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On a road towards applications and devices based on functional oxides with correlated electrons the crucial element is uncovering the effects of the reduced dimensionality on the electronic phase transition into a multi-ordered ground state. Towards this goal, we present a study of reduced dimensionality on charge and anti-ferromagnetic orderings in ultra thin EuNiO$_3$ (ENO) films on NdGaO$_3$ substrates with hard and soft resonant x-ray scattering to investigate the presence of electronic and magnetic orderings. Despite the ultra-thin nature of the films, they exhibit the bulk-like order parameters up to room temperature suggesting that the spontaneously coherent Mott ground state in the highly distorted rare-earth nickelates can be successfully sustained even when restrained towards two-dimensionality. The presence of charge ordering at room temperature and below opens prospects for their use in novel electric field controlled devices.

Transition metal oxides (TMO) are host to a vast array of collective phenomena with enormous potential for use in next generation electronic devices, including high temperature superconductivity, collosal magnetoresistance, metal-insulator transition (MIT), orbital, and charge ordering (CO)[1–5]. In particular, electric field induced changes in the CO state, where the modulated charge density acquires a periodic pattern typically leading to insulating behavior has received wide attention lately and been implemented in several devices[5–11]. In the ferrites, for instance, the application of an external electric field was found to induce a phase transition to a metallic state with a resistance change of several orders of magnitude, allowing their incorporation into devices[9–11]. These devices typically require ultra thin films or nanoparticles of materials making the study of size effects of paramount importance to future functionality. For instance, it was found that the bulk CO transition is rapidly suppressed in the nano-limit or under high pressure for CMR manganite systems[12,13]; while in thin films the CO transition temperature can be suppressed entirely or even increased from the bulk value[14–16]. Further, to be technologically viable a device typically needs to operate at room temperature and above, while in complex oxides CO is typically a low temperature phenomenon. This has stimulated our search for materials that fulfill all of the criteria, i.e. displays charge ordering, maintains this transition in nanometer size applications, and operates at room temperature.

As a prototypical TMO perovskite system, the rare-earth nickelates with chemical formula RNiO$_3$ (R = Pr, Nd, Eu, Y, ...) incorporate Ni ions in a low spin s=1/2 state and ionic 3d^7 (t$_{2g}^6$e$_g$) configuration, strongly covalent with oxygen placing these systems firmly in the charge transfer regime wit1h a significant 3d^8$\underline{L}$ component in the ground state[17,18]. This class of materials has received significant attention recently due to the MIT[17], E$'$-type anti-ferromagnetic transition (AFM)[19], structural transition[17], predicted high T$_c$ superconductivity[20], potential for device applications[6,7,21], and the charge-ordering transition[22–26]. The charge ordering transition, in particular,

has been a source of controversy and still requires further insight[27–30]. Indeed, devices utilizing less distorted NdNiO$_3$ (NNO) have already been realized, including electric field control, however the low transition temperature ($\sim$ 150K) limits the practically of such systems[7,18,21]. The rock-salt CO structure and the E$'$-type anti-ferromagnetic structure are shown in Fig. 1(a). In the rare-earth nickelates, the CO transition is invariably present in the bulk, but, as in the manganites, has been shown to be suppressed in hetero-epitaxial ultra-thin film of NNO[24,29–31]. Specifically, it was found that the interface is able to "pin" the symmetry in the non-CO *Pbnm* state, analogous to the effect of surface strain in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Sr$_2$RuO$_4$[12,32]. As changes in the ground state may render materials futile for applicability, it is important to find ways to mitigate the dimensionality effects. Within the nickelates, one possible route is the use of an R ion of smaller radius, which increases the distortion of the lattice and electron-phono coupling and correspondingly the T$_{MIT}$ at which CO arises in the bulk[17]. Determining whether this scheme can recover the typical bulk ground state or whether the two-dimensional geometry forbids its occurrence is crucial toward understanding the potential for this material to be used in future device applications.

