Optical line spectra in metallic $(Nd,Ce)_2CuO_{4-x}$

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Optical absorption lines characteristic of Nd^{3+} have been observed in semiconducting and metallic phases of $(Nd,Ce)_2CuO_{4-x}$ using a sensitive optical spectroscopic technique. Samples with controlled levels of impurities and controlled cerium content have been studied to verify that the lines observed are intrinsic to $(Nd,Ce)_2CuO_{4-x}$. Sharp absorption lines in the visible spectrum of these metallic materials are observed. The materials exhibit dichroism characteristic of a two-dimensional conductor. Both this dichroism and the oscillator strengths of certain transitions show variations that are correlated with the doping level, conductivity, and degree of orientation of the samples. It is believed that these variations are the result of changes, induced by the doping, in the charge distribution near the Nd ions and the indices of refraction of the material.

I. INTRODUCTION

The sharp spectral lines characteristic of optical f-f transitions of rare-earth ions provide an extremely useful probe of the properties of the solid state. However, because the oscillator strengths of these transitions rarely exceed 10^{-6}, past observations have been limited to the study of thick, transparent materials. Indeed, it is widely believed[1,2] that f-f transitions cannot be observed in metallic rare-earth solids using optical techniques. However, previous attempts to observe these sharp transitions in metallic solids[3-6] have failed principally because of the limited sensitivity of the spectrograph systems used.

We have recently constructed an optical spectrograph system,[7,8] sufficiently sensitive that sharp absorption lines due to very small levels of impurities in opaque solids have been observed.[9] This spectrograph was sensitive enough to observe sharp f-f transitions in metals, and this paper reports the observation of these lines.

The compound $(Nd, Ce)_2CuO_{4-x}$ was chosen for this study because it exists in both insulating and metallic phases. The structure of $(Nd, Ce)_2CuO_{4-x}$ is shown in Fig. 1. Without cerium doping the material is an opaque semiconductor. When more than 7.5% of the neodymium is replaced by cerium and more than 1% of the oxygen is removed, the material becomes metallic with no change in the crystal structure.[10,11] Also, the rare-earth atoms in this predominantly two-dimensional conductor are physically somewhat isolated from the conduction

electrons, as shown in Fig. 1, so that the $4f$ subshell of the Nd ions should be largely unperturbed by the presence of the conduction electrons. In Nd_2CuO_{4-x} the Nd atoms are located at a site which is not a center of symmetry with the result that electric dipole transitions within the $4f$ configuration are weakly allowed. For these reasons $(Nd,Ce)_2CuO_{4-x}$ served nicely as a first material for the observation of sharp absorption spectra in a metal. Indeed, f-f transitions were observed in all
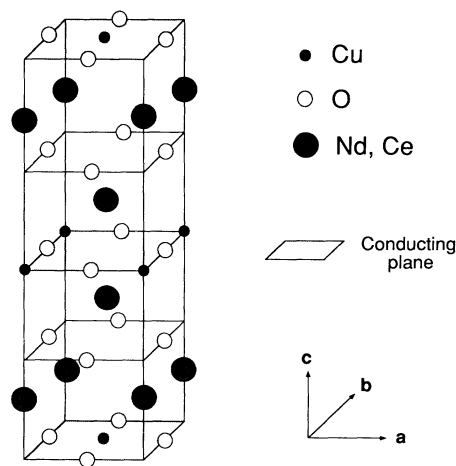

FIG. 1. The structure of $(Nd,Ce)_2CuO_{4-x}$.

phases of $(Nd,Ce)_2CuO_{4-x}$ in the form of polycrystalline pellets and oriented films. The spectra of both the pellets and the films exhibit variations in oscillator strength which are correlated with the conductivity and doping of the material. Also the oriented films display dichroism which differs dramatically between insulating and metal films.

II. EXPERIMENTAL PROCEDURE

The spectrograph system used in this experiment[7-9] consists of a white-light source, an optical Dewar, and a 1-m Czerny-Turner grating spectrograph with a photodiode array detector. With careful control of the spectrograph illumination and computer analysis of the output data, signal-to-noise ratios greater than 10^5 have been obtained with this system.

