High-resolution resonant inelastic extreme ultraviolet scattering from orbital and spin excitations in a Heisenberg antiferromagnet

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We report a high-resolution resonant inelastic extreme ultraviolet (EUV) scattering study of the quantum Heisenberg antiferromagnet KCoF3. By tuning the EUV photon energy to the cobalt M23 edge, a complete set of low-energy 3d spin-orbital excitations is revealed. These low-lying electronic excitations are modeled using an extended multiplet-based mean-field calculation to identify the roles of lattice and magnetic degrees of freedom in modifying the resonant inelastic x-ray scattering (RIXS) spectral line shape. We have demonstrated that the temperature dependence of RIXS features upon the antiferromagnetic ordering transition enables us to probe the energetics of short-range spin correlations in this material.

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I. INTRODUCTION

Resonant inelastic x-ray scattering (RIXS) spectroscopy [1] has emerged as a powerful technique for studying low-energy excitations in quantum materials [2–7]. In particular, it has been established that RIXS can probe the mutual coupling between distinct degrees of freedom and the corresponding collective excitations, such as electron-phonon [8] and spin-orbital [2] couplings.

Nowadays, high-energy resolutions (≤25 meV) can be achieved by RIXS spectrometers in the soft and hard x-ray regime [9–12]. However, extending the RIXS spectroscopy into the extreme ultraviolet (EUV) [13] regime can provide a wealth of benefits with respect to the soft x-ray energy range, for example, achieving superior energy resolution at moderate instrument resolution resolving power and potentially offering simpler interpretations for the spectral features [13–16]. EUV RIXS at the transition-metal M edges is not only of basic relevance to condensed matter physics, but also presents a unique opportunity to investigate elementary excitations in the time domain [13]. In fact, recent RIXS experiments [17] had demonstrated that it was possible to record RIXS spectra using a seeded EUV free-electron-laser (FEL) source. As such, subpicosecond time-resolved RIXS experiments are now achievable owing to the high FEL flux with a unique time resolution.

Here, we perform high-resolution EUV-RIXS (hereafter referred to as RIXS) measurements on the antiferromagnet KCoF3 to investigate how magnetic ordering affects low-energy orbital excitations. KCoF3 belongs to the actively researched family of insulating alkali-metal fluorides KMF3 (M = Cu, Mn, Fe, Co, Ni, and Zn) [18–20], a cubic perovskite family that displays a variety of intriguing phenomena such as high-temperature superionic behavior, and interesting physical properties such as piezoelectric characteristics, ferromagnetism, and nonmagnetic insulator behaviors. They are ideal candidates for studying the effects of superexchange interactions on the structural, electronic, and magnetic properties of a large class of ionic compounds. In addition, its highly ionic character, high crystallographic symmetry, and the low anion coordination of KMF3 are expected to offer simpler modeling to describe their electronic and magnetic properties [21–23]. KCoF3 has a G-type anisotropic antiferromagnetic structure with spins pointing along the c axis [24,25]. The magnetic unit cell contains two types of antiferromagnetically coupled neighbors and belongs to a nonsymmorphic D1h magnetic space group (see Fig. 1) [19,26]. Upon establishing the antiferromagnetic ordering at TN = 115.3 K, the Jahn-Teller effect changes the crystal structure from cubic to tetragonal [23,27]. We have studied the spectral line shape of orbital (dd) excitations across the Néel transition temperature. Using an extended atomic multiplet-based calculation to simulate the experimental RIXS spectra, we have determined the key energy scales for Co 3d orbitals. Our RIXS studies show that the onset of magnetic ordering, which quenches the spin-flip excitation channel, affects the overall energy of dd excitations.

II. EXPERIMENTS

Co M23-edge x-ray absorption spectroscopy (XAS) and RIXS spectra of a pure KCoF3 single crystal were acquired at beamline 4.0.3 (MERLIN) RIXS endstation (MERIXS) [29]
spectral features A, B, C, and D were fitted with a set of Voigt functions. The Gaussian width of the Voigt is fixed at 15 meV, which was evaluated from the lowest-temperature rising edge of peak A.

