

Thermoreflectance spectra of CrO₂

M. A. K. L. Dissanayake* and L. L. Chase

Department of Physics, Indiana University, Bloomington, Indiana 47405

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Measurements of the polarized thermoreflectance spectra of ferromagnetic CrO₂ films in the energy range of 0.5–6.0 eV are reported. Much of the observed structure is interpreted as resulting from the narrowing of the exchange-split cationic *d*-band gap with increasing temperature, possibly caused by the increase in spin disorder. These results substantiate the conclusions made earlier from the temperature dependence of the static reflectivity spectra.

I. INTRODUCTION

CrO₂ is one of a number of metallic dioxides having rutile-related crystal structures and a large range of transport and magnetic properties. With a 3*d*² outer electron configuration and metallic behavior, this material exhibits a ferromagnetic-paramagnetic phase transition at 392 K without any associated changes in transport properties. Optical properties of CrO₂ have been investigated by several workers¹⁻³ using transmission and reflectivity measurements. Thermomodulation techniques have been widely used in investigating the band structure of a number of materials, but very few transition-metal oxides have been so studied.⁴ In this work we report the polarized thermoreflectance spectra and the Kramers-Kronig analyzed dielectric function $\Delta\epsilon_2$ in the energy range of 0.5–6.0 eV. Although there are no band-structure calculations available on CrO₂, a phenomenological model proposed by Goodenough⁵ appears to explain some basic features of the structure of the cationic *d* bands, which seem to be primarily responsible for the observed physical properties of this material.

II. EXPERIMENTAL PROCEDURES

The samples used in the thermoreflectance measurements were oriented films of CrO₂, deposited on (100) and (110) faces of a TiO₂ substrate by a high-pressure decomposition process.⁶ Due to the metallic nature of the material the direct heating method was used to modulate the temperature of the sample. Two aluminum electrodes were evaporated onto the polished sample surface and the sample was then bonded to an aluminum heat sink. A 6.6-Hz square-wave current was passed through the sample to generate the temperature modulation. The reflectometer was described previously.³ The signal from the output of the spectrometer lock-in amplifier was separated into a dc part proportional to $I_0 R$ and a 6.6-Hz ac part

proportional to $I_0 \Delta R$, where I_0 is the intensity of the incident light, R is the static reflectivity, and ΔR is the change in reflectivity caused by the temperature modulation. A separate lock-in amplifier tuned to 6.6 Hz detected the ΔR signal. The magnitude of the temperature modulation was not measured, but it is the order of the 12 K increase in average temperature of the sample due to the thermomodulation.

III. RESULTS AND DISCUSSION

Figure 1 shows the thermoreflectance (TR) spectra of CrO₂ at room temperature taken with incident light polarized parallel and perpendicular to the rutile *c* axis. The static reflectivity spectra of CrO₂ (Ref. 3) are also shown in the figure for

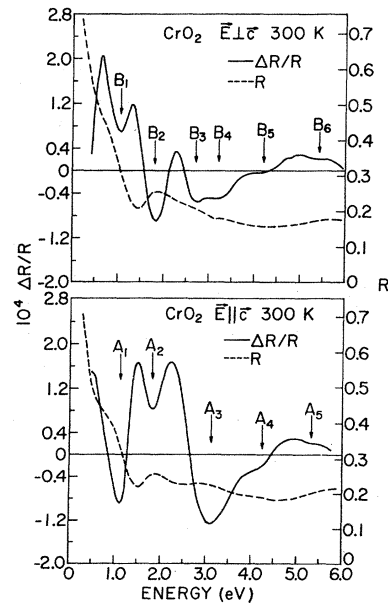


FIG. 1. Thermoreflectance spectrum (solid line) and the reflectivity spectrum (dashed line) of CrO₂ for $\vec{E} \perp \vec{c}$ and $\vec{E} \parallel \vec{c}$ at room temperature. The arrows indicate the energy positions of the dips in the TR spectrum.