The procedure used for this experiment was to observe the spectrum of the insulating phase and to study these features as a function of the cerium content. In all phases studied it was important to determine if the features observed originated from the compound of interest or from impurities. The Nd-Cu-O-H_2O system was studied first, to identify the spectra of any contaminants which might occur in the insulating phase Nd_2CuO_4. After the study of possible oxide and hydroxide contaminants was concluded, a study of the Nd-Cu-O system was undertaken. According to a published phase diagram[12] this system should contain only Nd_2O_3, copper oxides, and the insulating phase of interest, Nd_2CuO_{4-x}. By studying samples with varying composition the spectrum of Nd_2CuO_{4-x} was easily identified. As expected, the only other lines observed were characteristic of unreacted Nd_2O_3. In addition, one sample each of Pr_2CuO_{4-x} and Sm_2CuO_{4-x} was studied. No absorption lines were observed in either of these samples in the wavelength regions covered here. This leads to the conclusion that all of the lines observed in Nd_2CuO_{4-x} are due to the presence of the neodymium ions.

After the spectra of the insulating phase and its impurities were identified, the impurities which could be produced by adding cerium were studied. Only one was thought to contain absorption lines sufficiently narrow to be observed: $NdCeO_{3.5}$. Two samples of $NdCeO_{3.5}$ prepared at different temperatures were studied.[13] Other than the spectrum of Nd_2O_3, both samples contain only very broad absorption lines whose widths can be attributed to the difficulty in producing $NdCeO_{3.5}$ of uniform composition. It is important to note that none of the spectral lines reported here can be attributed to any of the impurity phases studied.

Next, the experiment turned to the study of the effects of cerium substitution. Six $(Nd,Ce)_2CuO_{4-x}$ samples were studied. Three were randomly oriented polycrystalline pellets with 0%, 4%, and 7.5% of the neodymium replaced with cerium, and the fourth was an oriented film with 0% doping. The other two were predominantly oriented films with 7.5% doping. All the samples with 7.5% doping were metallic.[14,15]

A pellet of insulating bulk Nd_2CuO_{4-x} was prepared using the standard solid-state reaction technique[10] and then analyzed using powder x-ray diffraction. No impurities were observed in the diffraction pattern.[14] The spectrum of this sample was indistinguishable from the spectra of other Nd_2CuO_{4-x} samples used in the impurity tests.

The 4% Ce doped semiconductor sample was prepared using the same solid-state reaction technique used for cerium-free samples. The measured resistance of this sample was more than two orders of magnitude lower than that of the cerium-free sample.

A pellet of metallic $(Nd_{0.925}Ce_{0.075})_2CuO_{3.96}$ was prepared using a more elaborate solid-state reaction technique.[16] This sample was then analyzed using powder x-ray diffraction and no impurities were observed. Other samples prepared with this technique have been analyzed using electron beam microprobe,[16] and the major impurities observed were copper oxides and nonstoichiometric Nd-Ce-O. Above $T_c \approx 20$–24 K,[14] the resistivity of the sample was less than 20 mΩ cm with only a slight increase in resistivity with increasing temperature.

The undoped insulating and 7.5% doped highly conducting metal film samples used in this experiment were produced by laser ablation from bulk targets.[17] Thicknesses were not independently measured but were calculated using known deposition rates. X-ray diffraction patterns for samples produced in this manner show that they contain no observable crystalline impurities and are oriented with the c axis perpendicular to the substrate.[17] An extensive study of the resistivity of films made in this way has been made.[18] The films typically show resistivities of the order of 1 mΩ cm above T_c increasing by a factor of 2–5 at room temperature.

When our spectrograph system was used to study these opaque materials the large background variations in reflectivity or transmissivity produced by interband transitions frequently dwarfed the sharp lines of interest. To allow observation of the sharp lines we typically fitted the broad background with a low-order polynomial and then subtracted this polynomial from the data. Although this allowed the sharp features to be seen more clearly, their exact shape can be distorted by inaccuracies in the background curve fitting.

