

Low-energy excitations in A-site ordered SmBaMn₂O₆

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The electron in a solid can be considered a bound state of the three independent, fundamental degrees of freedom creating quasiparticles: spinons, carrying the electron spin; plasmons, carrying the collective charge mode; and orbitons, carrying its orbital degree of freedom. These fundamental degrees of freedom could form ordering states in which dynamics or collective motions could occur and manifest as low-energy excitations. The exotic properties that appear in the materials exhibiting these electronic orderings are associated with these low-energy excitations. Although the orbital order (OO) and its coupling to the spin system creates very interesting phenomena, the microscopic origin of OO has been much less explored than other electronic properties as it is very difficult to directly access experimentally. Due to the recent improvement in energy resolution and flux, soft-x-ray resonant inelastic scattering (RIXS) allows for a reexamination of orbital excitations in manganites. Here, we present a study of low-energy excitations in half doped A-site ordered SmBaMn₂O₆ through a combination of RIXS and soft-x-ray resonant elastic scattering measurements. We confirm the existence of OO at $\mathbf{q} = (0.25, 0.25, 0)$ and find various low-energy excitations below 200 meV. While several excitations can be assigned to be of magnetic and phononic origin, a group of excitations between 80 and 200 meV show a temperature dependence closely following that of the OO, making them possible candidates for orbitons.

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I. INTRODUCTION

Quasiparticles characterize low-energy excitations in strongly correlated electron systems. This concept is used to describe the collective behavior by treating it as a single particle, which is important to simplify the many-body problem. While fermionic quasiparticles have been studied by angular-resolved photoemission (ARPES), bosonic quasiparticles can be probed by resonant inelastic scattering (RIXS). The orbital, spin, and charge degrees of freedom are quantum variables of electrons and have thus their own dynamics. In the same way as a magnon is a collective spin excitation in a magnetically ordered state, in a long-range orbitally ordered system a collective orbital excitation is predicted, and its quantized object is known as an orbiton.

Half-doped manganites represent the prototype of orbitally ordered systems. In these compounds, half of the Mn ions are in the Mn³⁺ state that has a $d^4(t_{2g}^3 e_g^1)$ configuration with one of the two e_g orbitals being occupied by an electron providing an orbital degree of freedom. Hole doping changes

the ground state due to the double-exchange interaction, and at half doping orbital order (OO) is formed [1]. Due to the strong electron-electron correlation, the theoretical description of the manganite systems is not straightforward. Even though some techniques, such as Raman scattering [2] and pump probe experiments [3], have claimed to have observed collective orbital excitations in manganites, these results are controversial [4] as these experiments cannot provide information on the momentum dependence of orbitons.

In recent years, resonant elastic x-ray scattering (REXS) has provided much information about orbital physics by directly observing the orbital order in different manganite compounds [5–14]. Several theoretical studies have predicted that orbital excitations are distinguishable by characteristic variations in the RIXS amplitude as a function of incident energy and momentum transfer [15–17] from other excitations in the solid. These studies predict that both single- and double-orbiton excitations are allowed, with intensities that are of the same order. In one-dimensional cuprates, orbitons are one of the three quasiparticles that electrons in solids are able to split into during the process of spin-charge separation. In two-dimensional cuprates, pure dispersive orbital excitations have been observed by RIXS [18]. However, the detection and study of the dispersion of orbitons in one of the prototypical orbital ordered materials, i.e., half-doped manganites, has been elusive so far. To our knowledge, only K-edge RIXS studies of doped manganites can be found in the literature to date [19–22].

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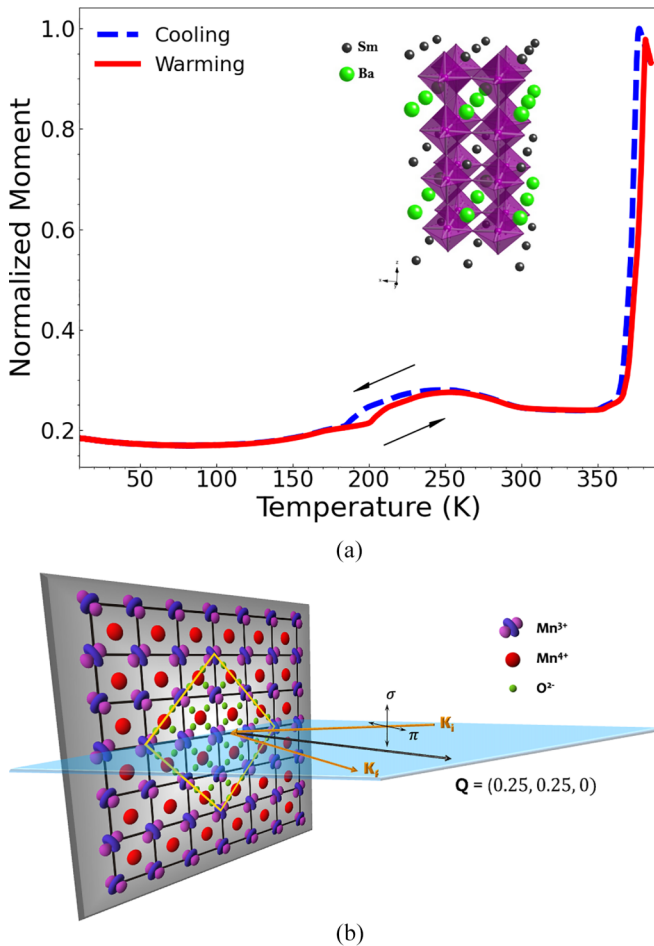