In this letter, high quality ultra thin films (14 unit cells, u.c., 5.3 nm) of EuNiO$_3$ (ENO) on NdGaO$_3$ (NGO) substrates, that feature moderate strain (1.5%) and symmetry matching (*Pbnm*) were probed by resonant x-ray scattering (RXS) in the hard and soft x-ray regime to determine the changes to the ground state due to the highly two-dimensional topology[33,34]. Structural diffraction confirmed that the film was of high quality and consist of *single-domain* in perfect registry with the substrate. Measurements of the (0 1 1)$_{or}$ [here *or* refers to orthorhombic structure; *pc* = pseudocubic] and ($\frac{1}{2}$ 0 $\frac{1}{2}$)$_{or}$ peaks at resonant edges were utilized to establish the presence of the bulk-like CO and E$'$-type AFM orderings, respectively. Our results demonstrate that ENO films display bulk-like multi-ordered ground states in sharp contrast to NNO, likely due to the larger distortion of the lattice and strong electron-phonon coupling destabilizing the substrate-induced symmetry pinning[35]. These findings increase the likelihood of fabricating multi-functional oxide based devices employ-

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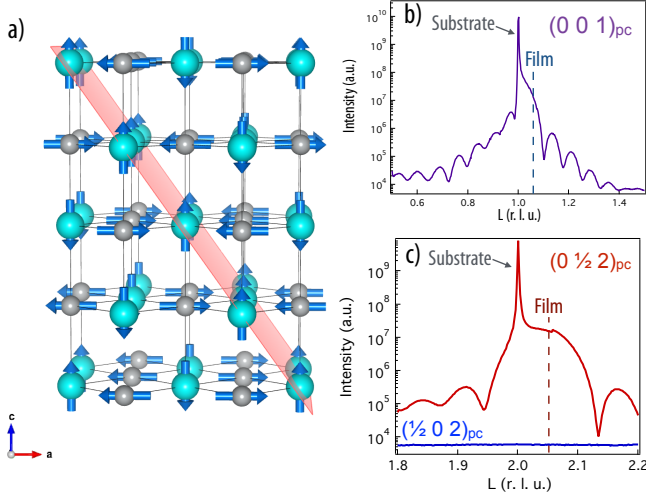
FIG. 1. (Color online) a) Charge ordered rock salt crystal structure with exaggerated $Ni^{3\pm\delta}$ radius variations. $(\frac{1}{2}\ 0\ \frac{1}{2})_{or}$ E'-type anti-ferromagnetic plane shown in red, with individual magnetic moment vectors for each Ni site. The c-direction shown is the psuedocubic growth direction of the film. b) L-scan through the $(001)_{pc}$ trunca-tion rods showing the high quality of the ultra-thin films. c) L-scan around the $(0\ \frac{1}{2}\ 2)_{pc}$ truncation rod.

ing room temperature charge ordering.

Ultra thin ENO samples were grown on NGO $(110)_{or}$ by pulsed laser deposition as described previously[36,37]. Reso-nant x-ray scattering (RXS) measurements were performed at both the 4.0.2 beam line of the Advanced Light Source, Lawrence-Berkeley National Laboratory (soft RXS), and the 6-ID-B beam line of the Advanced Photon Source, Argonne National Laboratory.

