Measurement of the Electronic Grüneisen Constant Using Femtosecond Electron Diffraction

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We report the first accurate measurement of the electronic Grüneisen constant γ_e using a novel method employing the new technique of femtosecond electron diffraction. The contributions of the conduction electrons and the lattice to thermal expansion are differentiated in the time domain through transiently heating the electronic temperature well above that of the lattice with femtosecond optical pulses. By directly probing the associated thermal expansion dynamics in real time using femtosecond electron diffraction, we are able to separate the contributions of hot electrons from that of lattice heating, and make an accurate measurement of γ_e of aluminum at room temperature. This new approach opens the possibility of distinguishing electronic from magnetic contributions to thermal expansion in magnetic materials at low temperature.

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The electronic Grüneisen constant (γ_e) defines the dimensional changes of a solid in response to the heating of its conduction electrons [1,2]. Like the electronic specific heat capacity, γ_e is an important physical quantity directly related to the density of electronic states at the Fermi level (n_{E_F}) [3]. Conventional means of measuring γ_e utilize either high precision dilatometry [4,5] or thermoelastic stress pulses [6,7] at a sample temperature of a few tens of Kelvin or less. At such low temperatures, however, dimensional changes associated with magnetic ordering set in, which make the measurement of γ_e in many magnetic materials virtually impossible [1,4,8].

Here, we report a new approach to circumvent these limitations. Instead of cooling down a sample under thermal equilibrium conditions, we transiently heat its conduction electrons well above the lattice temperature using femtosecond optical pulses. By directly probing the associated thermal expansion dynamics in real time using femtosecond electron diffraction [9–11], we are able to differentiate the contributions of hot electron from that of lattice heating [12], and make an accurate measurement of γ_e of aluminum at room temperature. This method opens the possibility of distinguishing electronic from magnetic contributions to thermal expansion in magnetic materials at low temperature.

When subject to any temperature variation, a solid responds by changing its geometrical parameters through expansion and/or contraction. This dimensional change is driven by the minimization of system free energy and occurs at the microscopic level through rearrangement of crystallographic cell dimensions and mean positions of atoms within the unit cell [2,4]. Contributions to the free energy come from the lattice, itinerant electrons, electric dipoles, magnetic ions, nuclear spins, and their mutual interactions. Accordingly, the behavior of thermal expansion is inherently related to the physics governing these subsystems and their interactions. Among them, the electronic thermal expansion is of particular importance, as γ_e is associated with the derivative of n_{E_F} with respect to the sample volume V, $\gamma_e = (\partial \ln n_E / \partial \ln V)_{T,E=E_\mathrm{F}}$ [3].

As is the case for specific heat, measurement of γ_e is confronted with the difficult problem of isolating it from the contributions of other subsystems. For a metal without magnetic ordering, including a magnetic metal at temperatures above its Curie point, the stress responsible for thermal expansion consists of two independent contributions: the stress related to the lattice anharmonicity (σ_l) and the pressure of hot electrons (σ_e) [4]. Assuming the electrons and lattice maintain separate states of equilibrium characterized by temperature deviations of δT_e and δT_l after a thermal perturbation, the combined stress can be written as [13,14]

$$\sigma = \sigma_e + \sigma_l = -\gamma_e C_e \delta T_e - \gamma_l C_l \delta T_l, \tag{1}$$

where C_e and C_l are heat capacities for electrons and phonons, γ_e and γ_l are the corresponding Grüneisen constants. For most metals, γ_e and γ_l have nearly the same magnitude; for example, for Al at room temperature, $\gamma_l = 2.16$, $\gamma_e = 1.6$ [5]. In traditional static thermal measurements, electrons and lattice are equally perturbed and always in thermal equilibrium with $\delta T_e = \delta T_l$. The contributions to thermal expansion from each component are, as a result, weighed by the magnitudes of their heat capacities (subsystem thermal energy). At room temperature, since C_l is nearly 2 orders of magnitude larger than C_e [15], the thermal expansion is completely dominated by the lattice contribution, thus obstructing measurement of γ_e. A traditional approach to getting around this obstacle relies on lowering the sample temperature below a few tens of Kelvin, at which C_e ($\propto T$) becomes comparable to or bigger than C_l ($\propto T^3$). At such low temperatures, however, ferromagnetic materials are magnetically ordered [15]. The associated dimensional changes, such as magnetostriction [16], display the same or similar temperature dependence as electronic thermal expansion. This makes the analysis of low temperature data difficult and prevents a reliable measurement of γ_e in many magnetic materials, such as rare earth elements [1,4].

