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Strain-tuned incompatible magnetic exchange-interaction in La₂NiO₄

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Magnetic frustration is a route for novel ground states, including spin liquids and spin ices. Such frustration can be introduced through either lattice geometry or incompatible exchange interactions. Here, we find that epitaxial strain is an effective tool for tuning antiferromagnetic exchange interactions in a square-lattice system. By studying the magnon excitations in La₂NiO₄ films using resonant inelastic x-ray scattering, we show that the magnon displays substantial dispersion along the antiferromagnetic zone boundary, at energies that depend on the lattice of the film's substrate. Using first principles simulations and an effective spin model, we demonstrate that the antiferromagnetic next-nearest neighbour coupling is a consequence of the two-orbital nature of La₂NiO₄. Altogether, we illustrate that compressive epitaxial strain enhances this coupling and, as a result, increases the level of incompatibility between exchange interactions within a model square-lattice system.

The square-lattice Heisenberg model is the subject of intense numerical and experimental investigations. In spin-1/2 systems—such as cuprates¹ and copper deuteroformate tetradeurate (CFTD)²—higher-order exchange interactions are inferred from observations of magnon dispersions along the magnetic zone boundary^{3,4}. While a detailed magnon characterization is useful to understand quantum-fluctuation effects⁵, exchange incompatibility is typically avoided in these systems. Indeed, the antiferromagnetic (AF) nearest-neighbor (NN) exchange interaction $(J_1 > 0)$ and the ferromagnetic next-nearest-neighbor (NNN) interaction $(J_2 < 0)$ in these systems stabilize the classical AF Néel order. Instead, magnetic exchange incompatibility requires both $J_1 > 0$ and $J_2 > 0$. This regime of the $J_1 - J_2$ model is the subject of extensive computational investigations for both spin $S = 1/2^{6-10}$ and $S = 1^{11,12}$ systems. In a narrow range near $J_2/J_1 \sim J_2$, magnetic frustration is found to dominate, and exotic quantum phases such as the spinliquid state¹³ are predicted. Several calculations show that the Néel order is destroyed there and the ground state has a valence-bond character¹³⁻¹⁵, although its exact nature is still the subject of debate^{8,16}. However, only very few square-lattice systems exhibit substantial magnetic frustration^{17,18}, and even fewer display tunable magnetic interactions¹⁹. As a result, approaching the interesting parameter regime in real materials remains an ongoing issue. In this article, we provide a high-resolution resonant inelastic X-ray scattering (RIXS) study of magnetic excitations in epitaxial thin films of the canonical S = 1 system La₂NiO₄, grown on different substrates. We discover a marked, upward dispersion along the AF zone boundary $\binom{1}{2}, 0 \rightarrow \binom{1}{4}, \binom{1}{4}$, which reveals the presence of AF NNN interactions that partly frustrate the NN ones. By employing ab initio calculations, we demonstrate that these results can only be explained by including the multi-orbital nature of $3d^8$ -Ni systems. Furthermore, we observe a correlation between the relative strength of the magnetic interactions and the strain applied to the films. Our results demonstrate that 214-type nickelates are a promising class of materials for the study of the AF square-lattice Heisenberg model. Moreover, the use of thin films provides a clear route to tune the magnetic frustration and explore so far inaccessible regions of the magnetic phase diagram.

Results

Our thin films of La₂NiO₄ (LNO) on SrTiO₃ (STO), LaAlO₃ (LAO), (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7} (LSAT), and NdGaO₃ (NGO) substrates are characterized by atomic force microscopy, X-ray diffraction, and X-ray absorption spectroscopy (see Fig. 1). The atomic force microscopy images

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Fig. 1 | Characterization measurements on thin films of La₂NiO₄. a X-ray diffraction (at 300 K) probing the (0, 0, ℓ) direction of 12-nm thin films of La₂NiO₄ on substrates as indicated. The inset represents the atomic force microscopy image showing the step-like morphology of the films (here for the NGO substrate). The color scale corresponds to film thickness. **b** *c*-axis lattice parameter versus in-plane epitaxial strain (at 300 K) calculated for La₂NiO₄ (purple dots) and La₂CuO₄³² (gray

dots) films grown on different substrates as a relative change of in-plane parameters in reference to bulk (diamonds) with a = 3.868 Å and c = 12.679 Å for an isomorphic La₂NiO₄ structure⁵⁹ and a = 3.803 Å and c = 13.156 Å for La₂CuO4⁶⁰. The errorbar correspond to the spread of in-plane parameters measured by X-ray diffraction. **c** X-ray absorption spectra around the Ni *L*-edge. The dominant peak corresponds to the La *M*-edge. **b**, **c** Dashed lines are guides to the eye.

display a step-like morphology indicating an excellent layer-by-layer growth. Diffraction patterns probing the $(0, 0, \ell)$ reciprocal direction demonstrate good single crystallinity and allow us to extract the *c*-axis lattice parameters of the films. The epitaxial strain applied by the substrates is supported by the film *c*-axis and in-plane lattice-parameter dependence (Fig. 1b). X-ray absorption spectra recorded on the LNO/STO and LNO/ NGO, shown in Fig. 1c, are consistent with observations on related nickelates^{20–23}. The Ni *L*-edge features on the tail of the La *M*-edge.