FIG. 1. (a) Magnetic moment measured as a function of temperature. The inset shows the crystal structure of the A-site ordered SBMO. (b) Experimental geometry, where the blue plane represents the horizontal scattering plane.

As RIXS experiments at the K -edge probe the $3d$ states indirectly [22], studies at the Mn $L_{2,3}$ -edge of doped manganites with high energy resolution are required to shed light on this issue.

Half-doped $\text{SmBaMn}_2\text{O}_6$ (SBMO) manganite crystallizes in the slightly distorted perovskite structure ABO_3 depicted in the inset of Fig. 1(a). In this compound, the MnO_6 octahedra are sandwiched by two distinct layers built of SmO and BaO [23] in contrast to the disordered $\text{Sm}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ with a random distribution of Sm and Ba ions. The A-site ordered RBaMn_2O_6 compounds with $R = \text{Sm, Eu, Gd, Tb, Dy, Ho, and Y}$ undergo a two-step charge-orbital order (COO) transition at temperatures $T_{\text{co1}} = 380$ K and $T_{\text{co2}} = 210$ K, while this transition is absent for the disordered compounds. Figure 1(a) shows magnetization measurements of SBMO single crystal where these transitions can be identified. Below $T_{\text{co2}} = 210$ K, a disappearance of the simple perovskite fourfold periodicity along the c -axis has been suggested to be caused by the restacking of the COO planes. The exact model, however, remains controversial [24–28]. The issue of the unresolved models arises partly from the fact that most experimental studies were performed on polycrystalline samples, which limits the direct observation of its microscopic physical properties.

A recent convergent beam electron diffraction experiment on a single crystal of A-site ordered SBMO determined that the space group for the T_{co2} and T_{co1} phases are $P21am$ and $Pnam$, respectively [29]. This space group change suggests that an even more complex structural arrangement occurs below T_{co2} as a consequence of the stacking of the COO. Some theoretical studies even predict a ferroelectric state in analogy to $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$ [29,30]. The existence of this second charge-order transition at 210 K, unique for the A-site ordered manganites, is responsible for a distinct temperature dependence of the OO parameter that will be discussed later.

In this paper, we present REXS and RIXS data which observe the orbital order and its low-energy excitations in a single crystal of SBMO. We employ REXS in the vicinity of the Mn $L_{2,3}$ edges to compare the OO signal to the previously published results on powder samples [10,11]. Using high-energy-resolution RIXS at these edges, we explore the existence of orbitons and other low-energy excitations.

Our results show that with the current available energy resolution, no orbiton could be detected in this compound at the OO ordering wave vector. However, for deviating momentum transfers, several low-energy excitations could be observed that exhibit correlations with the compound's electronic ordering phenomena.

We observed rich low-energy excitations up to ~ 200 meV at Mn L_3 and L_2 edges. Compared to the results obtained from Raman scattering and inelastic neutron scattering, the RIXS lower-energy excitations comprise at least magnons and phonons. However, the integrated spectral weight between 80 and 200 meV follows the distinct temperature evolution of the OO peak in A-site ordered manganites, suggesting the possible existence of orbitons in SBMO.

II. EXPERIMENTAL DETAILS

Single-crystalline SBMO was prepared in the following way: the mixed powders were calcined at 1273 K in air, pressed into a rod, and sintered at 1693 K under Ar atmosphere. At first, an A-site alloyed crystal of $\text{Sm}_{1/2}\text{Ba}_{1/2}\text{MnO}_3$ was grown at a rate of 4–10 mm/h in air by a floating-zone method. The melt-quenched crystal was treated in Ar atmosphere at 1693 K for 10 h to encourage the A-site ordering, and then annealed in O_2 at 973 K for 2 h. The structural characterization was performed by x-ray diffraction on a small part of the powdered crystal. The Rietveld analysis with Rietan2000 indicated perfect ordering of the Sm and Ba atoms [28]. The magnetic and transport properties of the studied sample were characterized using a SQUID magnetometer and are presented in Fig. 1(a). The crystal orientation was determined by a laboratory-based Laue diffractometer prior to the RIXS and REXS experiments.

