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Effect of growth temperature on the terahertz-frequency conductivity of the epitaxial transparent conducting spinel NiCo$_2$O$_4$ films

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We have measured the terahertz-frequency optical conductivity of the epitaxial inverse spinel NiCo$_2$O$_4$ films grown at different temperatures. The low-temperature-grown film exhibits a metallic behavior with ferrimagnetic ordering, while the high-temperature-grown film shows greatly suppressed magnetization and insulating behavior. Both films exhibit band-like coherent conduction at intermediate temperatures, albeit with very different carrier densities consistent with the proposed models of cation valencies in this mixed-valence material. Both films also display a crossover to incoherent transport at low temperatures, indicating a disorder-induced tendency toward localization. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4821548]

I. INTRODUCTION

Transition metal oxides exhibit a variety of fascinating and useful magnetic, electronic, and optical properties. While the oxides with perovskite structure traditionally attract most attention, spinel structure oxides have a long history of research of their own, with the most prominent example being the Verwey transition in magnetite.$^1$ More recently, magnetic spinel ferrites NiFe$_2$O$_4$ and CoFe$_2$O$_4$ have been investigated for spin filtering applications in spintronics.$^2$–$^5$ The inverse spinel nickel cobaltate NiCo$_2$O$_4$ (NCO) is extensively used and studied as electrode material for oxygen reduction$^6$, $^7$ and as a conducting oxide with infrared transparency$^8$–$^10$ for sensors and flat panel displays. The magnetic structure of NCO has long been known$^{11}$, $^{12}$ as ferrimagnetic with a Curie temperature $T_C \approx 400^\circ$C. The most common synthesis routes for the spinel rely on sol-gel and thermal decomposition methods$^7$, $^{13}$ that produce polycrystalline particulate samples with a rather low packing density and a low degree of sintering, which makes it difficult to characterize the material’s intrinsic transport properties.$^{12}$ In our previous work, we reported the synthesis of epitaxial films of NCO on spinel MgAl$_2$O$_4$ substrate at growth temperatures varying from 200°C to 600°C using pulsed laser deposition.$^{14}$ The low-temperature grown films (200°C-450°C) are magnetic and metallic with the lowest resistivity of 0.8 m$\Omega$cm, while the films grown at high-temperature (450°C-600°C) are insulating and non-magnetic. A recent polarized Raman spectroscopy study$^5$, $^{15}$ found that the high-temperature-grown films have the cation distribution that is close to the ideal inverse spinel $\text{Co}^{2+}[\text{Co}^{3+}\text{Ni}^{3+}]\text{O}_4^{2-}$, where the cations in the square brackets reside in the octahedral (B) sites. By contrast, the low-temperature-grown films display a mixed cation distribution with a diffusion of Ni cations into the tetrahedral (A) sites.

The $\text{AB}_2\text{O}_4$ spinel crystal structure is formed from the face-centered cubic lattice of $\text{O}^{2-}$ ions that allows 32 octahedral and 64 tetrahedral sites for transition metal cations. In a normal
spinel, the A cations occupy one eighth of the tetrahedral sites and the B cations occupy one half of the octahedral sites, with A cations typically found in the $2^+$ oxidation state and the B cations in the $3^+$ oxidation state. In the inverse spinel NCO, the Ni ions are mostly contained to the octahedral B sites and the Co ions are equally distributed between the octahedral B and tetrahedral A sites. The oxidation states of the cations in NCO have been the subject of much research and differing scenarios have been proposed\textsuperscript{7,12,13,16,17} that cover the range $0 \leq x \leq 1$ in the formula $\text{Co}^{2+}\text{Co}^{3+}[\text{Co}^{3+}\text{Ni}^{2+}\text{Ni}^{3+}]\text{O}_4$. Marco et al.\textsuperscript{7} and Battle et al.\textsuperscript{12} also reported a small occupation of A sites by Ni cations (up to 10%). The reported magnetization values fall in the 1.25-1.52 $\mu_B$/fu range in 0.8 T field, which also agrees with the magnetization measurements on epitaxial low-temperature-grown NCO films reported in our previous work.\textsuperscript{14} An intriguing feature of the NCO magnetic properties is the lack of magnetization saturation in fields up to 1.1 T,\textsuperscript{7,14,16,18} which was explained by the field-dependent charge distribution between the octahedral Ni and Co cations. The p-type thermally activated conductivity was observed in the recent work of Windisch et al. on sputtered NCO films,\textsuperscript{8–10} while the descriptions of Battle\textsuperscript{12} and Marco\textsuperscript{7} suggest the possibility of metallic band-like p-type transport in NCO.