All the spectra reported here were recorded with the samples partially or fully immersed in liquid helium. The only difference observed when measurements were made with the samples immersed in liquid nitrogen, even for the superconducting samples whose transition temperatures were below 25 K, was the presence of additional lines corresponding to transitions from thermally excited levels just above the ground level. For the bulk samples all the spectra were recorded in reflection. For the films, the spectra were recorded both in transmission and in reflection.

III. RESULTS AND ANALYSIS

The positions of all the observed lines are given in Table I. Assignments given in the table were based on comparisons to the observed spectra of other Nd solids. In particular, advantage was taken of the similarity of the

TABLE I. Positions in angstroms and assignments of observed transition in (Nd,Ce)$_2$CuO$_{4-x}$. Blank spaces correspond to transitions which were unobservable in a particular sample.

Nominal upper state	Number of lines expected	Undoped pellet	Undoped film	4% doped pellet	Metal pellet	Metal film No. 1	Metal film No. 2
$^4G_{7/2}$ and $^2K_{13/2}$	11		5339				5362
			5363				
$^4G_{5/2}$ and $^2G_{7/2}$	7		5745			5738	5738
			5785			5782	5782
			5813			5810	5810
			5824			5824	5822
			5839			5834	5835
			5917		5919	5913	5914
			5926				
		5942	5956	5944	5944	5947	5950
		5971	5975	5971	5970	5970	5970
			6020			6016	6016
$^4F_{7/2}$ and $^4S_{3/2}$	6	7428	7429	7429	7430	7431	7432
			7437				
			7483				7476
			7516	7517		7516	7514
		7525	7529	7529	7530	7533	
			7602				
$^4F_{5/2}$ and $^4H_{9/2}$	8	7932		7930	7931		
		7970		7969	7968	7971	7970
		8030	8029	8029	8029	8030	8028
		8069	8066	8063	8067	8068	
		8101	8103	8098	8100	8099	8096
			8144				
			8195				

spectrum of A-type Nd oxide and the Nd-Ce-Cu-O compounds. Because the films were not of optimum thickness and the pellet samples were weakly reflecting, low levels of light were observed in most cases. This typically reduced the signal-to-noise ratio to such a degree that only certain sets of lines could be observed and this is reflected in Table I.

The spectra of the bulk insulating, semiconducting, and metal samples are shown in Figs. 2–4. While the positions of the lines observed appear largely independent of doping there are small but consistent variations in the intensities of certain lines, in particular the lines marked with arrows. We interpret these variations in intensity as being caused by the combination of two effects: first, changes in oscillator strength due to the changes in the charge distribution near the Nd ions; second, orientation-dependent changes in the penetration length of different individual crystallites. The second effect will be discussed in detail later.

The first effect can be easily understood with the help of Fig. 1. When tetravalent cerium is substituted for Nd in the material it is likely that most of this extra charge is transferred to the copper oxide plane near the copper anions. The even parity component of the crystal field affecting the Nd atom is primarily produced by the oxy-
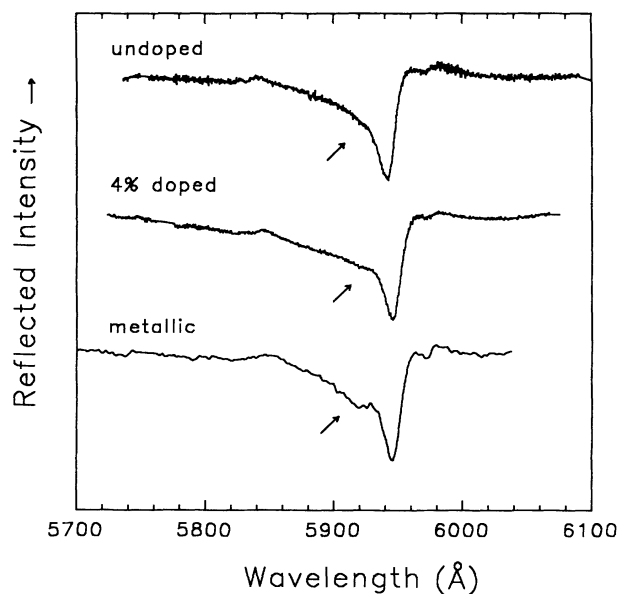