The RIXS spectra of La₂NiO₄ films were measured at the Ni L_3 edge (853 eV). These spectra exhibit key RIXS excitations, including high-energy *dd*-excitations (at ~0.5–3 eV), an elastic scattering contribution at 0 eV, as well as phonon and magnon excitations in between. The *dd*-excitations have a multi-peak structure, qualitatively similar to other $3d^8$ systems, such as NiO^{20–22,24}. As shown in Fig. 2a, the relative intensities of the peaks are different in the three samples, due to the different crystal-fields acting on the Ni atoms (see Fig. S1, Supplementary Note 1). However, all our La₂NiO₄ films display the most intense *dd*-excitation around 1.1 eV and a second less intense excitation just below 1.6 eV. This is consistent with what is reported in bulk La₂NiO₄²⁵ (see Fig. S2, Supplementary Note 1). The subtraction of the elastic peak clearly highlights the presence of multiple low-energy features (see Fig. 2b, c).

To extract the dispersion of magnetic excitations, we assumed a twomode model with the addition of a high-energy continuum "background" (Fig. 2b, c). Each of these components is represented by a Gaussian profile. This provides an effective fitting model of excitations for all measured film systems and momenta. Our interpretation of the proposed model is based on the hypothesis that the lower-energy mode (~40 meV) stems from an optical phonon, while the higher-energy mode (strongly dispersing between 60 and 120 meV) is a magnon. This assignment is supported by previous neutron scattering measurements that identified the phonon part via an outof-plane oxygen buckling mode^{26,27}. The interpretation of the higher-energy mode as a magnon is consistent with earlier RIXS²⁵ and neutron studies²⁸ of bulk La₂NiO₄. The resulting magnon dispersions are shown in Fig. 3.

Due to lower-energy resolution, the previous RIXS study²⁵ did not resolve any phonon excitations. The unresolved phonon excitation implied that the phonon and magnon spectral weights were merged. This, in turn influences the extraction of the magnon dispersion. Having access, in this work, to a higher-energy resolution, we can distinguish between the nearly momentum-independent phonon mode and the dispersive magnon branch along the three measured high-symmetry directions. In all the film systems explored, the magnon energy reaches its maximum at the AF zone boundary, at the Σ point (1/4, 1/4), referred to as E_{Σ} , while it displays a local minimum at the X point (1/2, 0), referred to as E_X . This evidently anisotropic shape of magnon dispersion was not reported in earlier studies^{25,28}, except for a recent inelastic neutron scattering experiment²⁹. Furthermore, the energy E_{Σ} is different for all three substrates. In particular, it increases as a function of compressive strain, with an enhancement of 18 ± 4 meV (~20%) from LNO/STO to LNO/LAO.

Discussion

By resolving both the phonon and magnon modes, we find that all samples exhibit a substantial dispersion of magnetic excitations along the AF zone boundary. This directly implies the presence of higher-order effective magnetic exchange interactions. In La₂CuO₄ and related Mott insulating cuprates, the zone-boundary dispersion has been interpreted in terms of a positive ring-exchange interaction that emerges naturally from a single-orbital Hubbard model^{30–32}. There is, however, an important difference between the zone-boundary dispersion of La₂CuO₄ and La₂NiO₄: in contrast to La₂CuO₄, the zone- boundary dispersion of La₂NiO₄ has its maximum at the AF zone boundary Σ point rather than at the X point. As such, the magnon dispersion of La₂NiO₄ is (as could be expected) inconsistent with a single-band Hubbard model in the strong coupling limit (where the projection onto a Heisenberg spin Hamiltonian is viable).

As a first step, we parameterize the magnon dispersion of La₂NiO₄ using a phenomenological spin-wave model that includes effective NN and NNN exchange interactions, respectively, J_1 and J_2 (Fig. 3), plus an easyplane anisotropy K, already reported by previous measurements^{28,29}. As a starting point, we employ the AF structure of the bulk La2NiO4 determined by neutron diffraction^{33–35}, with the spin direction parallel to the crystallographic a-axis. The model is solved in a linear spin-wave (large-S) limit, and the calculated dispersion is fitted to the measured one (see "Methods"). Fitting the experimental (exp) data yields an effective NN exchange interaction $J_1^{exp} \sim 30$ meV consistent with previous neutron and RIXS results^{25,36}. Due to the demonstrated finite zone-boundary dispersion, our spin-wave model fitting also yields a moderate NNN exchange interaction J_2^{exp} . Importantly, J_2^{exp} is positive and enhanced by compressive strain^{3,4}. In what follows, we wish to extract the frustration parameter $\mathcal{G} = J_2^{exp}/J_1^{exp}$ with the highest precision. Within our spin-wave model, $E_X = 4SZ_c(J_1 - 2J_2)$ and $E_{\Sigma} = 4SZ_c(J_1 - J_2)$, where Z_c is the quantum renormalization factor for spinwave energies, which is taken as $Z_c = 1.09^{37}$. This gives $\mathcal{G}^{-1} = 1 + \frac{E_{\Sigma}}{(E_{\Sigma} - E_{\chi})}$. The frustration parameter \mathcal{G} is thus derived directly from the experimental data, with high precision (E_{Σ} and E_X are extracted with error lower than 5 meV) and plotted as a function of the c lattice parameter in Fig. 4 (see also Table S1, Supplementary Note 2). Due to the Poisson effect, the c lattice parameter undergoes a proportional shrinkage when the in-plane