Fig. 1(b) displays scans along the $(L\ L\ 0)_{or}$ $((0\ 0\ L)_{pc})$ truncation rods with synchrotron based diffraction. The struc-tural quality is clearly evident from the appearance of Kiessig fringes spanning the $(1\ 1\ 0)_{or}$ truncation rod and film[37]. The spacing of the Kiessig fringes gives a film thickness of ~ 5.3 nm, perfectly corresponding to 14 u.c. of ENO consistent with reflection high energy electron diffraction (RHEED) oscilla-tions during growth. The high photon flux of the synchrotron source is of particular importance due to the relatively weak reflections used to probe CO. Beyond this, another basic in-dication of quality is the orientation of the orthorhombic c-direction of the film relative to the substrate, which corre-sponds to a doubling of the pseudo-cubic unit cell. The NGO substrates used are cut to have the $(1\ 1\ 0)_{or}$ direction out-of-plane, giving primary in-plane directions of $(1\ \text{-}1\ 0)_{or}$ and $(0\ 0\ 1)_{or}$. We have defined the $(0\ K\ 0)_{pc}$ direction to be parallel to the doubled orthorhombic c-axis for both the substrate and film. Thus, there exists a half-order peak along the $(0\ K\ 0)_{pc}$, but not along the $(H\ 0\ 0)_{pc}$ direction corresponding to the or-thorhombic c-direction for both the substrate and film indicat-ing an untwined film. Our scans across the $(0\ \frac{1}{2}\ 2)_{pc}$ half-order peak show a clear substrate and film peak, Fig. 1(c). Subse-quent attempts to locate the $(\frac{1}{2}\ 0\ 2)_{pc}$ found no peak. This indicates that there is no mixing of diffraction signals from
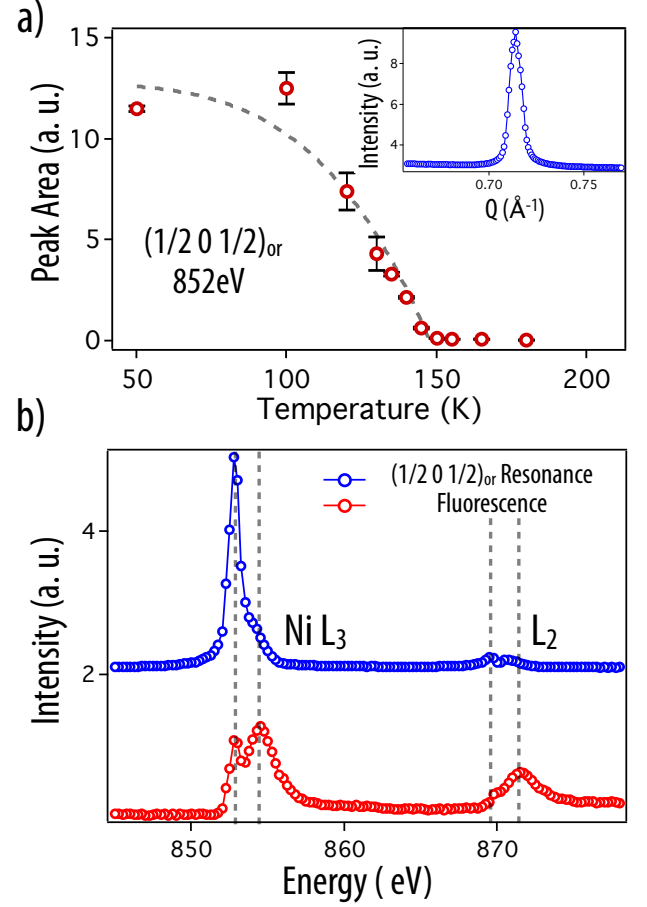

FIG. 2. (Color online) (a)Temperature dependence of the magnetic Bragg peak intensity corresponding to the magnetic order parameter. The inset shows the measured scattering at 50K. (b) 50K resonant and fluorescence measurements of the Ni L_3 and L_2 edges. The fluo-rence signal is enhanced 20x and the resonance data vertically offset for clarity. Dashed lines are guides to the eye.

in-plane twinned orthorhombic domains. This point is crucial for investigating CO as domains with different c-orientations will mix the signal from the $(H\ 0\ L)_{or}$ and $(0\ K\ L)_{or}$ peaks[30], thus adding a large Thompson scattering background which can obscure the resonant term.

