

## Structural Phase Transition of Aluminum Induced by Electronic Excitation

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The dynamics of a structural phase transition induced by interband electronic excitation in aluminum is studied by determining the time evolution of the dielectric constant at 1.55 eV through the measurement of the transient reflectivity induced by an ultrafast pump pulse. The threshold fluence and the time scale for this transition are significantly less than the values necessary for ultrafast heat-induced melting, indicating that this phase change is caused by band structure collapse and lattice instability resulting from strong electronic excitation.

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The understanding of structural phase transitions in metals induced by intense laser radiation is important because of its wide applications in materials processing and manufacturing. The dynamics associated with phase change, however, has only recently been explored using ultrafast optical techniques. Such techniques permit time-resolved measurements of nonequilibrium processes, revealing the dynamics of structural phase transitions with femtosecond time resolution.

During the past two decades, the study of ultrafast dynamics of low intensity laser interaction with metals has been vigorously pursued. Ultrashort pulses, with durations less than or comparable to the excited electron energy-loss lifetime, can heat electrons in a metal to a very high temperature while leaving the lattice relatively cool because the heat capacity of the electrons is much smaller than that of the lattice [1–4]. If the perturbing laser pulse is sufficiently weak, this transient nonequilibrium system will reach equilibrium within a few picoseconds through electron-phonon interactions as well as electron transport out of the excited region [1–4]. When the incident laser fluence is high enough to elevate the final lattice temperature to the melting point, the material will begin a solid to liquid phase transformation (a process that we refer to as ultrafast heat-induced melting throughout this paper). However, the understanding of the dynamics of ultrafast laser-induced melting of metals is in its infancy, and further investigation is required to understand the dynamics of the lattice deformation that leads to melting.

In this paper, we study the structural phase transition in aluminum (Al) induced by a direct electronic interband excitation generated by 1.55-eV, 130-fs laser pulses. The dynamics of the structural phase transition process in Al is studied by measuring the time evolution of its dielectric constant at 1.55 eV. The study of the change in the dielectric constant has fundamental advantages compared to studying only the optical reflectivity or second-harmonic generation because the dielectric constant reflects the intrinsic optical properties of a material [5,6]. The threshold laser fluence and the time scale required for melting Al are

found to be much less than the values necessary for ultrafast heat-induced melting discussed in the previous paragraph, indicating that interband electronic excitation in Al leads to lattice instability and a structural phase transition.

The experiment uses an amplified Ti:sapphire laser system running at a 1-kHz repetition rate, producing over 700  $\mu\text{J}/\text{pulse}$  in 130-fs pulses with a central wavelength of 800 nm. The repetition rate of the laser pulses can be further reduced with a pulse selector. A pump and two-angle probe technique is used to study the response of the dielectric constant in Al at 1.55 eV [5]. The pump pulse is weakly focused at normal incidence onto the sample, while two probe beams, incident at 47° and 58°, are focused to an area 10 times smaller than the pump beam to ensure probing of a uniformly excited area. The reflectance from two angles is recorded at each time delay and used to extract the dielectric constant through numerically inverting the Fresnel reflectivity formulas. The pump and probe beams are cross polarized ( $p$  polarization for probe) to minimize coherent artifacts when the pump and probe overlap temporally. In fact, no major conclusion in this paper is derived from the data points at zero time delay and therefore the possibility of coherent effects is relatively unimportant here. Polarizers allowing only the  $p$ -polarized light (probe) and 10-nm narrow bandpass interference filters for 800 nm are inserted in front of the probe detectors. The dielectric constant of Al at 1.55 eV is measured with this two-angle technique first without laser excitation, and the result shows excellent agreement with the published value [ $\text{Re}(\epsilon) = -63.6$ ,  $\text{Im}(\epsilon) = 47.2$ ] [7].

A polycrystalline Al sample is mounted on a motion system allowing for translation of the sample to a fresh spot between laser shots. The Al sample, prepared through high-vacuum deposition, has an rms surface roughness of 3.8 nm ensuring accurate optical measurements at 1.55 eV for Al [8]. A very thin layer of the surface oxide film on Al plays no role in affecting the measurement since infrared light does not interact with the oxide layer and therefore any absorption relating to the oxide layer is unimportant in our measurements [7,9]. In fact, the good agreement

with previously published values for the dielectric constant measured with  $p$ -polarized probe light (discussed above) reinforces the unimportance of this oxide layer.

