ESRF	**Experiment title:** **Validation of the excitonic scenario in Co3+ perovskites by means of high-precision 2p3d resonant inelastic X-ray scattering**	**Experiment number**: HC-3610
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Shifts:	**Local contact(s)**: Davide Betto, Nicholas B. Brookes	

Names and affiliations of applicants (* indicates experimentalists):

Ru-pan Wang*, Marte van der Linden*, Frank M.F de Groot*, Yohei Uemura*, Mahnaz Ghiasi*, Atsushi Hariki†, Andrii Sotnikov†, Jan Kuneš†, Davide Betto^, Nicholas B. Brookes^

*Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Universiteit Utrecht.

† Institute of Solid State Physics, TU Wien, 1040 Vienna, Austria

^ European Synchrotron Radiation Facility, France.

1. Background Information

The physics of ionic insulators at energies below the band gap opened between fully occupied and empty atomic states is often trivial. Under certain conditions, electron-electron interactions may alter this picture by giving rise to low-energy bosonic excitations. This is the case of $LaCoO_3$, a structurally simple quasicubic material with complex magnetic and transport properties studied since the 1950s. $LaCoO_3$, a diamagnetic insulator with a low-spin (LS, S = 0, $^1A_{1g}$) ground state and a band gap between filled t_{2g}^6 and empty e_g^0 subshells, becomes a paramagnetic insulator around 100 K. This behavior is traditionally attributed to thermal population of excited atomic multiplets. The high-spin (HS, S = 2, $t_{2g}^4e_g^2$, $^5T_{2g}$) or intermediate-spin (IS, S = 1, $t^5_{2g}e^1_g$, $^3T_{1g}$) nature of the lowest excited state has been the subject of an ongoing debate. Both HS and IS scenarios evoke an important question. Decorating the lattice with excited atoms leads to sizable distribution Co–O bond lengths due to breathing distortion around HS atoms or Jahn-Teller distortion around IS atoms. At experimentally reported concentrations, the excited atoms are expected to form a regular lattice, an effect favored by electron-lattice coupling, as well as electronic correlations. Nevertheless, no spin-state order nor Co-O bond-length disproportionation was observed in $LaCoO_3$. This leaves the possibility of dynamically fluctuating spin-state order, for which, however, the picture of thermal atom-bound excitations provides no mechanism.

2. Results

Our main observations are summarized in Fig. 1. The RIXS spectra exhibit low-energy features observed in previous studies. At 20 K, we observe a clear dispersion of the peak in 0.2–0.5 eV range that was assigned to the IS ($^3T_{1g}$) excitation. The HS ($^5T_{2g}$) excitation observed below 0.1 eV shows no dispersion. The IS dispersion is consistent with the theory and experiment of Ref., see Fig. 1(f), with substantially reduced error bars, provided by the present high energy resolution. Increasing the temperature above 100 K leads to a distinct narrowing and smearing of the dispersive feature, see Figs. 1(b)–1(e). Other spectroscopic studies indicated growing concentration of HS excitations with temperature, while the system remains a spatially uniform insulator. This work has been published on Phys. Rev. B (Phys. Rev. B **101**, 245162 (2020)).

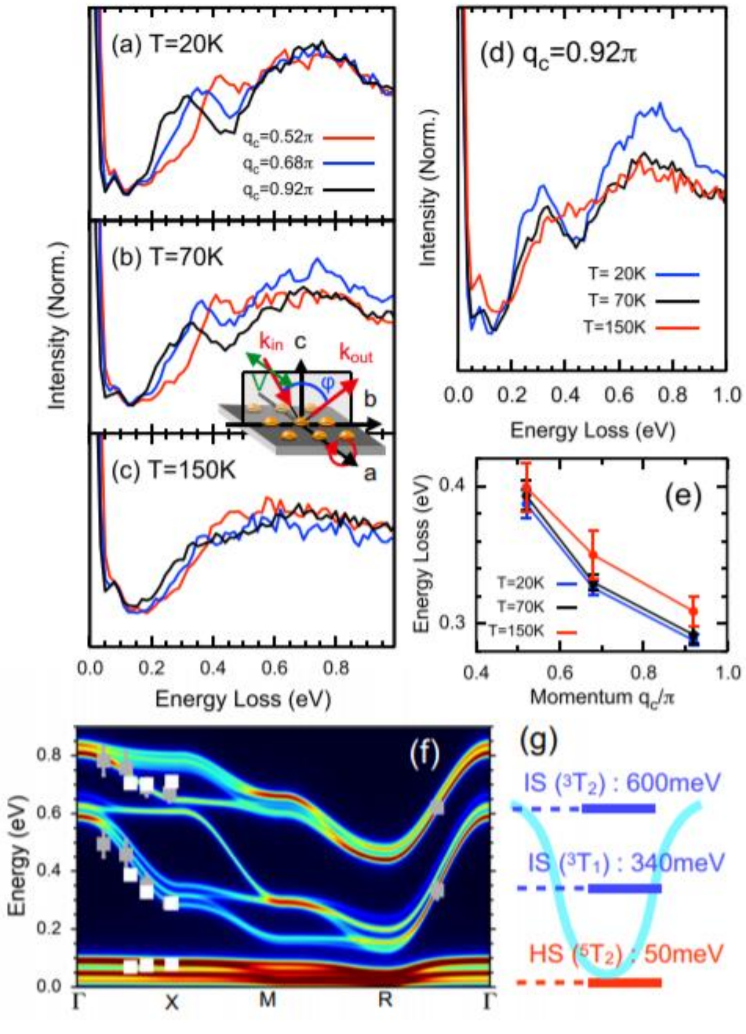

Figure 1: The experimental RIXS intensities for selected q = (0, 0, qc) measured at (a) 20 K, (b) 70 K, and (c) 150 K. (d) Temperature dependence at qc = 0.92π. Two distinct features located at 200–500 and 800 meV correspond to the $^3T_{1g}$ and $^3T_{2g}$ IS excitations, respectively. The experimental geometry and the definition of angle ϕ are illustrated in the inset. (e) The peak position of the $^3T_{1g}$ IS excitation obtained by the fitting analysis. (f) Comparison at 20 K between theory (color map), present RIXS data with $\triangle E$ = 25 meV (white), and previous RIXS data with $\triangle E$ = 90 meV (gray) . (g) Sketch of the excitonic scenario: the atomic-level energies and the IS dispersion on the LS background.