Giant electron-phonon coupling of the breathing plane oxygen phonons in the dynamic stripe phase of La$_{1.67}$Sr$_{0.33}$NiO$_4$

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Doped antiferromagnets host a vast array of physical properties and learning how to control them is one of the biggest challenges of condensed matter physics. La$_{1.7}$Sr$_{0.3}$NiO$_4$ (LSNO) is a classic example of such a material. At low temperatures holes introduced via substitution of La by Sr segregate into lines to form boundaries between magnetically ordered domains in the form of stripes. The stripes become dynamic at high temperatures, but LSNO remains insulating presumably because an interplay between magnetic correlations and electron-phonon coupling localizes charge carriers. Magnetic degrees of freedom have been extensively investigated in this system, but phonons are almost completely unexplored. We searched for electron-phonon anomalies in LSNO by inelastic neutron scattering. Giant renormalization of plane Ni-O bond-stretching modes that modulate the volume around Ni appears on entering the dynamic charge stripe phase. Other phonons are only weakly sensitive to stripe melting. Dramatic overdamping of the breathing modes indicates that dynamic stripe phase may host small polarons. We argue that this feature sets electron-phonon coupling in nickelates apart from that in cuprates where breathing phonons are not overdamped and point out remarkable similarities with the colossal magnetoresistance (CMR) manganites.

INTRODUCTION

In band as well as Mott insulators an energy gap at the Fermi surface prevents electronic conduction. These materials should become metallic when extra charge carriers are introduced by doping. However, many of them remain insulating or become very poor metals with large electrical resistivity and incoherent or diffusive transport [1][2]. This behavior is particularly common in transition metal oxides that have the potential to realize novel electronic phases with interesting and exotic properties from nontrivial topologies to superconductivity [3]. Poor electrical conductivity is typically associated with charge carrier localization arising from interactions between different quasiparticles [4]. Learning how to control these interactions is challenging, especially when strong electron-electron correlations are involved.

Electron-phonon coupling is often involved in localization of charge carriers in crystalline materials. For example, in the case of polaron formation, the carriers locally distort the atomic lattice and the distortions trap the carriers when the electron-coupling strength is large enough [5]. A detailed understanding of both electronic and phonon channels is necessary to accurately account for such phenomena. A lot of research focused on the former [4][5], but the latter is poorly characterized in many interesting materials.

Time-of-flight neutron scattering instruments can map the phonon spectra over hundreds of Brillouin zones, but comprehensive analysis of these datasets is extremely difficult and time-consuming. For example, small peaks in the background can be assigned to phonons. A broad peak may arise from a superposition of two or more closely-spaced peaks. Some phonons can be overlooked since most of them have appreciable structure factor only in a few zones, etc. Recently we developed new software-based data analysis that overcomes most of these and other difficulties [7].

We used this software to investigate the interplay between phonon modes and carrier localization in La$_{2-x}$Sr$_x$NiO$_4$ (LSNO), which is isostructural with La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), the family of cuprates in which high-temperature superconductivity was first discovered. LSNO is seen as a hole-doped antiferromagnetic Mott insulator where holes are confined within two-dimensional (2D) NiO$_2$ layers in which Ni atoms form a square lattice and O atoms bridge the nearest neighbors [8][10]. At low temperatures doped holes segregate into lines of charge that form antiphase domain walls between antiferromagnetic regions in the form of stripes that run along the diagonal direction with respect to the Ni-O bonds. The charge stripe period in real space equals $a/2(\delta)$ with $\delta \approx x$ [11][12]. Here we focus on the dopant concentration $x = 0.33$ (La$_{1.67}$Sr$_{0.33}$NiO$_4$) but our results apply to many other doping levels and materials as discussed below.

Stripe order locks the doped holes in place but when it melts above 240K the material does not become metallic [13][14]. The electrical resistivity continues to decrease...
up to about 300K and then stabilizes at a constant value until the maximum measured temperature of 600K [13]. It was proposed that insulating behavior of the resistivity is caused by polarons although their direct experimental signatures have been elusive [4, 13, 15].

