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Temperature, wavelength, and polarization dependent time resolved optical spectroscopy of half-metallic CrO_2

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CrO_2 is an important transition metal oxide due to its half-metallic behavior. We have performed ultrafast laser pump-probe differential transmission experiments on epitaxial CrO_2(110). Polarizations parallel and perpendicular to the *c* axis were used, at wavelengths corresponding to important magnetic excitations: 1300 (1 eV), 800 (1.5 eV), and 650 nm (2 eV). Anisotropy is observed in the polarization-dependent measurements and is attributed to the electronic orbital anisotropy. A critical change of transient transmission is also observed at the Curie temperature of 386 K. This behavior reveals the close relationship between the optical absorption and the spin dynamics of this material. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854417]

Half-metallic chromium dioxide, CrO_2, which had long been used as tape recording media, has recently attracted much attention.[1–3] A half metal has a different density of states for spin up and spin down electrons, and has a spin polarization at the Fermi level approaching 100%. The half-metallic property of CrO_2 deeply affects the transport properties of the material and makes it a potential candidate for spintronic devices and spin injectors.[4,5]

Half-metallic CrO_2 is a transition metal oxide with rutile structure and lattice constants of $a=b=4.421$ Å and $c=2.916$ Å.[6] It is a ferromagnetic metal below Curie temperature (386 K). The magnetic easy axis is along the (001) direction (corresponding to the *c* axis). The Cr^{4+} ion has a complete Ar shell plus two 3*d* electrons. Correspondingly, each O^{2-} ion in the crystal has a He shell plus two 2*s* and six 2*p* electrons. At the oxygen sites, the crystal field leads to two sp^2 combinations formed by the 2*s* and $2p_x$, $2p_z$ electrons, and a $2p_y$ state whose orbital plane is perpendicular to *c* axis. For the chromium sites, the crystal field splits the 3*d* bands into three t_{2_g} states and two e_g states. In the local coordinate system, the three t_{2_g} orbitals can be expressed as the natural base $3d_{xy}$, $3d_{xz-yz}$, and $3d_{xz+yz}$. One of the t_{2_g} states, namely $3d_{yz-xz}$, is hybridized with the oxygen $2p_y$ state and forms a π-type state near the Fermi level.[7,8] The strong orbital anisotropy has been previously investigated with optical spectroscopy[9] and polarization-dependent x-ray absorption spectroscopy.[8]

Band structure calculations have been performed using different approximations.[1,7,10] Although they are different in details, the main results in the vicinity of Fermi level are similar: One of the two 3*d* electrons occupies the $3d_{xy}$ state, which is localized and forms a spin up "core." Another 3*d* electron partly fills the Cr3d_{yz+xz} band and the hybridization band of the O2p_y and Cr3d_{yz-xz}, and is itinerant. It propagates through the spin up cores and aligns its spin with them resulting in a double exchange mechanism.

One of the difficulties in studying the band structure and electronic and spin dynamics of CrO_2 is that it is metastable at 300 K in air, and the top 1–2 nm of the thin films rapidly decomposes into an amorphous state with a stoichiometry similar to antiferromagnetic Cr_2O_3. Recently, ultrafast laser pump-probe spectroscopy has been used to study spin and magnetization dynamics in CrO_2 (Ref. 11) as well as other half metals.[12] Studying thin films by optical transmission should minimize surface effects. To investigate the electronic structure of CrO_2, we have performed polarization-dependent ultrafast spectroscopy on anisotropic CrO_2 thin films at different temperatures for different wavelengths. Our results are consistent with the band structure calculations, which predict strong orbital anisotropy.

The films studied were ~500 nm thick epitaxial CrO_2 grown by thermal decomposition of CrO_3 powder on TiO_2(110) substrates. The details of film growth and characterization are given elsewhere.[13] For transmission experiments, both sides of the TiO_2 were polished.