In this article, we use terahertz time-domain spectroscopy (THz-TDS) to determine the character of electronic transport in two NCO films grown at 300°C and 500°C, which we label NCO300 and NCO500. The NCO300 film undergoes a metal-insulator transition (MIT, $T_{MIT} = 300$K) and ferrimagnetic ordering at the same temperature ($T_C = 300$K). The NCO500 film possesses a much higher resistivity than NCO300 at room temperature and shows neither a metallic behavior in DC transport nor any appreciable magnetism.\textsuperscript{15} In spite of the significant differences in resistivity and magnetic properties between the two films, we find a remarkable similarity in the character of transport in the two films - both films show band-like coherent transport at intermediate temperatures (70-300 K). By contrast, previous studies of NCO reported p-type thermally-activated hopping conductivity, most likely due to the polycrystallinity of the samples they used.\textsuperscript{8–10} The present spectroscopic confirmation of the band-like transport is significant for the prospective applications of NCO as a transparent conducting oxide and further optimization of its functionality. The band-like conduction in NCO500 happens with a much lower carrier density, which we attribute to the different cation distributions in the two films: the more perfect inverse spinel structure in the NCO500 film provides a much lower level of carrier doping. In both NCO300 and NCO500 films, we find a crossover from coherent to incoherent transport below $\sim$70 K, which indicates the tendency of carriers toward localization. We suggest that this tendency results from disorder-induced localization effects,\textsuperscript{19} reminiscent of the localization tendencies found in magnetoresistive manganites\textsuperscript{20–24} and in Zn-doped cuprates.\textsuperscript{25}

II. EXPERIMENTAL DETAILS AND RESULTS

A. Experimental methods

The NCO samples used in this study are 300 nm epitaxial thin films on spinel MgAl$_2$O$_4$(001) substrates grown by pulsed laser deposition at substrate temperatures of 300°C and 500°C and 50 mT O$_2$ pressure inside the chamber. The thicknesses of the films were estimated from the thickness calculated from X-ray reflectivity scans on a set of thinner NCO films. The structural properties were analyzed using four-circle high resolution X-ray diffraction. The lattice constant along the c axis calculated from the vertical position of the (226) peak in reciprocal space mapping (RSM) scans for the NCO500 films is 8.50 Å, which is comparatively larger than 8.17 Å of the NCO300 film and than the bulk value (8.116 Å). Both films are fully strained and have same in-plane lattice constant (calculated from the horizontal (226) RSM peak position) as the MgAl$_2$O$_4$ substrate (8.083 Å). The full width at half maxima of the (004) peaks are 0.008° (NCO300) and 0.02° (NCO500), indicating the good crystalline quality of the films. The measurement of magnetic properties using a superconducting quantum interference device magnetometer and the resistivity measurement using a standard 4-probe method reported earlier showed ferrimagnetic behavior accompanied by metallicity for NCO300, while the NCO500 film showed insulating behavior with reduced magnetic moment.\textsuperscript{14} Hall resistivity measured with the magnetic field applied in a direction perpendicular to the film surface showed p-type conductivity.
THz-TDS was performed using a home-built spectrometer based on a 1-kHz repetition rate regenerative Ti:Sapphire laser amplifier and a commercial spectrometer made by Teraview. Both spectrometers are equipped with He flow cryostats that allow sample temperature control in the 4-320 K range. The two instruments produced identical spectroscopic data on the studied NCO films.

THz-TDS allows the measurement of the complex frequency-dependent dielectric function $\varepsilon(\omega)$ (or equivalently, the optical conductivity $\sigma(\omega)$) of a thin film on a substrate, which is accomplished by measuring the electric field of coherent THz pulses transmitted through the sample, $E_{\text{sam}}(t)$, and through the reference, $E_{\text{ref}}(t)$. In thin film studies, we take the reference to be a bare wafer of the same material as the film substrate and of similar thickness. Then, we compute the amplitude transmission coefficient as

$$
\tilde{t}(\omega) = \tilde{E}_{\text{sam}}(\omega)/\tilde{E}_{\text{ref}}(\omega),
$$

where $\tilde{E}_{\text{sam}}(\omega)$ and $\tilde{E}_{\text{ref}}(\omega)$ are Fourier transforms of the time-dependent quantities $E_{\text{sam}}(t)$ and $E_{\text{ref}}(t)$. The transmission coefficient of the film is determined by its dielectric function $\tilde{\varepsilon}(\omega)$ and the refractive index $\tilde{n}_3(\omega)$ of the substrate via the relation