Neutron scattering experiments revealed low energy charge fluctuations in the form of dynamic stripes illustrated in Fig. 1a with the strongest low energy spectral weight near the charge ordering temperature [16]. Similarly to the static stripe phase, these fluctuating charges form domain boundaries between the fluctuating magnetic domains. These were accompanied by low energy spin fluctuations in the form of magnetic stripes. Neutrons scatter from atomic lattice deformations, not the charges themselves, so the observed signal implies that the fluctuating charges are accompanied by atomic lattice deformations of the same wavevector. Charge carriers combined with these lattice deformations, which are distinct from phonons, behave as dynamic large polarons (as defined above for high carrier densities) spanning many unit cells as manifested by their narrow linewidth in momentum space. On the other hand, low energy optical response of LSNO has been interpreted in terms of small polarons [13].

In the present study we measured spectra of high energy phonons and found that some NiO$_2$ plane oxygen vibrations away from the Brillouin zone center are strongly damped in the dynamic phase, whereas others are affected relatively weakly (Fig. 1). The strongest effect is in the breathing mode, which becomes overdamped at 240K and partially recovers at higher temperatures. We argue that collapse of this mode indicates the formation of small polarons in addition to the dynamic stripes detected previously and discuss the universality of this phenomenon.

**EXPERIMENTAL DETAILS**

Since our primary focus is on the high-temperature homogeneous phase where the stripe order is melted, we choose a unit cell containing one Ni atom per layer with the in-plane lattice parameter $a \sim 3.8 \text{ Å}$ and the out-of-plane lattice parameter $c \sim 12.7 \text{ Å}$ (space group $I4/mmm$). The low temperature 3D spin ordering wavevector is then $(1/2 \pm \delta, 1/2 \pm \delta, 0)$ and the charge ordering wavevector is $q_{co} = (2\delta, 2\delta, \pm 1)$ in terms of reciprocal lattice units (r.l.u.) $(2\pi/a, 2\pi/a, 2\pi/c)$; in our sample, $\delta=0.33$. $[100]$ direction is defined to be parallel to the Ni-O bonds, and the $[110]$ direction is then along the diagonal.

The sample mounted with the scattering plane in the $ab$-plane, with the $c$-axis vertical and perpendicular to the beam, was measured on the ARCS spectrometer at the Spallation Neutron Source (SNS). This orientation is good for comprehensive measurements of phonons with atomic displacements in the Ni-O plane. Incident neutron energy $E_i$ was 120meV with the chopper running at 600Hz. $T_0$ chopper speed was 120Hz. The experiment was performed in two separate runs with the sample first mounted in the closed-cycle refrigerator set at 10K, 190K, and 240K, and in the high-temperature cryostat for the second run at 300K, 450K, and 600K. At most temperatures the sample orientation was scanned over $\sim 50^\circ$ by rotating it around the vertical axis and taking neutron scattering measurements every 0.25°. The resulting dataset contained the scattering function covering over 100 Brillouin zones. The sample rotation angular range was smaller at 450K and 600K covering reciprocal space around the 110-direction only. We used Phonon
the transverse direction along $(h,-h,0)$, where $1r.l.u. = 2\pi$. Binning was ±0.05 r.l.u. in the longitudinal direction along $(h,h,0)$ and ±0.035 r.l.u. in the transverse direction along $(h,-h,0)$, where 1 r.l.u. = $2\pi/a$. Binning along the c-axis was ±2.5 r.l.u. where 1 r.l.u. = $2\pi/c$. Note how the spectra around 70 meV for $|h| > 0.3$ change with temperature.

The data of interest do not depend significantly on L, so we used a relatively large binning interval along L to improve statistics. The energy resolution function was broader on the low energy side than on the high energy side, hence the peaks that are close to resolution-limited are also asymmetric.

