Dielectric signatures of lattice instabilities at 32K and 245K in La$_{2-y}$Sr$_y$MO$_{4+x}$

($M = Cu, Ni$) Cuprates and Nickelates

P. V. Parimi$^1$, N. Hakim$^1$, F. C. Chou$^2$, S. W. Cheong$^3$ and S. Sridhar$^1$

$^1$Physics Department, Northeastern University, 360 Huntington Avenue, Boston, MA 02115
$^2$Center for Material Science and Engineering, MIT, Cambridge, MA 02139
$^3$Physics Department, Rutgers University, Piscataway, NJ 08854

New dielectric transitions are observed at common temperatures 32K and 245K, in isostuctural La$_2$CuO$_{4+x}$ and La$_{5/3}$Sr$_{1/3}$NiO$_4$, that are signatures of local lattice (octahedral) instabilities. The present dielectric transitions reveal new aspects of the phase diagram of the perovskite cuprates and nickelates. They suggest that competition and coexistence of superconductivity with dielectricity occurs that is analogous to that between superconductivity and anti-ferromagnetism. These results also indicate that inhomogeneous electronic states, such as charge stripes and oxygen ordering, are strongly connected to underlying lattice instabilities.

The presence of intrinsic electronic inhomogeneities in La$_{2-y}$Sr$_y$MO$_4$ : $M = Cu, Ni$ (LSMO) is now becoming widely recognized [1,2]. Static stripe phases have been observed in La$_{2-y}$(Nd, Sr)$_y$CuO$_4$ [3], and in La$_{2-y}$Sr$_y$NiO$_4$ [6] with onset around 245K. Mechanisms suggested have been purely Coulombic (electron-electron) or magnetic in nature with a strictly 2D planar picture ignoring the involvement of lattice. In the La$_{2-y}$Sr$_y$CuO$_4$ and La$_{2-y}$Ba$_y$CuO$_4$ the global lattice transitions, such as LTO, Pcn, and LTT are well known to be associated with the tilts of the octahedra [3]. Phase separation into oxygen rich ($x > 0$) and poor ($x = 0$) regions around 245(±5)K and miscibility gap have been observed [3,2], leading to the coexistence of both superconductivity and antiferromagnetism in the phase separated regions, and formation of intercalated oxygen layers with staging. Significant jumps are seen in thermal expansion at $T_c$ in various HTS [3,4]. A correlation is observed between the lattice modes and electronic susceptibility in La$_{2-y}$Sr$_y$CuO$_4$ [3]. These results urge investigation of lattice-charge coupling and the resultant lattice-charge phase diagram similar to purely magnetic and structural phase diagrams that have been obtained from spin and lattice probes [10,17]. However, their sensitivity is limited for probing small displacements of atoms from centrosymmetric structures. The present work utilizes precision dielectric measurements, carried out using a highly sensitive superconducting (Nb) microwave cavity, which reveal signatures of subtle structural instabilities. The very high quality factor, $Q ≈ 10^8$, of the cavity makes this technique a powerful tool to investigate small displacements of atoms from centrosymmetric structure especially in non-magnetic insulators, where the polarization response dominates the spin response due to the high frequency, as has been evidenced by strong dielectric transitions in YBa$_2$Cu$_3$O$_{7−δ}$ [5].

High quality single crystals of La$_2$CuO$_{4+x}$ ($x = 0.0125, 0.0175$) [13] and La$_{5/3}$Sr$_{1/3}$NiO$_4$ [6] were prepared by the TSFZ method and have been well characterized by a variety of other techniques. The excess O concentration, $x$ in La$_2$CuO$_{4+x}$, was determined from dc magnetic SQUID susceptibility measurements and well-established relation between the Neel temperature $T_N$ and $x$. The sample is placed at the maximum of the microwave magnetic field $H_ω$ of the $TE_{011}$ mode resonant at 10GHz. The dielectric permittivity $\varepsilon(T) = \varepsilon^\prime(T) + i\varepsilon^\prime\prime(T)$ is determined from the measured parameters, shift in cavity resonant frequency $\delta f(T)$ and resonance width $\Delta f(T)$ [20]. In all the measurements $\varepsilon(T)$ is monitored as the sample is warmed slowly at the rate of 1.3K/min.

