Ellipsometric study of the electronic band structure of \(CrO_2\) across the ferromagnetic transition

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I. INTRODUCTION

According to band-structure calculations \(CrO_2\) is classified as a half-metallic ferromagnet with complete spin polarization at the Fermi energy.1–3 This has sparked a renewed interest in this material as a candidate for spin injection in spintronic applications. The prediction has been confirmed by point contact Andreev reflection measurements showing 96–98% spin polarization.4,5 Other experiments such as x-ray absorption,6 photoemission,7 and optical measurements8 performed below the Curie temperature show general agreement with band-structure calculations in the ferromagnetic state. Work done to study the electromagnetic response of this material across the ferromagnetic transition is limited to absorption9,10 and pump-probe transmission11 studies claiming to confirm a double-exchange mechanism of the ferromagnetic state. Within this latter scenario, major changes in the optical conductivity are expected across the ferromagnetic transition.12 A comprehensive study of the optical properties across \(T_C\) in both the \(c\) axis and \(ab\) plane directions should help further our understanding of this half-metal. While it is well known that the crystal structure of \(CrO_2\) is anisotropic,13 experimental studies of the anisotropy in the optical response of thin films are also very limited.11,14

In this paper, we study the frequency-dependent optical conductivity of \(CrO_2\) over a wide temperature and energy range in order to learn about its electronic band structure and carrier dynamics across the ferromagnetic transition. We employed variable angle spectroscopic ellipsometry (VASE): a technique that allows us to extract both the real and imaginary parts of the optical conductivity without recourse to Kramers-Kronig analysis.

II. EXPERIMENTAL METHODS

The samples are epitaxial \(CrO_2\) thin films grown on TiO2 substrates by chemical vapor deposition with \(CrO_3\) as a precursor. Sample growth and characterization using x-ray diffraction, Rutherford backscattering spectroscopy, several microscopy techniques, and a standard four-probe dc method are described elsewhere.15–17 We used two different samples: one deposited on TiO2 in the (100) orientation with a thickness of 175 nm and one in the (110) orientation, 150 nm thick. The (100) film is strained while the (110) film is strain-free.16–18 The reported Curie temperature of these films is \(T_C \approx 390–395\) K and the magnetic easy axis is the \(c\) axis.15

We performed the measurements using two commercial Woollam ellipsometers. One, a VASE model based on a grating monochromator, covers the energy range between 0.6 and 6 eV, to which we added a UHV cryostat in order to enable measurements at both low and elevated temperatures.19,20 The other one, an IR-VASE model, covers the range between 0.05 and 0.7 eV and is based on a Michelson interferometer. We first characterized the blank (100) and (110) substrates and then the films. Knowing that the crystal structure of \(CrO_2\) is elongated along the \(c\) direction, it is natural to expect the electronic properties to be anisotropic.11 In order to study the optical constants in the various crystallographic directions, it was necessary to measure the samples in two orientations: with the \(c\) axis in the plane of incidence and perpendicular to it. A schematic of these experimental geometries is shown in Fig. 1. Each measurement was performed at incidence angles of 60° and 75° and at temperatures ranging from 300 to 450 K, while some measurements in the visible and ultraviolet regions were extended down to 60 K. At each angle we measured the polarization state of the reflected light in the form of two parameters \(\Psi\) and \(\Delta\), as shown in Fig. 1, which are related to the Fresnel reflection coefficients for \(p\)- and \(s\)-polarized light \((R_p\) and \(R_s\)) through the equation \(R_p/R_s = \tan(\Psi)e^{i\Delta}\). We note that there is good agreement, better than 3%, between the data obtained from the two different ellipsometers in the overlapping frequency range.

In order to obtain the optical constants of the thin film samples, we first constructed a two-layer model taking proper account of the role of the substrate in raw ellipsometric data. The complex dielectric functions of the TiO2 required for this analysis were determined through ellipsometric measurements of the bare substrates, keeping in mind the
anisotropy of this uniaxial crystal. The same model of the optical constants tensor has been employed to fit the four sets of experimental data for TiO$_2$ collected at 60° and 75° with the c axis both perpendicular and parallel to the plane of incidence. In this way we were able to obtain the conductivity for both the c axis and the $ab$ plane of each of the two TiO$_2$ samples. Our data are in good agreement with those obtained in previous experiments.$^{21,22}$ To account for surface roughness in the substrate, we included in our model a top layer consisting of 50% void and 50% TiO$_2$ and described the response of such an effective layer with the Bruggeman effective-medium approximation.$^{23}$ The thickness of the layer was determined by the model fit to be 4 nm. Data for the CrO$_2$/TiO$_2$ films were modeled in a similar way. Specifically, we used the optical constants previously obtained for TiO$_2$ to characterize the substrate, so that the only fit parameters were the optical constants of CrO$_2$ in the c axis and $ab$ plane directions. The CrO$_2$ layer of the model is composed of two separate sets of eight Kramers-Kronig consistent Gaussian oscillators$^{24}$ and a Drude function, amounting to 26 fit parameters. Two sets of oscillators are necessary because we want to describe the response along each of the two crystallographic directions. Figure 1 shows experimental data and the model fits for measurements of the (110) sample performed at room temperature with the c axis in the plane of incidence. It can be seen that our model provides good fits, within 5%, for the data at both angles throughout the entire experimental range.