The main result of this work is summarized in figure 1. Ni-O bond-stretching phonons near the zone boundary soften and broaden (Fig. 1c) or become completely overdamped (Fig. 1d) as the stripe order melts on heating to 240K. In contrast, phonons that do not modulate crystallographic volume around Ni such as the zone center Ni-O bond-stretching phonon (Fig. 1b) are not affected beyond usual anharmonic effects.

Figures 2 and 3 show phonons at 10K and 240K dispersing in the longitudinal direction on both sides of the zone center at $h=0$ in the [110] and [100] directions to zone boundary wavevectors with $h=0.5$. The zone centers in both figures marked with the vertical dashed lines correspond to wavevectors $Q=(3,3,0)/(5,1,0)$ in Figs. 2/3 respectively. Zone boundary wavevectors in figure 2 at $Q=(2.5,2.5,0) / (3.5,3.5,0)$ on the left / right side of the figure both correspond to the reduced wavevector $q=(0.5,0.5,0)$. Zone boundary wavevectors in figure 3 at $Q=(4.5,1.0) / (5.5,1.0)$ on the left / right side of the figure both correspond to the reduced wavevector $q=(0.5,0,0)$. Note that the charge stripe ordering wavevector at 10K...
is $q_{lo}=(0.3,0.3,\pm 1)$

Figure 4 illustrates conventional temperature dependence of the zone center phonons. The peaks near 45meV/85meV originate from Ni-O bond-bending/bond-stretching vibrations respectively. As the atomic lattice expands on heating, the bond-stretching mode gradually shifts to lower energy and broadens due to anharmonic effects. However, it remains robust all the way up to 600K. The bond-bending vibrations, whose energy is less sensitive to lattice parameters, vary relatively little with temperature. Such weak temperature dependence is typical of all phonons that we investigated except for the bond-stretching LO phonons away from the zone center. Anomalous temperature-dependence of these modes is the main focus of this paper.

We start by discussing results at low temperature, which serve as a baseline for higher temperatures. At 10K the LO bond-stretching branch has a nearly flat dispersion in the 110 direction near the zone center, but then splits between $q=(0.3,0.3,0)$ and the zone boundary into the upper part at 85meV and the lower part at 75meV. On approach to the zone boundary, the upper part weakens, whereas the lower part intensifies. The data are consistent with earlier work [17].

The LO branch disperses downwards and broadens towards the zone boundary in the 100 direction as previously reported [17]. Our measurements suggest that this branch also splits into two (Fig. 3). Although these cannot be fully resolved in a single scan, we observed the variation of the lineshape from zone to zone, which points at two closely-spaced branches with different eigenvectors. We see a similar splitting of the 45meV zone center phonon at low temperature that disappears at 190K and above, which is consistent with infrared conductivity results [18]. This splitting is not understood but is probably related to the increased unit cell size in the presence of long-range stripe order [17].

The lowest branch in Figs 2,3 around 60meV originates from apical oxygen vibrations along the c-axis [19]. It mixes with the Ni-O bond-bending vibrations away from the zone center, which is responsible for nonzero scattering intensity observed in our measurements. This branch does not show strong coupling to charge fluctuations and we will not discuss it further.

Our primary focus is on the temperatures of 240K and above where we observe a single strongly renormalized branch in all directions. Near the zone center the effect of increased temperature is small as is typical of all phonon modes in LSNO that we looked at, except the LO Ni-O breathing bond stretching branches away from the zone center. The latter broaden and soften half-way to the zone boundary on heating and branch splitting is no longer observed. The phonon softening from 10K to 240K increases from 1meV at the zone center to about 4meV at the zone boundary $[q=(0.5,0,0)]$ and the peak broadens substantially (Fig. ??fig:Fig3) Fig. 4 shows the same effect in another Brillouin zone at $Q=(5.5,0,0)$, which rules out any spurious origin of the anomaly. On approach to the zone boundary M point $[q=(0.5,0.5,0)]$ in Fig. 2 phonon renormalization is even larger: The bond-stretching phonon evolves from a relatively narrow profile at 10K peaked at 74meV to a broad barely discernible overdamped lineshape at 240K (Also see Fig. [14]). The temperature effect at the zone boundary point $q=(0.5,0.5,0)$ extends in the transverse direction at least to $q=(0.6,0.4,0)$ (Fig. 5).