A strong interband transition around 1.55 eV in Al has been reported resulting from a parallel-band structure in planes parallel to the (200) faces of the Brillouin zone in fcc Al [10–12], as illustrated in Fig. 1. Therefore, a strong interband electronic excitation can be induced in Al with our 1.55-eV laser pulses. When an intense pump pulse excites many electrons to states above the Fermi level through this interband transition, a transient bleaching occurs and the reflectance of the probe pulse will increase. This can be seen clearly in Fig. 2(a), where the reflectance of probe pulse increases when Al is excited by a pump pulse with a fluence of 27 mJ/cm<sup>2</sup>. This reflectance increase due to the transient bleaching here is in contrast with a reflectance decrease normally induced by thermal heating in metals. (There could also be ultrafast heating in Al at 1.55 eV, but the reflectance increase indicates that electronic excitation dominates the process.) To see this, gold is also studied with the same pump-probe technique. Because there is no strong interband absorption for gold at 1.55 eV, we see a decrease of the probe reflectance due to the laser heating [Fig. 2(b)], consistent with previous experiments [13–16]. The data in Fig. 2 are both measured for laser pump fluences below the damage threshold, and we can see that the reflectance change in Al induced by the electronic excitation has a much slower relaxation time while the ultrafast heat-induced reflectance change in gold relaxes significantly within a few picoseconds, the time scale of the electron-phonon interaction in gold [17].

In Fig. 3, the change of reflectivity for Al is plotted versus pump fluence at probe delays of 2 and 10 ps. The probe reflectivity change increases with pump fluence sub-linearly up to a threshold fluence of 34 mJ/cm<sup>2</sup>, indicative of the nonlinear character of transient bleaching. When the pump fluence is further increased, the change of the probe reflectivity drops to a value of 1.2% and remains relatively unchanged as the pump fluence increases up to about 80 mJ/cm<sup>2</sup>. If the parallel band structure in Al were preserved despite the electronic excitation, we would expect the reflectance of the probe pulse to increase monotonically with pump fluence due to the transient bleaching,

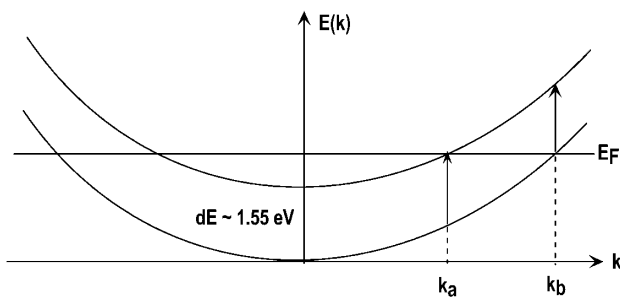


FIG. 1. Parallel band structure of aluminum.

especially at a time delay of 2 ps. (The decay of the electronic excitation, however, is slow at all fluences studied.) Therefore, the sudden drop of the reflectance when the pump fluence is above the threshold value can be attributed to a significant modification of the band structure induced by the electronic excitation. Moreover, examination of the Al samples under an optical microscope reveals that irreversible damage appears when the laser fluence is just above the threshold point of 34 mJ/cm<sup>2</sup>. This measurement strongly indicates that the structural phase change induced by electronic excitation is actually tied to the band structure collapse in Al, a phenomenon that has been observed in semiconductors [5].

To understand further the detailed dynamics of the structural phase change, the time evolution of dielectric constant at 1.55 eV is obtained through the simultaneous two-angle probe measurement. In Fig. 4, both real and imaginary parts of the dielectric constant are plotted versus pump-probe time delay for three excitation fluences. At a low fluence of 2.1 mJ/cm<sup>2</sup>, the change of dielectric constant is very small since Al is only weakly perturbed. At the damage threshold fluence of 34 mJ/cm<sup>2</sup>, we can see that the dielectric constant changes quite significantly after excitation. The imaginary part of the dielectric constant, characteristic of the material absorption, drops below the unperturbed value after excitation and starts to recover towards the initial value. (The relatively large fluctuation of dielectric constant at  $t = 0$  could be due to coherent artifacts or ultrafast heating at some level, but this is

