

# Observation of ultrafast lattice heating using time resolved electron diffraction

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We use ultrafast electron diffraction to study lattice heating of 20 nm noble metal films after femtosecond optical excitation with moderate excitation fluences. Using the Debye–Waller effect, the rise times of the lattice temperature were measured to be 1.1 ps in copper (5.9 mJ/cm<sup>2</sup> incident fluence) and 4.7 ps in gold (0.9 mJ/cm<sup>2</sup>). © 2009 American Institute of Physics.  
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Ultrafast electron and x-ray diffraction are relatively new techniques that provide both high temporal and atomic scale spatial resolution and enable the direct observation of atomic motions and changes in the atomic structure of matter with a time resolution of few hundred femtoseconds or better. In the first electron diffraction experiment with picosecond resolution Williamson *et al.* studied the laser-induced structural phase transition in aluminium.<sup>1</sup> The work by Zewail and his group<sup>2</sup> and also more recently by Miller and coworkers<sup>3</sup> has impressively demonstrated the great scientific potential of ultrafast electron diffraction.

We report here the application of ultrafast electron diffraction to study lattice heating after femtosecond optical excitation of thin metallic films. In the past, a variety of methods has been used to study the redistribution and energy relaxation of the excited electrons by performing measurements on the electronic system, for example, measurements of the optical reflectivity and absorption, or photoelectron spectroscopy. However, only in a few cases it has been possible to directly observe the excitation of lattice vibrations that results from the electronic energy relaxation (see, e.g., Refs. 4 and 5). We believe that electron diffraction is particularly useful to study this aspect of the energy relaxation.

Vibrations of the atoms about their equilibrium position lead to a reduction in the scattering intensity of the various elastic diffraction peaks—the Debye–Waller effect—which has previously been used to infer ultrafast laser-induced changes in the lattice temperature.<sup>6,7</sup> In electron diffraction, the matching of the penetration depth of the electrons and the laser excitation in a laser-pump/electron-probe experiment is readily accomplished, whereas this requirement restricts the choice of samples in x-ray experiments. Usually many diffraction orders are simultaneously accessible in electron diffraction, an important advantage for the unambiguous interpretation of diffraction experiments.

To observe ultrafast lattice heating we used a laser pump-electron probe scheme. Laser pulses of 50 fs duration were obtained from a titanium sapphire system (800 nm,  $\hbar\omega=1.55$  eV) running at a repetition rate of 1 kHz. One part of the output was frequency tripled and used for the illumination of a thin silver film serving as photocathode (transmission geometry). The photoelectrons were accelerated to a kinetic energy of 30 keV (De Broglie wavelength  $\lambda\approx0.007$  nm) and left the 3 mm long acceleration region

through a 100  $\mu\text{m}$  pinhole in the anode. A magnetic lens was used to focus the electron beam onto a multichannel plate (MCP) detector. The phosphor screen of the MCP was read out by a charge-coupled device (CCD) camera. The number of electrons per pulse was typically 2500. The broadening of the electron pulses under these conditions due to space charge effects and travel time dispersion<sup>8</sup> was calculated to be as follows: 280 fs pulse duration after the acceleration and 650 fs after travelling 75 mm from the anode to the sample.

The laser excitation pulses were suitably delayed and frequency doubled in a beta-barium borate crystal. Frequency doubling is advantageous because the optical reflectivity of the metal films used in this work is very high at the fundamental (800 nm). In our experimental setup, we were restricted to backside excitation at an angle of incidence of 45°. The resulting mismatch of the pulse fronts of the electrons and the laser pulse limited the overall time resolution to approximately 750 fs. This time resolution was demonstrated in a different experiment.<sup>9</sup>

Electron diffraction in transmission requires sample thicknesses of a few tens of nanometers. Freestanding thin Au and Cu films were prepared by electron-beam evaporation on top of carbon coated grids of 120  $\mu\text{m}$  spacing. The thickness was monitored by a quartz balance. The samples were placed behind the magnetic lens (75 mm from the anode).

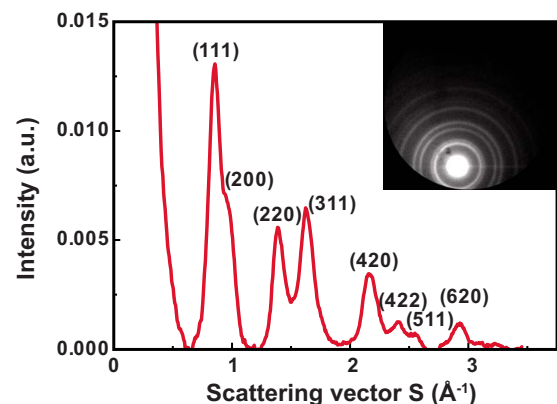


FIG. 1. (Color online) Diffraction pattern from the 20 nm gold film. The radial intensity profile has been corrected for background due to inelastic scattering and other causes. The scattering vector is  $S=(2/\lambda)\sin(\theta/2)$ , where  $\theta$  is the half angle of the Debye–Scherrer cone.