The ultrafast dynamics were measured by pump-probe experiments. The sample is excited by a pump laser pulse and measured by a delayed probe pulse. A mode-locked amplified Ti:Sapphire laser, with 1 kHz repetition rate and 150 fs duration, was used as the pump. The wavelength of the pump beam was 800 nm (1.5 eV). The probe beam was tuned to various wavelengths: 650 (2 eV), 800 (1.5 eV), and 1300 nm (1 eV). The 1300 nm pulses were obtained from an optical parameter amplifier. The 650 nm pulses were obtained by doubling the frequency of the 1300 nm pulses using a beta barium borate crystal. The pulse energy for the pump and probe were approximately 20 μJ and 10 nJ, respectively. The beam size of pump and probe are about 10 and 1 mm^2, which gives a fluence of 0.2 mJ/cm^2 and 1 $\mu J/cm^2$, respectively. The probe beam transmitted through the sample was measured by a silicon photodiode. The pump beam was chopped at 400 Hz and the differential transmission signal was measured by lock-in amplifier. The sign of the differential transmission was determined by setting the phase by the pump beam. The sign (induced absorption or transmission) was confirmed by checking the response of a

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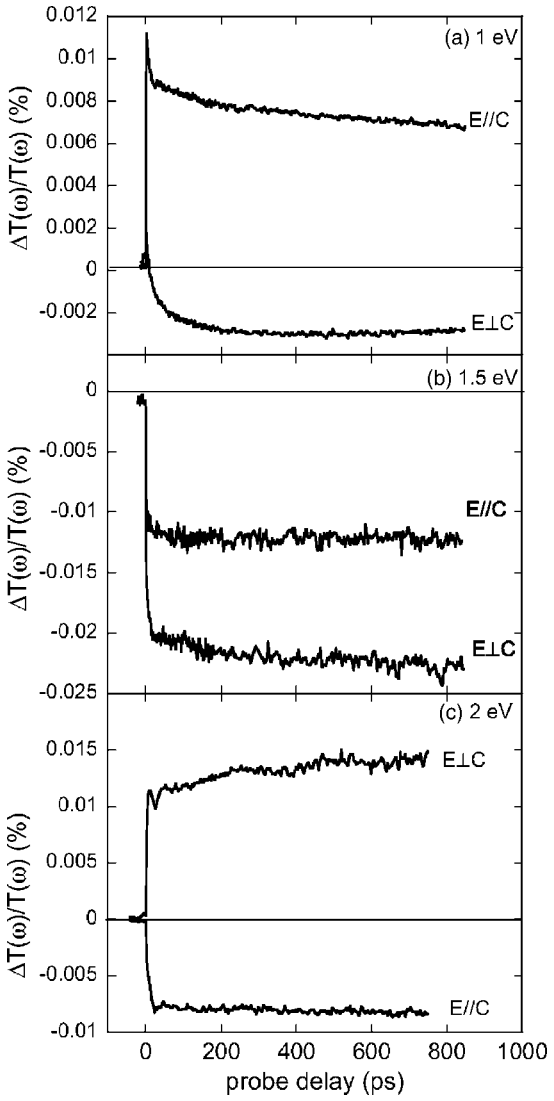

FIG. 1. Pump-probe differential transmission at 300 K with probe energy of (a) 1 eV, (b) 1.5 eV, and (c) 2 eV. The probe polarization is either parallel or perpendicular with the crystal easy axis, as indicated.

gold film. The experiments were conducted at various temperatures from 300 to 440 K.

The differential transmission results show a wavelength and polarization dependence of the probe beam, as shown in Fig. 1. In this figure, the differential transmission $[\Delta T(\omega)/T(\omega)]$ is shown at 300 K for the pump at various energies (wavelengths) and for polarizations parallel or perpendicular to the *c* axis. As shown in Figs. 1(a) and 1(b), the pump causes a greater increase in absorption $[\Delta T(\omega)<0]$ of the probe beam whose polarization (E) is perpendicular to the *c* axis than for the case of a probe polarization parallel to the *c* axis $[\Delta T(\omega)<0$ for 1.5 eV and $\Delta T(\omega)>0$ for 1 eV]. For a 2 eV probe energy, shown in Fig. 1(c), the opposite is true. The pump beam decreases the absorption $[\Delta T(\omega)>0]$ of the probe beam with polarization perpendicular to the *c* axis while increasing the absorption of the probe whose polarization is parallel to the *c* axis. The specific polarization or wavelength of the pump beam does not have a noticeable effect on the signals.

