Excitonic dispersion of the intermediate-spin state in $LaCoO_3$ revealed by RIXS

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Background

In strongly correlated insulators, the proximity of the excitonic insulator phase is reflected by the presence of dispersive electron-hole excitations with a small gap above a singlet ground state. Recently, such an excitation scenario was proposed to be realized in perovskite oxide $LaCoO_3$ [1], which is a material well-known by its notorious spin-state crossover. This crossover have been described as a thermal population of excited atomic multiplets from a low spin (LS) ground state to the high-spin (HS) or the intermediate-spin (IS) states. A coexistence of Co ions in the excited (IS or HS) and ground (LS) states in a lattice is expected to cause a sizable disproportionation of Co-O bond lengths. However, this disproportionation has never been observed.

The excitonic scenario of $LaCoO_3$ describes a propagation of a single IS exciton on the LS background due to superexchange mechanism to the nearest-neighbor [1,2]. As usual in periodic systems, the elementary IS excitations have the plane-wave form with the energy dependent on the quasi-momentum q. When the excitation gap is closed the excitations with q-vector of the band minimum form a condensate. For example, the metamagnetic transition observed in high fields has the temperature dependence consistent with exciton condensation without the HS-LS spin-state order [1]. Despite this indirect evidence an unambiguous proof of the excitonic physics in $LaCoO_3$ has been missing.

Method

We employee 2p3d resonant inelastic X-ray scattering (RIXS) of cobalt to reveal this excitonic scenario. The measurements were performed at 05A1 beamline in Taiwan Light Source [3]. A 90 meV energy resolution provides sufficient resolution to distinguish different spin states [4]. The $LaCoO_3$ single crystal was grown by the optical floating zone method and aligned to the c-axis in the (pseudo) cubic axis with a lattice constant a_{cub}~3.83Å. 2p3d RIXS spectra were collected from q=(0, 0, 0.26π) to (0, 0, 0.90π) at 20 K.

Result and discussion

The experimental spectra show four peaks at around 0.4, 0.7, 1.2, and 1.6 eV [4,5]. They are attributed to the excitations from LS ($^1A_{1g}$) ground state to IS ($^3T_{1g}$), IS ($^3T_{2g}$), LS ($^1T_{1g}$), and HS (^5E_g) states, respectively. The lowest HS ($^5T_{2g}$) state has a negligible RIXS intensity within the present approximation [4,5]. The IS $^3T_{1g}$ peak exhibits a clear q-dependent shift from 490 to 290 meV in the interval from q=(0, 0, 0.26π) to (0, 0, 0.90π). The q-dependence of the IS $^3T_{2g}$ peak at around 0.7 eV is much less pronounced. This sizable dispersion of the IS $^3T_{1g}$ branch, describing a propagation of a single IS $^3T_{1g}$ state on the LS background, which match well to the theoretical calculations for propagation of a single IS exciton [5].

Conclusion

This observation of the IS ($^3T_{1g}$) excitations dispersion with a sizable bandwidth point to an important role of IS excitations for the low-energy physics of the material. $LaCoO_3$, therefore, should not be viewed as a static collection of ions in particular atomic states, but rather as a gas of mobile bosonic excitons (IS) above (LS) vacuum.

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The authors are supported by by the European Research Council (ERC) with the grant agreement No. 646807-EXMAG and 340279-XRAYonACTIVE