III. RESULTS AND DISCUSSION

In order to analyze our results, it is useful to look at the real dissipative part of the optical conductivity, as it is related to the density of states. The complex optical conductivity can be obtained from the complex dielectric function using \( \sigma(\omega) = \frac{i\omega\varepsilon_{ab}^\prime - \varepsilon_{ab}^\prime\prime}{4\pi} \). Figure 2 shows conductivity data for both CrO$_2$ samples at room temperature. The spectra show three main features: (i) a Drude contribution at low frequencies, (ii) a broad peak in the mid-IR region (0.2–1.5 eV), and (iii) a sharp onset of interband absorption at 1.5 eV indicative of a prominent band gap. Comparing our data with band-structure calculations,$^{25-27}$ it is tempting to assign feature (iii) to transitions across the minority gap between the oxygen 2$p$ and the chromium 3$d$ bands, estimated by local spin-density approximation (LSDA) calculations to be 1.3 eV. Furthermore, transitions between the $t_{2g}$ and the $e_g$ levels (see right panel in Fig. 2) may contribute to absorption above 1.5 eV. Feature (ii) would correspond to interband transitions between the split $t_{2g}$ levels. Based on this analysis, one might conclude that our data support the LSDA calculations more so than LSDA+$U$ calculations. The latter include a Hubbard $U$ term to account for intra-atomic Coulomb repulsion and predict a larger spin-minority gap of 2.1 eV, which is inconsistent with our results. While existing band-structure calculations are valid at very low temperatures, dramatic changes in the band structure are not expected at higher temperatures below $T_c$.

Data in Figs. 2–4 reveal significant anisotropy in the CrO$_2$ films throughout the entire frequency range of our measurements. Figure 3 shows dc conductivity, scattering rate ($1/\tau$), and Drude plasma frequency ($\omega_p$) data obtained from the Drude functions in our models. These spectral features are related to the Drude contribution of the optical conductivity by $\sigma_{\text{Drude}}(\omega) = \frac{\omega_p^2}{\omega(\omega + i\tau)}$. The plasma frequency we have obtained experimentally is somewhat lower than the LSDA prediction of \( \sim 2 \) eV.$^{26}$ At room temperature, the dc conductivity and the Drude plasma frequency in the $ab$ plane are about 30% higher than in the direction of the c axis. Going back to Fig. 2 we note that this trend continues until about 0.5 eV. This is consistent with the knowledge that one of the $t_{2g}^\perp$ levels at the Fermi energy is hybridized with the oxygen 2$p_y$
state forming a II-type bond normal to the c axis.14 In this way, some of the electrons at the Fermi energy can contrib-
ute to conductivity in the ab plane only. In the mid-IR re-
gion, the c axis conductivity shows a well-defined peak while in the ab plane conductivity we see a broad shoulder.
At higher frequencies the anisotropy becomes smaller with
the conductivity along both directions showing a rapid in-
crease above 1.5 eV . In the ab plane response we see a more
pronounced peak at 2 eV followed by a slower increase in
conductivity at even higher energies. The response probed
along the c axis direction reveals a more uniform increase in
the conductivity, although peaks at 2 and 3 eV are still noticeable.