The RIXS and REXS experiments were conducted at the I21-RIXS beamline at Diamond Light Source, United Kingdom [31]. The sample was mounted with the $[110]$ plane lying in the scattering plane onto a copper sample holder fixed to a liquid He flow cryostat which achieves temperatures between 7 and 380 K. Experiments were performed using linear horizontal or vertical polarized light leading to π or σ incident photon polarization with respect to the horizontal scattering geometry. The REXS measurements were performed using a

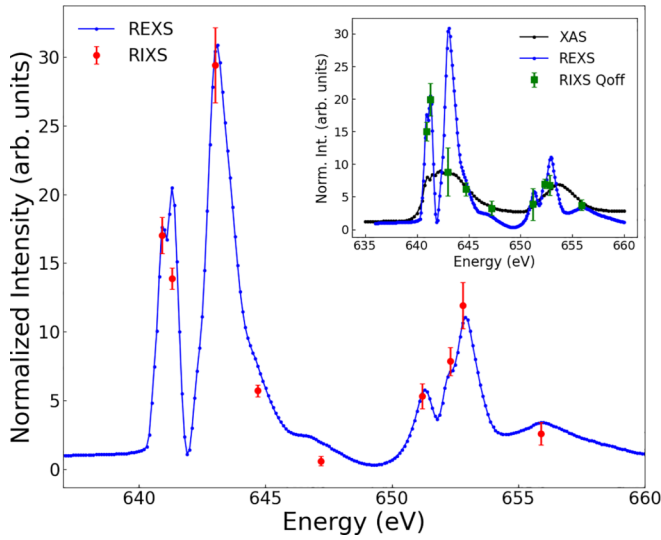


FIG. 2. Energy dependence of the (0.25, 0.25, 0) OO reflection together with the integrated intensity of the RIXS signal collected for different incident energies while maintaining the momentum transfer $\mathbf{q}$ constant. The inset shows the XAS taken in fluorescence mode together with the energy dependence of the Q_{off} reflection. The measurements were performed with σ incident polarization at $T = 15$ K.

photodiode as a detector without the possibility to differentiate the energy of the outgoing photons.

We tuned the incident photon energy to the resonance of the Mn $L_{2,3}$ absorption edges for the RIXS measurements. The total energy resolution achieved was about 24 meV FWHM. RIXS and REXS signals were collected without outgoing x-ray polarization analysis. For all RIXS spectra, the elastic (zero-energy loss) peak positions were determined by the elastic scattering spectrum from carbon tape placed near the sample surface and then fine adjusted by its Gaussian fitted elastic peak position. The Miller indices in this study are defined with reference to the crystal structure $a_p \times a_p \times 2a_p$, with $a_p \approx 3.9$ Å being the cubic perovskite unit cell. The experimental geometry of the sample is depicted in Fig. 1(b). The temperature of the measurements was 15 K unless otherwise stated. The REXS measurements were performed using a rotating photodiode inside the sample vessel. The RIXS measurements were collected through continuous rotation of the spectrometer arm due to the 3D nature of the investigated compound. The diffraction peaks have been analyzed using pseudo-Voigt functions while the inelastic peak were described using Gaussian functions.

III. RESULTS AND DISCUSSION

Figure 2 shows the REXS data of the energy dependence of the orbital (1/4 1/4 0) reflection in the vicinity of the Mn $L_{2,3}$ edges. The inset of Fig. 2 shows a comparison to the experimental x-ray absorption (XAS). Clearly, the resonant reflection intensity across the Mn $L_{2,3}$ edges is distinct from the XAS signal and evidences the OO [10,11,14]. More specifically, the present measurements on SBMO show the same differences with the layered $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ spectra

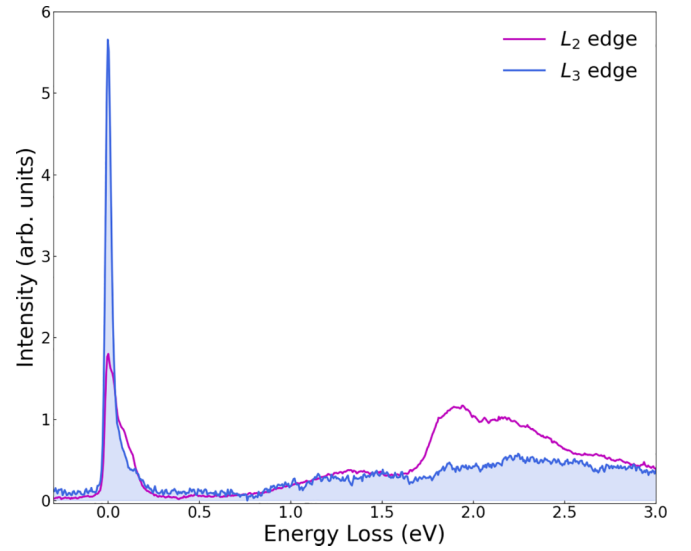


FIG. 3. Low energy-transfer RIXS line spectrum measured at the Mn L_2 and L_3 edge with σ incident polarization and $T = 15$ K plotted in different axes. The $\mathbf{q}$ for these measurements corresponds to (0.2347, 0.2347, -0.0130).

