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PHYSICAL REVIEW B **76**, 012301 (2007)

Optical excitation of a coherent transverse optical phonon in a polycrystalline Zr metal film

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(Received 2 March 2007; revised manuscript received 8 May 2007; published 5 July 2007)

Optical pump-probe measurements of transient reflectivity were made on a sputtered polycrystalline thin film of hcp Zr. On top of a slow multiexponential decay, an oscillatory signal was observed with frequency varying from the initial value of $f_0=2.24\pm0.06$ THz at zero time delay to a value of 2.56 ± 0.12 THz after 2 ps, which is similar to that of a transverse optical (TO) phonon near the Γ point of the Brillouin zone. From the data, the TO phonon relaxation time was determined to be 0.67 ps. The excitation of the coherent phonon was identified as being mediated by resonant coherent Raman scattering.

DOI: 10.1103/PhysRevB.76.012301 PACS number(s): 78.47.+p, 63.20.−e, 78.20.−e

Recently, much attention has been drawn to the study of terahertz phonons in semiconductors, semimetals, and metals. The motivation for these studies arises from the need for efficient means by which to quantify the elastic properties of solids, on one hand, and to analyze the integrity of nanoscale structures, on the other. Atomic dynamics determines new phase formation in solids and the kinetics of chemical reactions. The latest advances in ultrafast laser technology have allowed the subpicosecond nonequilibrium dynamics of phonons to be investigated in the time domain.[1–25] In most of these studies, acoustic modes were investigated. In such modes, neighboring atoms oscillate in phase, and so the characteristic length scale for associated nonuniformities is given by the phonon wavelength. At the same time, in crystals with two (or more) atoms in the unit cell, there also exist optical phonons. For these modes, the two basis atoms oscillate out of phase, and so by studying optical phonons, one may obtain information about interactions on the atomic length scale, even if the phonon wavelength is not small.

In striking contrast to semiconductors and semimetals,[6] there have only been a few reports of the observation of coherent optical phonons by optical pump-probe measurements in metals.[12,13,17,21,25] The observation of coherent longitudinal optical (LO) phonons in Gd was reported in Refs. 12, 13, 21, and 25. Coherent transverse optical (TO) phonons in Zn and Cd were observed in Ref. 17. The samples in those studies were single crystals. At the same time, many of the metallic nanostructures that are important for applications are prepared by sputtering and so are polycrystalline. Therefore, a question arises as to whether terahertz optical phonons can be excited and detected and, hence, used for characterization of polycrystalline metallic samples. In this Brief Reports, we show that coherent TO phonons near the center of the Brillouin zone can be optically excited and detected in a sputtered polycrystalline film of Zr.

Measurements were performed at room temperature with 90 fs (full width at half maximum) transform limited pulses with photon energy of 1.575 ± 0.005 eV from a Ti:sapphire laser with 80 MHz repetition rate. The pump and probe were focused to a 15 μm spot size, had energies of 2.25 and 0.04 nJ, and were incident on the sample at 7° and 27°, respectively. The probe was p polarized, while the pump polarization was varied continuously from p to a circularly polarized state by rotating a quarter wave plate placed after a polarizer. The delay between the two pulses could be varied with a step size of 1.67 fs. Coherent contributions to the signal were suppressed by modulating the time delay through a few wavelengths. The pump was chopped, and the pump-induced change in the intensity of the reflected probe was measured using a lock-in amplifier. Our experimental apparatus is described in more detail elsewhere.[26,27]

The sample was a 425.0 ± 0.7 Å thick polycrystalline Zr film sputtered onto a Si substrate. The thickness was determined from x-ray measurements, from which we also found that the film roughness was 4.7 ± 0.6 Å. A 25.0 ± 0.7 Å oxide layer with roughness of 4.46 ± 0.10 Å formed on the film surface. The measurements confirmed that the film had an hcp ($P63$-mmc) crystal structure with a (002) dominant orientation. The grain sizes were determined to be 147 ± 15 and 190 ± 19 Å in the [100] and [002] directions, respectively.