Figure 5 shows the full temperature-dependence of the phonon spectrum at $q=(0.5,0.5,0)$ up to 450K in two different Brillouin zones. The phonon at 74meV broadens at 190K where magnetic order melts and is completely washed out at 240K where charge order disappears. It recovers partially at 300K and 450K.

This behavior can be understood if one considers the volume of the oxygen octahedron around Ni. For the zone center phonon, the deformation due to lattice vibrations does not change the volume around Ni. Between the zone center and the zone boundary, modulated volume increases precisely as a sine function. The connection between the phonon anomaly and the modulation of octahedron volume around Ni is confirmed by Fig. 4. The transverse branches involving stretching of the same Ni-O bonds that do not modulate volume around Ni at any wavevector are narrow throughout the Brillouin zone at 240K, not just at the zone center.
FIG. 5. Raw data divided by the Bose factor at two zone boundary wavevectors: $Q=(2.5,2.5,0)$ (a) and $Q=(3.5,3.5,0)$ (b). The two wavevectors correspond to the same reduced wavevector $q=(0.5,0.5,0)$. Straight lines represent the background. Binning was the same as in Fig. 2. Arrows point at the peak from the breathing phonon that is well defined at low temperature, becomes overdamped at 240K, and reappears at higher temperature. The same behavior is observed in (a) and (b).

FIG. 6. Evolution of the phonon spectra in the transverse direction near wavevector $Q=(3.5,3.5,0)$. Arrows in (a) mark the phonons that become overdamped at 240K. Binning was the same as in Fig. 2.

FIG. 7. Phonon dispersion in the transverse directions. (a) along the Ni-O bond at wavevectors $Q=(5,k,0)$ (Binning was the same as in Fig. 3); (b) along the diagonal direction, $Q=(3-k,3+k,0)$ (Binning was the same as in Fig. 2); (c) Zone boundary phonons from (a) at 10K and 240K (d) Zone boundary phonons from (b) at 10K and 240K. Lines in c,d are guides to the eye.

DISCUSSION

LSNO received a lot of attention as the analogue of the high T$_c$ cuprates that are also characterized by a low temperature CDW [20,22]. However, LSNO is an insulating spin 1 antiferromagnet with small magnetic fluctuations and a large atomic lattice deformation that aides in trapping the doped holes in magnetic domain boundaries. In contrast, LSCO is a spin-1/2 system with...
large fluctuations, small lattice deformation and metallic charge transport. In fact the gapped low temperature phase of LSNO [15] is similar to undoped LSCO, which is an antiferromagnetic insulator. A lot of evidence exists that the dynamic component of the CDW in cuprates is strong and is important for the pseudogap and superconductivity [23]. Thus the high temperature phase of LSNO with strong low energy charge fluctuations is closer to the cuprates than the low-temperature phase is the one to study as an analogue of the cuprates. Our work highlights and characterizes strong electron-phonon interaction in this phase.

The electron-phonon interaction can be described by the following Hamiltonian:

\[
H_{\text{int}} = \frac{1}{\sqrt{N}} \sum_{q \mathbf{k}} \Gamma(q, \mathbf{k}) (c^\dagger_{\mathbf{k}q} c_{\mathbf{k}q} + c^\dagger_{\mathbf{k}q} c_{\mathbf{k}q}) .
\]  

(1)

It represents a process where an electron changes its momentum by \( q \) when it annihilates/creates \((b^\dagger_{\mathbf{q}}/b_{\mathbf{q}})\) a phonon with momentum \( q \). \( c^\dagger_{\mathbf{k}q}/c_{\mathbf{k}q} \) are creation/annihilation operators of electron with momentum \( \mathbf{k} \). \( \Gamma \) is the electron-phonon coupling.