observed previously in literature [10]. These data confirm that the OO of the e_g electrons is of $x^2 - z^2/y^2 - z^2$ type in A-site ordered SBMO, while a $3x^2 - r^2/3y^2 - r^2$ type of orbital order is present in the layered manganite.

Following the REXS measurements, we performed the energy-dependent RIXS measurements with the θ and 2θ angles ensuring a fixed momentum transfer at the (1/4 1/4 0) reflection when varying the x-ray energy. The integrated intensities between ± 80 meV of these RIXS spectra are shown as red dots in Fig. 2 together with the REXS signal. Both RIXS and REXS signals are very similar, confirming the excellent alignment of the spectrometer to $\mathbf{q}_{\text{OO}} = (0.25, 0.25, 0)$. To minimize the elastic signal, the RIXS measurements shown later were collected both at $\mathbf{q}_{\text{OO}}$ and off from the OO Bragg condition at $\mathbf{q}_{\text{off}} = (0.2347, 0.2347, -0.0130)$. In the inset of Fig. 2, a comparison with the observed energy dependence measured at fixed $\mathbf{q}_{\text{off}}$ with the REXS and the XAS signal is shown.

Figure 3 shows the difference of spectral weight between the measurements done at the L_3 and L_2 edges. Due to the self-absorption, the L_2 RIXS spectra show more clearly the $d-d$ and low-energy excitations, whereas the L_3 spectra are mainly dominated by the elastic signal. Keeping this information in mind, we proceeded to study the low-energy excitations at the incident energy of 652.85 eV in order to explore the potential existence of the collective orbiton.

We now discuss the inelastic excitation at the OO $\mathbf{q}_{\text{OO}} = (0.25, 0.25, 0)$. Given that the inelastic signal is stronger at the Mn L_2 edge compared to the L_3 edge, we collected the momentum-dependent RIXS spectra across the OO scattering peak at the Mn L_2 edge. Figures 4(a) and 4(b) show the momentum-dependent RIXS maps probed by the linear π and σ incident polarizations, respectively. However, the OO elastic scattering signal completely dominates the spectra with no appreciable spectral weight from the low-energy excitations, and no dependence with the incident polarization is observed.