The microwave dielectric permittivity $\varepsilon_a(T)$ when the microwave magnetic field $H_ω || a$-axis of La$_2$CuO$_{4+0.0175}$ shows a clear transition at 32K and two additional features whose onset is at 100K and 245K (Fig. 1). Below these transition temperatures the change in $\varepsilon^\prime(T)$ is accompanied by loss peaks in $\varepsilon^\prime\prime(T)$. The 32K transition is marked by a rapid increase in both $\varepsilon^\prime(T)$ and $\varepsilon^\prime\prime(T)$ as the temperature is decreased and is strongly thermal history dependent. This transition is found to be dependent on the cooling rate and annealing time at maximum temperature, 294K suggesting a glassy nature. A very strong transition is observed in $\varepsilon(T)$ when the sample had been slowly cooled down from 294K to 4K in about 16 hours. However, rapid cooling of the sample from 294K to 4K
in 2hrs and subsequent measurement of \( \varepsilon(T) \) results in a weak transition. The strength of the transition is dependent upon the previous maximum warm-up temperature \( T_{\text{max}} \), thus this transition has features of thermal aging that are often characteristic of dielectric transitions. An additional feature has been observed at low \( T = 17K \), which is associated with incipient superconductivity in micro domains as indicated by dc SQUID magnetization measurement. This transition is suppressed when the sample is cooled rapidly.

Remarkably, \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) also shows two dielectric transitions for \( H_{\| a} \) in \( \varepsilon(T) \) at 32K and 245K as shown in Fig. 2. As in the case of \( \text{La}_{2}\text{CuO}_{4,0175} \) the 32K transition in \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) is suppressed when the sample is quenched, indicating thermal aging, while the remainder of the data is less sensitive to thermal history. It was also observed that the 32K transition is unaffected when the sample was annealed at and above 200K for several hours. This indicates that the phase formed between 200K and room temperature appears to be crucial in giving rise to the 32K transition.

The present data can be analyzed in terms of multiple dielectric modes, \( \varepsilon(T) = \varepsilon_{\alpha}(T) + \varepsilon_{\beta}(T) + \varepsilon_{\gamma}(T) + \ldots \), each of which is well described by a Debye relaxation form with respect to the temperature dependence

\[
\varepsilon(T) = \varepsilon_{\alpha} + \varepsilon_{\beta} + \ldots = \sum_{i=\alpha,\beta,\gamma} \frac{\varepsilon_{i0}(T)}{1 - i\omega \tau_i(T)},
\]

where \( \varepsilon_{i0}(T) \) are static dielectric functions and \( \tau_i(T) \) relaxation times for each mode.

In \( \text{La}_{2}\text{CuO}_{4,0175} \) three contributions can be identified. \( \varepsilon_{\alpha}(T) \) indicates the onset of a new dielectric mode which turns on below 32K. We describe this mode with parameters \( \varepsilon_{\alpha0}(T) = 900(1 - T/T_{\alpha0}) \) with \( T_{\alpha0} = 32K \) and \( \tau_{\alpha}(T) = 6.5 \times 10^{-9} \text{sec} \cdot \text{K}/T \). \( \varepsilon_{\alpha0}(T) \) is similar to an order parameter which grows below a transition. As \( T \) is lowered, \( \varepsilon_{\alpha}(T) \) increases initially due to gradual displacement of Oxygen from centrosymmetric position leading to growing polarization as described in the octahedra model latter. However below a characteristic temperature \( \varepsilon_{\alpha}(T) \) begins to decrease because the dipoles are no longer able to follow the microwave field. In \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) the 32K dielectric mode has a much weaker strength with \( \varepsilon_{\alpha0}(T) \sim 0.5(1 - T/T_{\alpha0}) \), and requires a highly sensitivity measurement such as the present microwave measurement. \( \varepsilon_{\beta}(T) \) of \( \text{La}_{2}\text{CuO}_{4,0175} \) associated with \( T_{\beta} = 245K \) transition is described by \( \varepsilon_{\beta0}(T) = 10(1 - T/T_{\beta}) \) with and \( \tau_{\beta}(T) = 1 \times 10^{-9} \text{sec} \cdot \text{K}/T \). \( \varepsilon_{\gamma}(T) \) which is dominant at higher \( T \) is described with a relaxation time \( \tau_{\gamma}(T) = 8 \times 10^{-13} \text{sec}^{-1} \exp(1000/T) \) characterized by an activation energy 1000K.

