Melting of excitonic dispersion in LaCoO$_3$: theory and experiment

Atsushi Hariki,$^1$ Ru-Pan Wang,$^2$ Andrii Sotnikov,$^1,3$ Keisuke Tomiyasu,$^4,5$ Davide Betto,$^6$
Nicholas B. Brookes,$^3$ Yohei Uemura,$^5$ Mahnaz Ghiasi,$^2$ Frank M. F. de Groot,$^2$ and Jan Kuneš$^{1,7}$

$^1$Institute of Solid State Physics, TU Wien, 1040 Vienna, Austria
$^2$Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
$^3$Akkiezer Institute for Theoretical Physics, NSC KIPT, Akademichna 1, 61108 Kharkiv, Ukraine
$^4$Department of Physics, Tohoku University, Aoba, Sendai 980-8578, Japan
$^5$NISSAN ARC, LTD., 1, Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan
$^6$European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220, F-38043 Grenoble Cedex 9, France
$^7$Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czechia

(Dated: December 6, 2019)

We present Co $L_3$-edge resonant inelastic x-ray scattering (RIXS) of bulk LaCoO$_3$ across the thermally-induced spin-state crossover around 100 K. Owing to a high energy resolution of 25 meV, we observe unambiguously the dispersion of the intermediate-spin (IS) excitations in the low temperature regime. Approaching the intermediate temperature regime, the IS excitations are damped and the bandwidth reduced. The observed behavior can be well described by a model of mobile IS excitons with strong attractive interaction, which we solve using dynamical mean-field theory for hard-core bosons. Our results provide a detailed mechanism of how HS and IS excitations interact to establish the physical properties of cobaltite perovskites.

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, intra-atomic Coulomb interactions may alter this picture by giving rise to low-energy bosonic excitations. This is the case of LaCoO$_3$, a structurally simple quasi-cubic material with complex magnetic and transport properties that has been studied since 1950s $^{17,10}$.

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, $S = 2$, $t_{2g}^6e_g^2$, $2T_{2g}$) or intermediate-spin (IS, $S = 1$, $t_{2g}^5e_g^1$, $3T_{1g}$) nature of the relevant excited states has been the subject of an ongoing debate $^{7,19}$. Both HS and IS scenarios evoke an important question. Decorating the lattice with a regular or random pattern of excited atoms leads to sizeable 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 $^{20,21}$, as well as by electronic correlations $^{22,23}$. Nevertheless, no spin-state order or Co-O bond-length disproportionation was observed in LaCoO$_3$ $^{23}$. This leaves the possibility of dynamically fluctuating spin-state order $^{20}$, for which, however, the picture of thermal atom-bound excitations provides no mechanism.

Recently, Sotnikov and Kuneš $^{27}$ proposed a model of LaCoO$_3$, in which the IS excitations are viewed as mobile bosons (excitons) carrying spin $S = 1$, Fig. 1. Based on band-structure calculations and experimental evidence, they estimated the half-bandwidth of 250 meV to be comparable with the IS on-site energy of about $\epsilon_{1S} = 340$ meV. The HS excitations are viewed as immobile $S = 2$ bi-excitons formed by IS excitons of different orbital flavors with excitation energy of about $\epsilon_{HS} = 20$ meV $^{15,28}$, see Fig. 2. This implies a very strong local attraction $V$ between IS excitons $\epsilon_{HS} \approx 2\epsilon_{IS} - V$.

RIXS experiments performed at low temperature matched nicely with the generalized spin-wave theory based on first-principles parameters $^{29}$ and confirmed the estimate of Ref. $^{27}$. The low-temperature RIXS measurements map out the dynamics of a single IS or HS excitation on the LS lattice (ground state), i.e., a single-boson problem. The strong-coupling nature of the model $^{27}$ suggests a sizeable temperature dependence of the excitation spectrum when excited states start being populated.