Fig. 2 | Resonant inelastic X-ray scattering spectra of La₂NiO₄. a Raw spectra recorded in La₂NiO₄ films with substrates as indicated. a (inset) Schematics of the photon-in-photon-out resonant inelastic X-ray scattering (RIXS) geometry with horizontally polarized light (π) and azimuthal sample rotation angle ϕ . b, c Low-

energy part of the RIXS spectra with momentum transfer and film substrates indicated. The solid red line indicates a three-component fit with phonon, magnon (shaded), and multi-magnon (continuum) contributions. The elastic scattering channel is subtracted in (**b**, **c**).



Fig. 3 | Magnon dispersion of La_2NiO_4 films. a–c Magnon excitation energies (open dots) along high-symmetry directions for La_2NiO_4 on substrates as indicated. Solid lines represent the same spin-wave model evaluated for different exchange parameters within the confidence intervals of the fitted parameters. The curves

corresponding to the best-fit values (marked in bold in the legend) are reported as thicker lines. The middle segment, $X \rightarrow \Sigma$, is part of the antiferromagnetic zone boundary. The error bars are determined from the fitting uncertainty.

parameters expand. Our X-ray diffraction measurements confirm this relationship (Fig. 1b), indicating that the *c*-axis lattice parameter can serve as an indirect probe of the in-plane strain. Therefore, our findings demonstrate a nearly linear correlation between magnetic frustrations and epitaxial strain.

We stress that, for interaction strengths and hoppings that are realistic for cuprates and nickelates, $J_2 > 0$ is hard to reconcile with a single-band Hubbard model. A positive J_2 implies an effective AF NNN exchange interaction, at odds with what is observed in cuprates^{4,30} and d^9 infinite-layer nickelates^{38,39}. Both systems have indeed been successfully described using a single *d*-orbital framework^{3,4,40,41}. Therefore, we argue that the magnon zone-boundary dispersion in LNO signals physics beyond the single-orbital Hubbard model. We propose that the multi-orbital ($d_{x^2-y^2}$, d_{z^2}) nature of nickelates^{42–44} must be explicitly considered. Already in La₂CuO₄, due to the short apical oxygen distance, a small but significant orbital hybridization between d_{z^2} and $d_{x^2-y^2}$ has been reported⁴⁵. In La₂NiO₄ the apical oxygen distance is even shorter, as exemplified by the reduced *c* lattice parameter (see Fig. 1b), and hence an even more pronounced hybridization is expected.

To rationalize the trend in the exchange interactions obtained from our spin-wave fits, we derive a two-orbital low-energy model for La₂NiO₄ on different substrates from first principles (see the Method section). For the Ni d_{z^2} and $d_{x^2-y^2}$ orbitals (labeled α and β), we compute the (next) nearest-neighbor hopping parameters $t^{(\prime)}$, the crystal-field splitting Δ_{eg} , local Coulomb (Hubbard) interaction U and Hund's exchange J_H using experimental lattice constants from Table 1. Noteworthy⁴⁶, the hopping parameters and Coulomb interactions, listed in Table 1, hardly change under varying in-plane compression. This is different from calculations for the cuprate family, see ref. 32, and agrees with our experiments, which show substantially smaller changes in the magnon spectrum than for the cuprates. What is most affected by strain in Table 1 is the crystal-field splitting Δ_{eg} by which the Ni $d_{x^2-y^2}$ orbital is higher in energy than the d_{z^2} orbital. When going from the STO to the LAO substrate, in-plane strain



Fig. 4 | **Strain-dependent magnetic frustration.** The frustration parameter $\mathcal{G} = J_2^{\text{exp}}/J_1^{\text{exp}}$ derived from the experimental data (squares; left axis) is presented as a function of the *c*-axis lattice parameter. The error bars for the experimental data are calculated as a propagation of standard deviations extracted from the fits. The results for films are combined with data for bulk La₂NiO₄ from ref. 29. The experimental frustration \mathcal{G} is compared to the ratio $J_2^{\text{cal}}/J_1^{\text{cal,corr}}$ derived from the DFT and cRPA calculations (diamonds; right axis). Note that the calculated J_2^{cal} only contains a contribution to the full next-nearest-neighbor coupling J_2 . Therefore, the comparison merely highlights a similar trend of the frustration under in-plane compression. The dashed line is a guide-to-the-eye.

pushes the $d_{x^2-y^2}$ orbital further up in energy, as it is pointing towards the now closer in-plane oxygen sites that are charged negatively.