$$
\tilde{t}(\omega) = \frac{\tilde{n}_3 + 1}{\tilde{n}_3 + 1 - i\omega d(\tilde{n}_3 + \tilde{\varepsilon})/c} \exp \left( i \frac{\omega (d_s - d_f) \tilde{n}_3 (\tilde{n}_3 - 1)}{c} \right),
$$

where $d$ is the thickness of the film, and $d_s$ and $d_f$ are the thicknesses of the film substrate and of the bare reference wafer. Equation (2) accounts for multiple reflections of the THz pulse inside the film but assumes that the first and all subsequent reflections in both sample and reference substrates have been windowed out. The substrate thicknesses are typically measured by a precision micrometer with 1 $\mu$m accuracy. The refractive index $n_1(\omega)$ of the substrate is measured in a separate THz-TDS measurement with free space as the reference. Fig. 1 shows the temperature dependence of the dielectric function of the NCO300 film calculated from the transmission $\tilde{t}(\omega)$ using Eq. (2).
FIG. 2. The real part of the THz optical conductivity of the NCO300 film. The solid lines illustrate the extrapolation to find the DC conductivity $\sigma_0$. The solid lines at 100-300 K follow the Drude model of Eq. (4).

We interpret the measured dielectric function using the free-electron model of Paul Drude,\textsuperscript{29} which is written as

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_P^2}{\omega^2 + i\omega\gamma_D},$$  \hspace{1cm} (3)

where $\epsilon_{\infty}$ is the high frequency dielectric constant contributed by bound electrons and by high-frequency phonons. The second term in Eq. (3) is the contribution of free electrons for which $\gamma_D$ is the relaxation rate and $\omega_P$ is the plasma frequency. We treat $\epsilon_{\infty}$, $\omega_P$, $\gamma_D$ in Eq. (3) as fitting parameters and use a least-squares fitting procedure to determine their values (Fig. 1). This allows us to calculate the THz-frequency conductivity as

$$\sigma(\omega) = (\epsilon - \epsilon_{\infty}) \epsilon_0 \omega \frac{\epsilon_0}{\gamma_D - i\omega}. \hspace{1cm} (4)$$

The calculated conductivity of NCO300 at various temperatures is shown in Fig. 1.

**B. Spectroscopy of low-temperature-grown NiCo$_2$O$_4$**

The NCO300 film studied here displays a MIT at $T_{MIT} = 300$ K and undergoes ferrimagnetic ordering at the same temperature.\textsuperscript{14} Figure 1 shows the measured real and imaginary parts of the dielectric function $\epsilon(\omega)$ at various temperatures and Fig. 2 displays the corresponding optical conductivity. We extrapolate the optical conductivity to zero frequency to determine $\sigma_0$, the DC conductivity, and find that its temperature dependence follows closely that of the DC transport conductivity,\textsuperscript{14} displaying the MIT at 300 K and a resistivity upturn below 70 K (Fig. 3). To the best of our knowledge, the metallic behavior in the intermediate 70-300 K range has only been reported in the epitaxial NCO films.\textsuperscript{14} In other NCO specimens, e.g., sputtered polycrystalline films, the...
observed conduction showed resistive temperature-activated behavior that was attributed to small polaron hopping.\textsuperscript{9,30,31} We gain further insight into the nature of the metallic state in the intermediate temperature range from the observed frequency dependence of optical conductivity (Fig. 2), which follows well the Drude model dependence. At low temperatures below 70 K, we find a transfer of spectral weight from the zero-frequency Drude peak to higher frequencies, which leads to suppressed
FIG. 4. The real ($\epsilon_1$) and imaginary ($\epsilon_2$) parts of the measured dielectric function of the NCO500 film. Solid lines represent Drude model fits using Eq. (3).