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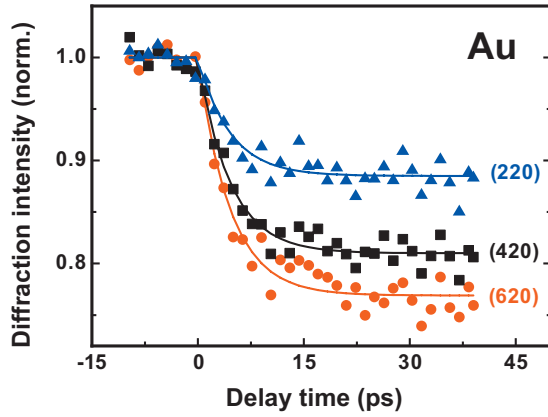


FIG. 2. (Color) Diffraction intensity versus delay time for the (220), (420), and (620) diffraction order of Au.

Figure 1 shows a typical diffraction pattern obtained from a 20 nm, polycrystalline gold film, and the radial profile integrated over the circumference of the individual rings. The picture was taken with an exposure time of 500 ms. Longer times resulted in an overexposure of the CCD by the zero order (transmitted) electron beam, which was measured to be  $6.3\% \pm 0.5\%$  of the incident beam. The Miller indices of the various diffraction rings can be readily identified using the well known fcc-selection rules and the lattice constant of Au ( $a=0.408$  nm).

In Fig. 2, we plot the measured diffraction intensity of three different rings as a function of the delay time between the laser and the electron pulses for the gold film (incident laser fluence  $0.9 \text{ mJ/cm}^2$ ). Time zero was determined by a separate experiment. Before the arrival of the laser excitation pulse the diffraction intensity remained constant within an error of less than 1%. A distinct decrease of the diffraction intensity was observed after the excitation. For all diffraction orders, the decrease could be fitted by an exponential function with a time constant of  $4.7 \pm 0.6$  ps. The diffraction reached an asymptotic value  $I_{\text{asy}}$  after approximately 20 ps. No further change was observed for delays up to 200 ps.

In Fig. 3, we plot the logarithm of the ratio  $I_{\text{asy}}/I_0$  of the asymptotic and the initial diffraction intensity at room temperature versus  $1/d_{hkl}^2$ , where  $d_{hkl}$  is the distance of the  $(hkl)$  lattice planes. The straight line indicates the scaling

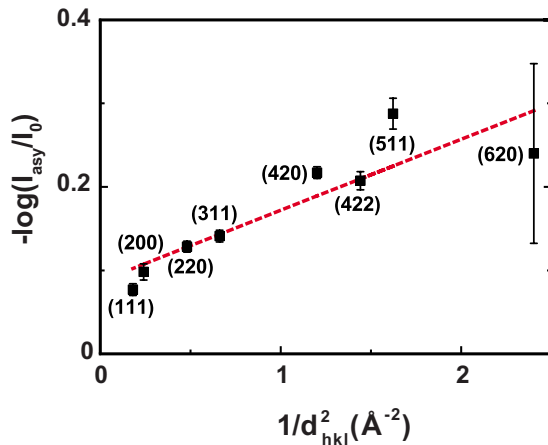


FIG. 3. (Color online) Drop of the diffraction intensity.  $d_{hkl}$  is the distance of the lattice planes. The exponential dependence is an indication of the Debye–Waller effect.

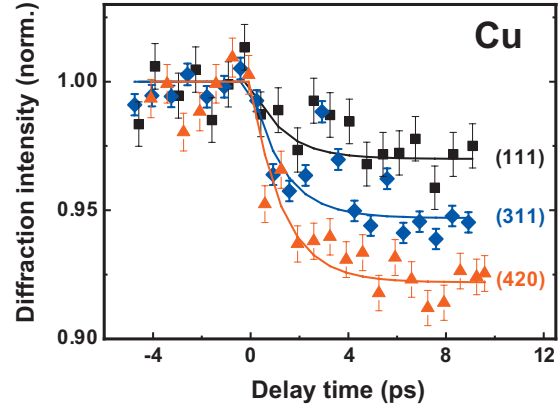


FIG. 4. (Color) Diffraction intensity versus delay time for the (111), (311), and (420) diffraction order of Cu.