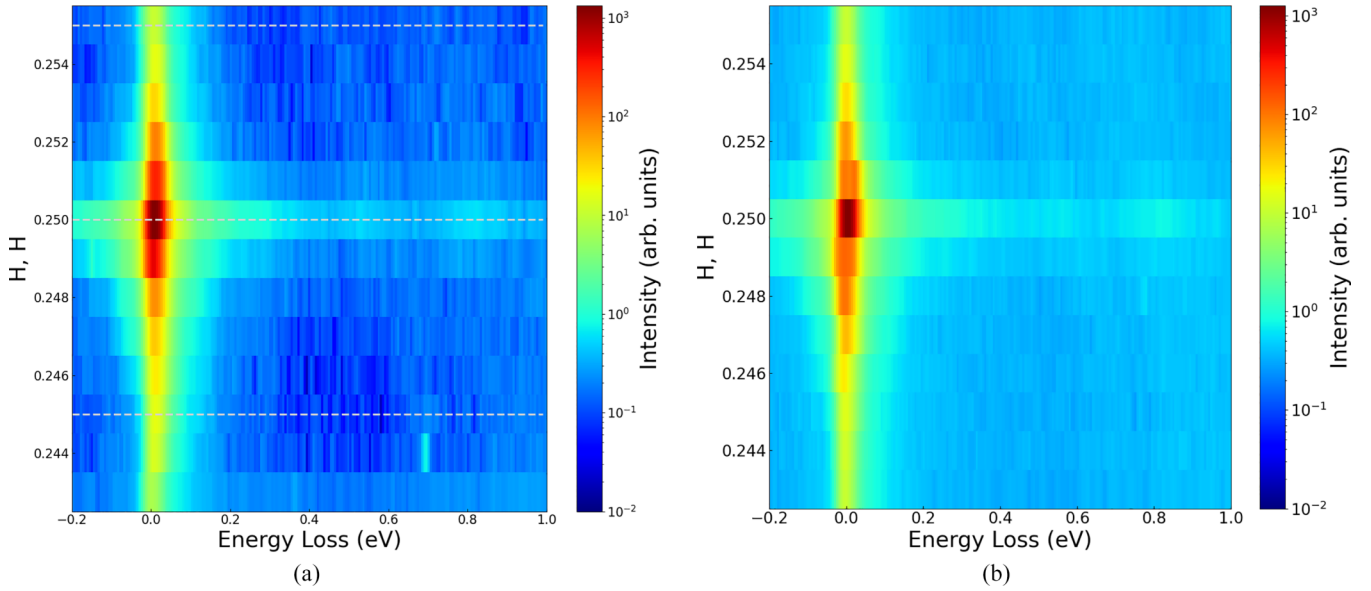


FIG. 4. Low energy excitations of SBMO measured in the vicinity of the OO (0.25, 0.25, 0) reflection revealed by Mn L_2 RIXS and $T = 15$ K. (a) Incident π polarization. The feature at HH 0.244 and energy loss 0.7 eV correspond to a cosmic ray in the detector. (b) Incident σ polarization.

This absence of polarization dependence of the OO Bragg peak is consistent with the previous REXS studies of OO in powder SBMO [10,11,14].

Figure 5 shows the normalized low-energy excitation spectra between 0 and 200 meV at three different $\mathbf{q}$ positions—(0.25, 0.25, 0), (0.245, 0.245, 0), and (0.255, 0.255, 0)—collected at $T = 15$ K and with linear horizontal incident polarization. These $\mathbf{q}$ positions correspond to the gray dashed lines in Fig. 4(a) and are shown together with the normalized elastic scattering spectrum from a carbon reference sample measured at the same geometry to illustrate the achieved energy resolution. The imperfect tail off the carbon tape Gaussian distribution reflects that the instrumental

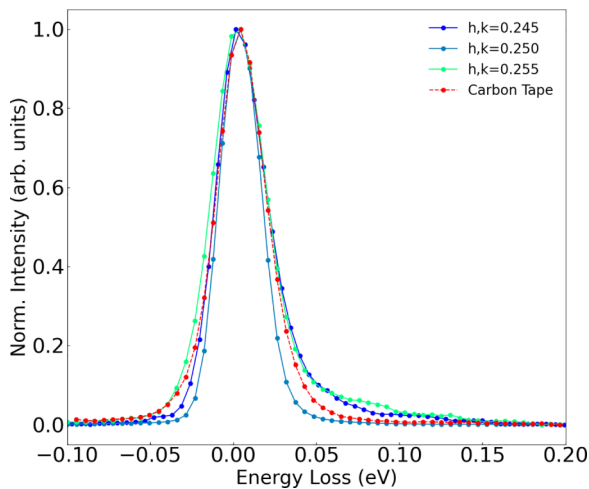


FIG. 5. Comparison of normalized RIXS spectra collected at different $\mathbf{q}$ values corresponding with the gray dashed lines in Fig. 4(a). The data are shown together with the normalized spectrum of a carbon tape measured at the same experimental conditions.

resolution function is distorted by the optics aberration. The near perfect Gaussian shape of the OO condition is due to the strong Bragg diffraction, which suppresses the aberration. When $\mathbf{q}$ is not exactly at the OO Bragg condition, weak low-energy excitations can be observed at around 80 meV. These data suggest that any possible low-energy excitations are shadowed by the OO scattering at this wave vector. The RIXS data at $\mathbf{q}_{\text{off}}$ are shown in Fig. 6, where several

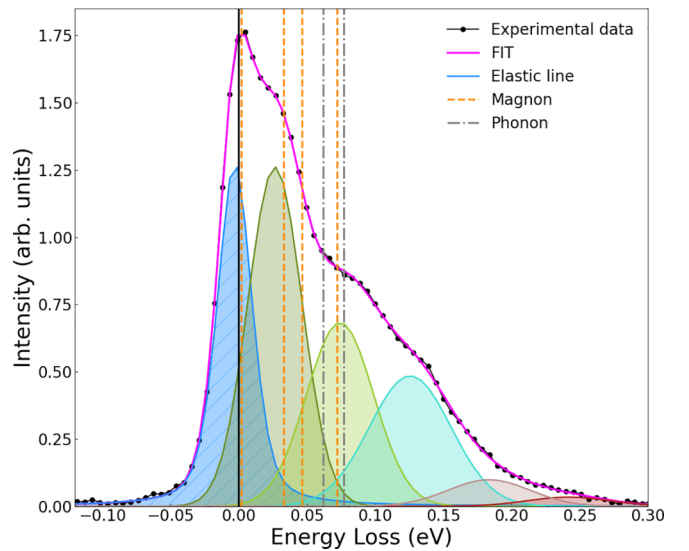


FIG. 6. Low-energy-transfer RIXS spectrum measured at the Mn L_2 edge with σ incident polarization at $T = 15$ K. The $\mathbf{q}$ vector corresponds to (0.2347, 0.2347, -0.0130) and the fits represent an elastic line and five low-energy excitations. The colors of the peaks are random as a way to help differentiate the individual contributions. The dashed lines correspond to the magnon energies and the dash-point lines to the phonon energies.