the purpose of comparing the corresponding structures in the TR and R spectra. The spectra of $\Delta\epsilon_2$ obtained by the derivative Kramers-Kronig analysis⁷ of the thermoreflectance spectra are shown in Fig. 2 for the two polarizations along with the corresponding ϵ_2 spectra obtained from the static reflectivity measurements. Each reflectivity peak of CrO₂ appears as a diplike structure in the $\Delta R/R$ spectra. The low-energy dip A_1 (B_1) in the ΔR spectra can be associated with the low-energy reflectivity shoulder around 0.8 eV in the R spectra. The higher-energy dips A_2 through A_5 for $\vec{E} \parallel \vec{c}$ and B_2 through B_6 for $\vec{E} \perp \vec{c}$ in the $\Delta R/R$ spectra appear to correspond to the respective higher-energy peaks in the R spectra. A similar comparison can be made between the peaks in the ϵ_2 spectra and the dips in the $\Delta\epsilon_2$ spectra. The energy positions of the various structures appearing in the static and thermomodulated (TM) spectra are compared in Table I. The structures in the TM spectra below 3 eV are sharper and more intense than those at higher energies. The higher-energy part of the TM spectra essentially consist of a set of shoulders. The intensities of various structures at low energies in the derivative spectra exhibit a more pronounced polarization dependence compared to that shown by the R and ϵ_2 spectra.

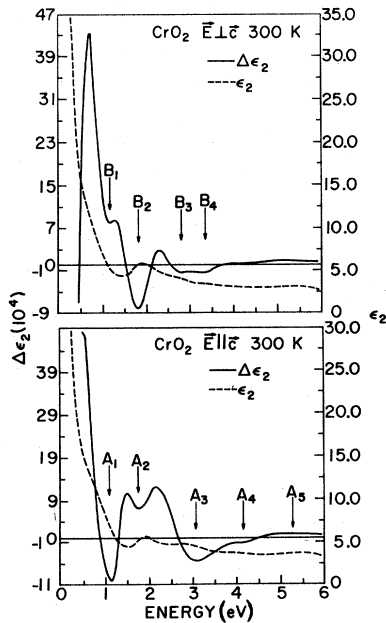


FIG. 2. Temperature derivation of ϵ_2 (solid line) obtained by the Kramers-Kronig analysis of the TR spectrum of CrO₂ and the ϵ_2 spectrum obtained by the Kramers-Kronig analysis of the reflectivity spectrum of CrO₂ for $\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ at room temperature.

TABLE I. Energy positions of the structures obtained from the static reflectivity measurements (R and ϵ_2) and the thermomodulated measurements ($\Delta R/R$ and $\Delta\epsilon_2$) for CrO₂ at room temperature. Energies are in eV. The signs of the shift coefficients, $\partial E_g/\partial T$, for various structures are also indicated.

$\vec{E} \parallel \vec{c}$	A_1	A_2	A_3	A_4	A_5	
R	0.80	1.90	3.00	4.25	5.50	
$\Delta R/R$	1.10	1.80	3.10	4.25	5.25	
ϵ_2	0.80	1.90	2.80	4.25	5.50	
$\Delta\epsilon_2$	1.10	1.80	3.10	4.25	5.25	
$\frac{\partial E_g}{\partial T}$	(-)	(+)	(-)	?	?	
$\vec{E} \perp \vec{c}$	B_1	B_2	B_3	B_4	B_5	B_6
R	0.75	1.90	2.75	3.35		5.75
$\Delta R/R$	1.10	1.80	2.75	3.30	4.25	5.50
ϵ_2		1.90	2.75	3.25		5.50
$\Delta\epsilon_2$	1.25	1.80	3.00			
$\frac{\partial E_g}{\partial T}$	(-)	(+)	(-)	?	?	?