The present transitions are strikingly similar to the microwave dielectric transitions at 60K and 110K observed in insulating \( \text{YBa}_{2}\text{Cu}_{3}\text{O}_{6.0} \), whose dielectric permittivity is also well described by eqn. (1). These transitions were identified with lattice instabilities - change in buckling angle for 110K transition - that have been observed in many measurements, including ion channeling [2].

It is important to stress that all these materials are \( \text{ABO}_{3} \) type perovskites, which are well known to show strong dielectricity, notable examples being the ferroelectric \( \text{BaTiO}_{3} \) and the quantum paraelectric \( \text{SrTiO}_{3} \). The perovskites readily display a variety of competing structural instabilities that lead to different ferroelectric states [2]. In these materials it is well established that the dielectricity (ferroelectricity) ensues from the strong polarizability of oxygen ion in the presence of cations (\( \text{Ba, La, Sr, Ti, Cu} \ldots \)) and that the relevant dynamical and critical features are controlled by a limited number of parameters such as the effective coupling between the cation (\( Ti, Cu \)) and \( O \). The presence of dipolar modes in \( Y\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7-\delta} \) arising from coupling of the buckled \( Cu - O \) planes with electric-dipole \( Ba - O \) layers has been theoretically addressed by Shenoy, et al. [23].

The surprising commonality of the dielectric transitions in both \( \text{La}_{2}\text{CuO}_{4,0175} \) and \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) strongly suggests contributions from a common unit with a characteristic energy scale that in these isostructural units is the \( \text{MO}_{6} \) octahedron. Such a description finds strong theoretical support from the work by Thomas [24], where it was shown that the dielectric response of \( \text{ABO}_{3} \) type perovskites was describable in terms of individual \( \text{BO}_{6} \) octahedra. The dielectric function of the present crystals is high and could arise from an induced dipole moment extended over a cation-anion bond distance, in this case \( M - O \) bond distance. Electron covalency between a cation and anion induces a large dipole moment [25] which originates from the charge transfer between the anion and cation sites. In the \( \text{La}_{2}\text{MO}_{4+x} \) and \( \text{La}_{2-x}\text{Sr}_{x}\text{MO}_{4} \) the \( \text{MO}_{6} \) octahedra are further coupled both electronically and vibrationally, and form arrays of weakly coupled rigid units. There are a certain number of very low frequency vibrational modes (or rigid unit modes, RUMs ) of these units which do not distort the units but flex the coupling between them. These RUMs are natural candidates for the soft modes that typically drive displacive dielectric phase transitions [24]. Since the large inter layer strains between the \( \text{MO}_{2} \) and \( \text{LaO} \) planes [27] can be relieved by tilting of the \( \text{MO}_{6} \) octahedra or correlated ferrodistortive buckling of \( \text{MO}_{2} \) plane with displacement of \( O \) atoms in the plane we attribute the 32K and 245K transitions to the onset of such a long wavelength, near- ferrodistortive distortion. These displacements would result in a change in bond lengths and thereby a change in effective \( \varepsilon(T) \).