DC conductivity. The coherent Drude peak at intermediate temperatures provides evidence for the band-like conduction as opposed to the incoherent hopping of small polarons. This band-like conduction and the positive sign of Hall resistivity in the NCO300 film are consistent with the cation valency models that allow the formation of p-type conduction bands, e.g., Battle and Marco. In the Drude model description, the conductivity is governed by two parameters - the plasma frequency $\omega_P$ and the scattering rate $\gamma_D$. The plasma frequency, which is in turn determined by the carrier density, is related to the area under the Drude peak (the spectral weight) in the real part of the optical conductivity, while the scattering rate represents the width of the Drude peak. The frequency window of our measurement includes only a small low-frequency part of the Drude peak, which may lead to systematic uncertainties in the determination of $\omega_P$ and $\gamma_D$, even though the functional form of Eq. (4) describes well the conductivity at intermediate temperatures. For example, a transfer of spectral weight from low to high frequencies may happen due to many-body interactions that is not captured in our measurement. With this caveat in mind, we compute the spectral weight in the 0.3-3 THz frequency range (Fig. 3(b)) and use its temperature dependence as an approximation for the temperature dependence of the total Drude spectral weight. The THz spectral weight increases with lowering temperature (Fig. 3(b)), which is indicative of an increased carrier density. Such behavior is consistent with the double-exchange nature of the MIT in NCO, which was suggested based on the MIT concomitant with the ferrimagnetic ordering and the observed negative magnetoresistance. In double-exchange-driven magnetoresistive manganites, the resistivity drop below the MIT is also governed mostly by the increase in the spectral weight of the Drude peak.

C. Spectroscopy of high-temperature-grown NiCo$_2$O$_4$

The high-temperature grown NCO500 film shows monotonic increase in resistivity during cooling from 400 to 2 K with no MIT and no magnetic order, with its room-temperature conductivity being six times lower than that of the NC300 film (Figs. 2 and 5). Figure 4 shows the measured di-
FIG. 5. The real part of the THz optical conductivity of the NCO500 film. The solid lines illustrate the extrapolation to find the DC conductivity $\sigma_0$. The solid lines at 250 and 300 K follow the Drude model of Eq. (4).

electric function of NCO500 at several temperatures. At all temperatures, the dielectric function and its frequency dependence are reminiscent of a metal, with a large imaginary part that is responsible for the absorption at THz frequencies. At the same time, the imaginary part is strongly suppressed compared to NCO300 (Fig. 1), as expected from a more resistive film. Figure 5 displays the real part of the optical conductivity of the NCO500 film. At temperatures above 150 K, the THz conductivity is Drude-like, which points to coherent band-like transport that is very similar to that of the NCO300 film (Fig. 2). The similar character of transport is an unexpected result, given the drastic differences in the temperature dependence of conductivity (Figs. 3(a) and 6(a)) and in the magnetic properties\(^\text{14}\) between the two films. The similar shapes of the THz spectra at intermediate temperatures (Figs. 2 and 5) and the different THz spectral weights (Figs. 3(b) and 6(b)) suggest that the difference in the measured conductivity between the films is determined by the differing carrier densities in the bands formed by the cation level overlap. Such different doping levels are likely the result of the different cation distributions between the tetrahedral and octahedral sites in the spinel structure, as determined by polarized Raman studies.\(^\text{15}\) In NCO500, the cation distribution is very close to the perfect inverse spinel $\text{Co[NiCo]O}_4$, while a diffusion of Ni cations into the tetrahedral sites happens in NCO300.

At low temperatures below 70 K, the NCO300 and NCO500 films both display a conductivity drop with lowering temperature (Figs. 3(a) and 6(a)), a behavior that agrees with the earlier DC transport study.\(^\text{14}\) More significantly, both materials undergo a transition from coherent to incoherent transport below $\sim 70$ K. The transition is observed in the real part of optical conductivity, where the low-frequency conductivity is reduced and the Drude peak slowly shifts to a higher frequency (Figs. 2 and 5). The optical conductivity increases with frequency, which signifies an activated hole mobility with holes needing to overcome a potential barrier for hopping.\(^\text{33}\) The low-temperature crossover to incoherent conduction is especially startling in NCO500, as it is difficult to deduce its
FIG. 6. NCO500: (a) The temperature dependence of the DC conductivity $\sigma_0$. (b) The temperature dependence of the THz spectral weight.
presence from the temperature dependence of the DC conductivity (Fig. 6(a)). At the first glance, the observed low-temperature activated mobility may be consistent with the reports of small polaron hopping conductivity in the spinels NCO and Co$_2$O$_4$. As the optical signature of polaronic hopping transport includes a high-frequency absorption band corresponding to the transfer of the small polaron from one localized site to an adjacent localized site. However, the simultaneous onset of polaronic transport in the two films with very different carrier densities is unlikely. Another possible origin of the low-temperature localization tendency is magnetic impurity or magnetic cluster scattering. Given that the NCO500 film is not magnetic but displays the stronger localization tendency, we do not consider the latter possibility here.

