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Optical conductivity of $LaNiO_3$: Coherent transport and correlation driven mass enhancement

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We report optical conductivity measurements of low resistivity $LaNiO_3$ thin films grown on $LaAlO_3$, $(LaAlO_3)_{0.3}$ $(Sr_2AlTaO_6)_{0.7}$, and $DyScO_3$ substrates, providing coherent compressive or tensile strain. The optical conductivity was measured by infrared reflectance and transmittance up to 3 eV and extrapolates well to the measured dc values. An unambiguous Drude response is clearly distinguishable from broad interband absorption extending beyond 3 eV. The measured spectral weight of the Drude response is substantially less than predicted by band theory, indicating an enhancement of the transport mass compared to the band mass by a strain-dependent factor of 2.5–5, characteristic of a strongly correlated metal.

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I. INTRODUCTION

$LaNiO_3$ is the only member of the rare-earth nickel oxide series, $RNiO_3(R=La,Pr,Nd,\ldots)$, which does not undergo a correlation-driven metal-insulator transition.[1,2] Its apparent proximity to a metal-insulator phase boundary makes it important to establish the strength of electron correlations in this material. In previous work, strong electron correlations were inferred from enhanced heat capacity and magnetic susceptibility, from a significant quadratic temperature dependence of the resistivity[3–5] and from photoemission[6] and electron spectroscopy.[7] Optical conductivity provides an important alternative measure of correlation-induced mass enhancement in terms of the ratio of the integrated intensity in the low-frequency "Drude" absorption peak to the prediction of single-electron band theory. The existing literature reports that $LaNiO_3$ exhibits a very incoherent optical response incompatible with conventional correlated-metal behavior. These data have been interpreted in terms of polaronic transport.[8] The present study is enabled by the recent successful growth of coherently strained, near stoichiometric single-crystal thin films of $LaNiO_3$ with lower resistivities than have previously been reported.[9] We find that the optical conductivity of these films is characterized by a coherent Drude low-frequency response consistent with the presence of metallic carriers with a renormalized mass. We estimate the mass renormalization by comparison to model calculations, finding reasonable agreement with previous thermodynamic, transport, and photoemission measurements.

$LaNiO_3$ has a $3d^7$ electron configuration with t_{2g}-e_g splitting due to the octahedrally coordinated oxygen surrounding each Ni site. The lower energy t_{2g} bands are completely filled and there is one electron in the two e_g bands, degenerate at $\mathbf{k}=0$ in unstrained material. The metal-insulator transition in the $RNiO_3$ series correlates with the ionic radius of R, which determines the magnitude of orthorhombic distortion and deviation of the Ni-O-Ni bond angle from 180°.[2] Epitaxial thin films may provide new approaches to control the Mott physics through bandwidth and band-filling control: in $LaNiO_3$, the strain induced by lattice mismatch is accommodated by further distortion of the bond lengths and angles[10] and electrostatic gating has been shown to alter transport.[11] The proximity to the metal-insulator transition suggests that a small change in the electron hopping due to strain could have a strong effect on the transport, similar to what is seen in other correlated oxides.[12–14] Here, we investigate the influence of strain on the strength of electron correlations in $LaNiO_3$ by comparing the optical conductivities of films grown coherently strained to several different substrates.

II. EXPERIMENTAL

Single-crystalline thin films of $LaNiO_3$ were grown epitaxially on rhombohedral $LaAlO_3$, cubic $(LaAlO_3)_{0.3}$ $(Sr_2AlTaO_6)_{0.7}$ (LSAT), and orthorhombic $DyScO_3$ substrates by rf magnetron sputtering. The lattice mismatches with $LaNiO_3$ are −1.1% (compressive strain), 0.6%, and 2.9%, respectively. Films as thick as 30 nm on $LaAlO_3$ and LSAT and 10 nm on $DyScO_3$ were shown to be coherently strained by x-ray diffraction with the out-of-plane lattice parameter adjusting to accommodate the in-plane strain; continuous films as thin as 2 nm have also been grown. The growth conditions were optimized to minimize the film resistivity, indicating good oxygen stoichiometry.[15] Details of the growth, resistivity, and film structure are described elsewhere.[9]