FIG. 2. The reflection of the three bulk (Nd,Ce)$_2$CuO$_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$. Note the changing relative intensities of the lines marked with an arrow.
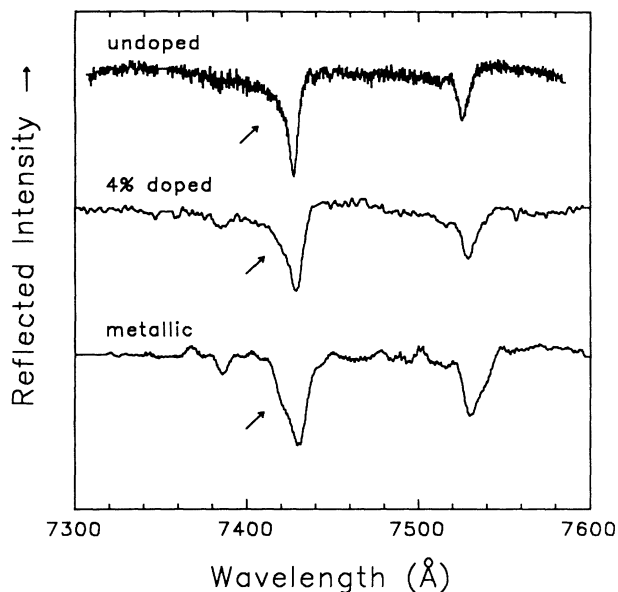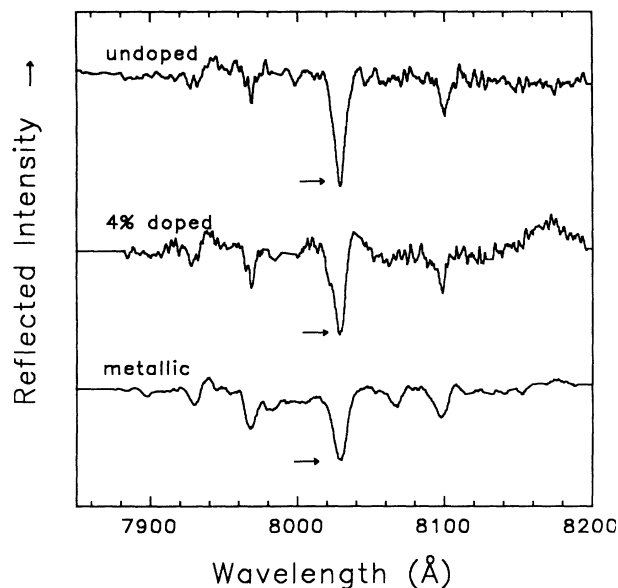
FIG. 3. The reflection spectra of the three bulk $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow ^4S_{3/2}$, $^4F_{7/2}$. Note the changing relative intensities of the lines marked with an arrow.

gen ions and trivalent rare-earth ions. Because the even parity part of the crystal field interaction is predominantly responsible for the splittings of the atomic levels, changes in the charge distribution near the copper and cerium sites should have only a limited effect on the positions of the crystal field levels. This is also consistent with the inelastic neutron scattering results which show no variation in the positions of the lowest crystal field levels.[19]

On the other hand, the odd parity component of the crystal field is primarily the result of the charge on the copper ions and any excess charge at a neighboring rare-earth site. The mixing of higher-lying configurations induced by the odd parity part of the crystal field entirely determines the intensities of the f-f transitions. The change in the charge density at the copper and cerium sites therefore can lead to variations in the relative intensities of lines.