This crystal-field splitting Δ_{eg} enters the calculated (cal) two-orbital superexchange as follows:

$$J_1^{\text{cal}} = \frac{t_{\alpha\beta}^2}{U + J_H - \Delta_{eg}} + \frac{t_{\alpha\beta}^2}{U + J_H + \Delta_{eg}} + \frac{t_{\alpha\alpha}^2 + t_{\beta\beta}^2}{U + J_H},\tag{1}$$

where we extend the formula of ref. 47 to finite Δ_{eg} (see Supplementary Note 3). As Δ_{eg} appears once with a plus and once with a minus sign in the denominator, the crystal-field splitting enters J_1^{cal} in a higher-than-linear order.

The magnetic exchange couplings J_1^{cal} determined by Eq. (1) are displayed in Table 1. They show the same qualitative tendency as in our experiment, i.e., an increase of both J_1^{exp} (see Fig. 3) and J_1^{cal} with compressive strain. Quantitatively, the ab initio calculated J_1^{cal} is however too large. This has two major origins: (i) The cRPA interactions are, here, taken at zero frequency $U = U(\omega = 0)$. Additional renormalizations from the frequency dependence $U(\omega)^{48}$ are often mimicked through an empirical enhancement of U. Increasing U, we could easily obtain quantitative agreement with the experimental J_1 , but at the cost of a free fit parameter and most likely only an accidental agreement. (ii) Eq. (1) only includes terms to second-order perturbation theory in t. For the one-band Hubbard model, higher-order processes have been calculated and yield a correction from $J_1 = 4t^2/U$ to a reduced $J_1 = 4(t^2/U - 16t^4/U^3)^{40,49}$. Higherorder terms are expected to reduce J_1 also in the two-orbital setting. Here, we estimate these corrections by the one-orbital prescription $t^2/U \longrightarrow t^2/U - 16t^4/U^3$. Then, e.g., for the NGO substrate, the leading contribution to J_1^{cal} , i.e., $t_{\beta\beta}^2/(U_{\text{eff}})$ with $U_{\text{eff}} = U + J_H$, reduces from 47 to 37 meV. Applying this substitution to Eq. (1) yields the corrected exchange couplings $J_1^{\text{cal,corr}}$ listed in Table 1, which are in better agreement with the measured values (see Fig. 3).

Table 1 also lists the next-nearest-neighbor exchange f_2^{cal} that can be obtained with the same second-order formula Eq. (1), except now using the hoppings *t'* instead of *t* (see Supplementary Note 3 for details). Crucially, our

LNO/LAO	3.793	12.78	0.74	-0.060	-0.447	-0.156	-5.5	80.5	3.02	3.08	1.93	0.50	71.6	1.83	56.8	
Crystal-field splitting and cRPA with the in- respectively. Estimat	I ∆ _{eg} , (next-)neare -plane lattice con :ing higher-order	est-neighbor hol Istant <i>a</i> of the th terms using a c	pping $t_{ij}^{(l)}$ betwee ree substrates; ı me-orbital anald	sn <i>i</i> th and <i>j</i> th Ni orbit: note that $t'_{lphaeta}=0$ by ι ogy, yields the redu	als (<i>a</i> and <i>β</i> here del symmetry. From th ced J ^{cal.corr} couplin	note the <i>z</i> ² and <i>x</i> ² – ese ab initio calcula ngs – see text. The I	y ² orbital, respe ted parameters bulk lattice para	ectively), the inter- , the spin coupling ameters refer to th	and intra-orbit: Is J ₁ and J ₂ are e low-tempera	al Coulomb inte calculated from ature tetragonal	raction <i>U_{ij},</i> and I superexchang polymorph of L	Hund's exchan ∋ (second-orde a₂NiO₄, after r	ge J _H between ther perturbation the ef. 29.	ie two orbital as eory), i.e., from l	calculated by DFT cq. (1) with <i>t</i> and <i>t</i> ',	

J₁ [meV] 51.0

J₂^{cal} [meV]

J₁^{cal} **[meV]** 60.7 62.2 62.3

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د ه ک

Uad [eV]

t^{'_{ββ} [meV] 74.9 74.5 76.3 76.7}

f^t^{aa} [meV] -8.6 -8.3 -7.4

t_{ab}

 $t_{\beta\beta}$

t_{aa} [eV]

Δeg [eV] 0.48 0.55 0.55

⊵ ∿

в

System

Table 1 | Parameters of the two-orbital Hubbard model

1.57 1.56 1.65

0.52 0.51 0.51

3.15 3.14

3.06

1.97

1.92

3.11

3.00

3.01

-0.156 -0.156

-0.395

-0.065

12.62 12.69

> LNO/LSAT LNO/NGO

La₂NiO₄ LNO/STO 12.71

-0.155

-0.414

-0.064

-0.161

-0.403

-0.070

12.55

3.890 3.905 3.868 3.859

1.97

3.16

49.7 51.8

51.9

calculations predict a positive J_2 , in agreement with the experiment. Moreover, J_2^{cal} shows the same qualitative tendency as in the experiment as a function of epitaxial strain. On a quantitative level, the calculated values are, however, a factor ~3–5 lower than the experimental results. The reason is that contributions to J_2 from higher-order exchange processes, of order t^4/U^3 and $t't^2/U^2$, become (relatively) more important for J_2^{cal} , as the secondorder terms are now based on the much smaller t'.

