Reply to "Comment on newly found Charge Density Waves in infinite layer Nickelates"

Charles C. Tam,[1,2,*] Jaewon Choi,[1,*] Xiang Ding,[3,*] Stefano Agrestini,[1] Abhishek Nag,[1,4] Mei Wu,[5] Bing Huang,[6] Huiqian Luo,[7,8] Peng Gao,[5] Mirian García-Fernández,[1] Liang Qiao,[3,†] and Ke-Jin Zhou[1,‡]

[1]*Diamond Light Source, Harwell Campus, Didcot OX11 0DE, United Kingdom.*
[2]*H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom.*
[3]*School of Physics, University of Electronic Science and Technology of China, Chengdu, 610054, China*
[4]*Laboratory for Non-linear Optics, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[5]*International Center for Quantum Materials and Electron Microscopy Laboratory,*
School of Physics, Peking University, Beijing 100871, China
[6]*Beijing Computational Science Research Center, Beijing 100193, China*
[7]*Beijing National Laboratory for Condensed Matter Physics,*
Institute of Physics, Chinese Academy of Sciences, Beijing 100190
[8]*Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China*

Charge density waves (CDW) have been reported in $NdNiO_2$ and $LaNiO_2$ thin films grown on $SrTiO_3$ substrates using Ni-L_3 resonant x-ray scattering in Refs. [1–3]. In their comment [4] on these reports, Pelliciari *et al.* found no evidence for a CDW in a $NdNiO_2$ film by performing fixed-momentum energy-dependent measurements. Instead, they observed a nearby non-resonant scattering peak, attributed to the (101) substrate reflection, made accessible at Ni-L_3 due to third harmonic light contamination. Here we present fixed-momentum energy-dependent resonant inelastic x-ray scattering measurements across Ni-L_3 on $NdNiO_2$, used in the preceding study [1]. We see intrinsic Ni-L_3 energy profiles at all measured $\mathbf{Q}$ values, including a strong resonance effect at $\mathbf{Q}_{CDW} = (-1/3, 0, 0.316)$ reciprocal lattice units. Attempts to measure the (101) substrate peak using third harmonic light at Ni-L_3 at I21, Diamond were unfruitful. Our results clearly demonstrate the electronic origin of the scattering peak published in Ref. [1] and lack of a detectable structural component in the peak.

INTRODUCTION

The infinite-layer nickelate superconductors contain two-dimensional NiO_2 layers, nominal $S = 1/2$ $3d^9$ Ni^{1+} ions and an active $d_{x^2-y^2}$ orbital near the Fermi level, making them in many ways analogous to cuprate superconductors. Despite the absence of long-range antiferromagnetic ordering, highly dispersive magnons confirm the existence of strong electronic interactions [5]. Strong electronic correlations often give rise to symmetry-breaking orders, which was confirmed in measurements of CDWs in $LaNiO_2$ [2], $NdNiO_2$ [1, 3], and $PrNiO_2$ [6].

In Refs. [1–3, 6], scattering peaks were found around $\mathbf{Q}_{CDW} = (1/3, 0, L)$ reciprocal lattice units (where $L \sim 0.3$) with a clear resonance effect around the Ni-L_3. In our previous work on $NdNiO_2$ [1], the resonant effect (Fig. 1e, Ref. [1]) and polarisation dependence (Figs. S11, S12, Ref. [1]) suggest the observed scattering peak originates from charge correlations rather than spin correlations or structure. Energy dependence around the Ni-L_3 absorption edge were performed at a fixed scattering angle 2θ (defined as Ω hereafter).

With a fixed Ω, the total momentum transfer $\mathbf{Q}$ varies with E as $\mathbf{Q} = (4\pi/hc)E\sin(\Omega/2)$ where h is Planck's constant and c is the speed of light. To fix the in-plane momentum transfer (*i.e.* $Q_{H,K} = 1/3$), the incident angle θ needs to be changed as $Q_{H,K} = Q\sin(\theta - \Omega/2)$. This leaves the out-of-plane momentum transfer $Q_L = Q\cos(\theta - \Omega/2)$ variable. We will explain at the end of

the reply that this type of measurement is valid if the CDW is sufficiently broad in L.