The transmission spectra of the c-axis oriented insulating and metal film samples are shown in Figs. 5 and 6. The spectra of the two metallic films were essentially identical and so only data from the second metal film are shown in Figs. 5–8. The thickness of the insulating film was estimated, using known deposition rates, to be approximately 1000 Å, and the second metal film was approximately 2000 Å in thickness. Table II contains oscillator strengths for the transitions shown in Fig. 5 calculated using these thicknesses and assuming a Gaussian profile. Since the films used were highly oriented these values correspond to the projection of the full dipole onto the a-b plane. The transitions shown in Fig. 6 overlap too greatly to make such a calculation reliable. As discussed above, the changes in the charge distribution produced by the doping cause many of the transitions to have different relative intensities in the metal film. However, because these films are similarly oriented, a change in the anisotropic background absorption should not produce a change in the relative absorptions of differently oriented dipoles as it does in the polycrystalline samples.
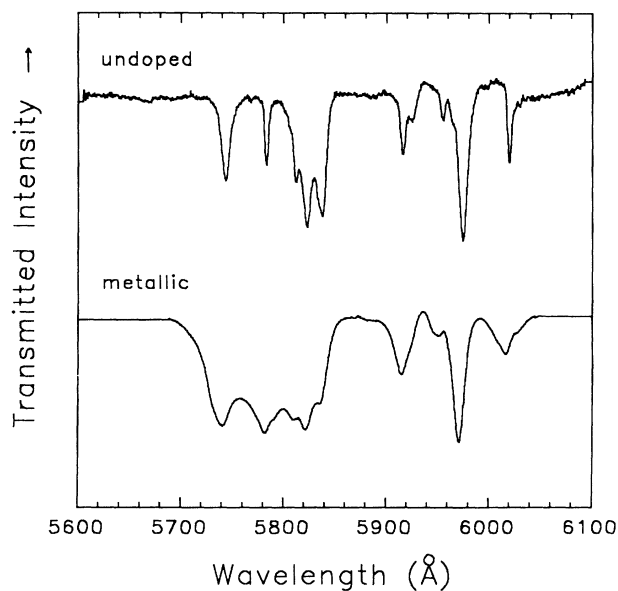

FIG. 4. The reflection spectra of the three bulk $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$. Note the changing relative intensities of the lines marked with an arrow.

FIG. 5. The transmission spectra of the film $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow ^2G_{7/2}$, $^4G_{5/2}$. Note the broadening of the lines in the metallic phase which is believed to be an inhomogeneous broadening produced by the cerium doping.

TABLE II. Oscillator strengths of the transitions $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ in $(Nd,Ce)_2CuO_{4-x}$ films for transmitted light parallel to the c axis.

Insulator		Metal	
Position in angstroms	Oscillator strength	Position in angstroms	Oscillator strength
5745	20×10^{-7}	5738	30×10^{-7}
5785	6×10^{-7}	5782	30×10^{-7}
5813	2×10^{-7}	5810	10×10^{-7}
5824	10×10^{-7}	5822	20×10^{-7}
5839	20×10^{-7}	5835	30×10^{-7}
5917	7×10^{-7}	5914	20×10^{-7}
5926	4×10^{-7}		
5956	5×10^{-7}	5950	4×10^{-7}
5975	40×10^{-7}	5970	30×10^{-7}
6020	7×10^{-7}	6016	8×10^{-7}

Several other characteristics of these spectra are notable. First, the line near 5940–5950 Å which is so strong in the reflection spectra of the polycrystalline samples is much weaker in the film spectra. This indicates that the forced dipole involved in this transition is aligned almost exactly along the c axis, and thus parallel to the incoming light. Second, several of the lines in the metallic film are much broader than in the undoped film, as broad, in fact, as in the polycrystalline samples. The strains induced by the heavy doping are probably sufficient to induce inhomogeneous broadening of this order. Unfortunately, this probably masks any small contributions to the broadening due to interactions with the conduction electrons. Not surpr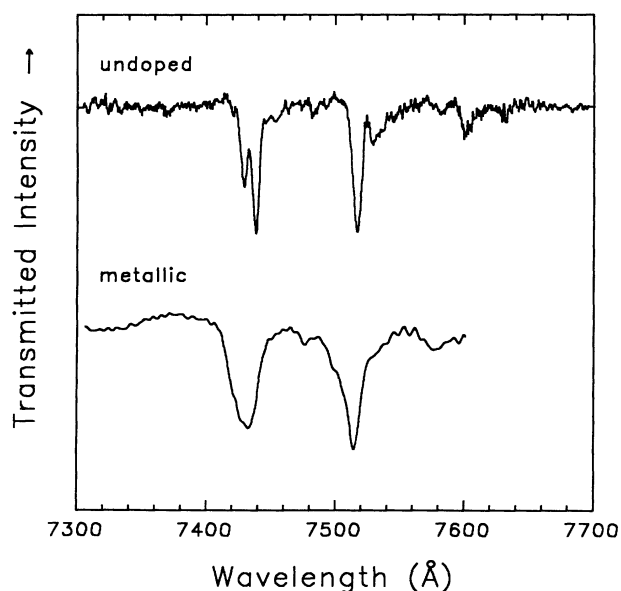isingly, the same transitions which display the greatest integrated intensity variation due to the doping also display the greatest doping-induced broadening.