The suppression of \( \varepsilon_{\alpha}(T) \) in the quenched samples of \( \text{La}_{2}\text{CuO}_{4,0175} \) and \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) is a manifestation of competition between order and disorder. In the well annealed, slow cooled \( \text{La}_{2}\text{CuO}_{4,0175} \) the excess oxygen forms intercalated layers as shown in Fig. 3a and in \( \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_{4} \) the holes form charge ordered stripes. However, rapid cooling does not result in ordering but highly disordered oxygen as shown in Fig 3b. An in-
tercalated oxygen atom displaces the apical oxygens and thereby leads to the distortion and tilt of the octahedra. In the ordered state the majority of octahedra chains are unperturbed by the excess-oxygen which leads to a strong transition. However in the disordered state since the excess O are randomly distributed above or below the octahedra plane as interstitial impurities they will have a bearing on the entire plane. Consequently in the Debye model for the disordered state $\varepsilon_\alpha(T)$ is well described by $\varepsilon_\alpha(T) = 100(1 - (T/T_{d\alpha})$ (solid line Fig.1) with $T_{d\alpha}(T)$ being same as that of the ordered state for this mode. The role of disorder in suppressing the 32K transition is evidenced in the measurement on flux grown crystals of La$_2$CuO$_4$ (not shown) where our 10GHz dielectric data shows suppression of the 32K transition, consistent with earlier dielectric measurements [28,29].

In the case of La$_{5/3}$Sr$_{1/3}$NiO$_4$ suppression of $\varepsilon_\alpha(T)$ indicates that high temperature ($ > 245K$ ) annealing determines the strength of transition at 32K. We further argue that charge ordering per se has a driving lattice component in it because purely electronic states are not expected to be dependent on thermal annealing. We believe that quench disorder (rapid cooling) would lead to a change in the structure of charge stripe formation which would affect the tilts of octahedra at 32K resulting in a weak dielectric transition.

Another temperature scale that is common to La$_2$CuO$_{4+x}$ and La$_{5/3}$Sr$_{1/3}$NiO$_4$ is around 245K (see Figs.1 & 2). The 245K transition in $\bar{\varepsilon}(T)$ of La$_2$CuO$_{4+x}$ is attributed to oxygen ordering observed in neutron diffraction measurements by Tranquada, et. al. [6]. In La$_{2-x}$Sr$_x$NiO$_4$, a detailed elastic neutron diffraction study has demonstrated charge ordering around $T_{c\text{CO}} = 245K$ into domain walls or stripes [28]. In the dielectric response this leads to the onset of a dielectric mode associated with the stripe formation (see Fig.2). In both these materials we can associate a dielectric mode $\bar{\varepsilon}_\beta(\omega,T)$ with the 245K feature. That Oxygen ordering and charge ordering take place at the same temperature in LCO and LSNO is now understandable since it is the underlying lattice instability, observed here as a dielectric transition at 245K, that drives these transitions in these two isostructural compounds.

Observation of the 32K dielectric transition and its relation to the MO$_6$ octahedra modes also explains the origin of anomalies at this temperature in NQR, thermal expansion and specific heat. Thermal expansion measurements [14] reveal changes at 32K and 36K in the coefficient of thermal expansion indicating lattice changes. Migliori et al. [28] have observed a feature with onset at 32K in the specific heat of La$_2$CuO$_4$. NQR measurements [37] reveal a change in the $^{139}$La spin-lattice relaxation rate and spin-spin dephasing rate between 30K and 38K [3]. Anelastic measurements revealed softening of La$_2$CuO$_4$ lattice with onset around 32K [29]. Recently, Takao, et. al. [22] observed a change in sound velocity at 36K in La$_2$CuO$_{4,05}$ which is found to be present even after suppression of superconductivity by magnetic field. While all these measurements indicate a structural change at 32K (and 36K) our microwave dielectric measurements connect these changes to the instability of the octahedra. The MO$_6$ octahedron is strongly coupled to the La nuclear moment through an orbital hybridization mediated by apical oxygen [3]. Therefore, the subtle tilt/distortion of the octahedra directly affects the $^{139}$La spin-lattice relaxation rate. Thus our microwave measurements indicate that dipolar-phonon mediated mechanisms are important and play a significant role in inducing many electronic transitions in these materials.

The coexistence of , and competition between dielectricity and superconductivity is clearly evident in the result obtained on a single crystal La$_2$CuO$_{4,0125}$, for $H_{\text{mew}} || a$ a dielectric transition is observed at 31K followed by onset of superconductivity at 27K (inset Fig. 1b). This observation coupled with the results on $x = 0.0175$ crystal (Fig. 1) suggests that the dielectric and superconducting transitions are independent of each other, and when the crystal superconducts the dielectric response is overshadowed below $T_c$. Its important to note that the competition between ferroelectricity and superconductivity is well-known in the A-15 compounds, and its possible relevance to perovskite oxides was noted shortly after the discovery of high temperature superconductivity [3].