The differential transmission signals studied as a function of temperature (T) show abrupt changes around the Curie temperature of the CrO_2, as shown in Figs. 2 and 3, indicating that the behavior seen is related to the magnetic properties. For the probe energy at 1 eV with $E \perp c$, as shown in Fig. 2(a), the differential transmission signal shows

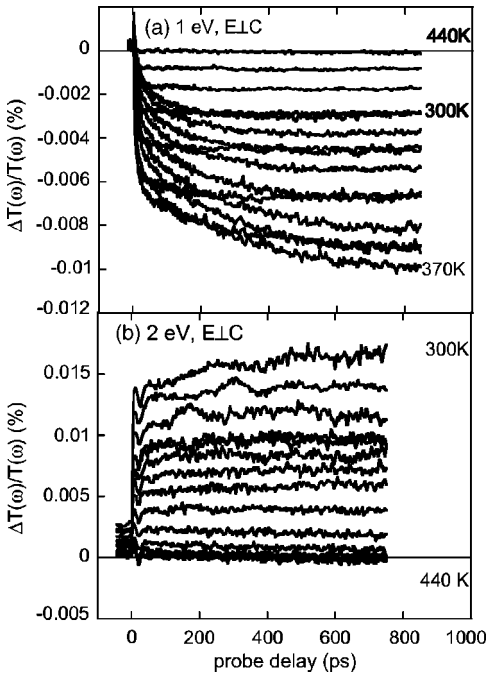

FIG. 2. (a) Pump-probe differential transmission at various temperatures from 300 to 440 K for probe polarization perpendicular to the *c* axis, with a probe energy of (a) 1 eV and (b) 2 eV. In (a), the differential absorption increases from 300 K up to approximately 370 K, and decreases to zero afterwards. In (b), there is a continuous decrease of the differential transmission signal to zero from 300 to 440 K.

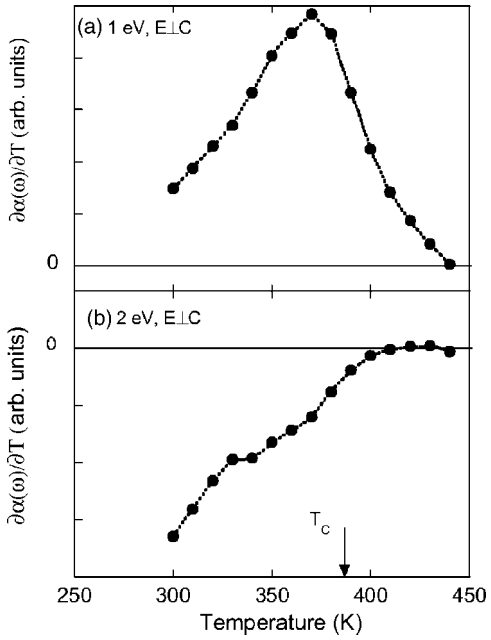

FIG. 3. Behavior of the differential absorption as a function of temperature for probe polarization perpendicular to the *c* axis, with a probe energy of (a) 1 eV and (b) 2 eV. The differential absorption change is determined from the differential transmission shown in Fig. 2, averaged from 600 to 700 ps, as described in the text. Note the characteristic "λ" shape around the Curie temperature in (a) and the decrease of the signal to zero in (b).