The key difference between the multi-orbital case of LNO and the oneorbital cuprates is the larger $U(U_{cRPA} \approx 3.1 \text{ eV})$ for two-orbitals while $U_{cRPA} \approx 1.9 \text{ eV}$ for a one Ni $d_{x^2-y^2}$ orbital setup) and the additional Hund's $J_H \approx 0.5 \text{ eV}$ in the denominator of Eq. (1). As a consequence, the balance for the NNN exchange coupling shifts from a ferromagnetic ring exchange $J_2 \sim -t^4/U_{eff}^3 < 0$, that overpowers the AF second-order exchange $J_2 \sim t'^2/U_{eff} > 0$ in the one-orbital cuprates, toward dominance of the latter in the multi-orbital LNO. This change in hierarchy explains the main qualitative differences in magnon dispersion between LNO and cuprates: the opposite sign of the effective J_2 . For LNO, with a positive J_2 , the zoneboundary dispersion shows a notable minimum at (1/2, 0), see Fig. 3, whereas a maximum occurs for the negative J_2 in cuprates.

Conclusions

The ab initio calculations indicate that the magnetic frustration in La₂NiO₄ is caused by the multi-orbital nature of $3d^8$ nickelates. More importantly, our results demonstrate that the degree of frustration is amplified by compressive strain (see Fig. 4), with a pivotal role played by the crystal-field splitting. Indeed, with the substrates used, the magnetic frustration increases four-fold with respect to the bulk, bridging half the way toward the exotic realm anticipated for $J_2/J_1 \sim {}^1/_2$. Thus, our study suggests an effective tool for tuning antiferromagnetic interactions within square-lattice systems. We speculate that the approach is applicable beyond La₂NiO₄ and may offer an experimental route to reach so far unexplored regions of the magnetic-phase diagram, potentially allowing to investigate exotic states induced by magnetic frustration.

Methods

Film growth and characterization

Thin films of La₂NiO₄ were grown by RHEED-equipped Radio-frequency off-axis magnetron sputtering⁵⁰ on (001) STO, (001) LAO, (001) LSAT and (110) NGO substrates. These films were grown in an argon atmosphere at 700 °C. Their qualities were confirmed by atomic force microscopy and x-ray diffraction. Their insulating character was confirmed by resistivity measurements of the LNO/STO film (see Fig. S3, Supplementary Note 4).

RIXS experiments

Ni L-edge RIXS experiments for STO, LAO and NGO substrates were carried out at the I21 beamline⁵¹ at the DIAMOND Light Source. All spectra were collected in the grazing exit geometry using linear horizontal polarized incident light with the scattering angle fixed to $2\theta = 154^\circ$. The energy resolution was estimated from the elastic scattering on amorphous carbon tape and was between 37 and 41 meV (full-width-at-half-maximum, FWHM). All films were measured at base temperature T = 16 K. We define the reciprocal space (q_x, q_y, q_z) in reciprocal lattice units $(h, k, \ell) = (q_x a / l_z)$ 2π , $q_v b/2\pi$, $q_z c/2\pi$) where a, b, and c are the pseudo-tetragonal lattice parameters. RIXS spectra were acquired along three in-plane paths: $(0,0) \rightarrow (0, \frac{1}{2}), (0,0) \rightarrow (\frac{1}{4}, \frac{1}{4}) \text{ and } (0, \frac{1}{2}) \rightarrow (\frac{1}{4}, \frac{1}{4}).$ Extraction of low-energy excitations around (0, 0) is limited by energy resolution. Due to kinematic constraints Γ points at higher zones cannot be reached, as well. RIXS intensities are normalized to the weight of the dd-excitations⁵². The data for the LSAT substrate were collected at the ID32 beamline at the European Synchrotron Radiation Facility (ESRF) (see description in Supplementary Note 5, Fig. S4).

Phenomenological spin-wave model

The effective superexchange parameters were extracted from the measured dispersion using a linear spin-wave model. We included effective couplings

between the first and second nearest neighbors, plus an easy-plane anisotropy *K*, with the resulting Hamiltonian:

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle \langle i,j \rangle \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + K \sum_i (S_i^z)^2$$
(2)

where $\langle i, j \rangle$ and $\langle \langle i, j \rangle \rangle$ denote pairs of first and second nearest neighbors Ni atoms, respectively. The fitting procedure has been carried out using the SpinW package⁵³. As an input we have used the AF structure of the bulk La₂NiO₄ determined by neutron diffraction^{33–35}, with the spin direction parallel to the crystallographic *a*-axis. The dispersion in the approximation of the linear spin-wave theory is represented by^{4,29}:

$$\begin{split} \hbar\omega &= Z_c \sqrt{\left(A_{\mathbf{q}}^2 - B_{\mathbf{q}}^2\right)} \\ A_{\mathbf{q}} &= 4S \left[\frac{K}{4} + J_1 - J_2(1 - \nu_h \nu_k)\right] \\ B_{\mathbf{q}} &= 4S \left[J_1 \frac{\nu_h + \nu_k}{2} - \frac{K}{4}\right] \end{split} \tag{3}$$

where $\nu_x = \cos(2\pi x)$. The quantum renormalization factor for spin-wave velocity is fixed to $Z_c = 1.09$, as usual for S = 1 systems³⁷. The value of the easyplane anisotropy *K* mostly controls the size of the magnon gap at the Γ point. Since this value is very hard to obtain from RIXS spectra, we have fixed K = 0.5 meV in agreement with previous inelastic neutron scattering data²⁸. We have also neglected other interactions $<10^{-1}$ meV, such as easy-axis anisotropy, inter-layer coupling, and Dzyaloshinskii–Moriya interactions^{29,34}.

Ab initio calculations

Electronic structure calculations were performed with density functional theory in the local density approximation using a full-potential linearized muffin-tin orbital (FPLMTO) code⁵⁴, after the structures were optimized with WIEN2k⁵⁵ using the PBE functional. We mimicked the influence of the substrates by simulating bulk La2NiO4 using the experimental lattice constants of the thin films. The reference calculation for the bulk uses lattice constants from ref. 29. All calculations assume the space group I4/ mmm and are paramagnetic. The resulting band structures are displayed in Fig. S5, Supplementary Note 6. The FPLMTO calculations were converged using 12^3 reducible k-points and include local orbitals for the Ni-3p and La-5p states. The internal atomic positions were relaxed with WIEN2k using 6^3 reducible k-points, a cutoff parameter RMTKMAX = 7 and partial waves inside the atomic spheres up to l = 5, until the forces were below 1 mRy per Bohr radius (for details of the relaxed structures, see Supplementary Note 7, Table S2). The tight-binding hopping and crystal-field parameters have been extracted from a projection onto maximally localized Wannier orbitals^{56,57} of Ni $3d_{x^2-y^2}$ and $3d_{z^2}$ character. Matrix elements of the static ($\omega = 0$) and local screened Coulomb interaction (Hubbard U and Hund's J_H) have been estimated from calculations in the constrained random phase approximation (cRPA)⁴⁸ for entangled band structures⁵⁸ in the Wannier basis⁵⁷ using $6 \times 6 \times 6$ reducible momentum-points in the Brillouin zone. For the two-particle product basis, states are kept up to an angular cutoff of l = 4 and down to an overlap eigenvalue of 10^{-4} .

Data availability

Data supporting the findings of this study are available from corresponding authors upon reasonable request.

Code availability

Code supporting the data processing of this study is available from corresponding authors upon reasonable request.