FIG. 1. The KCoF₃ lattice structure and a pictorial representation of the mean-field magnetic Hamiltonian. A single Co atom (red arrow) is coupled to six neighbors, each of which has a mean-field spin moment (yellow arrow) for the second sublattice.

at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL).RIXS data were recorded using the slitless Variable Line Spacing grating spectrometer (VLS) based x-ray emission spectrometer equipped with a commercially available in vacuum CCD detector [29,30]. The sample and the spectrometer were placed at a 20° grazing incidence angle and 90° relative to the incoming x-ray beam, respectively. Photon polarization was maintained in the scattering plane in order to minimize the elastic scattered radiation. XAS measurements were recorded in the total electron yield (TEY). The atomic multiplet calculation was performed using the Kramers-Heisenberg formalism [13,31–33].

The Slater-Condon parameters were renormalized to 75% of the Hartree-Fock values for 3d-3d interactions, and to 67% for 3p-3d interactions. Spin-orbit couplings for core and valence levels were not renormalized. The crystal field strength was set to 10Dq = 0.90 eV at T = 0 K. The temperature effect was accounted for by applying a correction factor of (1 + T/20 000 K)^−5/3. The standard −5/3 exponent [34] and a volumetric thermal expansion coefficient were estimated from Ratuszna et al. [35]. The ground states in the scattering equation were a Boltzmann weighted ensemble of low-energy multiplet states. This weighting is the origin of the pseudo-anti-Stokes effect, in which RIXS features become broader on the energy gain side at higher temperatures. The intensity ratio between the elastic and inelastic features is around 10⁴, similar to previous M-edge RIXS results on other compounds [32,36,37]. Because of that, background curves produced by polynomial fitting to the experimental RIXS spectra in [0.5 eV, 1.55 eV], [1.15 eV, 3.2 eV] energy windows were used for subtraction to reveal the weak inelastic features in Figs. 2(c), 3(a), and 3(b). All inelastic features occurred at a constant energy loss, and no charge transfer features were observed in the spectra. In order to retrieve the peak energy positions, the spectral features A, B, C, and D were fitted with a set of Voigt functions. The Gaussian width of the Voigt is fixed at 15 meV, which was evaluated from the lowest-temperature rising edge of peak A.

FIG. 2. (a) Co M₉/₅-edge XAS spectrum recorded in total electron yield (TEY) mode at 80 K. (b) Stacked plot of Co M₉/₅-edge RIXS spectra measured at 80 K. The RIXS spectra are plotted as a function of energy loss. The excitation photon energies are listed next to the curves and also denoted by red and blue squares in (a). A strong elastic peak at zero energy loss is not fully displayed. (c) Comparison of two RIXS spectra measured above (150 K) and below (80 K) the Néel temperature. Each spectrum at the respective temperature is produced by summing individual spectra taken at the excitation photon energies marked by the blue squares in (a). The blue dashed line is the optical absorption spectrum of KCoF₃ reproduced from Ferguson et al. [28].

The main visible absorption bands are labeled in the figure.