low-energy excitations are visible. We describe the spectra using five Gaussian functions while the elastic peak is described with a pseudo-Voigt function. The available energy resolution does not allow for a univocal fit of the data, and different solutions with similar fitting errors can be achieved. However, all the tested fit solutions indicate that the observed peaks are not higher harmonics of each other.

These results are interesting when compared to results from inelastic neutron scattering [32], which studied the magnetic excitations of the canonical half-doped manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in its magnetic and orbitally ordered phase. The neutron study demonstrated the existence of four gapped dispersive magnon modes. By using an effective Heisenberg-Hamiltonian model $\mathcal{H} = -\sum_{(ij)} J_{ij} S_i S_j$, the magnon dispersion and the dynamical structure factor were calculated. The gapped spin wave dispersion is consistent with the Goodenough model with strong nearest-neighbor ferromagnetic interactions along the zigzag chains and weak antiferromagnetic interactions between them.

Given the same magnetic structure between PCMO and SBMO, we used the Heisenberg Hamiltonian and the optimized exchange parameters obtained from PCMO to mark the magnetic excitations of SBMO at the given momentum transfer. The obtained energies for the magnon excitations for $\mathbf{q}_{\text{off}}$ are $E_{m_1} = 2$ meV, $E_{m_2} = 33.09$ meV, $E_{m_3} = 46.62$ meV and $E_{m_4} = 71.98$ meV as displayed in Fig. 6 by dashed orange lines.

In addition to the magnons, we also expect phonons to be present in this range of energy. Akahoshi *et al.* [28] studied SBMO using optical conductivity and Raman scattering. These techniques are restricted to $\mathbf{q} = \mathbf{0}$ and are not sensitive to the dispersion of the observed excitations. Two major peaks are observed in the Raman spectra around 500 and 620 cm^{-1} (62 and 77 meV) that are assigned to the Jahn-Teller (JT) and breathing modes, respectively. These phonon energies are displayed in Fig. 6 as dashed gray lines.

To better understand the origin of the low-energy excitations, we probed its dispersion by collecting its momentum-dependence between $\mathbf{Q} = 0.4864$ and 0.8453 with σ incident polarization at $T = 15$ K. The collected RIXS spectra are presented in Fig. 7 and are vertically displaced for clarity. The intensity of the RIXS spectra are normalized by the $d-d$ excitations, as these are not expected to be dispersive or have significant structure factor modulations. The momentum-dependent low-energy modes do not show sizable dispersion. Four dashed lines represent the calculated dispersion of the magnetic excitations. The comparison demonstrates that the magnons very likely contribute to the low-energy excitations in RIXS. However, other modes, including phonons and orbitons, likely also contribute to the RIXS spectra as the calculated magnon peaks cannot reconcile the observed evolution of low-energy excitations.

Another way to differentiate between these modes is to study their temperature evolution. Figure 8(a) shows the RIXS spectra at the Mn L_2 edge at $\mathbf{q}_{\text{off}}$ for three different temperatures. Comparing with the temperature dependence of the magnetization recorded during cooling and heating of SBMO presented in Fig. 1(c) allows us to establish the correlation between the RIXS signal and the phase diagram. The three chosen temperatures are $T = 15$ K corresponding to the $T_{\text{CO}2}$

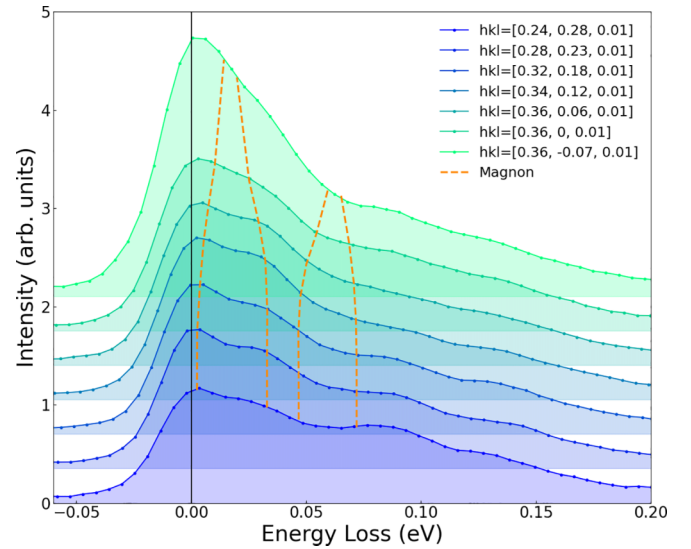


FIG. 7. RIXS spectra taken at the Mn L_2 edge with σ incident polarization at $T = 15$ K and at different $\mathbf{q}$ vectors. The dashed lines represent the dispersion of the magnon energies for the same $\mathbf{q}$ vectors obtained from theoretical calculations.