Optical conductivity measurements were carried out in a Bruker 66v/S Fourier transform infrared (FTIR) spectrometer in near normal reflectance (~13°) and normal transmittance geometries with photon energies from 3 meV to 3 eV. Measurements were referenced to Au and Ag mirrors. A sliding backside clamping sample holder allowed repeatable sample changing while the spectrometer was under vacuum with minimal alignment variation. The throughput of the spectrometer was adjusted to avoid detector nonlinearity. Various sources, beamsplitters, and detectors were used to cover the entire spectral range with the small amount of disagreement in overlapping regions used as an estimate of sys-

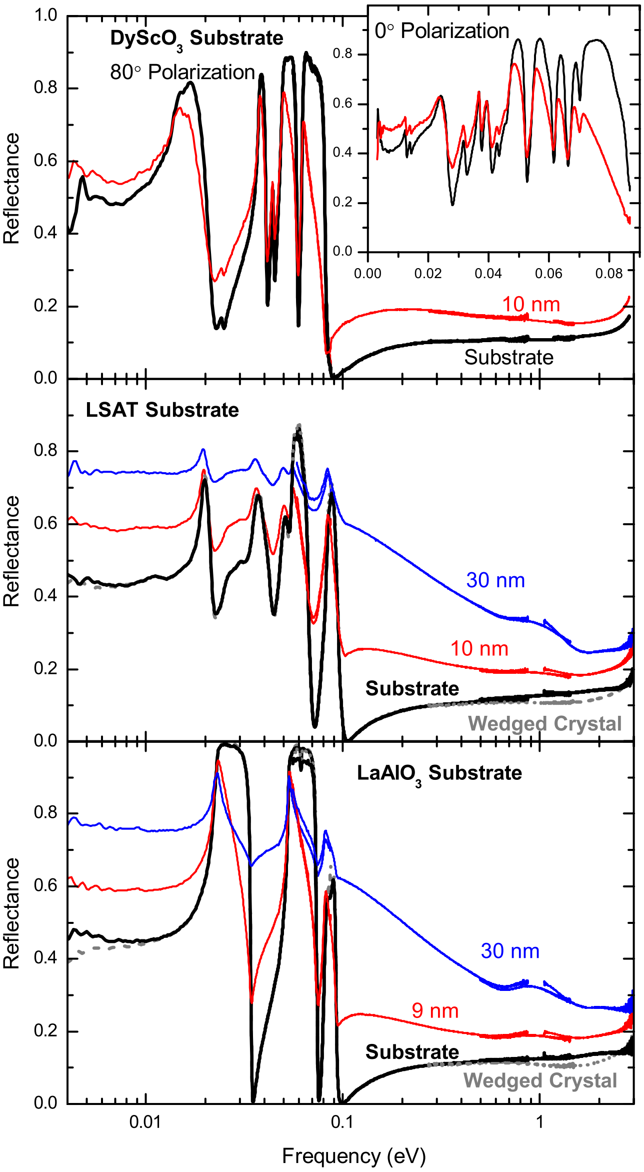

FIG. 1. (Color online) Reflectance spectra for thin films and bare substrates. The overlap between the various spectral ranges of the FTIR is shown. The two-side polished $LaAlO_3$ and LSAT substrates are compared to wedged crystals of the same material to expose sensitivity to the reflectance from the backside of the samples. The polarization angles are referenced to the [001] direction of the (110) oriented $DyScO_3$ substrates, in orthorhombic notation.

tematic errors. All measurements were made at 295 K.

For all $LaNiO_3$ films and frequencies studied here, the penetration depth of radiation is larger than the thickness of the film and thus the substrates have a profound effect on the infrared reflectance and transmittance. This is clearly seen in the reflectivity spectra shown in Fig. 1, where the strong optical phonon features of the substrate influence the reflectivity of the thin-film samples. Whenever the penetration depth in the film is much greater than the thickness of the film, the reflectivity and transmittance depend only on the sheet conductance of the film and the substrate dielectric function. The film may then be modeled as a two-dimensional conductance on the surface of the substrate; application of electrostatic boundary condition give the complex reflectivity r as

$$r = \frac{\epsilon^{1/2} + g/Y_0 - 1}{\epsilon^{1/2} + g/Y_0 + 1}, \tag{1}$$

where ϵ is the dielectric function of the substrate, g is the (complex) sheet conductance of the film, and $Y_0 = 1/(376.7\ \Omega)$ is the wave admittance of free space. We refer to this as the "thin-film approximation." In the limit that the penetration depth is much greater than the film thickness, the measured quantity $|r|^2$ given by Eq. (1) is in exact agreement with the full electrostatic solution of the vacuum-film-substrate interfaces. This limit is applicable for most of the data as the penetration depth is never less than ~60 nm and is much greater at the middle to far-infrared frequencies where the $LaNiO_3$ Drude peak is observed. A key advantage to using this approximation is that by treating the problem as a single interface, the Kramers Kronig (KK) relations for the phase shift at reflection are applicable.[16] To extract the film conductivity from Eq. (1), the dielectric functions of the substrates were first obtained from the KK transformed reflectivity of the bare substrates.