III. RESULTS AND DISCUSSION

The x-ray absorption spectrum recorded in total electron yield mode around the Co M₉/₅ edge at 80 K is shown in Fig. 2(a). The XAS spectrum exhibits a prominent double-peak structure from Co 3p₁/₂,3/₂ core levels in the 61–67 eV energy range and two well-resolved pre-edge features in the 57–59.5 eV energy range. The overall XAS line shape bears a similarity to that of CoO, suggesting comparable energy scales for these two materials despite their different crystallographic structures. The experimental RIXS spectra at 80 K are shown in Fig. 2(b), with their excitation photon energies listed next to the curves and labeled by red and blue squares in Fig. 2(a). These spectra are dominated by a strong elastic peak at zero energy loss, which is not fully displayed in this figure; however, when zooming in on the low-intensity tail region around the elastic peak, four distinct inelastic features labeled A, B, C, and D can be identified in the [0.8 eV, 2.9 eV] energy loss window. These features show a strong resonance enhancement when excitation photon energies are tuned to Co M₉ resonance [blue squares in Fig. 2(a)], confirming their origin from Co 3d orbitals. They also resemble the ones in a similar system, CoO [32]. But due to the higher ionicity of KCoF₃, features B and C are more pronounced in this material and we also observe a very sharp inelastic feature at a higher-energy loss [feature D, 27 meV full width at half maximum (FWHM)] that is absent in the CoO spectra.
In Fig. 2(c), we show two RIXS spectra measured at 150 K (red line) and 80 K (black line), above and below \( T_N \). Each spectrum is obtained by summing individual spectra measured at the excitation photon energies around the Co \( M_2 \) edge [blue squares in Fig. 2(a)] at respective temperatures. The four main RIXS features can be correlated with their counterparts in the optical absorption spectrum in the visible and near-infrared regimes [28] (blue dashed line): Features A, B, C, and D correspond to excitations with \( T_{2g} \), \( A_{2g} \), \( T_{1e} \), and \( 2T_{1g} \) symmetries. A comparison between them shows that the high-temperature spectrum exhibits a shallower slope on the energy gain side of all inelastic features, consistent with the pseudo-anti-Stokes effect identified in CoO [32]. This pseudo-anti-Stokes effect is particularly visible in feature A [see Fig. 3(a)] because in the atomic multiple calculation, the multiplets forming this feature are confined to only within \( \sim 20 \) meV energy range at 0 K. Thus, as temperature is increased, the thermally excited states involved in the RIXS process manifest additional spectral weight in the energy gain side [for example, the red shaded area in Fig. 3(a)] that increases with temperature. Besides this pseudo-anti-Stokes effect, one can see that the line shape of feature A is highly asymmetric with an extended tail on the higher-energy loss side, which gives a FWHM around 120 meV at 10 K [for example, see the blue shaded area in Fig. 3(a)]. This tail suggests the presence of other contributions from the shakeup process. Unlike in the case of CoO where a strong nearest-neighbor magnetic interaction along the [111] direction was proposed to explain this energy loss tail, there are no nearest neighbors along the [111] direction in this perovskite compound. On the other hand, the high ionicity of \( \text{KCoF}_3 \) may enhance the contribution from the lattice degree of freedom, as in the RIXS process where the occupancy of poorly screened Co 3d orbitals is changed, and the Co-F bond length can be affected accordingly to lead to a phonon shakeup (see discussion below).

In that regard, we follow the approach in Ref. [32] to simulate the RIXS spectra with the consideration of a pseudo-anti-Stokes effect on the energy gain side and the contribution from interatomic many-body dynamics on the energy loss side of the excitations. A major contribution to the energy loss shakeup part of the spectra is a continuumlike distribution of states spread over \( \sim 150 \) meV, which likely represents simultaneous excitations of multiphonons with matrix elements that shrink upon increasing the number of phonons. We also adopt the self-consistent mean-field approach for the temperature dependence of the magnetic interaction. In mean-field theory, the 115.3 K Néel temperature implies an exchange field of \( J = 10.56 \text{ cm}^{-1} \) between neighboring Co sites, which is in agreement with the 10.3–10.6 \text{ cm}^{-1} values reported in Raman and neutron studies [26,38]. The local exchange field is set equal to the mean-field value from the six antiferromagnetically coupled neighboring Co atoms. Representative simulated RIXS spectra are shown as red dashed lines in Figs. 3(a) and 3(b).

Following the \( 3d^7 \) Tanabe-Sugano diagram and in agreement with the assignment in Ferguson et al. [28], the best candidate for the 2.6 eV feature is a \( 2T_{1g} \)-symmetry feature that comes from a spin \( \frac{3}{2} \) to \( \frac{1}{2} \) high spin to low spin transition. There are actually two excitations very close in energy (\( T \) and \( 2A \) symmetry), both of which are high spin to low spin excitations. However, the \( 2A \) state shows a negligible RIXS intensity in our calculation.