phase, $T = 300$ K with $T_{\text{CO}2} < T < T_{\text{CO}1}$, and finally at $T = 380$ K, which is above the metal-to-insulator transition $T > T_{\text{CO}1}$.

There are two regions in the spectra that exhibit an opposite temperature dependence. Below 50 meV, the intensity of the elastic and lowest energy excitations increases with increasing temperatures. However, for intensities above 50 meV, we observe a drastic intensity reduction up to $T = 300$ and 380 K. The temperature evolution of the RIXS spectra is in agreement with Raman, which reported that both the JT and the breathing modes are rapidly suppressed with increasing temperature towards $T_{\text{CO}2}$ and bear little intensity in the temperature range of $T_{\text{CO}2} < T < T_{\text{CO}}$. Remarkably, we observe the presence of several excitations around 100 meV whose energies do not correspond either to magnons or phonons. These excitations exhibit a more pronounced temperature dependence. Ishihara *et al.* [33] postulated in their theoretical study of orbital excitations in LaMnO_3 that the orbiton energy is of the order of J and larger than the Jahn-Teller phonon energy. Hence, the observed excitations around 100 meV might correspond to orbital excitations. To test this scenario, we collected RIXS spectra at further temperatures and we compared their spectral weight around 100 meV with the temperature dependence of the orbital order reflection. The RIXS spectra were fitted using a skewed Gaussian peak to describe the elastic signal and two Gaussian peaks to describe the inelastic low-energy excitations. The first Gaussian peak was used to describe the excitations below 50 meV, which, as Fig. 8(a) shows, increase in intensity with increasing temperature. The second Gaussian peak describes the energy region between 50 and 200 meV that exhibits a decreasing spectral weight as a function of rising temperature. Figure 8(b) compares the integrated intensity of the REXS signal as a function of temperature with the integrated intensity of the inelastic excitations between 50 and 200 meV. A remarkable agreement in their temperature