The reflection spectra of the insulating and metal film samples are shown in Figs. 7 and 8. Two characteristics of Fig. 7 are to be noted. First, for light polarized perpendicular to the c axis (s polarized) all of the spectral lines produce increased reflection, with respect to the background, in the insulating film and decreased reflection in the metallic film. Second, for light not polarized strictly perpendicular to the c axis (p polarized or unpolarized) the strong line near 5940 Å produces decreased reflection in both insulating and metallic films. These characteristics are believed to result from a combination of the following: (1) The orientations of the forced dipoles responsible for the different absorption lines, (2) the highly anisotropic indices of refraction of these materials, and (3) the change in the indices of refraction produced by the doping.

A brief description of the optical properties of $(Nd,Ce)_2CuO_{4-x}$ is in order at this time. The insulating (semiconducting) phase is transparent in the infrared but opaque above about 1.5 eV due to a charge transfer exci-
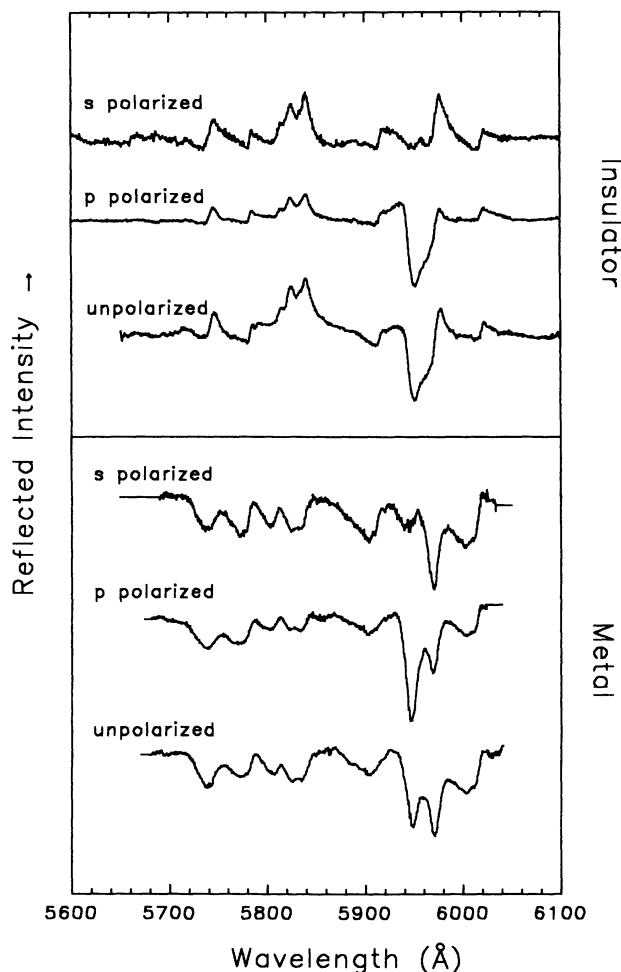

FIG. 6. The transmission spectra of the film $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow {}^4S_{3/2}$, $^4F_{7/2}$. Note the broadening of the lines in the metallic phase which is believed to be an inhomogeneous broadening produced by the cerium doping.