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References

- Lee, P. A., Nagaosa, N. & Wen, X.-G. Doping a Mott insulator: physics of high-temperature superconductivity. *Rev. Mod. Phys.* 78, 17–85 (2006).
- Christensen, N. B. et al. Quantum dynamics and entanglement of spins on a square lattice. *Proc. Natl. Acad. Sci. USA* **104**, 15264–15269 (2007).
- Headings, N. S., Hayden, S. M., Coldea, R. & Perring, T. G. Anomalous high-energy spin excitations in the high-T_c superconductor-parent antiferromagnet La₂CuO₄. *Phys. Rev. Lett.* **105**, 247001 (2010).
- Coldea, R. et al. Spin waves and electronic interactions in La₂CuO₄. *Phys. Rev. Lett.* 86, 5377–5380 (2001).
- Wang, Q. et al. Magnon interactions in a moderately correlated Mott insulator. *Nat. Commun.* 15, 5348 (2024).
- 6. Choo, K., Neupert, T. & Carleo, G. Two-dimensional frustrated $J_1 J_2$ model studied with neural network quantum states. *Phys. Rev. B* **100**, 125124 (2019).
- 7. Capriotti, L. & Sorella, S. Spontaneous plaquette dimerization in the $J_1 J_2$ Heisenberg model. *Phys. Rev. Lett.* **84**, 3173–3176 (2000).
- Capriotti, L., Becca, F., Parola, A. & Sorella, S. Resonating valence bond wave functions for strongly frustrated spin systems. *Phys. Rev. Lett.* 87, 097201 (2001).
- Zhang, G.-M., Hu, H. & Yu, L. Valence-bond spin-liquid state in twodimensional frustrated spin-1/2 Heisenberg antiferromagnets. *Phys. Rev. Lett.* **91**, 067201 (2003).
- 10. Gong, S.-S., Zhu, W., Sheng, D. N., Motrunich, O. I. & Fisher, M. P. A. Plaquette ordered phase and quantum phase diagram in the spin $\frac{1}{2}J_1 J_2$ square Heisenberg model. *Phys. Rev. Lett.* **113**, 027201 (2014).
- Sushkov, O. P., Oitmaa, J. & Weihong, Z. Quantum phase transitions in the two-dimensional J₁ – J₂ model. *Phys. Rev. B* 63, 104420 (2001).
- 12. Jiang, H. C. et al. Phase diagram of the frustrated spatially-anisotropic S = 1 antiferromagnet on a square lattice. *Phys. Rev. B* **79**, 174409 (2009).
- 13. Anderson, P. W. The resonating valence bond state in La_2CuO_4 and superconductivity. *Science* **235**, 1196–1198 (1987).
- Dagotto, E. & Moreo, A. Phase diagram of the frustrated spin-1/2 Heisenberg antiferromagnet in 2 dimensions. *Phys. Rev. Lett.* 63, 2148–2151 (1989).
- Schulz, H. J., Ziman, T. A. & Poilblanc, D. Magnetic order and disorder in the frustrated quantum Heisenberg antiferromagnet in two dimensions. *J. de Physique I* 6, 675–703 (1996).
- Beach, K. S. D. Master equation approach to computing RVB bond amplitudes. *Phys. Rev. B* 79, 224431 (2009).
- 17. Wang, Q. et al. Magnetic ground state of FeSe. *Nat. Commun.* **7**, 12182 (2016).
- Gu, Y. et al. Frustrated magnetic interactions in FeSe. *Phys. Rev. B* 106, L060504 (2022).
- Mustonen, O. et al. Spin-liquid-like state in a spin-1/2 square-lattice antiferromagnet perovskite induced by d¹⁰ – d⁰ cation mixing. Nat. Commun. 9, 1085 (2018).
- 20. Nag, A. et al. Many-body physics of single and double spin-flip excitations in NiO. *Phys. Rev. Lett.* **124**, 067202 (2020).
- Ghiringhelli, G. et al. NiO as a test case for high resolution resonant inelastic soft x-ray scattering. *J. Phys.: Condens. Matter* **17**, 5397–5412 (2005).
- Lin, J. Q. et al. Strong superexchange in a d^{θ-δ} nickelate revealed by resonant inelastic x-ray scattering. *Phys. Rev. Lett.* **126**, 087001 (2021).
- Kuiper, P. et al. Polarization-dependent nickel 2p x-ray-absorption spectra of La₂NiO_{4+δ}. *Phys. Rev. B* 57, 1552–1557 (1998).
- Ghiringhelli, G. et al. Observation of two nondispersive magnetic excitations in NiO by resonant inelastic soft-X-ray scattering. *Phys. Rev. Lett.* **102**, 027401 (2009).
- Fabbris, G. et al. Doping dependence of collective spin and orbital excitations in the spin-1 quantum antiferromagnet La_{2-x}Sr_xNiO₄ observed by X rays. *Phys. Rev. Lett.* **118**, 156402 (2017).

- Pintschovius, L. et al. Lattice dynamics of La₂NiO₄. *Phys. Rev. B* 40, 2229–2238 (1989).
- Pintschovius, L. et al. Phonon anomalies in La₂NiO₄. Europhys. Lett. 5, 247 (1988).
- Nakajima, K., Yamada, K., Hosoya, S., Omata, T. & Endoh, Y. Spin-wave excitations in two dimensional antiferromagnet of stoichiometric La₂NiO₄. *J. Phys. Soc. Japn.* 62, 4438–4448 (1993).
- 29. Petsch, A. N. et al. High-energy spin waves in the spin-1 square-lattice antiferromagnet La₂NiO₄. *Phys. Rev. Res.* **5**, 033113 (2023).
- Peng, Y. Y. et al. Influence of apical oxygen on the extent of in-plane exchange interaction in cuprate superconductors. *Nature Phys.* 13, 1201–1206 (2017).
- Ivashko, O. et al. Damped spin excitations in a doped cuprate superconductor with orbital hybridization. *Phys. Rev. B* 95, 214508 (2017).
- Ivashko, O. et al. Strain-engineering Mott-insulating La₂CuO₄. Nat. Commun. 10, 786 (2019).
- 33. Aeppli, G. & Buttrey, D. J. Magnetic correlations in $La_2NiO_{4+\delta}$. *Phys. Rev. Lett.* **61**, 203–206 (1988).
- 34. Yamada, K. et al. Magnetic structure and weak ferromagnetism of $La_2NiO_{4+\delta}$. *Physica C: Superconductivity* **191**, 15–22 (1992).
- Rodriguez-Carvajal, J., Fernandez-Diaz, M. T. & Martinez, J. L. Neutron diffraction study on structural and magnetic properties of La₂NiO₄. *J. Phys.: Condens. Matter* **3**, 3215 (1991).
- Yamada, K. et al. Complete two-dimensional antiferromagnetic spinwave dispersion relation of La₂NiO₄ determined by chopper spectrometer installed at the pulsed neutron source. *J. Phys. Soc. Jpn.* **60**, 1197–1200 (1991).
- Igarashi, J. 1/S expansion for thermodynamic quantities in a twodimensional Heisenberg antiferromagnet at zero temperature. *Phys. Rev. B* 46, 10763–10771 (1992).
- Lu, H. et al. Magnetic excitations in infinite-layer nickelates. *Science* 373, 213–216 (2021).
- Gao, Q. et al. Magnetic excitations in strained infinite-layer nickelate PrNiO₂ films. *Nat. Commun.* 15, 5576 (2024).
- Delannoy, J.-Y. P., Gingras, M. J. P., Holdsworth, P. C. W. & Tremblay, A.-M. S. Low-energy theory of the t - t' - t'' - U Hubbard model at half-filling: Interaction strengths in cuprate superconductors and an effective spin-only description of La₂CuO₄. *Phys. Rev. B* **79**, 235130 (2009).
- Dalla Piazza, B. et al. Unified one-band Hubbard model for magnetic and electronic spectra of the parent compounds of cuprate superconductors. *Phys. Rev. B* **85**, 100508 (2012).
- Horio, M. et al. Two-dimensional type-II Dirac fermions in layered oxides. *Nat. Commun.* 9, 3252 (2018).
- 43. Uchida, M. et al. Orbital characters of three-dimensional Fermi surfaces in $Eu_{2-x}Sr_xNiO_4$ as probed by soft-X-ray angle-resolved photoemission spectroscopy. *Phys. Rev. B* **84**, 241109 (2011).
- Uchida, M. et al. Pseudogap of metallic layered nickelate R_{2-x}Sr_xNiO₄ (*R* = Nd, Eu) crystals measured using angle-resolved photoemission spectroscopy. *Phys. Rev. Lett.* **106**, 027001 (2011).
- 45. Matt, C. E. et al. Direct observation of orbital hybridisation in a cuprate superconductor. *Nat. Commun.* **9**, 972 (2018).
- Tomczak, J. M., Miyake, T., Sakuma, R. & Aryasetiawan, F. Effective Coulomb interactions in solids under pressure. *Phys. Rev. B* 79, 235133 (2009).
- Lemanski, R. & Matysiak, J. Two-orbital Hubbard model vs spin S = 1 Heisenberg model: Studies on clusters. *Condens. Matter Phys.* 21, 33301 (2018).
- Aryasetiawan, F. et al. Frequency-dependent local interactions and low-energy effective models from electronic structure calculations. *Phys. Rev. B* **70**, 195104 (2004).
- MacDonald, A. H., Girvin, S. M. & Yoshioka, D. Reply to "Comment on 't/U expansion for the Hubbard model". *Phys. Rev. B* 41, 2565–2568 (1990).