In the new method of measuring γ_e proposed here, the contributions of σ_e and σ_l to thermal expansion are differentiated in the time domain through transiently heating the electronic temperature well above that of the lattice with fs optical pulses. In contrast to the static heating, σ_e is first activated by photoexcitation of the conduction electrons. The subsequent evolution of σ_e and σ_l follow the kinetics of energy flow from electrons to lattice, obeying energy conservation [17]: $C_e \delta T_e + C_l \delta T_l = E_{\mathrm{pump}}$. In metals, the time scale of this energy flow ($3t_{e\text{-ph}}$) is governed by the dynamics of electron-phonon interactions [18,19]. It is ultrafast and lasts only a few ps or less [20–22]. This indicates that σ_e persists only during the first few ps before the electrons and lattice reach a thermal equilibrium. However, if this time is comparable to a quarter period ($T/4$) of the induced coherent lattice vibration, that is, $3t_{e\text{-ph}} \sim T/4$, σ_e will make a significant contribution to drive the lattice motion [12]. In the following we show the first accurate measurement of γ_e at room temperature using this new approach when the above condition is fulfilled.

The experiments are conducted on the femtosecond electron diffraction instrument [9], composed of an amplified Ti:sapphire laser system, a femtosecond electron gun, a streak camera, and a two-dimensional single electron detector. The output laser pulses at 1 kHz repetition rate, centered at 790 nm with ~50 fs temporal duration and averaged pulse energy of up to 1 mJ, are first divided into pump and probe pulses by a beam splitter. The pump pulses, containing about ~90% of original beam energy, are directed through a path mounted on a precision linear translation stage and are used to initiate the structural dynamics. The remaining 10% optical pulses are sent to a frequency tripler. The tripled fs pulses, with photon energy of ~4.7 eV, were converted to fs electron pulses via photoemission. These electron pulses are accelerated to a 60 keV beam energy (de Broglie wavelength $\lambda = 0.0487$ Å) and used to record the temporal evolutions of structural changes by taking a snapshot of transmission diffraction patterns inside a UHV chamber with a base pressure less than 3×10^{-10} torr. The delay times between the excitation optical and the probe electron pulses are controlled by varying the relative optical path length difference between the two beams.

The polycrystalline thin-film aluminum samples, with thickness of 20 ± 3.0 nm measured with a quartz crystal thickness monitor, are prepared by thermal evaporation of Al in high vacuum on freshly cleaved NaCl single-crystal substrates. The films on NaCl substrates are subsequently detached in a solvent and transferred to TEM grids as freestanding films.

To maintain the optimal time resolution, the electron beam intensity is set very low, containing on the average less than 1000 electrons per pulse. The corresponding temporal pulse width is less than 400 fs determined *in situ* with our streak camera. The pump laser (~2 mm beam size) and probe electron (~330 μm beam size) beams are arranged in a nearly collinear configuration with less than 10° cross angle. The overall temporal resolution, convoluting the excitation laser pulse width, the probe electron pulse width, and the temporal degradation, is less than 500 fs [11]. In the experiment, the laser excitation fluence is approximately 1.3 mJ/cm^2, and no sample damage is observed even after extended exposure to the pump laser pulses. In addition, the diffraction patterns without the pump laser are also recorded at each time delay and used as a reference for data analysis to correct any extraneous changes, such as probe electron beam walking and the long-term system drift.

The thermal expansion of the film, in the form of a single-mode one-dimensional (1D) standing acoustic wave breathing along the surface normal, was generated