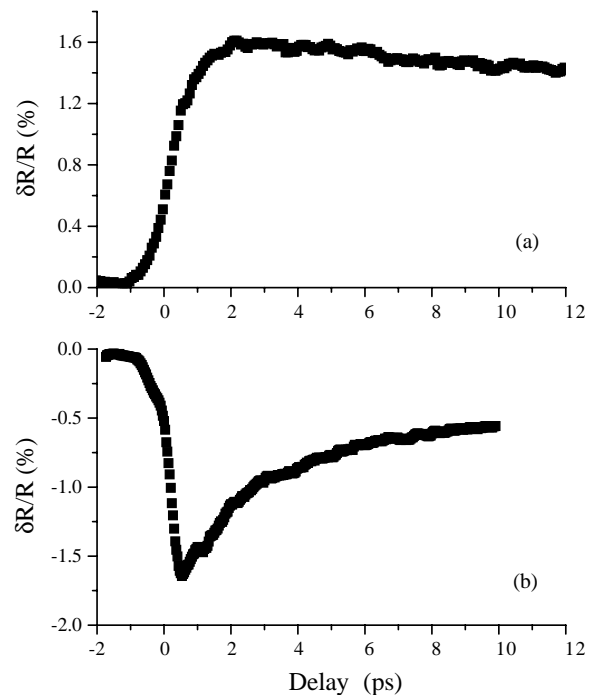


FIG. 2. Reflectance of probe beam at 58° for (a) aluminum excited by a 1.55-eV, 27-mJ/cm<sup>2</sup> pump pulse; (b) gold excited by a 1.55-eV, 177-mJ/cm<sup>2</sup> pump pulse.

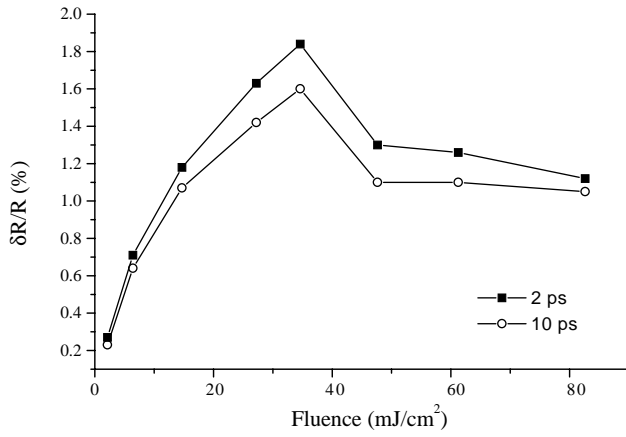


FIG. 3. Fluence dependent change of probe reflectance, incident at  $58^\circ$ , in aluminum at time delays of 2 and 10 ps.

irrelevant to the further discussions in this paper.) The dielectric constant will fully recover to the initial value in about 200 ps, and, therefore, the process is reversible at this threshold fluence even though the dielectric constant experiences a relatively large change. When the fluence is further increased above the damage threshold, the change of dielectric constant becomes irreversible. As shown in the plot for the fluence of  $1.8F_{th} = 63 \text{ mJ/cm}^2$ , the real and imaginary parts approach stable values about 500 fs after excitation, which is much shorter than the electron-phonon coupling time for the ultrafast heat-induced melting. At this high fluence, we can also see that the final pump-induced values of the dielectric constant show excellent agreement with those of liquid phase Al, as reported in Ref. [18]. This indicates that a laser-induced solid-liquid phase transition in our case occurs about 500 fs after excitation when the laser fluence is above threshold. Finally, we note that the previously reported absence of

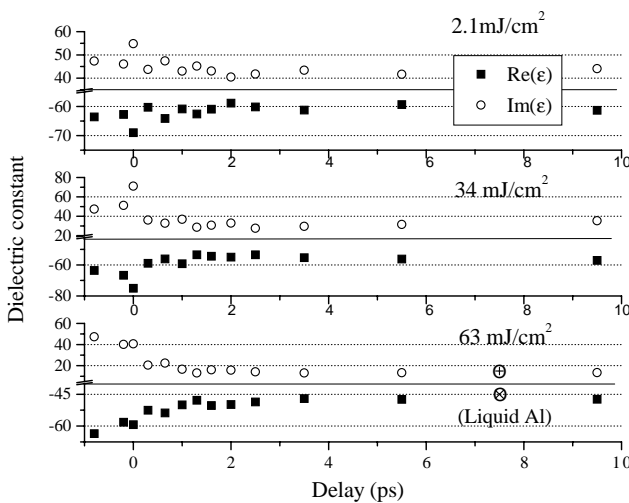


FIG. 4. Time evolution of dielectric constant of aluminum (Al) at three different pump fluences. The circled “x” and “+” in the bottom figure denote, respectively, the real and imaginary parts of dielectric constant of liquid Al from Ref. [18].

the strong interband absorption at 1.55 eV in liquid phase Al (Ref. [18]) is consistent with the decreased value of the imaginary part of the dielectric constant in Fig. 4 and the nearly constant reflectance observed for pump fluences above the damage threshold in Fig. 3.