6

- Podkaminer, J. P., Patzner, J. J., Davidson, B. A. & Eom, C. B. Realtime and in situ monitoring of sputter deposition with RHEED for atomic layer controlled growth. *APL Mater.* 4, 086111 (2016).
- Zhou, K.-J. et al. I21: an advanced high-resolution resonant inelastic X-ray scattering beamline at Diamond Light Source. *J. Synchrotron Rad.* 29, 563–580 (2022).
- Wang, Q. et al. High-temperature charge-stripe correlations in La_{1.675}Eu_{0.2}Sr_{0.125}CuO₄. *Phys. Rev. Lett.* **124**, 187002 (2020).
- Toth, S. & Lake, B. Linear spin wave theory for single-Q incommensurate magnetic structures. J. Phys.: Condens. Matter 27, 166002 (2015).
- Methfessel, M., van Schilfgaarde, M. & Casali, R. A full-potential Imto method based on smooth Hankel functions. In *Electronic Structure* and *Physical Properties of Solids: The Uses of the LMTO Method, Lecture Notes in Physics.* (ed. Dreysse, H.) 535 (Springer, 2000).
- 55. Blaha, P. et al. WIEN2k: An APW+lo program for calculating the properties of solids. *J. Chem. Phys.* **152**, 074101 (2020).
- Marzari, N., Mostofi, A. A., Yates, J. R., Souza, I. & Vanderbilt, D. Maximally localized Wannier functions: theory and applications. *Rev. Mod. Phys.* 84, 1419–1475 (2012).
- Miyake, T. & Aryasetiawan, F. Screened Coulomb interaction in the maximally localized Wannier basis. *Phys. Rev. B* 77, 085122 (2008).
- Miyake, T., Aryasetiawan, F. & Imada, M. Ab initio procedure for constructing effective models of correlated materials with entangled band structure. *Phys. Rev. B* 80, 155134 (2009).
- Goodenough, J. & Ramasesha, S. Further evidence for the coexistence of localized and itinerant 3*d* electrons in La₂NiO₄. *Mater. Res. Bull.* **17**, 383–390 (1982).
- Radaelli, P. G. et al. Structural and superconducting properties of La_{2-x}Sr_xCuO₄ as a function of Sr content. *Phys. Rev. B* 49, 4163–4175 (1994).

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Author contributions

I.B. and L.M. have contributed equally to this work. G.D.L., C.B.E., A.D., L.G., A.E., S.J., and M.G. grew and characterized the La_2NiO_4 films. I.B., J.Choi, M.G.-F., S.A., K.-J.Z., K.K., N.B.B., and Q.W. carried out the RIXS experiments. I.B., L.M., and Q.W. analyzed the RIXS data. P.W., J.M.T, and K.H. conceived, executed, and analyzed the ab initio calculations. I.B., Q.W., and J.C. conceived the project. All authors contributed to the writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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