In their comment, Pelliciari *et al.* performed resonant elastic x-ray scattering (REXS) measurements on a $NdNiO_2$ film grown on a $SrTiO_3$ (STO) substrate [4]. For the sake of the reader we will briefly summarise their comment, referring to their main results as **(A)** and **(B)**.

(A) Lack of resonance effect near $\mathbf{Q}_{CDW}$ in $NdNiO_2$

When doing energy dependence with a fixed scattering angle (now referred to as $E_{fix\Omega}$), Pelliciari *et al.* observed an enhancement centred around the Ni-L_3 edge. However, an energy dependent measurement at a fixed momentum transfer (now referred to as E_{fixQ}) at $\mathbf{Q} = (1/3, 0, 0.31)$ yielded no resonance effect. They explored reciprocal space and found the (101) reflection of the STO substrate in proximity, made accessible at Ni-L_3 by third harmonic contamination *i.e.*, making (101) appear at $(1/3, 0, 1/3)$.

(B) Observation of $(1/3, 0, 1/3)$ on $SrTiO_3$ at Ni-L_3

To confirm this, Pelliciari *et al.* directly measured the STO substrate material. Similar to result **(A)**, the $E_{fix\Omega}$ scan shows a resonance effect, while the E_{fixQ} scan does not. Based on this, Pelliciari *et al.* concluded that scat-

tering at $\mathbf{Q} = (1/3, 0, 0.31)$ contains substantial contamination from the substrate from higher order light. They proposed a *new standard* procedure $E_{\text{fix}Q}$ scans at different $\mathbf{Q}$ locations to determine the resonant contribution to the quasi-elastic scattering.

In this reply, we conduct resonant inelastic x-ray scattering (RIXS) experiments, including the proposed *new standard* measurement, to address results **(A)** and **(B)**. We show in the experimental conditions of Ref. [1], charge scattering is indeed observed at the CDW position, with negligible scattering originating from the substrate.

RESULTS AND DISCUSSION

Reply to (A) - Observation of resonance effect at $\mathbf{Q}_{\text{CDW}}$ on NdNiO$_2$ film

First, we self consistently determined the scattering peak position in 3D reciprocal space. To do this, we placed the incident energy at the main peak of Ni^{1+} in the x-ray absorption spectra (XAS) at $E_i = 853$ eV, where the scattering peak was seen to resonate [1, 3]. Plotted in Fig. 1a is an H scan at fixed L, and in Fig. 1b an L scan at fixed H. We find the scattering peaked at $\mathbf{Q}_{\text{CDW}} = (-0.337, 0, 0.316)$.

With the exact value of $\mathbf{Q}_{\text{CDW}}$ determined, we then moved onto the *new standard* $E_{\text{fix}Q}$ measurements. Energy scans across the Ni-L_3 edge were performed at three fixed $\mathbf{Q}$ positions. Off the peak and at a strictly non-resonant location $\mathbf{Q} = (-0.2, 0, 0.316)$ (Fig. 1c), the measurement is purely fluorescence and resembles closely XAS. This indicates the presence of Ni, which is an intrinsic signal from the film. On the peak at $\mathbf{Q} = (-0.337, 0, 0.316)$ (Fig. 1e), the signal becomes clearly resonant, as the energy profile is distinct from XAS and the overall intensity is $\sim \times 100$ stronger. Slightly away from the peak, at $\mathbf{Q} = (-0.29, 0, 0.316)$, (Fig. 1d), the energy profile is still distinct from XAS, albeit with less intensity than on the peak, demonstrating the finite correlation length in H ($\xi_H \approx 60$ Å [1]).

The $E_{\text{fix}Q}$ scans clearly show an evolution from the fluorescence-like signal off the peak to the strong resonant behaviour on the peak, in contrast to the non-resonant profile on the peak in Ref. [4]. From this, we conclude the $\mathbf{Q} = (-0.337, 0, 0.316)$ scattering peak has electronic origin.