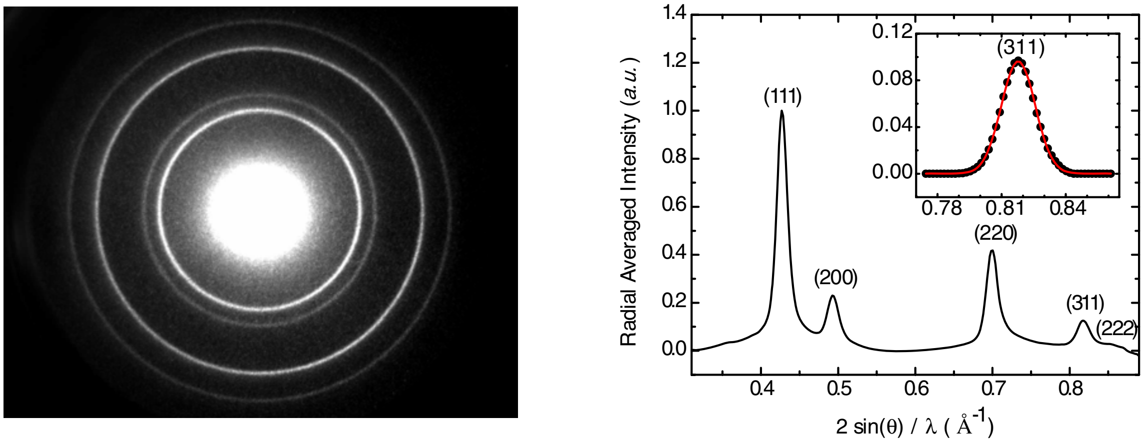

FIG. 1 (color online). Left: Diffraction pattern of polycrystalline freestanding thin-film aluminum of 20 nm thickness. It is recorded with $\sim 2 \times 10^7$ electrons of 60 keV beam energy ($\lambda = 0.0487$ Å) at approximately 1.3 mJ/cm^2 laser excitation fluence. Right: The corresponding radial averaged intensity curve. Inset: A typical fit of (311) Bragg peak to a Gaussian profile. The peak center position is determined to be $0.817\,80 \pm 0.000\,03$ (Å^{-1}) (474.99 ± 0.02 pixel).

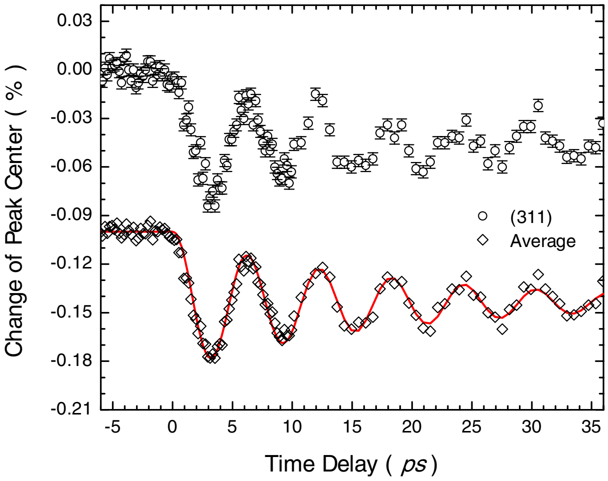

FIG. 2 (color online). Temporal evolution of Bragg peak positions. The averaged data are obtained by arithmetic averaging of all the Bragg peak vibration data and shifted for viewing clarity. Positive time delays correspond to probe electron pulses arriving after the excitation laser pulses. The error bars represent one standard deviation in the Gaussian peak profile fitting for determining the peak centers. The solid curve is a fit to the experimental data using Eqs. (2) and (3).

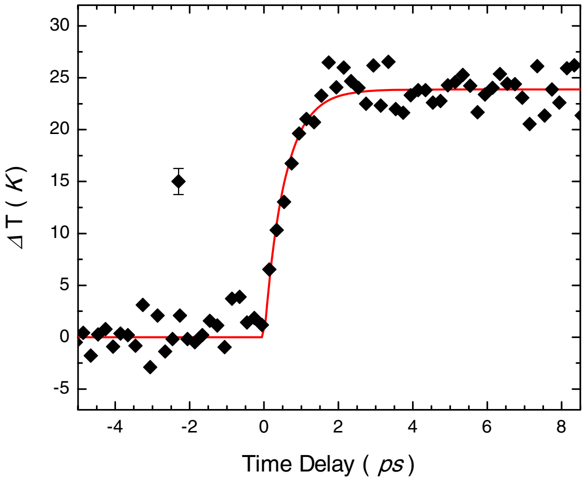

FIG. 3 (color online). Temporal evolution of lattice temperature as a function of delay time. The solid line is a fit to the data using an exponential function with a time constant $t_{e\text{-ph}} = 550 \pm 80$ fs.

by ultrafast and nearly uniform heating of the film with fs optical pulses [10,11]. The associated coherent and thermal lattice motions were recorded in real time by taking snapshots of electron diffraction patterns (see left panel of Fig. 1) at different time delays [9,11]. To obtain a quantitative measurement of structural dynamics, we first convert a two-dimensional diffraction pattern to a diffraction intensity curve as a function of diffraction angle (momentum transfer $S = 2\sin\theta/\lambda$), as shown in the right panel of Fig. 1. Then, we fit each Bragg peak in the intensity curve with a Gaussian line profile to determine its peak center (peak position), peak intensity, and peak width.