To further understand the band structure of CrO2 it is
crucial to study the temperature dependence of the conduc-
tivity, especially near $T_C$ and across the ferromagnetic trans-
ition. Figure 4 shows temperature dependence of the optical
conductivity for both films. It is important to note that the
absorption region (iii) with onset at 1.5 eV exhibits virtually
no temperature dependence, prevailing well above $T_C$. No-
ticeable temperature dependence is observed in the midinfr-
ared region. In the case of the (110) film, the amplitude of this
peak increases and its center becomes redshifted as tempera-
ture increases. In the (100) film we observe that, in the c axis
direction, this peak broadens but its amplitude does not in-
crease, while in the ab plane we see no clear peak in this
region. The Drude free-carrier absorption at the lowest ener-
gies is modified as well. As shown in Fig. 3, the dc conduc-
tivity decreases and the scattering rate increases with increas-
ing temperature. Above $T_C$, hints of saturation in the
scattering rate are apparent, presumably due to the small
electron mean-free path expected in the paramagnetic state.26
The Drude plasma frequency remains approximately con-
stant at all temperatures. This finding is in conflict with the
double-exchange scenario of ferromagnetism in CrO2 predict-
ing a noticeable spectral weight transfer from high to low
energy as temperature is reduced below $T_C$.27 This expecta-
tion is substantiated by IR data for manganites, where the
effective number of carriers decreases continuously with in-
creased temperature, finally vanishing at $T_C$.12 This result
is also inconsistent with LSDA calculations predicting higher
Drude plasma frequency in the paramagnetic state.26 Similar
behavior of the Drude plasma frequency across $T_C$ is also
found in ferromagnetic III-V semiconductors.28,29 Dc con-
ductivity in the ab plane remains higher than that in the c axis
direction throughout our entire temperature range, with
no discontinuous changes at $T_C$. These data are in good
agreement with resistivity measurements performed on simi-
lar (100) CrO2 samples.15 We observe a higher scattering rate
in the ab plane than in the c axis direction. From Fig. 3 we
note that the dc conductivity of the (100) film is 30–35 %
higher than that of the (110) film.

![Figure 3](image-url)

**FIG. 3.** (Color online) Dc conductivity (top), scattering rate, and Drude plasma frequency (bottom) as functions of temperature obtained from the Drude function in our model. The vertical bars indicate the Curie temperature. The left column shows data for CrO2 on (110) TiO$_2$ and the right column is for CrO2 on (100) TiO$_2$.

![Figure 4](image-url)

**FIG. 4.** (Color online) Optical conductivity in ab plane and c axis directions of each film at temperatures between 300 and 450 K for the (100) sample and between 60 and 450 K for the (110) sample.
An unanticipated result of our work is that we observe no significant changes either in the Drude absorption or in the interband resonance throughout the broad temperature range covering both the ferromagnetic and paramagnetic states. It is known that strain and strain-induced defects can affect the electronic and magnetic properties of thin films. This is a possibility in the (100) film, but not in the (110) film which has been shown to be strain-free. Therefore, we expect to see a dramatic difference between the spectra at the low and high ends of our temperature range, the former corresponding to a fully spin-polarized ferromagnetic state well below $T_C$ and the latter to a paramagnetic regime well above $T_C$.

However, while the small peaks present at lower temperatures near 2 and 3 eV disappear quickly with increased temperature, the general trend of a sharp absorption starting at 1.5 eV remains unchanged. Therefore, assignment of the temperature, the general trend of a sharp absorption starting at 1.5 eV remains unchanged. Therefore, assignment of the high-energy absorption to transitions across the minority gap of a half-metallic ferromagnet becomes problematic and is in disagreement with our results. The more noticeable temperature dependence in the mid-IR region might be explained by recalling that this peak could correspond to interband transitions between the split $t_{2g}$ levels. As the temperature is increased and the sample enters the paramagnetic state, the minority-spin levels would presumably go down to the Fermi energy. This would allow excitations of minority spins into the conduction band with less energy, which could contribute to the broadening and increase in magnitude of this peak. In the case of the (100) film we expect the strain along the $b$ axis to be greater than that along the $c$ axis due to larger lattice mismatch in the direction of the $b$ axis. Since the splitting of the $t_{2g}$ levels is due to the elongation of the oxygen octahedra along the $c$ axis, one might expect that the way in which the $t_{2g}$ levels split will be affected by this strain along the $b$ axis, causing a difference in the conductivities of the two films in the mid-IR region. The lack of temperature dependence in the plasma frequency as well as in the sharp absorption region above 1.5 eV is in disagreement with the dramatic changes expected in the double-exchange scenario and in the current picture of the band structure of this material.

**IV. CONCLUSION**

We have obtained optical conductivity data for CrO$_2$ across the ferromagnetic transition at 390 K. The main features observed in our room-temperature data appear to be in good agreement with band-structure calculations for the fully spin-polarized ferromagnetic state. A study of the temperature dependence of the conductivity, however, poses new questions about the electronic band structure of this material. We see that the peak which, according to calculations, would correspond to transitions across the minority gap remains quite prominent at temperatures well above $T_C$. Furthermore, the Drude plasma frequency we obtained is temperature independent, which is inconsistent with the double-exchange scenario. We also observe an important anisotropy in the optical conductivity of CrO$_2$ and a difference in the conductivities of the two films. These observations are consistent with what is known about the crystal structure of this half-metal and about the strain in the films.

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