In this Letter, we report the thermal evolution of the IS dispersion in LaCoO$_3$ obtained with Co $L_3$-RIXS and its theoretical modelling using dynamical mean-field theory for hard-core bosons (HB-DMFT). Our main results are: i) observation of the low-temperature IS dispersion in the 0.2-0.5 eV range in the accessible part of the Brillouin zone with a high energy resolution, ii) observation of ‘melting’ of the sharp IS dispersion into a narrow band of damped excitations at elevated temperatures, iii) theoretical modelling of the observed behavior by multi-flavor attractive Hubbard model for hard-core bosons.

* These two authors contributed equally to this work.
FIG. 1. The experimental RIXS intensities for selected $q = (0,0,q_z)$ measured at (a) 20 K, (b) 70 K and (c) 150 K. The experimental geometry and the definition of the angle $\varphi$ is illustrated in the inset. Two distinct features locating around 200–600 meV and 800 meV correspond to $^3T_{1g}$ IS and $^3T_{2g}$ IS excitations [29]. (d) comparison at 20 K between theory (color map), present RIXS data with $\Delta E = 25$ meV (white) and previous RIXS data with $\Delta E = 90$ meV (gray) in Ref. [29]. (e) A sketch of the excitonic scenario in LaCoO$_3$: the atomic-level energies together with the dispersion of the IS ($^3T_{1g}$) state on the LS background in the lattice.

At elevated temperatures, finite population of the excitonic states on the LS background in the lattice.

FIG. 2. Sketch of the IS-exciton $(IS_x,y)$, ellipses correspond to the charge distribution) propagation on the LS background (black circles) and the formation of the immobile HS bi-exciton $(HS_x)$. IS$_x$ (IS$_y$) with the $dz^2 \otimes dz^2$ $(dxz \otimes dxz)$ orbital character in the IS $(^5T_{1g})$ manifolds can propagate in $yz$ ($zx$) plane [27, 29, 31]. The HS bi-exciton can be formed/melted by/into the two IS excitons via the local attractive interaction between IS excitons.

Our main observations are summarized in Fig. 3a. The RIXS spectra exhibit low-energy features observed in previous studies [28, 29]. At 20 K, we observe a clear dispersion of the peak in the 0.2-0.5 eV range that was assigned to the IS $(^3T_{1g})$ excitation [28, 29]. The dispersion is consistent with the theory and experiment of Ref. [29] see Fig. 3a, with substantially reduced error bars in the experimental data, provided by the present high energy resolution. Increasing the temperature above 100 K leads to a distinct narrowing and smearing of the dispersive feature, Figs. 3b and 3c. Other spectroscopic studies [7, 28] indicate an increasing concentration of HS atoms with temperature, while the system remains a spatially uniform insulator. Thus theoretical modelling of the heating effect on the dispersive IS excitations is a challenge that we address next.

Theory. Analysis of the low-temperature RIXS spectra using the generalized spin-wave theory is described in Ref. [29]. It proceeds in following steps. After a density functional calculation, a Hubbard model spanning the Co-$d$ bands is constructed [32, 34]. The next step is the Schrieffer-Wolff projection [35] on the subspace containing the lowest Co 3$d^5$ multiplets. Keeping only the terms that describe creation/annihilation of an atomic excitation out of the LS ground state, we arrive at a non-interacting bosonic Hamiltonian, which describes dynamics of a single excitation relevant at low temperature.

At elevated temperatures, finite population of the excited multiplets must be taken into account. We start
with the bosonic model of Ref. [29]. To make the problem tractable, while keeping the key effect, i.e., the formation and thermal population of HS bi-excitons, we make the following approximations to the bosonic model: i) we neglect the spin structure of the problem, ii) instead of three orbital IS flavors that can form three HS orbital flavors, we work with two IS flavors and single HS flavor, iii) we neglect the spin-orbit coupling, iv) we neglect the nearest-neighbor interaction and keep only the on-site attraction of the IS excitons, v) we adopt the DMFT approximation [30–37].