For frequencies above 0.1 eV the substrates were sufficiently transparent to allow transmittance measurements. Using reflectivity and transmittance together, the film optical conductivity was obtained above 0.1 eV without use of the KK transformation or the thin-film approximation. This was accomplished by exact numerical solution of the boundary conditions at the vacuum-film and film-air interfaces, considering the wave propagation in the film. This result is in good agreement with the conductivity obtained from the KK transformed reflectivity [Fig. 2(a)], except for the 30-nm-thick films above 2 eV, where the thin-film approximation is no longer valid. In regions where the substrate is transparent, we accounted for the small systematic error due to the reflectivity of the backsides of the samples; wedged crystals of $LaAlO_3$ and LSAT whose backsides did not contribute to the measurement were used as a reference. This procedure was not necessary for the $DyScO_3$ substrates since they were less transparent and had unpolished backsides.

Below the lowest frequency phonon mode, the $LaAlO_3$ and LSAT substrates are characterized by slowly varying polarization insensitive dielectric functions, providing accurate data and straightforward extrapolation of the film conductivity to dc. The dc extrapolation is in good agreement with dc measurements of the same films obtained by the Van der Pauw method (Fig. 2). The extrapolation and low-frequency measurement were more difficult with the $DyScO_3$ substrate, owing to a strongly anisotropic phonon spectrum with a large number of modes. A data point at 1 meV, obtained using the Fabry-Perot resonance of the $DyScO_3$ substrate, was consistent with dc. The sample on the $DyScO_3$ substrate was measured with polarized radiation for frequencies below 0.5 eV to account for the anisotropy and to execute an accurate KK analysis.[17] The low sheet conductance of this film and a strong substrate phonon spectrum prohibited a clean extraction of the optical conductivity between 0.01 and 0.1 eV for

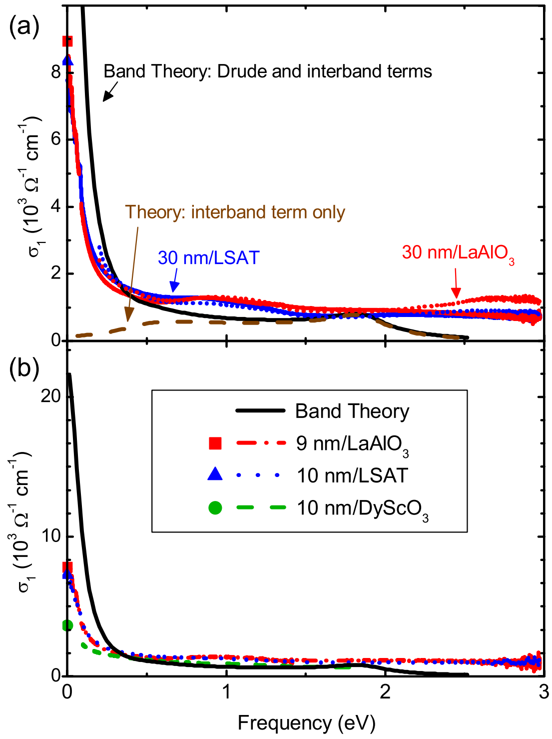

FIG. 2. (Color online) Measured and calculated optical conductivity spectra, with substrates indicated. The data points at zero show dc electrical measurements. (a) Comparison of the real part of the optical conductivity of 30 nm films obtained from KK transformed reflectivity (solid lines) with that from reflectivity and transmittance together (dotted lines). (b) Conductivity of the 10 nm films obtained from the reflectivity. The optical conductivities of the 30 nm (a) and 9–10 nm (b) films agree well.

this sample but our observation of the Drude response was not compromised.