Reply to (B) - No evidence of third harmonic Ni-L_3 contamination at I21, Diamond

Next we address the issue of third harmonic contamination at beamline I21, Diamond, by searching for the (101) reflection directly on the STO substrate material using third harmonic light. To begin, we started with the

conditions where the CDW has been most frequently reported, namely with $E_i = 853$ eV, at the resonance of the Ni^{1+} XAS peak, at fixed $\Omega = 154°$, and scanned along $(H, 0)$. Only a background-like signal was seen (Fig. 1f). To investigate further, we went to $E_i = 767$ eV, where the third harmonic light (2301 eV) fulfils exactly the (101) diffraction condition of STO when $\Omega = 154°$. Again, only a background-like signal was seen (Fig. 1g).

Independent of this measurement, we examined the theoretical transmission of each optical component at the I21 beamline, and obtained a total transmission ratio of third harmonic to the primary beam at 853 eV to be around 2.3×10^{-10} [7]. Details of the calculation are in the Methods section. It is clear that the third harmonic contamination at the Ni L_3 edge at I21, Diamond is negligible, resulting in the lack of detection of the (101) substrate peak.

$\mathbf{E}_{\text{fix}Q}$ vs $\mathbf{E}_{\text{fix}\Omega}$

Finally, we comment on the validity of the $E_{\text{fix}\Omega}$ scan. For the $E_{\text{fix}\Omega}$ scan employed in the previous study at $\Omega = 154°$, the out-of-plane momentum transfer Q_L was changed from 0.365 to 0.368 r.l.u. in the energy window 851 to 855 eV [1]. Comparing to the FWHM of the CDW (0.08 r.l.u.) in L (Fig 1b), ΔQ_L (0.003 r.l.u.) is significantly smaller. In this case, although the CDW has clear L dependence, it is broad enough so that $E_{\text{fix}\Omega}$ is a sufficient approximation of $E_{\text{fix}Q}$.

CONCLUSION

We reexamined the CDW in the same sample, using the same RIXS instrument as in Ref. [1]. Following the determination of the exact $\mathbf{Q}_{\text{CDW}}$, we performed the *new standard* procedure suggested by Pelliciari *et al.*, namely $E_{\text{fix}Q}$ scans at various $\mathbf{Q}$ locations. This revealed a distinct evolution of energy profiles from off to on the CDW peak, in contrast to results of Pelliciari *et al.* Searching for the (101) reflection on a bare piece of the STO substrate material using third harmonic light at Ni-L_3 yielded no results.