We study the two-flavor attractive Hubbard model

$$\hat{H} = \epsilon_{\text{IS}} \sum_{i} \sum_{\gamma} \hat{n}_{i,\gamma} - V \sum_{i} \hat{n}_{i,x} \hat{n}_{i,y}$$

$$+ t \sum_{i} \sum_{\gamma} \sum_{\gamma'} (\hat{b}_{i,x}^{\dagger} \hat{b}_{i,y} + \hat{b}_{i,y}^{\dagger} \hat{b}_{i,x}),$$

(1)

The operator $\hat{b}_{i}^{\dagger}$ creates a boson of flavor $\gamma = x, y$ that can propagate by nearest-neighbor hopping in the $yz$- and $xz$-plane, respectively. A hard-core constraint per flavor is assumed. The 2D confinement mimics the behavior of $^{3}T_{1g}$ IS excitons in LaCoO$_3$, in particular, reproduces the IS bandwidth. Only the local spectral function is relevant in the DMFT treatment of the spatially uniform state, nevertheless, we use the above lattice to compute the $k$-resolved spectral functions.

We treat Eq. (1) using the bosonic DMFT [37–40] with strong-coupling continuous-time quantum Monte-Carlo (CT-QMC) impurity solver [39, 41] in a parameter range without condensate. The hard-core constraint can be implemented dynamically by introducing a large intra-flavor interaction or explicitly. We have checked on several cases that both approaches lead to the same low-energy physics of interest. Nevertheless, the explicit constraint has computational advantages and is more elegant. While enforcing the constraint in the CT-QMC calculation is straightforward, care must be taken by definition of the self-energy, because the Green’s function does not have the canonical $\frac{1}{\iota \omega_n}$ high frequency limit, where $\omega_n = 2\pi n / \beta$ is the bosonic Matsubara frequency with the inverse temperature $\beta = 1 / k_B T$. An analogous problem arising in the $t - J$ model for fermions was discussed by Shastry [42], introducing the concept of extremely correlated Fermi liquid. Perepelitsky and Shastry [43] showed that in the DMFT limit of the infinite dimension the Green’s function can be written in the form

$$G_{\text{loc}}(i\omega_n) = \frac{1 - 2 \langle \hat{n} \rangle}{i\omega_n - (1 - 2 \langle \hat{n} \rangle) \epsilon_k - \Sigma(i\omega_n)},$$

(2)

where the spectral weight in the numerator depends on the flavor occupation $\langle \hat{n} \rangle$ and thus differs from 1, while the self-energy $\Sigma(i\omega_n)$ is local and has the standard $\Sigma(i\omega_n \rightarrow \infty) \sim \Sigma' + \sum_{\omega_n} \Gamma_{\text{loc}}$ high-frequency behavior. Note that the numerator in the case of hard-core bosons differs from the fermionic case and can go negative. The Green’s function in the present case is diagonal in the bosonic flavor and $\epsilon_k = \epsilon_{\text{IS}} + 2t \cos(k_z) + \cos(k_y)$, where $k_z = k_x, k_y$ depending on the flavor. The DMFT self-consistent loop is closed by calculating the hybridization function (Weiss field) of the auxiliary impurity problem

$$\Delta(i\omega_n) = \frac{i\omega_n - \Sigma(i\omega_n)}{1 - 2 \langle \hat{n} \rangle} - \epsilon_{\text{IS}} - G_{\text{loc}}^{-1}(i\omega_n),$$

(3)

where $G_{\text{loc}} = \sum_{k} G_{k}$ is the local Green’s function, which is the same for both bosonic flavors in our model.