III. RESULTS

The measured optical conductivity spectra shown in Fig. 2 exhibit a clear Drude response emerging at low frequency from the broad high-frequency absorption. The half width of the coherent response is about 90 meV for films on LaAlO$_3$ and LSAT and somewhat greater on the DyScO$_3$ substrate. No systematic differences in the optical conductivity were observed between the 9–10 and the 30 nm films on LaAlO$_3$ and LSAT, indicating that the measurement is dominated by bulk conduction which is largely independent of distance from the surface or interface. Above $\sim$0.4 eV the conductivity spectra of films on the three substrates are very similar; however, the spectral weight in the Drude response of the film on DyScO$_3$ is less than that of the other films. It is clear from these measurements that experimentally distinguishing the coherent response requires samples with resistivity lower than 10^3 $\mu\Omega$ cm and low scattering rate, perhaps accounting for the difference between previous optical data and those presented here.

IV. ANALYSIS

To interpret the data we turn to LDA band-theory calculations,[18] which predict that LaNiO$_3$ is a metal with near Fermi surface states derived from antibonding combinations of Ni e_g and O $2p_\sigma$ states. We have fit the low-lying part of the band structure to a two-band tight-binding model characterized by nearest-neighbor t and second-neighbor t' hopping parameters. Standard gauge-invariance arguments determine the optical matrix elements in terms of the hopping parameters. From these we calculate the conductivity using a frequency-independent scattering rate chosen for definiteness to match the width of the coherent response measured on LaAlO$_3$ and LSAT substrates. It is, however, important to note that the gauge-invariance arguments apply strictly only to the coherent $\omega=0$ part of the optical absorption. As the frequency is increased, changes in matrix elements may occur and interband transitions involving bands not contained in the tight-binding model may become important. Thus, we make a quantitative comparison only for the calculated and measured Drude response and not for the interband absorption. Our fits to the band structure yield $t=0.63$ eV and $t'/t=0.11$. This t'/t is about three times smaller than the value 0.3 extracted by analyzing photoemission[6] and transport[9] data, however, the calculated Drude weight changes very little as t'/t is varied from 0.1 to 0.3 (the e_g-e_g interband transitions are more sensitive). It is also important to note that the band parameters are sensitive to the Ni-Ni distance and to the Ni-O-Ni bond angle. These issues introduce uncertainties at the level of 15% in our calculation of the Drude spectral weight.

Comparison of the band-theory prediction with the measurement at low frequencies (Fig. 2) indicates a significant reduction in the spectral weight in the coherent peak. The absorption above 1 eV, which appears to be dominated by interband transitions, is in rough agreement with earlier work,[19–22] but the measured conductivity is somewhat greater than the calculated spectrum. The latter difference may be due to a combination of interband transitions from the Ni t_{2g}/O antibonding complex present in band theory[18,23] but not included in the tight-binding model and to redistribution of weight from the coherent part by many-body interactions. However, the differences between calculation and data in this higher frequency range are not relevant to the comparison of the Drude weight.

The coherent spectral weight is quantified in Fig. 3(a), where we show the integrated conductivities defined as

$$f(\hbar\omega) = \frac{2\hbar a}{\pi e^2}\int_0^{\hbar\omega} \sigma_1(\hbar\omega')d(\hbar\omega'), \qquad (2)$$

where the prefactors serve to normalize the conductivity to the conductance quantum $e^2/\hbar = 1/(4100\ \Omega)$ and the LaNiO$_3$ lattice constant $a=3.9$ Å so that f has dimension of energy. Integrating only the coherent part gives the kinetic energy associated with free carrier motion, which may be expressed in terms of the carrier density n and carrier mass m as $\hbar^2 na/m$. The kinetic energy predicted by band theory is 0.29 eV. For reference, assuming one free electron per Ni and taking the mass to be the electron mass would give 0.50 eV; this difference is a single-electron band-structure effect. The integrated Drude part of the experimental conductivity is substantially less the predictions of the single-electron band

