in organic spintronic devices, *Org. Electron.* **13**, 2653 (2012).
- [20] J. S. Parker, P. G. Ivanov, D. M. Lind, P. Xiong, and Y. Xin, Large inverse magnetoresistance of CrO_2/Co junctions with an artificial barrier, *Phys. Rev. B* **69**, 220413(R) (2004).
- [21] D. M. Edwards and J. A. Hertz, Electron-magnon interactions in itinerant ferromagnetism. II. Strong ferromagnetism, *J. Phys. F Met. Phys.* **3**, 2191 (1973).
- [22] R. Skomski, Finite-temperature depolarization in half metals, *J. Phys.: Condens. Matter* **19**, 315202 (2007).
- [23] M. I. Katsnelson, V. Y. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Half-metallic ferromagnets: From band structure to many-body effects, *Rev. Mod. Phys.* **80**, 315 (2008).
- [24] L. Chioncel, Y. Sakuraba, E. Arrigoni, M. I. Katsnelson, M. Oogane, Y. Ando, T. Miyazaki, E. Burzo, and A. I. Lichtenstein, Nonquasiparticle states in Co_2MnSi evidenced through magnetic tunnel junction spectroscopy measurements, *Phys. Rev. Lett.* **100**, 086402 (2008).
- [25] H. Fujiwara, M. Sunagawa, K. Terashima, T. Kittaka, T. Wakita, Y. Muraoka, and T. Yokoya, Observation of intrinsic half-metallic behavior of $\text{CrO}_2(100)$ epitaxial films by bulk-sensitive spin-resolved PES, *J. Electron Spectrosc. Relat. Phenon.* **220**, 46 (2017).
- [26] H. Fujiwara, K. Terashima, M. Sunagawa, Y. Yano, T. Nagayama, T. Fukura, F. Yoshii, Y. Matsuura, M. Ogata, T. Wakita, K. Yaji, A. Harasawa, K. Kuroda, S. Shin, K. Horiba, H. Kumigashira, Y. Muraoka, and T. Yokoya, Origins of thermal spin depolarization in half-metallic ferromagnet CrO_2 , *Phys. Rev. Lett.* **121**, 257201 (2018).
- [27] A. Weh, J. Otsuki, and L. Chioncel, Finite-temperature many-body effects in half-metallic ferromagnets, *JPS Conf. Proc.* **30**, 011005 (2020).
- [28] J. M. D. Coey, J. J. Versluijs, and M. Venkatesan, Half-metallic oxide point contacts, *J. Phys. D Appl. Phys.* **35**, 2457 (2002).
- [29] L. Chioncel, H. Allmaier, E. Arrigoni, A. Yamasaki, M. Daghofer, M. I. Katsnelson, and A. I. Lichtenstein, Half-metallic ferromagnetism and spin polarization in CrO_2 , *Phys. Rev. B* **75**, 140406(R) (2007).
- [30] K. Miyamoto, A. Kimura, Y. Miura, M. Shirai, M. Ye, Y. Cui, K. Shimada, H. Namatame, M. Taniguchi, Y. Takeda, Y. Saitoh, E. Ikenaga, S. Ueda, K. Kobayashi, and T. Kanomata, Absence of temperature dependence of the valence-band spectrum of Co_2MnSi , *Phys. Rev. B* **79**, 100405(R) (2009).
- [31] S. Ueda, Y. Miura, Y. Fujita, and Y. Sakuraba, Direct probing of temperature-independent bulk half-metallicity in Co_2MnSi by spin-resolved hard x-ray photoemission, *Phys. Rev. B* **106**, 075101 (2022).
- [32] D. Kan, I. Suzuki, and Y. Shimakawa, Influence of deposition rate on magnetic properties of inverse-spinel NiCo_2O_4 epitaxial thin films grown by pulsed laser deposition, *Jpn. J. Appl. Phys.* **59**, 110905 (2020).
- [33] Y. Shen, D. Kan, Z. Tan, Y. Wakabayashi, and Y. Shimakawa, Tuning of ferrimagnetism and perpendicular magnetic anisotropy in NiCo_2O_4 epitaxial films by the cation distribution, *Phys. Rev. B* **101**, 094412 (2020).
- [34] D. Kan, M. Mizumaki, M. Kitamura, Y. Kotani, Y. Shen, I. Suzuki, K. Horiba, and Y. Shimakawa, Spin and orbital magnetic moments in perpendicularly magnetized $\text{Ni}_{1-x}\text{Co}_{2+y}\text{O}_{4-z}$ epitaxial thin films: Effects of site-dependent cation valence states, *Phys. Rev. B* **101**, 224434 (2020).
- [35] X. Xu, C. Mellinger, Z. G. Cheng, X. Chen, and X. Hong, Epitaxial NiCo_2O_4 film as an emergent spintronic material: Magnetism and transport properties, *J. Appl. Phys.* **132**, 020901 (2022).