A detailed analysis of the TM spectrum of CrO₂ is not possible at this stage because energy-band-structure calculations for the material are not available. It is possible, nevertheless, to draw some conclusions regarding the energy-band structure by considering the basic features in the spectra on a qualitative basis using the phenomenological energy-band scheme proposed by Goodenough⁵ and the results deduced from the static reflectivity measurements.³ A change in temperature usually produces two effects on the interband optical transitions of solids: a shift of the energy bands and a change of the Lorentz broadening parameter, Γ . Therefore, one can write the change in ϵ_2 for transitions between a single pair of bands as

$$\frac{\partial \epsilon_2}{\partial T} = \frac{\partial \epsilon_2}{\partial E_g} \frac{\partial E_g}{\partial T} + \frac{\partial \epsilon_2}{\partial \Gamma} \frac{\partial \Gamma}{\partial T}, \quad (1)$$

where E_g is the energy separation between the bands which are involved in the transition. The temperature modulation of ϵ_2 caused by the shift of energy bands is expected to give rise to a TM spectrum which looks similar to the energy derivative spectrum, $\partial \epsilon_2/\partial E$, as can be seen from the relation

$$\frac{\partial \epsilon_2}{\partial E_g} \frac{\partial E_g}{\partial T} = - \frac{\partial E_g}{\partial T} \frac{\partial \epsilon_2}{\partial (\hbar\omega)}, \quad (2)$$

where $E = \hbar\omega$ is the photon energy. The modulation

of ϵ_2 caused by thermal broadening of energy bands, however, gives rise to a TM spectrum which resembles the $(\partial^2\epsilon_2/\partial E^2)$ -type spectrum. Therefore, if the temperature modulation of ϵ_2 is caused solely by interband transitions, one expects the TM spectrum to exhibit diplike structures at the energy positions of the corresponding peaks in the ϵ_2 spectrum because of the $(\partial^2\epsilon_2/\partial E^2)$ -type contribution. If a derivative-type contribution arising from the shift of energy bands is present, however, the energy positions of the dips may shift to slightly higher or lower energies relative to the corresponding ϵ_2 peaks, depending on the sign of the shift coefficient, $\partial E_g/\partial T$, in Eq. (2). Thus, if the energy position of a dip in the TM spectrum is slightly higher than the energy position of the corresponding peak in the ϵ_2 spectrum then this peak must be associated with a negative shift coefficient as illustrated in Fig. 3. This

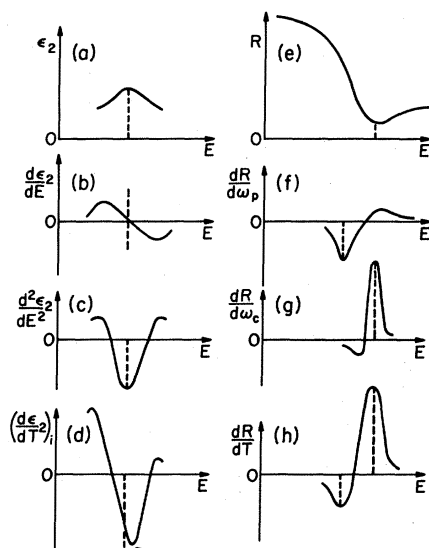


FIG. 3. Schematic representation of various contributions to the $\Delta\epsilon_2$ and ΔR spectra of CrO_2 : (a) Interband contribution to ϵ_2 . (b) Interband contribution to the TM spectrum $\Delta\epsilon_2$ from the shift of energy bands with negative shift coefficient ($\partial E_g/\partial T < 0$). (c) Interband contributions to the TM spectrum from thermal broadening. (d) Net interband contribution to a dip having a negative shift coefficient. Note that the energy position of the dip is shifted to a slightly higher energy compared to the energy position of the ϵ_2 peak. (e) Free-electron contribution to the reflectivity of CrO_2 below ~ 2 eV. (f) Contribution to the ΔR TM spectrum from a plasma resonance, showing a dip at $\hbar\omega_p \approx 0.9$ eV. (g) Contribution to the TM spectrum from collision frequency showing a peak at the energy corresponding to R_{\min} . (h) Net contribution to the TM spectrum expected from the free-electron response. The TM spectrum of CrO_2 below ~ 2 eV, shown in Fig. 3 appears to originate from an interband contribution (d) and a free-electron contribution (h) to the modulation of ϵ_2 .

means that the energy gap between the two bands involved in the interband optical transitions decreases with increasing temperature. Similarly, if the energy position of a dip in the TM spectrum is slightly lower than the energy position of the corresponding peak in the ϵ_2 spectrum, such a peak can be associated with a positive shift coefficient ($\partial E_g/\partial T > 0$). This indicates that the energy separation between the two bands concerned increases with increasing temperature.