The reflectivity response of the sample is shown in Fig. 1. The top and bottom panels represent signals that were acquired using a circularly and linearly (p-) polarized pump, respectively.[28] One can see that the two signals differ through the presence of a sharp peak at short time delays. Although present in both signals, it is only visible in the signal with the pump and probe polarized in the same plane. The peak is associated with the transient linear dichroism induced by the pump pulse.[29] The signal contains oscillations that sit on top of the multiexponential shape. The frequency and amplitude of the oscillations appear to be independent of the pump helicity. As shown in Fig. 2, the fast Fourier transform (FFT) of the signal with the multiexponential background subtracted yielded an average frequency of about 2.4 THz (9.4 meV), which is much higher than the value of ~0.01 THz expected for a standing acoustic phonon in a Zr film of this thickness. To analyze the transient behavior of

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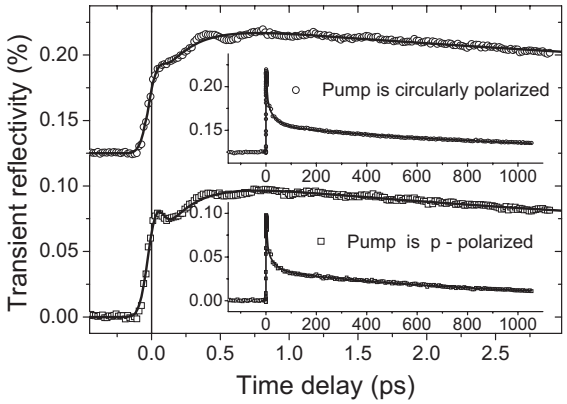

FIG. 1. The transient reflectivity signal is shown for excitation with circularly (top panel) and linearly (bottom panel) polarized pumps. The symbols are data points and the lines show the fitted background. The insets show the signals on a longer time scale.

the frequency in more detail, we fitted the oscillatory part of the signal to the damped chirped harmonic oscillator function $e^{-t/\tau}\cos(2\pi(f_0+bt)t+\varphi_0)$, where f_0, τ, b, and φ_0 are the initial frequency, relaxation time, chirp parameter, and initial phase, respectively (Fig. 3). The fit showed that the phonon frequency experiences a transient blueshift from the initial value of $f_0=2.24\pm0.06$ THz at zero time delay to a value of 2.56 ± 0.12 THz after 2 ps.

The observed mode can be identified as the TO phonon near the Γ point of the Zr phonon spectrum (E_{2g} mode). The energy of this phonon mode was calculated to be 9.7 meV at 295 K in Ref. 30. The inelastic neutron scattering measurements of Ref. 31 yielded a somewhat greater value of 10.59 meV at the same temperature while reporting a decreased value of 9.6 meV at 773 K. To compare these values with our measurements, we should bear in mind the transient increase of the temperature induced in the pump-probe experiment. Indeed, it is known that the lattice temperature of a metal excited by a short laser pulse reaches its maximum after some delay (typically after a few picoseconds), mainly determined by the interplay between electron-phonon thermalization and heat diffusion.[7] Following this, the lattice cools down on time scales typically longer than 100 ps. From the reflectivity signals shown in Fig. 1, one can see that this is indeed the case in our experiment.[32] For our pump pulse parameters, one can expect a rise of the lattice temperature of the order of 100 K. Thus, the phonon energy of 10 meV observed here at 2 ps after excitation compares rather well with the neutron scattering data from Ref. 31. At the same time, at shorter time delays, the system stays in a highly nonequilibrium state,[25] and so it makes no sense to compare the initial or average values of the phonon frequency with the data obtained at equilibrium.

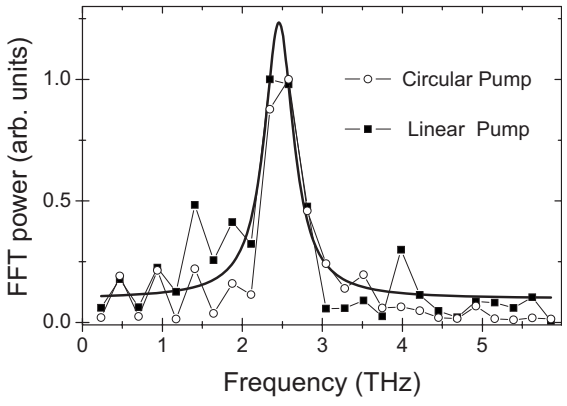

FIG. 2. The FFT spectra of the difference between the measured signals and the fitted background are presented for excitation with the circular and linear pumps. The curves with and without symbols represent the data points and Lorentzian fit, respectively.