Next we turn our attention to magnetism. Previous studies by several groups, including our recent work on NNO, have shown the E' -type AFM order in the nickelates is very ro-bust and likely plays a significant role in the MIT transition in the less distorted nickelates[19,29,30,38]. In ENO, however, the separation of the MIT and the AFM transitions is nearly 300 K allowing independent investigation of each. Note, the E'-type AFM ordering period contains 4 consecutive Ni moments along the $[1\ 1\ 1]_{pc}$ direction, thus this ordering can then be probed via the $(\frac{1}{2}\ 0\ \frac{1}{2})_{or}$ peak $((\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})_{pc})$.

In figure 2(a) (inset), scans across this diffraction spot re-vealed a strong peak at low temperature. Temperature de-pendence of the integrated intensity is shown in Fig. 2(a). As seen, a clear transition to the magnetically ordered state is found around 150K. This is 55K below the value reported
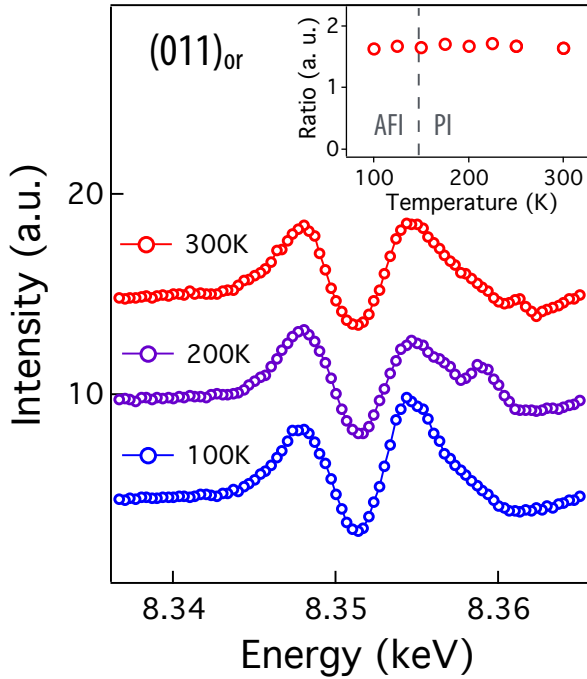
FIG. 3. (Color online) Resonant scattering at the $(0\ 1\ 1)_{or}$ peak at various temperatures. Data offset for clarity. The inset shows the ratio of the peak around 8.348 keV to the background at 8.34 keV across the AFM transition up to room temperature.

in bulk, which is consistent with previously reported measurements on thin film nickelates[17,39]. Here we stress that the magnetic Bragg peak corresponding to the bulk-like E'-type AFM order was observed despite the ultra-thin nature of the films, thereby displaying the robustness of this transition down to a thickness less than 4 full magnetic unit cells.

Having established the high structural quality, single domain phase, and the presence of AFM transition, the temperature dependence of the $(0\ K\ L)_{or}$ peaks $((-\frac{K}{2}\ \frac{L}{2}\ \frac{K}{2})_{pc})$, associated directly with charge order, can be investigated[22–25]. Figure 3 shows the results of resonant energy scans around the $(0\ 1\ 1)_{or}$ peak. A clear energy dependence is observed at the Ni K-edge with no apparent temperature dependence. The line shape has strong similarities with what was observed for thick and bulk NNO samples, with a small peak at higher energy (~ 8.36 keV) likely due to multiple scattering[22,23]. While the scattering around the Ni K-edge is due to the resonant term of the total scattering factor, the off-resonance scattering indicates additional contribution from the Thompson scattering off the Ni sites, whereas the Eu and O sites do not contribute by symmetry[22,23]. As with the resonant peak, no temperature dependence was observed for this contribution. Further analysis, taking the ratio of the peak at 8.348 keV to the background Thompson scattering, (inset of Fig. 3) verifies the lack of any significant temperature dependence for this peak. Upon cooling bulk ENO, the CO and MIT transitions initiate at ~ 470K[17,18]. In many films CO continues to develop with cooling, stabilizing at ~ 100K below the MIT[22]. Thus, the absence of any temperature dependence here, ~ 170K below

the bulk transition, is expected.