Apart from exotic cases, the interaction \( \Gamma(k, q) \approx \Gamma(q) \) depends only on phonon momentum \( q \). In the case of long-range Fröhlich Hamiltonian arising from the Coulomb interaction, the strongest coupling is at \( q=0 \):

\[
\Gamma(q) \sim \frac{\sqrt{\alpha}}{q^{d-1}/2}
\]  

(2)

\( \alpha \) is a dimensionless coupling constant and \( d = 3 \) or \( d = 2 \) is the dimension of the system [24]. Since this interaction is peaked at the BZ center, it should have the biggest impact on phonons near the zone center, which is inconsistent with our findings.

As an alternative, Holstein type coupling based on short-range electron-phonon interaction is characterized by momentum independent \( \Gamma \): [25]

\[
\Gamma(q) = g
\]  

(3)

However it is also inconsistent with our results, which show strong \( q \)-dependence of electron-phonon coupling.

Instead our results point at a breathing-type electron-lattice interaction peaked at the zone boundary [26] and characterized by the coupling of electronic charge fluctuations to vibrations of lighter ions modulating the volume around a heavier one. It is similar to coupling to nonzero wavevector charge fluctuations discussed in [27, 28]. Strong manifestations of this type of interaction were first experimentally observed [29, 30] and explained [26, 31] in mixed valence compounds. In our case

\[
\Gamma(q) \sim g \sin \frac{q}{2}
\]  

(4)

which peaks at the Brillouin zone boundary [26, 32].

The important difference between our findings and models of Ref. [27, 28] is the observation of strong broadening of the phonons not accounted for in purely harmonic models based on dynamical matrices. The adiabatic part of the electron-lattice coupling takes into account high-energy electronic excitations leading to well-defined phonon modes of zero width. It was noticed long ago [33] and clearly re-established recently [34] that the existence of low-lying electronic excitations, whose energy is comparable with that of the lattice vibration is necessary for phonon broadening caused by electron-phonon interaction. In this case the nonadiabatic part of the interaction caused by soft electronic excitations, leads to the damping of otherwise perfectly stable lattice vibrations.

Thus our results point at a considerable spectral weight of soft electronic excitations at energies comparable to the Debye energy above charge ordering temperature. Strong electron-phonon interaction increases effective mass facilitating charge localization inside the stripe magnetic domain boundaries as the temperature is lowered.

The interplay between low energy dynamic stripes and small polarons in the high temperature phase follows from the interaction of doped holes with phonons and magnetic degrees of freedom. Magnetic fluctuations in LSNO above 240K do not have a structure in \( \mathbf{q} \)-space at the energy of the bond-stretching phonons but they are robust at low energies. [16]. Therefore dynamic charge fluctuations at low energies are pinned at \( \mathbf{q}, \alpha \) by domain boundaries of spin fluctuations and do not strongly interact with phonons. At high energies they extend to the zone boundary and damp the breathing modes. These observations point at a complex highly cooperative behavior between charge, spin, and lattice degrees of freedom.

Recent RIXS experiments showed considerable electronic charge character in cuprates associated with an analogous Cu-O bond stretching phonon [35], which softens with doping on approach to the zone boundary [19, 36, 37]. However in cuprates La\(_{2-x}\)Sr\(_x\)CuO\(_4\) or YBa\(_2\)Cu\(_2\)O\(_{6+x}\) breathing modes are not overdamped in any part of the phase diagram [37, 40]. In both cuprates and nickelates, holes reside primarily on the oxygen orbitals [41] but in the nickelates the Ni character of the doped holes [42], which tends to attract the surrounding O ions, is stronger than the Cu character in cuprates [43]. This difference enhances the breathing character of electron-phonon coupling in the nickelates and makes them more susceptible to small polaron formation as discussed below.

The theory of polarons was originally applied to lightly doped semiconductors with dilute carrier concentrations. Long-range interaction represented by the Fröhlich Hamiltonian leads to large polarons where dis-
tortions induced by a single electron or hole span many unit cells and a continuum approximation to the lattice can be made.