These results demonstrate that the scattering peak observed in our nickelate films are primarily electronic in origin, with a negligible structural part. Results shown by Pelliciari *et al.* are self-consistent but only demonstrate the lack of charge correlations in their nickelate sample, while higher amounts of third harmonic contamination at the REXS instrument used allow for the detection of the (101) substrate reflection. Therefore, their interpretation cannot be validly applied to data collected in Refs. [1–3].
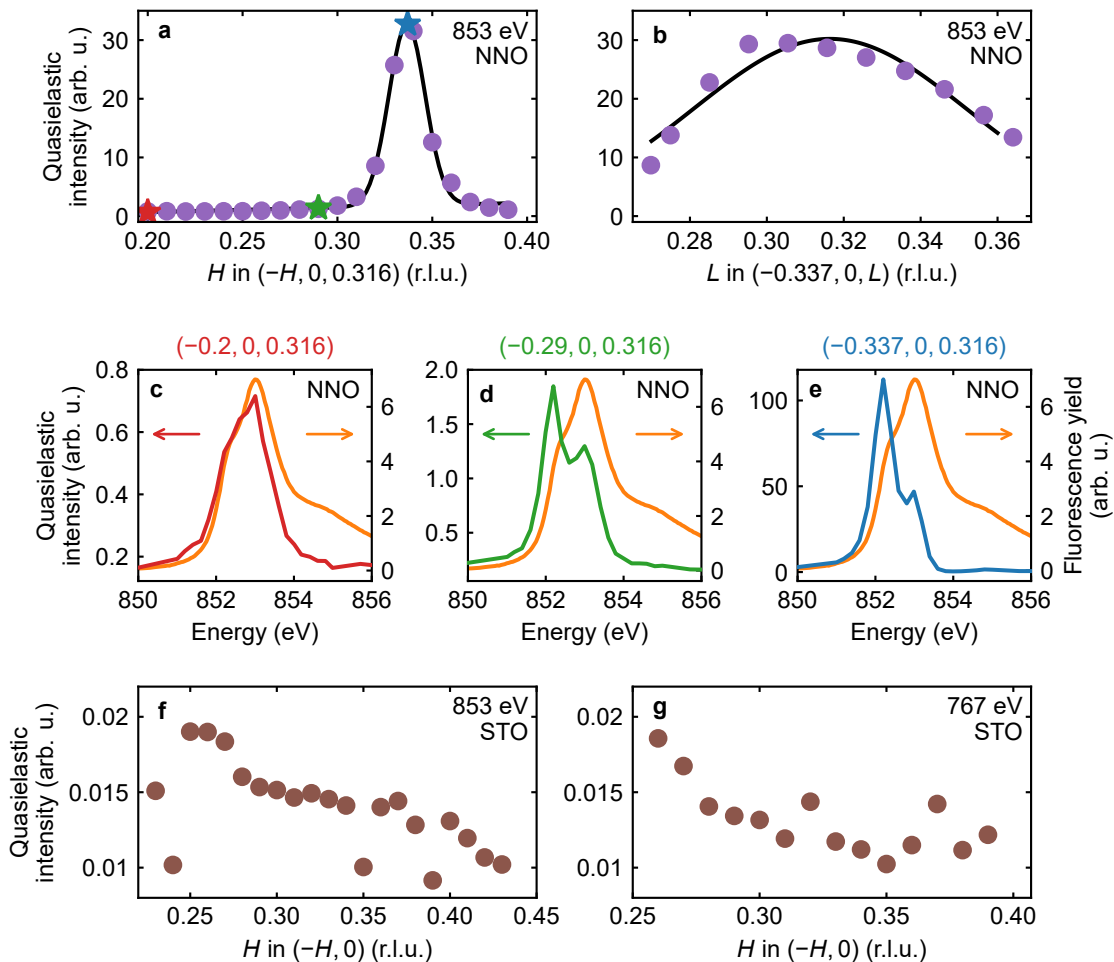
FIG. 1. **a** Quasi-elastic RIXS intensity of NdNiO$_2$, along H at $L = 0.316$, taken with incident energy at the maximum of the Ni-L_3 absorption peak at 853 eV. **b** Quasi-elastic RIXS intensity of NdNiO$_2$, along a small L range limited by soft x-ray RIXS, at $H = -0.337$, taken at 853 eV. Black lines are Gaussian fits. **c-e** Fixed $\mathbf{Q}$ energy scans of NdNiO$_2$, taken at fixed $\mathbf{Q} = (-0.2, 0, 0.316)$, $(-0.29, 0, 0.316)$ and $(-0.337, 0, 0.316)$, respectively. Fluorescence yield XAS taken with σ polarisation at grazing incidence are plotted on the secondary axis. **f** H scan of SrTiO$_3$ taken at 853 eV. **g** H scan of SrTiO$_3$ taken at 767 eV. All measurements were conducted at 20 K with σ polarised x-rays.

METHODS

A nickelate film sample (called NNO-1 in Ref. [1]) used in our previous study was chosen for the current measurement [1]. Samples were grown on SrTiO$_3$ substrates by pulsed laser deposition followed by topotactic reduction with CaH$_2$. The sample does not have a capping layer. More sample growth and characterisation details can be found in Ref. [1].

We performed RIXS measurements at the I21 beamline, Diamond Light Source, UK, where previously published nickelate CDW data were collected [1, 2]. All measurements were performed at 20 K with an energy resolution of 37.2 meV (FWHM). The sample was aligned with the same geometry as previously, namely the crystallographic a–c plane aligned with the horizontal scattering plane. To maximise the CDW signal we used σ polar-

isation and a grazing-in geometry ($\theta < \Omega/2$ as shown in Ref [1] Fig. S8). Ω was fixed at 154° in the $E_{\text{fix}\Omega}$ geometry. Reciprocal space is labelled reciprocal lattice units (r.l.u.) of the tetragonal structure of NdNiO$_2$, using refined lattice parameters $a = b = 3.908$ Å and $c = 3.543$ Å.