FIG. 7. The reflection spectra of the film $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ for different polarizations of the incoming light.
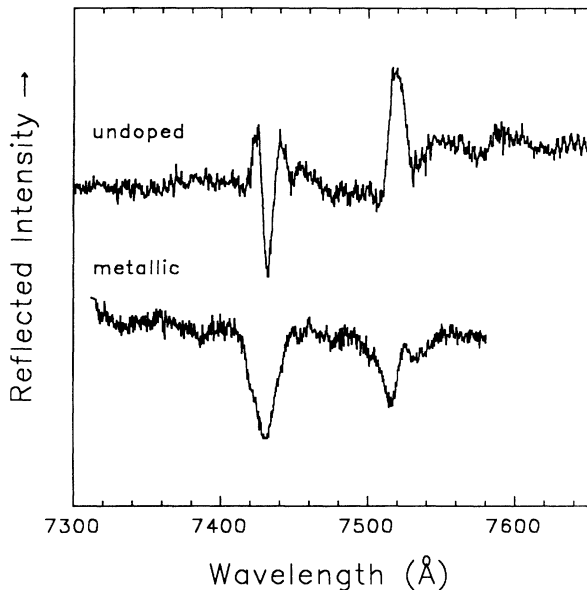
FIG. 8. The reflection spectra of the film $(Nd,Ce)_2CuO_{4-x}$ samples for the transition $^4I_{9/2} \rightarrow {}^4S_{3/2}$, $^4F_{7/2}$. Note the broadening of the lines in the metallic phase which is believed to be an inhomogeneous broadening produced by the cerium doping.

tation.[20,21] The metallic phase is opaque in the infrared with a plasma edge around 1 eV, but surprisingly in the visible the conductivity of the metal is not as high as the conductivity of the semiconductor.[21] The indices of refraction of all phases of these materials are highly anisotropic with the dominant absorption occurring for light polarized in the a-b plane.[22]

Returning to Figs. 7 and 8, all lines which produce an increase in reflection, with respect to the background, correspond to dipoles superimposed on a highly absorptive background index of refraction. In this case the observed spectra are dominated by front surface reflection. The addition of a resonant absorption merely produces an increase in the net reflection.

When the background optical conductivity is low, then transmission through the sample and reflection from the substrate becomes important. The decrease in the total amount of reflected light produced by an added resonant absorption results from the relatively large decrease in

transmission followed by second-surface reflection. In fact, this mechanism is responsible for the absorption dips observed in reflection from the polycrystalline pellets. Also, the resulting orientation-dependent changes in penetration length cause the spectra of the randomly oriented pellet samples to vary with doping level.

Finally, with the current results it is not possible to determine the specific source of the extra lines observed in the region of the transition to the $^4G_{5/2}$ level (see Table I). These lines are believed to not be due to distinct impurity phases but instead are believed to be the result of regular variations in the morphology and composition of $(Nd,Ce)_2CuO_{4-x}$. Similarly, the well-known spectrum of Nd_2O_3 exhibits many extra lines whose exact origin is still unknown.[23,24]

IV. CONCLUSIONS

Sharp optical absorption lines have been observed in all phases, including the metallic phase, of $(Nd,Ce)_2CuO_{4-x}$. We note that this was an observation of sharp absorption lines in the visible spectrum of a metal. The spectra show variations in oscillator strength which are correlated with the doping level and conductivity of the samples. It is believed that these variations are the result of doping-induced changes in the charge distribution near the Nd ions. The materials exhibit dichroism characteristic of a two-dimensional conductor, and this dichroism changes dramatically as the optical conductivity of the materials changes with doping.

ACKNOWLEDGEMENTS

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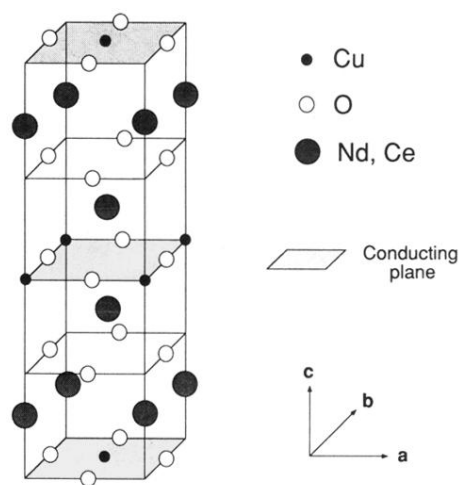[24]J. R. Henderson, M. Muramuto, and J. B. Gruber, J. Chem. Phys. **46**, 2515 (1967).

FIG. 1. The structure of $(Nd,Ce)_2CuO_{4-x}$.