When charge density is high, classic large polarons, where charge carriers do not interact with each other, cannot form. However, in this case the combination of electron-phonon and electron-electron interactions may underlie correlated ordered or disordered states that localize charge degrees of freedom in a similar way. These states are sometimes called polaronic as in the case of the paramagnetic phase of the colossal magnetoresistance (CMR) manganites. In this context a large polaron necessarily involves many electrons interacting with each other and the atomic lattice. Localization occurs due to quasiperiodic cooperative modulations of electronic charge density locked to a deformation of the atomic lattice of the same wavevector. Such collective polarons are characterized by specific wavevectors, $q$, whereas polarons based on isolated electrons are characterized by $q=0$.

A number of theoretical models propose carrier localization via small polarons, which arise from short range interactions with the lattice and involve only a few unit cells or even just one unit cell. Due to their small size, small polarons based on isolated electrons or holes can form at high carrier densities.

In either case most of the electronic quasiparticle spectral weight is pushed below the Fermi surface and electrical conductivity is suppressed.

One may think that the Holstein Hamiltonian is most favorable to small polarons since it is already purely local: It is nonzero at the position of the electron and zero on neighboring sites. In fact as the interaction strength increases, the Holstein interaction has a much sharper transition into the strong-coupling regime necessary for polaron formation than the long range Fröhlich interaction. However, the breathing interaction involves volume contraction on a site accompanied with an anti-phase volume expansion on neighboring sites, i.e. the electron is attracted to the site it occupies while being repelled from surrounding sites. This interaction has a stronger on-site confinement than the Holstein interaction, which is zero on the neighbors. Indeed the transition into the strong-coupling regime with increasing coupling strength is even sharper for the breathing type coupling, implying that the formation of small polarons is most probable in the case of breathing interaction.

Based on our observations and these theoretical considerations we conjecture that small polarons form in the high temperature phase of LSNO. To prove it, angle resolved photoemission measurements (ARPES) in the high temperature phase should show that most of the electronic quasiparticle spectral weight is pushed below the Fermi level and has sidebands that correspond to the breathing phonons.

Coexistence of dynamic stripes and small polarons at high temperatures can explain why optical conductivity can be fit by the small polaron model only at low frequencies whereas the high energy part of the response is not reproduced. Slowly fluctuating dynamic stripes are essentially static on the energy scale (order of 0.5eV) under consideration and play a role of an impurity potential. It was shown that that the optical response of such trapped carriers significantly contributes only to the high frequency part of the optical conductivity leaving the low-energy response of small polarons almost intact.

Our results indicate that LSNO has many similarities to colossal magnetoresistance (CMR) manganese oxides. For example, La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) was reported to have overdamped zone boundary LO phonons in the high temperature paramagnetic phase. This material is a metallic ferromagnet at low temperatures but its electrical resistivity jumps dramatically above the Curie temperature where large Jan-Teller polarons characterized by short range charge/orbital order at the transverse wave vector $q=(1/4,1/4,0)$ also appear. Striking similarity in the breathing phonons between nickelates and manganites with very different low energy physics indicates that small polarons based on breathing LO modes may be generic in doped perovskite oxides and possibly other similar systems such as the photovoltaic perovskites.

Presence of strong electron-phonon interaction of the breathing type, which favors small polaron formation in many doped Mott insulators, may explain why they do not display metallic behavior. Copper oxides where where zone boundary LO phonons are not overdamped and small polarons do not form are a notable exception.

Theoretical treatment of correlated perovskites often ignores electron-phonon coupling, but we demonstrated that it is very strong for breathing Ni-O modes in the high temperature phase of LSNO. This interaction favors small polarons of the breathing type that would coexist with dynamic stripes and make the system more susceptible to correlations and localization. We hope our work will stimulate the inclusion of this interaction into theoretical models of materials with correlated electrons. Tuning it opens an additional way to control their electronic properties.

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