The calculations were performed for $t = 58$ meV ($W_{\text{IS}} = 468$ meV), $\epsilon_{\text{IS}} = 340$ meV, following the estimation above, see Fig. (a) and SM (b). We have used several values of the on-site attraction $V$ (the results are summarized in SM (c)), out of which we picked $V = 620$ meV. In Fig. (b) we show evolution of the $k$-resolved spectral function $A_k(\omega) = -\frac{1}{\pi} \text{Im} G_k(\omega^+)$ with increase of density of excitations. Despite its simplicity, the model [1] captures the essential features of the experimental data shown in Figs. (a)–(c). The zero temperature ground state is the bosonic vacuum (all atoms in the LS state) and excitation spectrum reduces to that of the non-interacting boson. By construction, this spectrum reproduces the $^{3}T_{1g}$ spectrum of Ref. [23] except for the minor modifications due to the spin-orbit coupling, which is neglected.
here. Upon heating, the equilibrium state changes due tothermal population of the excited states. These are dominated by HS excitations, i.e., the concentration of doubly occupied sites \( n_{\text{HS}} = \langle \hat{n}_{\text{HS}} \rangle \), with a non-negligible IS population, i.e., the concentration of singly occupied sites \( n_{\text{IS}} = \langle \hat{n}_{\text{IS}} \rangle \), being 5 to 3 times smaller. The increasing concentration of excitations results in band narrowing and decreasing life-time of the IS excitons, broadening of the spectral lines, Figs. 3 and 4.

Even a model with single \( b \)-flavor exhibits some \( T \)-dependence of the spectrum, because it is a strongly interacting problem due to the hard-core constraint. However, the thermal population of excited states and the \( T \)-dependence of the spectrum in this case is negligible. Formation of HS excitations represented by the attractive

\[
e_{\text{HS}}(T) = T \ln \frac{1 - n_{\text{HS}}(T)}{n_{\text{HS}}(T)}, \tag{4}
\]

where \( n_{\text{HS}} \) is the HB-DMFT value. In Fig. 4, we show the \( T \)-dependence of \( e_{\text{HS}} \) and compare it to available experimental data. We find that the low-\( T \) value of \( e_{\text{HS}} \) is substantially smaller than \( e_{\text{HS}}^0 \) (the value for isolated atom). While the HS bi-exciton is a stable object, it is not localized on a single atom. Quantum fluctuations on the nearest-neighboring bonds of the type \( |\text{HS},\text{LS}\rangle \rightleftharpoons |\text{IS},\text{IS}\rangle \) lower the energy of the HS bi-exciton. A simple perturbation theory \( e_{\text{HS}} - e_{\text{HS}} \approx \frac{8t^2}{V} \), yielding about 40 meV gain, describes the calculated \( T = 0 \) data quite well. It should be pointed out that the on-site energies \( e_{\text{HS}} \) and \( e_{\text{HS}}^0 \) are not purely atomic energies, but already contain renormalization due to virtual electron hopping [29, 40].

Similar to the experimental observations, we find that \( e_{\text{HS}} \) increases with temperature. While the calculated \( de_{\text{HS}}/dT \) has a realistic order of magnitude, it is smaller than the experimental observations. This point is not unexpected. The \( e_{\text{HS}} \) increase with \( n_{\text{HS}} \) is caused by interatomic HS-HS repulsion. While the model of Ref. 29 contains a nearest-neighboring HS-HS repulsion in the 100-200 meV range, this is neglected in our simplified model [1]. The effective repulsion in the present calculation arises from blocking the above quantum fluctuations with increasing \( e_{\text{HS}} \) and represents only one contribution to the HS-HS repulsion in real material. While interatomic interaction, realistic number of flavors (3 IS and 3 HS) as well as the inclusion of the explicit spin structure are important to describe the relative stability of different phases, e.g., uniform vs spin-state ordered, we expect only quantitative changes (stronger \( T \)-dependence) to the present spectra when including these aspects.

Finally, we would like to comment on recent inelastic neutron measurements [17] reporting unusual delocalized magnetic form factor in LaCoO\(_3\) at intermediate temperatures. The present picture of HS excitation as bi-exciton dressed with \( |\text{HS},\text{LS}\rangle \rightleftharpoons |\text{IS},\text{IS}\rangle \) on nearest-neighboring bonds fits very well with this observation.