For the estimation of the third harmonic transmission of the beamline, the efficiency of each optical element was calculated by either reflectivity (for mirrors) or a diffraction calculation (for gratings). Details of the optical elements can be found in Ref. [7]. The results of these calculations are listed in Table. I. The transmission ratio of the beamline (up to and including M4) is estimated to be 2.4×10^{-6}. The spectrometer (M5 and SVLS2) cuts down the transmission by a further 9.8×10^{-5}, resulting in a total transmission of third harmonic light at Ni-L_3 of around 2.3×10^{-10}.

Optical element	Primary (853 eV)	3rd harmonic (2559 eV)	3rd/1st ratio	
ID flux (photons sec^{-1})	2.24×10^{15}	6.1×10^{14}	0.27	
M1 reflectivity (C coating)	0.92	0.93	1	
M2 reflectivity (C coating)	0.89	0.1	0.11	
M3 reflectivity (Pt coating)	0.59	0.35	0.59	2.4×10^{-6}
VPG2 grating reflectivity	0.12	2.7×10^{-5}	2.25×10^{-4}	
M4 reflectivity (Pt coating)	0.8	0.49	0.6	
M5 figure of merit (Pt coating)	0.028	0.0028	0.1	9.8×10^{-5}
SVLS2 grating reflectivity	0.045	4.45×10^{-5}	9.8×10^{-4}	

TABLE I. Photon flux and calculated efficiency of optical components for Ni-L_3 (853 eV) and third harmonic light (2559 eV) of optical components in use at I21, Diamond (at the time of writing). The beamline transmission ratio is 2.4×10^{-6}, while the spectrometer is 9.8×10^{-5} giving a total transmission ratio of third harmonic to primary light of 2.3×10^{-10}.

COMPETING INTERESTS

The authors declare no competing interests.

DATA AVAILABILITY

Relevant data are available from the corresponding authors upon reasonable request.

---

* These authors contributed equally
† liang.qiao@uestc.edu.cn
‡ kejin.zhou@diamond.ac.uk

[1] C. C. Tam, J. Choi, X. Ding, S. Agrestini, A. Nag, M. Wu, B. Huang, H. Luo, P. Gao, M. García-Fernández, L. Qiao, and K.-J. Zhou, Nature Materials 21, 1116 (2022).

[2] M. Rossi, M. Osada, J. Choi, S. Agrestini, D. Jost, Y. Lee, H. Lu, B. Y. Wang, K. Lee, A. Nag, Y.-D. Chuang, C.-T. Kuo, S.-J. Lee, B. Moritz, T. P. Devereaux, Z.-X. Shen, J.-S. Lee, K.-J. Zhou, H. Y. Hwang, and W.-S. Lee, Nature Physics 18, 869 (2022).

[3] G. Krieger, L. Martinelli, S. Zeng, L. Chow, K. Kummer, R. Arpaia, M. M. Sala, N. Brookes, A. Ariando, N. Viart, M. Salluzzo, G. Ghiringhelli, and D. Preziosi, Physical Review Letters 129, 027002 (2022).

[4] J. Pelliciari, N. Khan, P. Wasik, A. Barbour, Y. Li, Y. Nie, J. M. Tranquada, V. Bisogni, and C. Mazzoli, Comment on newly found charge density waves in infinite layer nickelates (2023).

[5] H. Lu, M. Rossi, A. Nag, M. Osada, D. F. Li, K. Lee, B. Y. Wang, M. Garcia-Fernandez, S. Agrestini, Z. X. Shen, E. M. Been, B. Moritz, T. P. Devereaux, J. Zaanen, H. Y. Hwang, K.-J. Zhou, and W. S. Lee, Science 373, 213 (2021).

[6] X. Ren, R. Sutarto, Q. Gao, Q. Wang, J. Li, Y. Wang, T. Xiang, J. Hu, F.-C. Zhang, J. Chang, R. Comin, X. J. Zhou, and Z. Zhu, Symmetry of charge order in infinite-layer nickelates (2023).

[7] K.-J. Zhou, A. Walters, M. Garcia-Fernandez, T. Rice, M. Hand, A. Nag, J. Li, S. Agrestini, P. Garland, H. Wang, S. Alcock, I. Nistea, B. Nutter, N. Rubies, G. Knap, M. Gaughran, F. Yuan, P. Chang, J. Emmins, and G. Howell, Journal of Synchrotron Radiation 29, 563 (2022).