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Electron dynamics in chromium probed with 20-fs optical pulses

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Electron excitation and relaxation in chromium are probed with 20-fs time resolution using an ultrafast optical technique. We obtain good fits to the data for the transient reflectivity and transmittivity changes in a thin film using a simple model of electron relaxation, suggesting the existence of an efficient electron-electron thermalization process on ultrashort-time scales. Quantitative analysis allows the extraction of thermo-optic coefficients and dielectric constant variations related to both the electron and the lattice temperatures.

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Nonequilibrium electron distributions can be excited in metals with an ultrashort light pulse. The subsequent energy exchange between the electrons and the lattice is governed predominantly by the electron-phonon (e-p) scattering time, but is also affected by the electron-electron (e-e) scattering time. The noble metals, possessing simple band structures, have provided a fertile testing ground for theories of nonequilibrium electron relaxation and diffusion. It is now possible to investigate the electron dynamics on time scales of the order of the e-e scattering time, typically 10–50 fs for excess electron energies ~1 eV. Although in the noble metals and in the alloy CoPt3, where the e-p interaction is relatively weak, the evolution of such transient athermal electron distributions was investigated with ~20-fs time resolution, in other transition metals no studies have been made on these time scales, to the best of our knowledge.

The group-VIB transition metals (Cr, Mo, W) are interesting because they have large values of the e-p coupling constant, resulting in short electron energy relaxation times ~200 fs compared to the noble metals (~1 ps). Their band structure is complicated, there being a significant density of states due to d electrons in the region around the Fermi level. Understanding the short-time electron dynamics in such metals with strong e-p coupling should become essential for applications in future ultrafast devices with ultrahigh switching speeds. The electron relaxation in thin films of chromium and tungsten under spatially homogeneous conditions was measured by Brorson et al. with optical pulses of duration 60 fs. But only the reflectivity change was probed, thus preventing access to the transient dielectric constant. In this report we monitor both the reflectivity and transmittivity changes in a thin polycrystalline film of chromium with 20-fs optical pulses to elucidate the ultrafast dynamics of the electrons therein.

The film of Cr on a crown glass substrate is excited and probed from the front side with near Fourier-transform-limited optical pulses from a Ti:sapphire laser (Kapteyn-Murmanc Labs) of central wavelength 790 nm, repetition rate 87 MHz, pulse duration \( \tau_p = 20 \text{ fs} \) [full width at half maximum (FWHM) intensity], and spectral width ~50 nm (FWHM). A schematic diagram of the apparatus is shown in Fig. 1. Interband transitions of electrons within the photon energy (1.57 eV) of the Fermi surface (at \( E_F = 7 \text{ eV} \)) are primarily induced. The optical pulse duration is controlled by two prisms. It is measured at the sample position by a noncollinear cross-correlation technique, through the temporal insertion of a 25-\( \mu \)m slab of beta barium borate that combines the cross-polarized pump and probe beams at 0° and 10° (p-polarized) incidence, respectively. At the sample the optical spot radius at 1/e intensity is \( a = 9.5 \mu \text{m} \), the typical incident pump pulse energy is \( E = 0.75 \text{ nJ} \) (maximum incident fluence \( E/\pi a^2 = 0.26 \text{ mJ cm}^{-2} \)), and the probe pulse energy is 0.007 nJ. The predicted electron temperature change (for a thermalized electron gas) is 220 K and that of the lattice is 8 K. The pump light is chopped mechanically at 2 kHz, and a synchronous signal proportional to the reflected or transmitted intensity variation of the probe light is fed to a lock-in amplifier. Multiple scanning with an optical delay line allows a resolution for relative intensity changes \( \sim 5 \times 10^{-6} \) (with a total integration time of ~2 s per point with 280 points, using 60 scans).