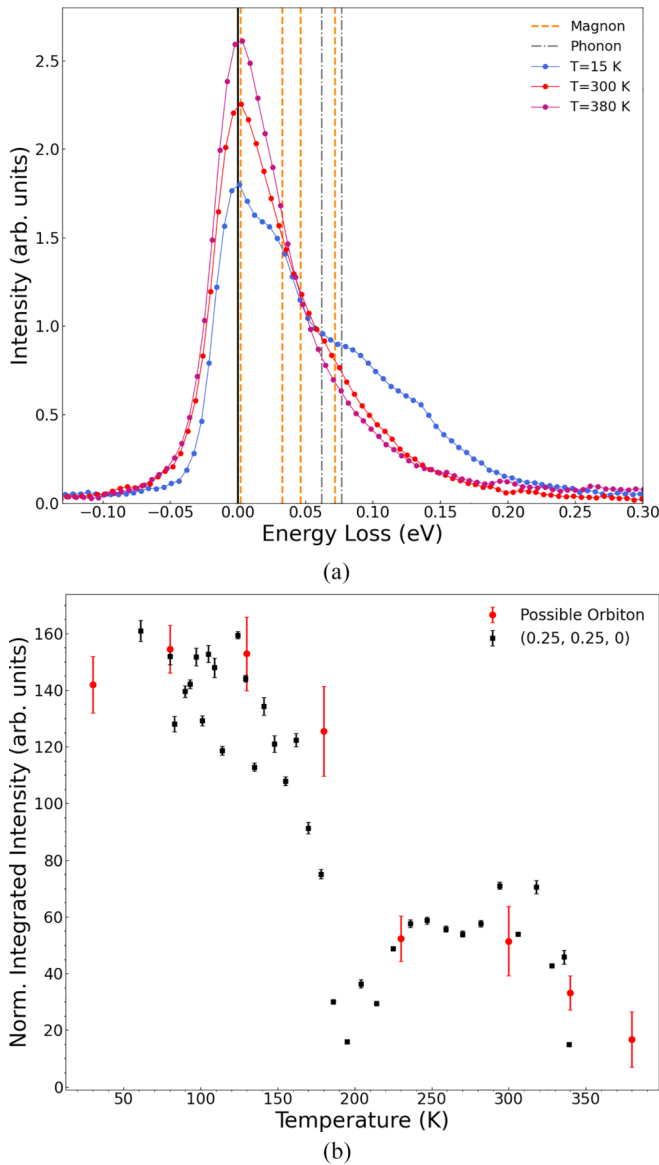


FIG. 8. (a) RIXS spectra measured at the Mn L_2 edge and $\mathbf{q}_{\text{off}} = (0.2347, 0.2347, -0.0130)$. The spectra were collected with σ incident polarization and temperatures of 15, 300, and 380 K. (b) Comparison of the integrated intensity of the $(0.25, 0.25, 0)$ orbital order peak measured by REXS with the integrated intensity of the energy excitations between 80 and 200 meV in the RIXS spectra.

dependence can be observed. For more details about the data fitting, see the Supplemental Material [34].

One of the specific properties of the A-site ordered manganites is the transition at $T_{\text{CO}_2} = 210$ K associated with a change in the stacking of the orbitally ordered planes along the z axis. In the OO temperature dependence, it results in a steep increase of intensity by a factor of 2. This peculiar behavior was already observed in a previous REXS study of SBMO powder samples [10] and appears also in our REXS measurements of this single crystal. Remarkably, the temperature dependence of the integrated intensity of the excitations around 100 meV also follows this behavior, including the doubling of intensity compared to below T_{CO_2} , which indicates a correlation between orbital order and the excitations. This

evolution is in strong contrast with that of the excitations at energies below 50 meV.

Several works have considered orbital excitations in the parent compound LaMnO_3 [17,35–37], with significant variation of the role attributed to phonons. Van der Brink [35] used self-consistent second-order perturbation theory in the orbital-phonon coupling and found that the orbital dispersion is strongly reduced by the electron-phonon coupling. In addition, he found that this coupling also mixes the orbital and phonon modes and causes satellite structures in the orbital and the phonon spectral function. In this context, the observed excitations between 80 and 200 meV could be explained as the orbital collective excitations plus these phonon satellites, whose energy would involve contributions from both the orbital and the lattice components.

Schmidt *et al.* [37] performed a calculation to provide information on the nature of orbital excitations in the presence of substantial orbital phonon coupling. In their model, they considered quantitatively the dynamic orbital-phonon interaction that corresponds to the creation or annihilation of a local distortive phonon in the presence of an orbital. Their results show that the system becomes more local when increasing the orbital-phonon coupling, i.e., the effective bandwidth of the orbital band decreases as the orbital-phonon coupling increases. In a later work, that focused completely on the observation of orbital excitations in LaMnO_3 using RIXS, Forte *et al.* [17] used the ultrashort core-hole lifetime expansion for RIXS and obtained a gapped orbital spectrum. Since their calculated orbital Hamiltonian did not have a continuous symmetry, the Goldstone modes were absent. In addition, they found that at high symmetry points in the Brillouin zone, the intensity of specific orbital branches vanishes. This result is consistent with our experimental data, which show that at the OO $\mathbf{q}$ vector the OO diffraction peak dominates the spectra.

We are aware that these experimental observations are not sufficient to univocally claim that the observed excitations correspond to the elusive orbitons. However, the observed correlation is a strong motivation for further studies. We believe that in order to properly explore the low-energy excitations in half-doped manganites, further improved energy resolution and additional polarization analysis of the scattered radiation would be essential to clarify the electronic nature of the observed excitations, as it would enable us to distinguish the excitations that are present in each of the four polarization channels. Note that for coupled orbital-phonon modes, one can only see the “orbital” contributions, as is the case for the measurement of phonons at the oxygen K -edge; see, e.g., Ueda *et al.* [38].

IV. CONCLUSIONS

Thanks to the improved flux and energy resolution of the new generation of soft-x-ray RIXS instruments, a re-examination of low-energy excitations in half-doped A-site ordered SBMO combining RIXS and REXS measurements was performed. At the OO wave vector, the OO diffraction peak dominates the spectra completely. When moving slightly

away from the Bragg condition, several low-energy excitations became observable.

The observed low-energy excitations fall within the energy region in which both magnetic and phonon excitations are expected to appear. Comparing to neutron inelastic and Raman scattering results, we identified the energies at which magnons and phonons would be expected. We find additional excitations between 80 and 200 meV that could not be identified as magnons or phonons. They could potentially correspond to the elusive orbiton. The temperature dependence of the RIXS and REXS signals shows a clear correlation for the energy excitations between 80 and 200 meV. The unique temperature dependence indicates a clear correlation between orbital order and the excitations. This observed correlation hints at the

possibility that these excitations could correspond to the long sought-after orbiton.

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DATA AVAILABILITY

The data that support the findings of this article are available from the authors upon reasonable request.

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