- [36] C. Wu, L. Liu, R. Xu, K. Zhang, C. Zhen, L. Ma, and D. Hou, Theoretical analysis on O vacancy and cation inversion in NiCo_2O_4 , *Mat. Sci. Eng. B* **263**, 114886 (2021).
- [37] K. Dileep, B. Loukya, P. Silwal, A. Gupta, and R. Datta, Probing optical band gaps at nanoscale from tetrahedral cation vacancy defects and variation of cation ordering in NiCo_2O_4 epitaxial thin films, *J. Phys. D Appl. Phys.* **47**, 405001 (2014).
- [38] X. Shi, S. L. Bernasek, and A. Selloni, Oxygen deficiency and reactivity of spinel NiCo_2O_4 (001) surfaces, *J. Phys. Chem. C* **121**, 3929 (2017).
- [39] T.-C. Chang, Y.-T. Lu, C.-H. Lee, J. K. Gupta, L. J. Hardwick, C.-C. Hu, and H.-Y. T. Chen, The effect of degrees of inversion on the electronic structure of spinel NiCo_2O_4 : A density functional theory study, *ACS Omega* **6**, 9692 (2021).
- [40] Y. Shen, D. Kan, I.-C. Lin, M.-W. Chu, I. Suzuki, and Y. Shimakawa, Perpendicular magnetic tunnel junctions based on half-metallic NiCo_2O_4 , *Appl. Phys. Lett.* **117**, 042408 (2020).
- [41] O. Rader, A. Varykhalov, J. Sánchez-Barriga, D. Marchenko, A. Rybkin, and A. M. Shikin, Is there a Rashba effect in graphene on 3d ferromagnets? *Phys. Rev. Lett.* **102**, 057602 (2009).
- [42] R. Skomski and P. A. Dowben, The finite-temperature densities of states for half-metallic ferromagnets, *Europhys. Lett.* **58**, 544 (2002).
- [43] G. K. Wertheim, D. M. Riffe, and P. H. Citrin, Anharmonic surface vibrations in photoemission from alkali metals, *Phys. Rev. B* **49**, 2277 (1994).
- [44] F. W. de Wette and A. D. Kulkarni, Phonon dispersion, phonon specific heat, and Debye temperature of high-temperature superconductors, *Phys. Rev. B* **46**, 14922 (1992).
- [45] K. Ishizaka, R. Eguchi, S. Tsuda, A. Chainani, T. Yokoya, T. Kiss, T. Shimojima, T. Togashi, S. Watanabe, C.-T. Chen, Y. Takano, M. Nagao, I. Sakaguchi, T. Takenouchi, H. Kawarada, and S. Shin, Temperature-dependent localized excitations of

- doped carriers in superconducting diamond, *Phys. Rev. Lett.* **100**, 166402 (2008).
- [46] I. Saafi, R. Dridi, A. Mami, J. Ben Naceur, A. Amlouk, R. Chtourou, and M. Amlouk, Some physical investigations on NiCo_2O_4 thin films for potential applications, *Appl. Phys. A* **127**, 651 (2021).
- [47] V. Y. Irkhin, M. I. Katsnelson, and A. I. Lichtenstein, Non-quasiparticle effects in half-metallic ferromagnets, *J. Phys.: Condens. Matter* **19**, 315201 (2007).
- [48] P. Dai, H. Y. Hwang, J. Zhang, J. A. Fernandez-Baca, S.-W. Cheong, C. Kloc, Y. Tomioka, and Y. Tokura, Magnon damping by magnon-phonon coupling in manganese perovskites, *Phys. Rev. B* **61**, 9553 (2000).
- [49] G. Venkat, C. D. W. Cox, D. Voneshen, A. J. Caruana, A. Piovano, M. D. Cropper, and K. Morrison, Magnon diffusion lengths in bulk and thin film Fe_3O_4 for spin Seebeck applications, *Phys. Rev. Mater.* **4**, 075402 (2020).
- [50] K. Yaji, A. Harasawa, K. Kuroda, S. Toyohisa, M. Nakayama, Y. Ishida, A. Fukushima, S. Watanabe, C. Chen, F. Komori, and S. Shin, High-resolution three-dimensional spin- and angle-resolved photoelectron spectrometer using vacuum ultraviolet laser light, *Rev. Sci. Instrum.* **87**, 053111 (2016).
- [51] T. Okuda and A. Kimura, Spin- and angle-resolved photoemission of strongly spin-orbit coupled systems, *J. Phys. Soc. Jpn.* **82**, 021002 (2013).
- [52] T. Tadano, Y. Gohda, and S. Tsuneyuki, Anharmonic force constants extracted from first-principles molecular dynamics: Applications to heat transfer simulations, *J. Phys.: Condens. Matter* **26**, 225402 (2014).
- [53] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [54] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [55] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [56] T. Greber, T. J. Kreutz, and J. Osterwalder, Photoemission above the Fermi level: The top of the minority *d* band in nickel, *Phys. Rev. Lett.* **79**, 4465 (1997).