The polycrystalline Cr sample of thickness \( d_0 = 19 \text{ nm} \) is prepared on a crown glass substrate of thickness 1 mm at a pressure of \( 5 \times 10^{-6} \) Torr by electron-beam deposition at 0.3 nm s\(^{-1}\). The grain size was estimated by atomic force microscopy to be 100–200 nm. The thickness is measured by spectroscopic ellipsometry and confirmed with picosecond ultrasonics. The refractive index of the film \( n + i \kappa = 3.65 \)
+ 3.09i) and substrate (n s = 1.52) at 790 nm are also measured by ellipsometry. This value of k corresponds to a 20-nm optical-absorption depth. The measured static reflection and transmission coefficients for the sample for ultrashort optical pulses are, respectively, R = 0.46 and T = 0.12. These values are close to those (R = 0.43 and T = 0.16) expected from the measured optical-absorption profile in the depth direction in the film. With the steady-state sample temperature in the probed region estimated at ≈470 K, 14 Cr is in its paramagnetic state. (Exposure to a temperature of 470 K or higher can increase the native oxide layer thickness on the sample, of the order of a few nm in thickness, that should have a negligible effect on the present measurements. 15)

Figure 2(a) shows the experimental relative reflectivity and transmittivity changes (solid curves) as a function of delay time. The initial change in the signals is compared with the integral (dash-dotted curves) of the cross-correlation (dashed curves) for the pump and probe optical pulses. The data follow closely behind this integral in the initial stages. The sign of ΔR (dependent on film thickness 16) is opposite to that of ΔT. The simplest theoretical model that can account for this data reasonably well is the two-temperature model: 17 the electrons and the lattice are assumed to be described by separate temperatures T e and T l, coupled by the e-p interaction. In a one-dimensional approximation, valid since a ≫ d, 0,

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -g(T_e - T_I) + S(z, t),$$  

$$C_l \frac{\partial T_l}{\partial t} = g(T_e - T_I),$$

where z is the depth coordinate. The e-p coupling constant g and the lattice heat capacity C l are assumed to be constant because of the relatively small transient change in lattice temperature (≪10 K). 18 The electron heat capacity, about 35 times smaller than C l (≈3.6 Jm −3 K −1 at 470 K), is given by C e(T e) = γ T e (γ = 193 Jm −3 K −2). 19 The source term due to the optical pulse is taken as

$$S(t) = 2K \sqrt{F} \exp \left[ -4 \ln 2 \left( \frac{t}{\tau_L} \right)^2 \right],$$

where the factor K = 1 2 here is calculated to account for the spot size of the probe beam. Because of the poor air and substrate thermal diffusivities, we assume no transport of heat (or electrons) across the film boundaries on our experimental time scales.

Neglecting the small modulation from the substrate on our time scales, the reflectance (r) and transmittance (τ) changes (≪1) for the present geometry can be calculated from the transient dielectric constant change Δε ∼ (n + ik) 2 of the film by assuming monochromatic incident radiation and spatially homogeneous modulation: 20

$$\frac{\partial r}{r} = \frac{ik_0 \Delta \varepsilon}{2a_0 b_0} \int_0^{d_0} (a_1 e^{ikz} + b_1 e^{-ikz})^2 dz,$$

$$\frac{\partial \tau}{\tau} = \frac{ik_0 \Delta \varepsilon}{2a_0} \int_0^{d_0} (a_1 e^{ikz} + b_1 e^{-ikz})(a_1' e^{ikz} + b_1' e^{-ikz}) dz,$$

where k 0 and k 1 are wave numbers and a 0, b 0, a 1, b 1, a 1', and b 1' are constants, 21 for which 0 refers to air and 1 to the film. The measured relative reflectivity (∆R/R) and transmittivity (∆T/T) changes are related to Eqs. (3) and (4) by ΔR/R = 2 Re(∂r/∂t), ΔT/T = 2 Re(∂τ/∂t) [since R = |r| 2 and T = |τ| 2]. Here, Δε is assumed to be linearly related to the electron and lattice temperature changes for our range of fluences. Measurements and fits for ∆R at different pump fluences (with τ L = 34 fs—see Fig. 2 inset) confirm that this first-order approximation is reasonable: 22

$$\Delta \varepsilon = \Delta \varepsilon_1 + i \Delta \varepsilon_2 = (a \Delta T_e + b \Delta T_I) + i(c \Delta T_e + d \Delta T_I),$$

where a = ∂ε/∂T e, b = ∂ε/∂T l, c = ∂ε/∂T e, and d = ∂ε/∂T l. We treat these thermo-optic coefficients and g as fitting parameters, substituting the numerical solution of the nonlinear Eqs. (1) and (2) obtained by the finite-difference technique into Eqs. (3)–(5). 23 By least-squares fitting using parameters a, b, c, d, and g common to the two data curves in the presence of an optical pulse.
good agreement with that found in low-frequency thermomodulation, the changes in the density of states and in the multiparameter fitting.