Having established that the temperature dependence of the $(0\ 1\ 1)_{or}$ peak indicates a bulk-like CO transition, we next compare the charge disproportionation,δ ($Ni^{3\pm\delta}$), of the film to the bulk. Low temperature resonance scans at the $(\frac{1}{2}\ 0\ \frac{1}{2})_{or}$ magnetic Bragg peak and the accompanying flouresence background are shown in Fig. 2(b). The typical Ni L_3 and L_2 features are seen for the fluorescence data, with the higher energy L_3 peak corresponding to the Ni 3+ state around 855 eV and the lower energy multiplet split peak, characteristic of the insulating state, around 853 eV as also previously reported[37].

The resonance of the L_3 edge, besides indicating a strong Ni contribution to the observed magnetic Bragg peak, can reveal the degree of charge disproportionation $Ni^{3\pm\delta}$ in the sample[19,38,40]. Specifically, Scagnoli *et al* used a configuration interaction model to demonstrate that the value of δ strongly influences the line shape of the resonant peak[38,41]. Surveying the available compounds, Bodenthin *et al* found, for $RNiO_3$ *powder* samples spanning several rare earth ions, no deviation in the magnitude of δ[19]. This result is quite surprising as the degree of the monoclinic distortion increases with decreasing rare-earth radius and this was expected to increase the value of δ. For our $EuNiO_3$ ultra thin films, the line shape for the σ incident light is nearly identical to what was observed for the bulk samples, and, based upon the similarity with the calculated spectra of $\delta = 0.32$e from Ref.[19], is within the 0.05e range found for all the $RNiO_3$ bulk powder compounds. Combining the results of the $(0\ 1\ 1)_{or}$ CO peak and the $(\frac{1}{2}\ 0\ \frac{1}{2})_{or}$ magnetic peak, it is therefore clear that the CO in the ENO film maintains a bulk-like value despite the highly constraining two-dimensional geometry in contrast to the lattice pinning found for NNO thin films[29,30].

Thus, we find the higher distortion in this nickelate incorporating a smaller RE ion, Eu, is able to recover the bulk-like phase transitions that were suppressed for NNO in the same two-dimensional geometry[39,42]. Previous work on rare-earth nickelate thin films showed that heterointerface with the substrate can readily suppress the monoclinic symmetry, bulk-like CO, and the MIT transitions under compressive strain[7,27,43–46]. Further, some films have been found to maintain a MIT and yet show no symmetry breaking on crossing the MIT[27,29,30]. We conclude that the higher distortion and stronger electron-phonon coupling in ENO allows CO to persist in the insulating, tensile-strained sample. Moreover, it is quite remarkable that, based upon the line shape of the Ni L_3 edge resonant scattering, the degree of charge disproportionation appears unchanged from the bulk value based upon the resonance at the $L_{3,2}$ edges[19]. We have therefore uncovered a mechanism to overcome the suppression of bulk functional properties that has been observed previously in other nickelate films.

In conclusion, we synthesized ultra thin films of ENO films on NGO substrates to investigate the stability of the AFM and CO orderings against the ultra thin geometry via hard and soft XRS. An AFM transition is found to occur near the expected temperature with the Q-value corresponding to the bulk-like E' type ordering. Interestingly, the magnitude of the CO δ parameter, derived from magnetic scattering, was found to be the

same as was reported for both bulk and thick films of various RNiO$_3$. In ENO, despite the ultra thin geometry and altered electronic bandwidth, our findings revealed that the CO and AFM transitions remain bulk-like. Moreover, CO is observed at room temperature rendering ultra-thin ENO films and heterojunctions potential use for novel electric field controlled devices along with CMR manganites and ferrites[5–11].

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