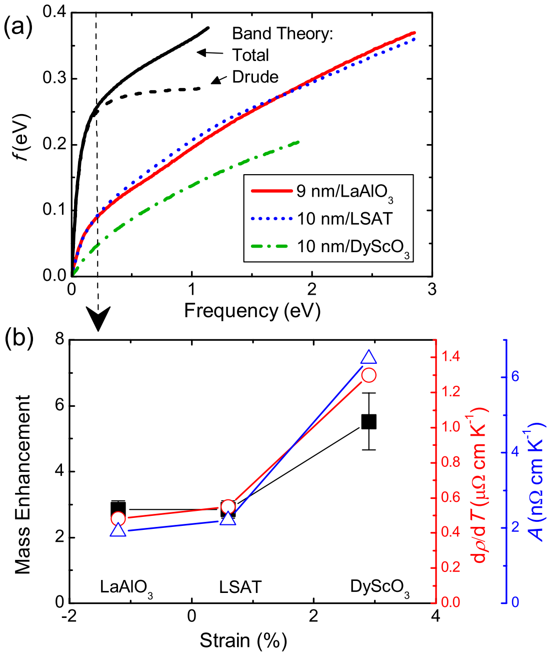

FIG. 3. (Color online) (a) The integrated optical conductivity is compared to the prediction of band theory. (b) The mass enhancement obtained from the Drude spectral weight reduction (filled squares, black online, left axis) is compared to the temperature dependence of the resistivity by Son *et al.* (Ref. 9) (open symbols, right axis): the slope at near room temperature (circles, red online) and the quadratic coefficient at low temperature (triangles, blue online). Error bars represent the uncertainty in separating the measured coherent peak from the broad absorption.

theory and we attribute this lost spectral weight to a correlation-driven mass enhancement, noting that much of it has been transferred to frequencies beyond those studied here. The mass enhancement has been quantified by integrating to a cutoff frequency of 0.2 eV corresponding to the change in frequency dependence visible in Fig. 3(a), where most of the coherent peak is included and the interband transitions are still relatively weak. The precise choice of cutoff frequency does not have a large influence on the value of the mass obtained on the LaAlO$_3$ and LSAT substrates; however, on DyScO$_3$, separation of the coherent peak from the broad absorption is less certain.

In Fig. 3(b), the strain dependence of the mass enhancement is compared to transport measurements of similar films measured by Son *et al.*[9] Near room temperature, the resistivity increased approximately linearly with temperature and its slope $d\rho/dT$ was assumed to scale with m/n; at low temperatures the resistivity is of the form $\rho=\rho_0+AT^2$ with the coefficient A providing a measure of the strength of electron correlations. All three parameters are seen to scale similarly with strain, consistent with a narrowing of strongly correlated Ni e_g bands. This is in agreement with the effect of pressure in bulk PrNiO$_3$, where compression induces the metallic state,[24] but is in contrast to the bulk RNiO$_3$ phase diagram,[2] where the smaller lattice constant leads to the insulating state. The mass enhancement obtained here is similar to the value of 3.3 obtained by photoemission measurements[6] of films on SrTiO$_3$ substrates (whose lattice mismatch with LaNiO$_3$ is between that of LSAT and DyScO$_3$) or to the value of 2 or 3 from comparison of magnetic susceptibility[3,18] of bulk samples to the same band theory.

V. CONCLUSIONS

We have measured the optical conductivity of epitaxial, near stoichiometric, coherently strained thin films of LaNiO$_3$ from 0.0 eV (dc) to 3 eV. Relatively low extrinsic scattering allows a clear separation of the Drude response from interband absorption. A tight-binding model of the band structure partially accounts for the interband absorption; comparison of the calculated and measured coherent Drude response indicates a 2.5–5 fold enhancement of the transport mass, characteristic of strong electron correlations. The enhancement is largest in the LaNiO$_3$ film on DyScO$_3$, which suffers the largest tensile strain, consistent with other transport measures of the carrier mass. Although further work is needed to identify the structural mechanism by which strain influences transport in the Ni e_g bands, these results suggest that epitaxial strain may provide a route to bandwidth control of the correlated electron phenomena in the RNiO$_3$ series.

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[16] The KK relations do not strictly apply to layered structures because of singularities at the Fabry-Perot resonances. It should be noted for completeness that for a conducting film of finite thickness, the phase angle calculated from the KK relations may no longer be interpreted physically as the actual phase shift of the reflected wave. Regardless, whenever the thin-film approximation is valid, the phase angle given by the KK relations leads to the correct value of the sheet conductance according to Eq. (1). This is because whenever the penetration depth is much greater than the film thickness, the measured reflectivity is identical to if the film was indeed infinitesimally thin and is easily verified numerically.

[17] We note that strictly speaking, KK relations cannot be applied to rhombohedral symmetry dielectrics without consideration of off-diagonal elements in the dielectric tensor (Ref. 25). We neglect this here because the small magnitude of the rhombohedral distortion in $\mathrm{DyCsO_3}$ means that the contribution of any off-diagonal terms is expected to be less than the effects arising from non-normal incidence and low sheet conductance.

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