The experimental results are shown in Fig. 2, and including a convolution with the probe pulse temporal profile, theoretical curves (dotted lines) are obtained that are very similar to experiment. This relative success of the two-temperature model may well extend to a wide range of optical wavelengths, considering the broad features in the joint density of states of the electrons in the VIB transition metals.11,24

The fitted value of \( g = (470 \pm 30) \times 10^{-15} \text{Jm}^{-3} \text{K}^{-1} \) is in good agreement with (relatively temperature-insensitive) literature values.10,25 The thermo-optic coefficients obtained are \( \beta_1 = -2.4 \times 10^{-5} \), \( \beta_2 = -4.1 \times 10^{-5} \), \( \beta_3 = -1.2 \times 10^{-5} \), and \( \beta_4 = 2.0 \times 10^{-5} \) (solid curve) in units of \( \text{K}^{-1} \). The uncertainties are typically \( \pm 30\% \), owing mainly to the errors in the measurement of the pump fluence and in the multitemperature fitting. These coefficients, sensitive to the band structure, are strong functions of wavelength.11,26 Our low value for the ratio of \( \beta_2 / \beta_3 - 2 \beta_4 / \beta_2 \) at 790 nm is consistent with that found in low-frequency thermomodulation measurements, although the comparison is not exact because our experiments are done under conditions of approximately constant (zero) strain as opposed to constant (zero) stress.

The experimental \( \Delta R/R \) and \( \Delta T/T \) variations are difficult to interpret physically in terms of microscopic theories. The transient dielectric constant variation is more fundamental and is directly related to changes in the density of states governing the relevant electronic transitions. For our homogeneously excited thin film, the changes in \( \Delta R \) and \( \Delta T \) are linearly related to those in the dielectric constants,4,5,8

\[
\Delta R/R = \alpha_1 \Delta \varepsilon_1 + \alpha_2 \Delta \varepsilon_2, \tag{6}
\]

where the coefficients \( \alpha_1, \alpha_2, \beta_1, \beta_2 \) can be obtained from Eqs. (3) and (4). Knowing the fitted \( \Delta R/R \) and \( \Delta T/T \) variations allows one to solve for the theoretical \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) variations, and in turn from Eqs. (3)–(5) for the theoretical electronic and lattice contributions to \( \Delta R/R \) and \( \Delta T/T \), as shown in Fig. 3 (based on values of \( \alpha_1, \alpha_2, \beta_1 \) and \( \beta_2 \) equal to 0.0025, 0.024, 0.0037 and -0.050, respectively). The lattice contribution for both the relative reflectivity [Fig. 3(a)] and transmissivity [Fig. 3(b)] changes tends to a constant value as the electron temperature relaxes. The contribution from the electron temperature change is dominant at short times in both cases.