expected for the Debye–Waller effect,  $I_{\text{asy}}/I_0 = \exp(-(4\pi^2/3)(\langle u^2 \rangle - \langle u^2 \rangle_{\text{RT}})/d_{hkl}^2)$ , where  $\langle u^2 \rangle$  and  $\langle u^2 \rangle_{\text{RT}}$  is the mean square atomic displacement at the high temperature and at room temperature, respectively. We conclude from this result that the observed laser-induced decrease of the diffraction intensity is indeed due to the Debye–Waller effect.<sup>10</sup> For our conditions,  $\langle u^2 \rangle$  is proportional to  $T/\Theta_D^2$  (Ref. 11) and represents the thermal motion of the lattice atoms caused by transfer of electronic energy to the lattice ( $\Theta_D$  denotes Debye temperature). From the slope of the line in Fig. 3, we obtain  $\langle u^2 \rangle - \langle u^2 \rangle_{\text{RT}} = 6.6 \times 10^{-5} \text{ nm}^2$ . The corresponding absolute temperature  $T_{\text{asy}}$  is calculated to be 380 K. This value is in reasonable agreement with the temperature of approximately 420 K from the estimated deposited laser energy.

We have used the two-temperature model<sup>12</sup> to simulate the evolution of the lattice heating. The observed time constant for the rise of the lattice temperature corresponds to an electron-phonon coupling parameter of  $g=2.1 \times 10^{16} \text{ W/m}^3 \text{ K}$ . This value is in good agreement with estimates of  $g$  from earlier all-optical experiments.<sup>13</sup>

Similar measurements were also performed on a polycrystalline copper film of 20 nm thickness. The transmission of this film was only  $2.6\% \pm 0.2\%$  and therefore longer CCD exposure times were necessary. Figure 4 depicts the temporal evolution of the diffraction intensity of selected rings. Although a higher excitation fluence of  $5.9 \text{ mJ/cm}^2$  was used, the drop in the diffraction was only 7% for the (420) ring, the highest order that could be observed for copper. Presumably the lower Debye–Waller drop can be explained by the relatively high Debye temperature of copper ( $\Theta_D=343$  K for Cu and 165 K Au).

The exponential fit yields a time constant of  $1.3 \pm 0.6$  ps. Deconvolution taking into account the experimental time resolution of 0.75 ps suggests a time constant of 1.1 ps for the lattice heating in copper. Using the two temperature model to fit our data, we obtain a coupling constant of  $g=10^{17} \text{ W/m}^3 \text{ K}$ , which is in agreement with the value reported in Ref. 14.

In summary, time resolved electron diffraction reveals lattice heating on a time scale of a few picoseconds in femtosecond laser-excited gold and copper. Our experiments indicate much faster lattice heating and stronger coupling of the electrons to the lattice for Cu than for Au.

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<sup>1</sup>S. Williamson, G. Mourou, and J. C. M. Li, *Phys. Rev. Lett.* **52**, 2364 (1984).

<sup>2</sup>D. Shorokhov and A. Zewail, *Phys. Chem. Chem. Phys.* **10**, 2879 (2008).

<sup>3</sup>B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, *Science* **302**, 1392 (2003).

<sup>4</sup>D. von der Linde, J. Kuhl, and H. Klingenberg, *Phys. Rev. Lett.* **44**, 1505 (1980).

<sup>5</sup>J. A. Kash, J. C. Tsang, and J. M. Hvam, *Phys. Rev. Lett.* **54**, 2151 (1983).

<sup>6</sup>H. Park, X. Wang, S. Nie, R. Clinite, and J. Cao, *Solid State Commun.* **136**, 559 (2005).

<sup>7</sup>M. Harb, R. Ernstorfer, T. Dartigalongue, C. T. Hebeisen, R. E. Jordan, and R. J. D. Miller, *J. Phys. Chem. B* **110**, 25308 (2005).

<sup>8</sup>B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, *J. Appl. Phys.* **92**, 1643 (2002); **94**, 807 (2003).

<sup>9</sup>I. Rajkovic, M. Ligges, P. Zhou, T. Payer, F. J. Meyer zu Heringdorf, M. Horn-von Hoegen, and D. von der Linde, *Ultrafast Phenomena XVI*, Springer Series in Chemical Physics, edited by P. Corkum, K. Nelson, E. Riedle, R. Schoenlein, S. De Silvestri (Springer, Berlin, in press).

<sup>10</sup>There is some constant vertical offset of the data not accounted for by the Debye–Waller formula.

<sup>11</sup>B. C. Larson, J. Z. Tischler, and D. M. Mills, *J. Mater. Res.* **1**, 144 (1986).

<sup>12</sup>S. I. Anisimov, B. L. Kapeliovich, and T. L. Perelman, *Sov. Phys. JETP* **39**, 375 (1974).

<sup>13</sup>J. Hohlfeld, S. S. Wellershoff, J. Güdde, U. Conrad, V. Jähnke, and E. Matthias, *Chem. Phys.* **251**, 237 (2000).

<sup>14</sup>H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou, *Phys. Rev. Lett.* **58**, 1212 (1987).