NCO is an intrinsically disordered material, as Ni and Co ions are randomly distributed over the occupied octahedral sites. Therefore, we conjecture that the low-temperature localization could result from quantum interference effects rooted in disorder-enhanced electron-electron interactions and/or weak localization. Both these mechanisms were invoked to explain the upturns in resistivity below $\sim$60 K found in magnetoresistive manganites, and different authors reported one or the other mechanism as prevalent in their studies. The two mechanisms predict different signs of magnetoresistance, but the presence of the magnetoresistance due to the double exchange can mask this distinction. In the picture of the disorder-induced localization, NCO500 is expected to exhibit a stronger localization tendency (as observed here) as it possesses a lower carrier density than NCO300. Spectroscopically, our observation is similar to the localization tendency in Zn-doped cuprates, where the Zn impurities provide the disorder potential and the low-temperature optical conductivity exhibits a broad peak in the 3-4 THz range attributed to a disorder-induced bound state.

III. SUMMARY

We presented a THz spectroscopic study of epitaxial films of the mixed-valence inverse spinel NCO. The measurement of real and imaginary parts of the dielectric function and optical conductivity provides the evidence for the band-like conduction in both NCO300 and NCO500 at intermediate temperatures, despite the overall insulating behavior and drastically different magnetic properties of NCO500. Until recently, only a thermally activated hopping conductivity was reported in NCO, even though the cation valency models allow the possibility of band-like conduction. The present confirmation of the coherent band-like transport provides a basis for further improving the transport properties of NCO for applications as a transparent conducting oxide. We also find that both films undergo a crossover to incoherent transport at low temperatures, which indicates a localization tendency likely rooted in the effects of disorder.

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Supplementary material for:

Terahertz time-domain spectroscopy of the crossover from coherent band-like to incoherent transport in transparent conducting spinel NiCo$_2$O$_4$

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The schematic diagram of our home-built terahertz time-domain spectroscopy (THz-TDS) system is shown in Fig. 1. It uses a Spectra-Physics Spitfire ACE Ti:sapphire laser amplifier seeded by a mode-locked Spectra-Physics MaiTai laser. The output wavelength is 800 nm, the repetition rate is 1 KHz, and the pulse width is 35 fs. The maximum average power output is 4 Watts. The laser beam is divided into two arms by a beam splitter: a stronger generating beam (70%) for THz pulse emission and a weaker gating beam (30%) for THz detection. The generating beam is then modulated by a mechanical chopper. A ZnTe (110) crystal emitter of 0.5 mm thickness is used at normal incidence to generate THz pulses by the optical rectification process. The released sub-picosecond pulse of THz radiation is then collimated and focused by two off-axis parabolic mirrors in a helium-flow cryostat. The transmitted THz pulse is collected and focused onto a 0.5 mm (110) ZnTe detector crystal by two other parabolic mirrors. The phase-sensitive detection is accomplished by a lock-in-amplifier and the data are recorded onto a computer. The detected signal results from the polarization rotation of the gating pulse due to the birefringence induced in the detector ZnTe by the THz electric field. By varying the time delay between the generating and the gating pulses, the amplitude of the THz pulses transmitted through sample and reference is recorded in time domain.
Fig. 1. The schematic representation of our home-built THz-TDS system.

Ambient humidity can be problematic as water has absorption lines in the THz regime. Hence all the optical components and samples are enclosed in a purge box and purged with dry air to avoid water absorption. To enable low and high temperature measurement we have installed a continuous flow cryogenic system. The sample holder consists of two circular apertures of 6 mm diameter. To provide thermal contact, samples are glued on the sample holder with a thin layer of silver paste. The cryostat is mounted on the computer controlled motorized XY stage to move the sample in the horizontal and vertical directions transverse to the THz beam. Transmission measurements through sample and reference apertures are measured one after the other by moving the cryostat the appropriate distance to place the right aperture in the path of the THz pulses. We then compared the transmission through NCO film on MAO substrate sample to the bare MAO substrate reference to isolate the response of the NCO films. The measured THz amplitude for NCO 300°C film (sample) and MAO (reference) at 300K is shown below in Fig. 2(a) and the ratio of the amplitudes after Fourier transform is shown in Fig. 2(b). The inset shows the difference between the phases of the sample and reference.
Fig. 2. (a) The measured amplitude of the transmitted terahertz pulse through the sample and reference for NCO 300°C at 300K. In the time-domain spectra, the first transient is the primary pulse passed directly through the medium. The second transient is due to the reflections of the primary pulse from the back and the front surfaces of the sample. Since the main transmitted pulse is well separated from the first reflected pulse, for the analysis, the data were windowed around the main transmitted pulse. (b) The amplitude of the ratio of the sample and reference Fourier transforms of the time-domain data. The inset shows the difference between the phases of the sample and reference Fourier transforms.