Equations (6) and (7) also allow one to derive the experimental \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) variations (independent of any dynamical model), as shown in Fig. 4(a). Some salient points regarding these are as follows: (i) the temporal shape of \( \Delta \varepsilon_2 \) is similar to that of \( \Delta R/R \) and \( \Delta T/T \), and \( \Delta \varepsilon_2 \) is dominated by the electronic contribution; (ii) the temporal shape of \( \Delta \varepsilon_1 \) is different, and is strongly influenced by the lattice contribution; (iii) the noise level for \( \Delta \varepsilon_1 \) is significantly larger than that for \( \Delta \varepsilon_2 \). The results are a direct consequence of the signs and relative magnitudes of \( \alpha_1, \alpha_2, \beta_1, \beta_2 \) and of \( a, b, c, d \). (iv) The magnitude of \( \Delta \varepsilon_1 \) is larger than that of \( \Delta \varepsilon_2 \), both quantities being negative. The sign of \( \Delta \varepsilon_2 \) indicates a decrease in absorption during the transient heating. The derived electronic contributions to the experimental dielectric constant variations, \( \Delta \varepsilon^e_1 \) and \( \Delta \varepsilon^e_2 \), are shown in Fig. 4(b). Comparison with the predictions of the two-temperature model (dashed curves) shows good agreement at times \( t > 100 \text{fs} \), suggesting that \( T_e \) is well defined at these
times and that the electron distribution is internally thermalized within \( \sim 100 \) fs by e-e scattering. By fitting the experimental \( \Delta e^* \) decays to the approximate function \( \exp(-t/\tau_{e,2}) \), the effective electron energy relaxation times \( \tau_{e,1} \) for \( \Delta e^*_1(t) \) and \( \tau_{e,2} \) for \( \Delta e^*_2(t) \) are found to be \( 230 \pm 50 \) and \( 210 \pm 20 \) fs, respectively. These values are larger than the value \( \tau_{e}(T_e = T_l = 470 \) K) = \( C_e/g \approx 190 \) fs expected for the same initial lattice temperature in the limit of small \( \Delta T_e \). This increase in \( \tau_e \) with increasing \( T_e \) is in agreement with rough estimates based on an approximate first-order solution to Eqs. (1) and (2) at constant \( T_l \): \( \tau_e \approx \tau_e(T_l)(1 + T_e/T_l)/2 \) (see Ref. 2). In a more sophisticated treatment the effect of the finite e-e relaxation time\(^{27} \) and the band structure\(^{11} \) should be taken into account. The variations \( \Delta e^*_1(t) \) and \( \Delta e^*_2(t) \) arise from a sum of all allowed electronic transitions at the probe wavelength originating in different regions of \( k \) space whose populations are perturbed by the pump optical pulse. These variations cannot be ascribed to a single interband transition in the complex band structure of Cr\(^{11,26} \). A more detailed analysis of the \( \Delta e \) variations is beyond the scope of this report.

In conclusion we have investigated the nonequilibrium dynamics of electron relaxation in chromium with 20-fs time resolution using an ultrafast optical technique. The two-temperature model produces good agreement with the experimental data, implying electron-electron thermalization within \( \sim 100 \) fs in this metal. This efficient thermalization and the short electron energy relaxation time in chromium bode well for future applications in ultrafast control of charge distributions and transport in transition metals.

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12 Another sample of similar thickness made by the same technique at \( 5 \times 10^{-7} \) Torr and 0.7 nm s\(^{-1} \) gave an identical reflectivity response, allowing us to conclude that the residual oxygen content of our film did not influence the results. See A. K. Kulkarni and L. C. Chang, Thin Solid Films 301, 17 (1997).
14 This value, averaged over the probe beam profile, is estimated from a three-dimensional heat conduction model using the average absorbed pump power (12.4 mW), the Gaussian pump spot radius \( a \), and the thermal conductivities of the substrate (1.4 Wm\(^{-1}\)K\(^{-1} \)) and film (94 Wm\(^{-1}\)K\(^{-1} \)).
21 Here \( k_0, k_1, \) and \( k_2 \) are the wave numbers in the air, film, and substrate, respectively, and
\[
a_0 = (k_0 + k_1)(k_1 + k_2) + (k_0 - k_1)(k_1 - k_2)e^{2ik_1d_0} \]
\[
b_0 = (k_0 - k_1)(k_1 + k_2) + (k_0 + k_1)
\times(k_1 - k_2)e^{2ik_1d_0}, \quad a_1 = 2k_0(k_1 + k_2), \quad b_1 = 2k_0(k_1 - k_0)e^{2ik_1d_0},
\]
\[
a_1' = (k_1 - k_0) / 2k_1, \quad \text{and} \quad b_1' = (k_0 + k_1) / 2k_1.
\]
22 The measurements in the inset of Fig. 2 were also repeated in the range 0–150 fs at higher resolution to check the short-time response at different fluences. The characteristic slightly delayed response at short times compared to the two-temperature model was more clearly evident at both fluences.