A study of the conductivity spectrum of CrO_2 has shown that the properties at energies up to ~ 2 eV are dominated by the conduction-electron response and a single absorption band.^{1,3} At energies near and above 2 eV, however, the optical properties of CrO_2 are largely determined by the interband transitions. Therefore, the structures in the TM spectra at these energies are due to the thermal broadening and shift of energy bands, as discussed above. Comparison of the energy positions of the static and thermomodulated spectra (Table 1) shows that the dip A_2 (B_2) has shifted to a lower energy relative to the corresponding peak in the static spectra. On the basis of the qualitative arguments discussed above, this shift can be explained by associating a positive shift coefficient, $\partial E_g/\partial T > 0$, to the A_2 (B_2) structure. Such an assignment implies an increase of the energy separation between the two bands under consideration with increasing temperature. Similarly, the shift of the A_3 (B_3) structure in the $\vec{E} \parallel \vec{c}$ ($\vec{E} \perp \vec{c}$) TM spectrum to a slightly higher energy relative to the corresponding peak in the static spectra can be explained by assigning a negative shift coefficient, $\partial E_g/\partial T < 0$, to this structure. This implies a narrowing of the band gap with increasing temperature for the interband transitions associated with the A_3 (B_3) structure.

The situation becomes quite different when one considers the TM spectrum below ~ 2 eV, because at these energies there is a contribution to the thermal modulation of ϵ_2 coming from the conduction-electron response, in addition to the normal interband contribution. As evidenced by the nature of the conductivity spectrum of CrO_2 below ~ 2 eV,^{1,3} it is reasonable to separate the low-energy shoulder around 0.8 eV in the ϵ_2 spectrum into two parts: One is a "peak" at 0.8 eV presumably resulting from the interband transitions between cationic d bands separated by ~ 0.8 eV. The other is a low-energy Drude-type response characteristic of free carriers. The peak at 0.8 eV has been attributed to normal interband transitions,³ and therefore the thermal modulation of ϵ_2 gives rise to a diplike structure in the TM spectrum around this energy due to the thermal broadening contribution to ϵ_2 . However, due to the derivative-

type contribution arising from the shift of energy bands the energy position of the dip may shift to a lower or higher energy relative to 0.8 eV depending on the sign of the shift coefficient, $\partial E_g/\partial T$. The appearance of the well-defined low-energy dip at 1.10 eV in the TM spectrum is explained on this basis if one assigns a negative shift coefficient to this structure. Further, the appearance of a low energy peak at 0.65 eV in the TM spectra for $\vec{E} \perp \vec{c}$ strongly suggests that this combined structure, consisting of the peak at 0.65 eV and the dip at 1.10 eV, must be due to the thermal modulation of ϵ_2 arising from interband transitions and not from the thermal modulation of free-carrier response, as described below. This assignment is further supported by the larger magnitude of the A_1 dip compared to B_1 , which is consistent with the greater magnitude of the 0.8 eV shoulder in the R and ϵ_2 data for $\vec{E} \parallel \vec{c}$ compared with the $\vec{E} \perp \vec{c}$ data. The negative shift coefficient associated with this interband transition, therefore, indicates a narrowing of the energy gap concerned with increasing temperature for the corresponding transitions.