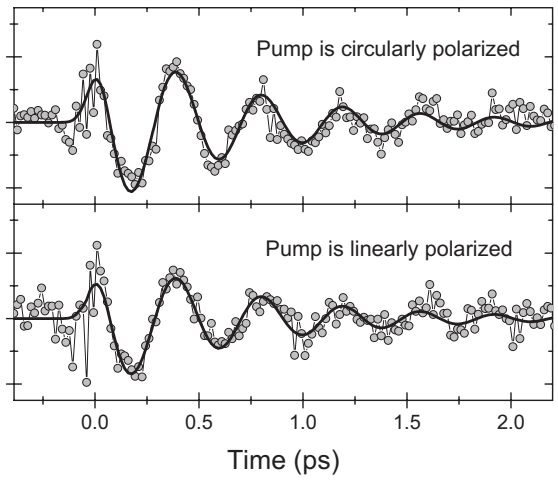

FIG. 3. The oscillatory components of the measured signals are presented for excitation with the circular and linear pumps. The curves with and without symbols represent the data points and fits to the damped chirped harmonic oscillator function, respectively.

In Ref. 17, Hase *et al.* outlined the conditions that must be met in order to excite a coherent optical phonon mode in a metal. The first condition is the existence of a Raman active $k=0$ optical phonon.[17] The hcp structure of Zr supports six normal modes, which belong to the irreducible representations $A_{2u}+B_{1g}+E_{1u}+E_{2g}$ and of which only the doubly degenerate E_{2g} mode is Raman active.[33] The second condition is the existence of a spectral peak in the imaginary part of the dielectric function that is related to an interband transition.[17] Due to the interband absorption between parallel bands along the P direction (between K and H points) in the Brillouin zone,[34] the imaginary part of the dielectric function of hcp Zr has a peak at 1.58 eV,[35] which matches the photon energy of our experiment. However, the real part of the dielectric function also has a peak at nearly the same photon energy. This corresponds to phonon excitation via a mechanism that is not purely displacive,[3] as observed in Ref. 17, but is mediated by the resonant coherent Raman scattering (CRS), introduced by Garrett *et al.*[5] The value of $17°\pm4°$ obtained from the fit for the initial phase of the coherent phonon φ_0 in the present work is consistent with the resonant CRS mechanism of excitation.[5,6] In a similar experiment, Bovensiepen *et al.* suggested that the bulk LO mode in Gd was excited *indirectly* due to interaction with a resonantly excited surface phonon mode.[13,25] Although Gd and Zr have similar crystal symmetry and elastic properties, making the latter mecha-

nism plausible in Zr at least in principle, it is unable to explain the excitation of the bulk TO phonon mode observed in the present work.

The fit in the present study showed that the TO phonon frequency in Zr experiences a transient *blueshift* with increasing time, with a fitted value of the chirp parameter $b = 0.16 \pm 0.03$ THz/ps. While no transient frequency shift was observed in Zn and Cd by Hase *et al.*,[17] they observed a blueshift similar to ours at the frequency of the A_{1g} phonon in Bi under strong photoexcitation and attributed it to the effect of the cubic anharmonicity of the atomic potential.[9] The same effect might be responsible for our observation, although the pump intensity in our experiment is an order of magnitude smaller than that in Ref. 9. In the case of the bulk LO mode in Gd, Bovensiepen *et al.* observed a transient *red* frequency shift of −0.12 THz/ps, which is very similar in magnitude to our result, and attributed it to a transient modification of the ion potential due to a redistribution of valence electrons around the Fermi level.[13,25] It is unclear, however, why this effect should be different for TO and LO modes. An alternative explanation could be that the optical excitation leads, or is equivalent, to a transient increase in pressure that subsequently relaxes on the picosecond time scale. It is known that, due to softening of the C_{44} elastic constant, the TO mode frequency in Zr and Gd shifts to the red with increasing pressure,[36–38] while it is plausible that the LO mode frequency might simultaneously shift to the blue. Therefore, the relaxation of the transient pressure in the time resolved experiments should lead to the transient blueshift of the TO mode frequency in Zr observed here and to the transient redshift of the LO mode frequency in Gd observed in Refs. 13 and 25. For the relaxation time, the fit yielded a value of $\tau = 0.67 \pm 0.07$ ps, which is similar to that obtained for Gd by Bovensiepen *et al.*[13,25]

In summary, we have observed the excitation of a coherent TO phonon by an intense laser pulse incident on a sputtered polycrystalline thin film of hcp Zr. The frequency of the phonon shows a transient blueshift that is discussed in terms of the cubic anharmonicity of the atomic potential and of the transient pressure induced by the optical pump pulse. The mechanism of excitation of the coherent phonon is identified to be resonant coherent Raman scattering.

The authors acknowledge the financial support of the UK Engineering and Physical Sciences Research Council (EPSRC) and the New Energy and Industrial Technology Development Organization (NEDO).

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