The temporal evolutions of Bragg peak positions are shown in Fig. 2. Each data point is obtained by dividing the peak position with the pump laser on by that with the pump beam blocked. The average value for a given peak before time zero is set to zero. The coherent lattice motions, displayed as the oscillation of Bragg peak positions, exhibit the typical features of film breathing motion along the surface normal, with all Bragg peaks oscillating perfectly in phase with one another and with the same vibrational period. These vibrations are centered at a newly established and reduced Bragg ring radius (expanded equilibrium lattice constant). Similar to the displacive excitation of coherent phonons [23], the vibration has a maximum displacement at time zero and displays a nearly cosine time dependence. Importantly, the Fourier transform of vibration data for the (311) Bragg ring yields a single peak centered at 0.17 THz. The corresponding ~6.0 ps vibrational period is in an excellent agreement with that predicted by the 1D standing wave condition $T = 2L/v$, where L is the nominal average film thickness of 20 ± 3.0 nm and the velocity of sound in the film is 6420 m/s [24].

The temporal evolution of concurrent lattice heating (driving force) is displayed in Fig. 3. The lattice temperature change is obtained by first calculating the normalized (311) peak intensity with respect to the (111) peak for each diffraction intensity curve at a given time delay. The normalized intensity is converted to the lattice temperature using the Debye-Waller factor [25]. The temperature rise of 23 K is estimated by measuring the amount of optical energy absorbed by the Al film and dividing it with the film heat capacity calculated using the bulk value. A time constant of $\tau_{e\text{-ph}} = 550 \pm 80$ fs, along with the uncertainty of time zero of 60 fs, are determined by fitting the data with an exponential function: $\delta T_l = T_l^0(1 - e^{-(t-t_0)/\tau_{e\text{-ph}}})$ (solid line in Fig. 3). The corresponding 1.7 ps time scale for lattice heating is in excellent agreement with the ~2 ps value observed in recent transient optical reflectivity measurements [26,27].

The value of γ_e is determined by fitting the above data of coherent lattice motions to a damped harmonic oscillator driven by both lattice and electron heating. For sufficiently small lattice vibrations associated with a single acoustic mode as observed in our FED measurements, its temporal evolution $Q(t)$ can be described by a classical harmonic oscillator as [12,23]

$$\frac{d^2Q}{dt^2} + 2\beta\frac{dQ}{dt} + \omega_0^2 Q = \sigma(t), \tag{2}$$

where ω_0 is the angular vibrational frequency, β is a phenomenological damping constant, and σ is the driving force given by Eq. (1). Assuming energy conservation [17], the transient stress in Eq. (1) can be further simplified to [28]

$$\sigma = A - Be^{-t/\tau_{e\text{-ph}}} \tag{3a}$$

$$\text{with } \gamma_e = \gamma_l(1 - B/A) \tag{3b}$$

where A and B are two constants related by Eq. (3b). Hence, by fitting the FED data to Eqs. (2) and (3), we obtain the values for A and B. Then, given γ_l, the electronic Grüneisen constant γ_e can be calculated.

For better signal-to-noise ratio, the averaged temporal evolution for all the Bragg peaks is used to extract the value of γ_e (lower curve in Fig. 2). In the fitting, the lattice heating time constant ($\tau_{e\text{-ph}} = 550$ fs) and time zero ($t_0 = 0 \pm 60$ fs) are fixed to the values measured by FED, and the other four parameters, ω_0, β, A, and B are floated. The fitting results, with phonon angular frequency $\omega_0 = 1.04 \pm 0.01$ THz and damping constant $1/\beta = 17 \pm 1$ ps, are plotted as a solid curve in Fig. 2, and in very good agreement with the coherent lattice vibration data. Using the fitted values of $A = 0.048 \pm 0.001$, $B = 0.016 \pm 0.003$, and $\gamma_l = 2.16$ [5], we found $\gamma_e = 1.4 \pm 0.3$, where the uncertainty of 0.3 is calculated by convoluting the errors in all the parameters involved in the fitting. This γ_e value is in excellent agreement with that of 1.6 obtained in the low temperature measurement [5,29].

We believe that the accurate measurement of the electronic Grüneisen constant in a polycrystalline Al thin film reported here is a critical step forward in the study of electronic thermal expansion. It opens the way to determining γ_e in many magnetic materials, such as rare earth elements with low Curie temperatures, where the accurate measurement of γ_e is not amenable with other traditional techniques. The new approach reported here can also be extended to femtosecond optical measurements, provided that both thermal and coherent lattice motions can be recorded and differentiated in real time.

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[29] The highest electronic temperature induced by the laser heating is estimated to be less than 1200 K, much smaller than the Fermi temperature $T_{E_{\text{F}}} \approx 136\,000$ K in Al. Therefore, the γ_e value measured with FED should be the same as that of low temperature measurement. In addition, we use γ_l value at room temperature in the calculation, considering the 23 °C lattice temperature jump is very small.

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