To quantify the temperature dependence of elementary excitations shown in Figs. 3(a) and 3(b), we carried out the fitting procedure outlined in the experimental sections to determine the peak positions for all the features. Figure 3(c) shows the experimental (blue squares) and theoretical (open and solid red squares; from an atomic multiple calculation) temperature dependence of the peak positions. Two theoretical curves are shown in each subpanel: The curve with solid red squares takes the mean-field thermalization of nearest-
neighbor magnetic moments into account, whereas the curve with open red squares has fixed nearest-neighbor magnetic moments at their $T = 10$ K value (assuming the magnetic order is preserved over the whole temperature range). Both curves include the effects of lattice expansion [35] and thermalization of the electronic states.

The theoretical curves reproduce nicely the observed temperature dependence of the experimental peak positions, implying that the lattice expansion and thermalization of the electronic states are essential ingredients for simulating the RIXS spectra. However, there are subtle differences. As can be seen from a comparison of two theoretical curves [open and solid red squared curves in Fig. 3(e)], the presence of antiferromagnetic ordering affects the energy shift. However, the effect of magnetic ordering is different for different features. For example, for features B and C, excluding antiferromagnetic ordering above $T_N$ only slightly increases the dispersion (a 10 meV increase over 60 meV for feature B and a 2 meV increase over 24 meV for feature C), and the effect for feature D is much larger (a 8 meV increase over 17 meV). Within the model, the relatively large discontinuity of the energy position of feature D across the magnetic transition occurs because this is a high spin to low spin excitation ($S = 3/2$ to $S = 1/2$), which intrinsically weakens the local antiferromagnetic correlations.

Generally, the magnetic part of the total energy shifts is less than $\frac{1}{2}$ of the lattice part, upon heating from 10 to 150 K. Above 150 K, only the lattice part matters in a mean-field picture, though in reality a magnetic contribution due to short-range exchange interactions continues to play a role. The major exception to this picture is the 2.6 eV feature, where the magnetism contributes almost 50% of the total energy shift. Notably, the highly resolved experimental data clearly show a ~20 meV discontinuity in the energy shift of that feature when crossing the magnetic transition temperature. This is corroborated by a calculated value of ~17 meV in our mean-field many-body modeling of the magnetic interaction between neighboring Co sites.

The full theoretical RIXS map across the Co $M_{23}$ edge at low temperature, with a broadening of the spectral features to account for the experimental resolution, is shown in Fig. 4. In the same figure, we also list the amount of charge density that is transferred into the $e_g$ states, relative to the ground state, for each excitation (averaged over incident energy). The change in occupation numbers $\Delta e_g$ gives a qualitative understanding of how strongly the excitation couples to the shakeup phonons. This can be understood from the fact that reducing the number of $e_g$ electrons will reduce the equilibrium distance between Co and the neighboring F, as well as the capability to shield the core hole created in the RIXS process. If this distance is greatly changed upon creating excitations in the RIXS process, a quenching of the core hole is expected to produce multiphonons. It is important to note that this kind of phonon coupling only matters for phonons created in the RIXS process and does not depend strongly on temperature. Correspondingly, $\Delta e_g$ only have a connection to the feature width FWHM at low temperature. This effect is discussed for the transition-metal $L$ edge in Lee et al. [15].

Finally, the thermal dispersion of the inelastic features increases monotonically with the amount of $\Delta e_g$ electron density, because $e_g$ electron orbitals directly overlap with the fluorine sigma orbitals. This picture can explain the remarkable energy stability of the lattice component of the 2.6 eV feature energy (i.e., disregarding the discontinuity across the magnetic transition).

### IV. CONCLUSIONS

In conclusion, we report a comprehensive high-resolved EUV-RIXS investigation of the excitation spectrum of orbital and spin degrees of freedom of the antiferromagnet KCoF$_3$, revealing a binding energy shift of these excitations across the antiferromagnetic phase transition. An interpretation from the perspective of short-range magnetic energetics suggests that this energy shift arises through the cobalt high spin to low spin flips, which weakens the local antiferromagnetic correlations. It follows that, owing to the unquenched spin-orbit interaction of cobalt, the energy stability of the spin and orbital states is affected by the local spin excitations when antiferromagnetic order is established. More in general, our results unveil the effects of magnetic exchange energetics on the low-energy landscape in this class of materials.

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