In summary, by measuring Co L\(_3\) RIXS spectra of LaCoO\(_3\) with state of the art energy resolution, we have demonstrated a sizeable mobility of \(^3\)T\(_{1g}\) IS excitations. Melting of the corresponding dispersion into a narrow band of damped excitations, observed between 70 and 150 K, points to a strongly interacting nature of the IS excitations. The experimental data are well described by modelling the low-energy state of LaCoO\(_3\) as a gas of mobile IS excitons and immobile HS bi-excitons, in contrast to the paradigm of atom-bound (immobile) IS or HS excitations. Our numerical results show that even at low temperatures, where the IS concentration is negligible, the virtual fluctuations \( |\text{HS},\text{LS}\rangle \rightleftharpoons |\text{IS},\text{IS}\rangle \) on the nearest-neighbor bonds have an important impact of the low-energy physics and the IS excitations cannot be neglected. The classic cobaltite question whether the low-energy physics is determined by HS or IS excitations is therefore ill posed.

The authors acknowledge A. Kauch, J. Fernández Afonso, D. J. Huang and J. Okamoto for valuable discussions. The authors thank M. van der Linden and F. Frati for their support in RIXS experiment. A.H., A.S., and J.K. work are supported by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 646807-EXMAG). The experiments were supported by ERC advanced grant (grant agreement No. 340279-XRAYonACTIVE). K.T. was fi-
nancially supported by the MEXT and JSPS KAKENHI (JP17H06137, JP15H03692, JP18K03503). The calculations were performed on the Vienna Scientific Cluster (VSC).

[1] J. B. Goodenough, J. Phys. Chem. Solid 6, 287 (1958)
[2] R. Heikes, R. Miller, and R. Mazelsky, Physica 30, 1600 (1964)
[3] P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967)
[4] M. Abbate, J. C. Fuggle, A. Fujimori, L. H. Tjeng, C. T. Chen, R. Potze, G. A. Sawatzky, H. Eisaki, and S. Uchida, Phys. Rev. B 47, 16124 (1993)
[5] K. Asai, A. Yonedata, O. Yokokura, J. M. Tranquada, G. Shirane, and K. Kohn, J. Phys. Soc. Jpn. 67, 290 (1998)
[6] S. Stelen, F. Grønvold, H. Brinks, T. Atake, and H. Mori, Phys. Rev. B 55, 14103 (1997)
[7] M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. 97, 176405 (2006)
[8] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. 9, 766 (1954)
[9] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B 42, 5459 (1990)
[10] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüniger, P. G. Radaelli and S.-W. Cheong, Phys. Rev. B 66, 094408 (2002)
[11] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B 42, 5459 (1990)
[12] A. Ishikawa, J. Nohara, and S. Sugai, Phys. Rev. B 54, 5309 (1996)
[13] J.-Q. Yan, J. S. Zhou, and J. B. Goodenough, Phys. Rev. B 69, 134409 (2004)
[14] Z. Ropka and R. J. Radwanski, Phys. Rev. B 67, 172401 (2003)
[15] A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Ponomakushina, K. Conder, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, Phys. Rev. Lett. 97, 247208 (2006)
[16] S. Noguchi, S. Kawanata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B 66, 094404 (2002)
[17] G. Maris, Y. Ren, V. Volotchaev, C. Zobel, T. Lorenz, and T. T. M. Palstra, Phys. Rev. B 67, 224423 (2003)
[18] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B 67, 140401 (2003)
[19] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B 55, 4257 (1997)
[20] R. A. Bari and J. Sivardière, Phys. Rev. B 5, 4466 (1972)
[21] K. Knížek, Z. c. v. Jirák, J. c. v. Hejtmanek, P. Novák, and W. Ku, Phys. Rev. B 79, 014430 (2009)
[22] J. Kuneš and V. Krápek, Phys. Rev. Lett. 106, 256401 (2011)
[23] M. Karolak, M. Izquierdo, S. L. Molodtsov, and A. I. Lichtenstein, Phys. Rev. Lett. 115, 046401 (2015)
[24] G. Zhang, E. Gorelov, E. Koch, and E. Pavarini, Phys. Rev. B 86, 184413 (2012)
[25] P. G. Radaelli and S.-W. Cheong, Phys. Rev. B 66, 196402 (2007)