Since Al does undergo a structural phase transition with the laser excitation fluence above the threshold value, it is necessary to understand further the relationship between ultrafast heat- and electronic-induced phase changes. Previous experimental investigations have shown that metals have very high damage threshold when excited with ultrashort pulses, even if superheating is properly avoided [19,20]. Such a high damage threshold can be explained by considering that the heat deposited in the electrons diffuses a distance exceeding the laser skin depth before being transferred to the lattice. The formula derived for the damage threshold accordingly agreed with experimental findings [20]. The resulting heat penetration depth,  $z_0$ , when melting occurs is

$$z_0 = (128/\pi)^{1/8} (\kappa_0^2 C_i / T_m g^2 \gamma)^{1/4}, \quad (1)$$

where  $\kappa_0$  is the heat conductivity,  $C_i$  is the lattice heat capacity,  $T_m$  is the melting temperature,  $g$  is the electron-phonon coupling constant, and  $\gamma$  is the coefficient for electron heat capacity  $C_e = \gamma T_e$ . In the case of Al, we use  $\kappa_0 = 2.37 \text{ W/cm K}$ ,  $C_i = 2.4 \text{ J/cm}^3 \text{ K}$ ,  $\gamma = 125 \text{ J/m}^3 \text{ K}^2$ , and  $g = 1 \times 10^{17} \text{ W/m}^3 \text{ K}$  [21], and this yields a heat deposition length of about 170 nm. The threshold fluence for melting based on this depth is calculated from  $F_{th} \alpha_{abs} = C_i \Delta T_m z_0$ , where  $\alpha_{abs} \approx 13\%$  is the energy absorption coefficient for Al at 1.55 eV, and  $\Delta T_m$  is the difference between initial and melting temperatures. This yields a threshold fluence for melting in Al of about  $200 \text{ mJ/cm}^2$ , which is much larger than the threshold fluence we measured experimentally ( $34 \text{ mJ/cm}^2$ ). Therefore, the ultrafast heating process does not play a significant role in our experimental observation since the above formulas accurately predict the heat-induced damage thresholds for metals under ultrashort pulse excitation [20]. This discrepancy is not unexpected since the damage is mainly due to the electronic excitation in our Al experiments.

To confirm our hypothesis that the observed melting transition is induced by electronic excitation rather than ultrafast heating, we repeated the experiment with the pump photon energy of 3.1 eV (400 nm), where Al behaves as a well-known free-electron metal following the Drude model (no strong interband transition) [18]. The heat penetration depth from Eq. (1) does not depend on the wavelength but the energy absorption in Al changes to about 8% for 400-nm light, and this yields a calculated ultrafast heat-induced damage threshold of about  $310 \text{ mJ/cm}^2$  at 400 nm. The 3.1-eV pump pulses were generated by frequency doubling the 1.55-eV pulses from the Ti:sapphire amplifier. By carefully filtering out any residual fundamental at 1.55 eV, the observed damage threshold at

3.1 eV agrees with the calculated ultrafast heat-induced value. Therefore, we conclude that the low damage threshold in Al at 1.55 eV is the result of strong interband electronic excitation rather than ultrafast heating.

If we again examine the electronic band structure of Al in Fig. 1, the excitation across the parallel bands occurs between  $k_a$  and  $k_b$  when the upper band exceeds the Fermi level, away from the high symmetry point  $k = 0$ . The pair of parallel bands, originally formed from  $s$  and  $p$  free electron bands in Al, will have a larger mixture between  $s$  and  $p$  levels farther away from the high symmetry point  $k = 0$  due to the interaction between  $s$ - and  $p$ -like electrons in neighboring sites of the Al lattice. Therefore, the part of the two bands involving the electronic excitation is highly hybridized (all three conduction electrons in Al are now in the lower band while the upper band is empty, which is different from the occupation configuration of  $s$  and  $p$  free electron bands) resulting in bondinglike and antibondinglike bands [22]. When a substantial number of electrons are excited into the upper antibondinglike band from the bondinglike band, the lattice structure should be weakened and structural instability should occur. Such an effect has been studied previously in semiconductors [23–26], and a similar volume expansion has also been seen in itinerant magnetic transitions [27]. An estimate reveals that more than 15% of the electrons in the lower conduction band have been excited into the upper band at the threshold fluence in our experiments, resulting in band structure collapse and structural phase transition in Al with much lower fluence than that of ultrafast heat-induced melting.

In summary, we present the first observation of a structural phase transition in Al predominantly induced by electronic excitation across a pair of parallel bands. The dynamics of this structural change is revealed through the measurements of the time evolution of dielectric constant at 1.55 eV. In contrast with the high heating damage fluence at 3.1 eV, the threshold fluence to melt Al at 1.55 eV is found to be significantly less than the value needed for ultrafast heat-induced melting. This lower transition threshold and the shorter time scale compared to those for the heat-induced melting lead us to conclude that the structure phase transition in Al is due to band structure collapse and lattice instability induced by the strong electronic excitation. The results presented in this paper will serve as a springboard for stimulating further theoretical investigations on high intensity ultrafast laser interactions with

metals, providing new insights for designing the optimal procedures for metal processing and manufacturing.

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