The response of free carriers to temperature modulation can give rise to sharp structure near a plasma resonance.⁷ This structure may be due either to a modulation of the plasma frequency, ω_p , or to a modulation of the collision frequency, ω_c . In metals, a sharp diplike structure occurs in the ΔR spectrum very close to ω_p due to the decrease in ω_p with increasing lattice constant as the temperature increases. In addition, a peak in the ΔR spectrum occurs very close to the minimum in the reflectivity due to the increase of ω_c with temperature. A value of $\hbar\omega_p \sim 0.9$ eV for CrO_2 has been estimated previously by fitting the free-electron contribution to the conductivity of a Drude response, with $\hbar\omega_c \sim 0.15$ eV and the high-frequency dielectric constant, $\epsilon_\infty \approx 5$. A contribution to the diplike structure at 1.10 eV in the TM spectrum of CrO_2 could, therefore, result from the thermal modulation of the plasma frequency, and the peak in the TM spectrum around 1.5 eV, where the reflectivity goes through a minimum, could be augmented by the thermal modulation of the collision frequency. The strongly temperature dependent spin-disorder scattering in CrO_2 (Ref. 8) would contribute to a rather large modulation of ω_c at temperatures below T_c . This change in collision frequency may dominate the modulation of ω_p in determining the overall shape of the free-carrier contribution to the TM spectrum of CrO_2 around 1 eV, in contrast with the findings of Matatagui and Cardona⁹ for the alkali metals, where modulation of the plasma frequency produced the largest changes in the TM spectrum.

Since it is possible, however, to qualitatively account for the observed TM structure by modulation of the interband transitions alone, no definitive evidence is found for these free-carrier contributions to the TM spectra of CrO_2 .

The structures observed in the TM spectrum of CrO_2 may be assigned to possible electronic transitions with the help of the phenomenological model illustrated in Fig. 4. According to this model, the primarily cationic d bands in CrO_2 are split by the intra-atomic exchange interaction into α -spin and β -spin subbands. As deduced from our static reflectivity measurements,^{1,3} the energy separation between the primarily anionic valence band, π , and the Fermi level in the half-filled conduction band, $\pi^*-\alpha$, is about 1.5 eV whereas the energy separation of the $\pi^*-\alpha$ and $\pi^*-\beta$ bands, split by the ferromagnetic exchange interaction is about 0.8 eV at room temperature. Increase in spin disorder, as the temperature is increased through T_c , gives rise to a narrowing of the exchange-split cationic d -band gap, effectively raising the $\pi^*-\alpha$ band and lowering the $\pi^*-\beta$ band, relative to the π valence band. Therefore, the assignment of the low-energy dip A_1 (B_1) in the TM spectrum to electronic transitions between the $\pi^*-\alpha$ and $\pi^*-\beta$ bands is consistent with the negative shift coefficient associated with this structure. Similarly, the dip A_2 (B_2) with its positive shift coefficient is assigned to interband transitions between the π valence band and the $\pi^*-\alpha$ conduction band, whereas the dip A_3 (B_3) with its negative shift coefficient is assigned to interband transitions between the π valence band and the empty $\pi^*-\beta$ band. The signs of the shift coefficients associated with these two structures are therefore consistent with the raising of the $\pi^*-\alpha$ band and lowering of the $\pi^*-\beta$ band relative to the π valence band, as the temperature is increased through T_c .

The appearance of only one diplike structure around 1 eV in the TM spectrum suggests that there is no substantial difference between the widths of the π^* band and the $d_{||}$ band in CrO_2 in contrast to Goodenough's energy band scheme.⁵ If

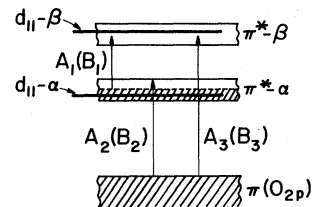


FIG. 4. Assignment of the diplike structures observed in the TM spectrum of CrO_2 to possible interband electronic transitions on the basis of the qualitative energy-band model proposed by Goodenough (Ref. 5).

the widths of the d_n and π^* bands were significantly different, then additional structures associated with these levels would be expected to appear in the TM spectra, even if they could not be resolved in the static spectra. This is because the sharp structures are usually greatly enhanced by modulation techniques. These assignments of the low-energy structures support the conclusions derived from the temperature dependence of less resolved structure in the optical conductivity of CrO_2 ,³ and provide stronger evidence for the narrowing of

the exchange-split cationic d -band gap in this material with increasing temperature, evidently caused by the disappearance of the long-range ferromagnetic order.

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*Present address: Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka.

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