The importance of the present results is emphasized in a new phase diagram (Fig. 4) constructed from the present microwave observations and other results reported earlier on LMO and LSMO, which together reveal unambiguously new structural instabilities at 32K and 245(±5)K. The structural instability at 245(±5)K leads to charge ordering in the case of LSNO and oxygen ordering in the case of LCO. The fact that these compositions have different hole doping suggests that these transitions are purely structure dependent and almost independent of hole doping in the low doping regime. In contrast the magnetic ($T_N$) and superconducting transitions ($T_c$) are well-known to be doping dependent. It is important to note a striking similarity of the present transitions in LSCO and LSNO to multiple temperature scales observed in ion channeling measurements on YBa$_2$Cu$_3$O$_{7-\delta}$ [21]. The present observation of signatures of octahedra instability at common temperatures in both underdoped (no stripes) and doped (presence of stripes) regimes confirms that charge stripes and oxygen ordering are coupled to the underlying lattice instabilities rather than resulting purely from magnetic or electronic interactions. There are a few other temperatures where lattice anomalies were reported previously [14]. However, not all the lattice instabilities would effect the octahedra (RUMs) and correspondingly have dielectric signatures. In the phase diagram we emphasized only those results that show anomalies at 32K and 245K and are related to the present dielectric transitions. The present dielectric transitions at common temperatures underscore the importance of subtle local structural instabilities that result in dramatic changes in the electronic properties of
perovskite oxides.

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FIG. 1. Microwave (10GHz) dielectric constant $\varepsilon'(T)$ and $\varepsilon''(T)$ of $La_2CuO_4.0125$. Note the onset of dielectric modes at $T_{d\alpha} = 32K$ and $T_{d\beta} = 245K$, and the difference in the strength of dielectric function between slow cooling and rapid cooling. Solid lines are fits to Debye relaxation form. Inset (bottom panel) shows the $T_{d\alpha}$ transition in $La_2CuO_4.0125$.

FIG. 2. Microwave (10GHz) dielectric constant $\varepsilon'(T)$ and $\varepsilon''(T)$ of $La_{2-x}Sr_xNiO_4$ (top panel). Inset (top panel) shows suppression of 32K mode in the quenched sample. Note that the dielectric modes at 32K and 245K are present in both LCO and LSNO (bottom panel).

FIG. 3. Schematic diagram of intercalated oxygen ordered (a) and disordered (b) lattice showing cross section of the rigid units of $MO_6$ (shaded squares) that lie in a plane. M occupies center of each shaded square and O at its center. Dashed square represents $MO_2$ plane of one unit cell. Solid circles represent excess oxygen that lie below and above the $MO_6$. The tilt pattern of the octahedra determines $\varepsilon(T)$. The distortion of the octahedra tilt pattern in the disordered phase explains the suppression of 32K mode in quenched samples.

FIG. 4. Phase diagram of LMO and LSMO. Two temperature scales 32K and 245K are found which are characteristic of these isostructural systems. Note that these two temperature scales are independent of (small) hole doping. Solid diamonds represent present microwave dielectric transitions. Several other experimental results also reveal anomalies at 32K and 245K including neutron diffraction $\bullet$ [8], sound velocity $\Diamond$ [32], thermal expansion $\circ$ [14], NMR triangle [4], thermoelectric power solid square [5], resistivity, dc magnetization square [34], and thermal expansion solid triangle [14]. The dashed lines representing $T_{\alpha}$ and $T_{\beta}$ are for $La_{2-y}Sr_yCuO_{4+y}$ system.
$\varepsilon'(T), \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$

$T_{d\alpha} = 32\text{K}$

$T_{d\beta} = 245$

slow cooled

quenched

$\varepsilon'(T), \text{La}_2\text{CuO}_{4.0175}$

$\varepsilon'(T), \text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$