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a pump-induced increase in absorption which increases in magnitude up until T_C, after which the signal decreases to zero. In Fig. 2(b) the signal for the probe energy at 2 eV with $E \perp c$ is shown, for increasing temperatures from 300 to 440 K. The signal drops abruptly with increasing temperature and disappears at and above T_C. This behavior can be qualitatively represented by a plot of $\partial\alpha/\partial T$, shown in Fig. 3, where α is the absorption coefficient and $\partial\alpha/\partial T$ is proportional to $-\Delta T(\omega)/T(\omega)$. Each data point in Fig. 3 is an average over the range from 600 to 700 ps since the change of the signal is small in this range. In Fig. 2(a), the signal for the probe at 1 eV, with $E \perp c$ is shown. The temperature dependence of this signal shows a characteristic lambda shape around the Curie temperature. The 2 eV probe with $E \perp c$, however, experiences a pump-induced decrease in absorption which decreases as the temperature increases, as shown in Fig. 3(b). For the $E \| c$ cases the absorption decreases as the temperature increases. For the 1.5 eV data (not shown here), both the $E \perp c$ and $E \| c$ configurations give an increasing absorption as the temperature increases, which indeed is consistent with the temperature dependent absorption measurements.[14]

The optical anisotropy revealed in these experiments is consistent with the general features of the CrO_2 band structure. The π-type state formed by the hybridization of oxygen P_y state and the chromium d_{xz-yz} state is expected to play an important role in the differential transmission anisotropy. It is close to the Fermi surface and thus can be easily excited optically. Its orbital, as we have discussed, is perpendicular with the c axis and thus the electrons in the band are more sensitive to the laser pulse of $E \perp c$ because the E vector is in the orbital plane. Moreover, this π-type state is also the origin of the anisotropy of x-ray absorption spectroscopy and the x-ray magnetic circular dichroism.[8,15]

The fact that 2 eV probe with $E \perp c$ is less absorbed than the $E \| c$ probe, while 1 and 1.5 eV probes of $E \perp c$ are more absorbed than the $E \| c$ probe pulses can be explained by assuming this π-type band as the upper level of the 1 and 1.5 eV optical transitions and the lower level of the 2 eV transition. This assumption is strongly supported by the temperature dependent optical absorption experiments.[14] According to this assumption, the electronic population of the π-type state is important to the 1, 1.5, and 2 eV transitions. The pump pulse heats the electrons and redistributes them near the Fermi level. More empty states are then created in the π-type band, which is situated near the Fermi surface. The increase of the empty states in the π-type band enhances the 1 and 1.5 eV optical transitions, whose final states are in the band, and decreases the absorption of the 2 eV photons because of the electronic population decrease.

This picture is confirmed by the temperature dependence of the signals (Fig. 3). For example, in Fig. 3(b), $\partial\alpha(\omega)/\partial T$ is negative, which means the absorption coefficient decreases as the temperature increases. If we take the absorption as an indication of the electronic population, we can easily see the reasonable result that the electronic population at the energy level near the Fermi surface is decreased by the rising temperature.

The "λ" shape shown in Fig. 3(a) is a characteristic shape of specific heat near the magnetic phase transition. Here if we assume the 1300 nm optical transition is an intraband transition, then all the absorbed photon energy is converted to heat. Therefore it is reasonable to expect at this wavelength the absorption coefficient has a similar feature with the thermal properties of the material near the magnetic phase transition temperature. Although not very prominently, the same "λ" shape is also observed in the 1.5 eV experiments. But no such curve is observed in the 2 eV case [Fig. 3(b)]. This implies that the 1 and 1.5 eV transitions are the intraband transitions in which most of the absorbed energy is converted to the form of heat, while a large part of the energy absorbed in the 2 eV transitions produces interband excitations and thus the "λ" shape of the specific heat is not evident. Instead, we see an absorption related with the electronic population. Therefore, we believe there is a band gap of about 1.5–2 eV near the Fermi surface that separates the interband and intraband transitions. This gap could be the predicted minority gap.[7,16]

In summary, we have performed ultrafast transmission measurements on anisotropic CrO_2 thin films. We have observed optical anisotropy which is consistent with the Cr -3*d* and O-2*p* bands hybridization model. The wavelength and temperature dependent measurements imply there is a band gap of 1.5–2 eV near the Fermi surface. These results indicate that ultrafast optical spectroscopy is a useful tool for studying magnetic transitions and magnetization dynamics in half metals.

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