Electronic Grüneisen parameter and thermal expansion in ferromagnetic transition metal

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We report the measurement of the electronic Grüneisen parameter \( \gamma_e \) of the ferromagnetic transition metal nickel. In this measurement, the electronic thermal expansion was differentiated from other thermal contributions by simultaneously monitoring the laser-induced ultrafast stress and structural dynamics in the time domain using femtosecond electron diffraction. This method overcomes the restriction of traditional low temperature methods and offers a unique path to study electronic thermal expansion in magnetic metals. The result indicates that the local magnetic moment, which persists in the paramagnetic state of nickel, does not significantly contribute to the thermal expansion. © 2008 American Institute of Physics. [DOI: 10.1063/1.2902170]

In thermodynamics, the Grüneisen parameter connects two important physical properties of a solid, the specific heat capacity and the volume thermal expansion coefficient. It determines the magnitude of the system dimensional change in response to its thermal energy variation induced by changing temperature. Differentiating the various contributions to the Grüneisen parameter is of great importance to clearly understand the thermal expansion mechanism of solids. In particular, the electronic Grüneisen parameter (\( \gamma_e \)) has attracted much attention since it is directly related to the density of electronic states at Fermi level. For nonmagnetic metals, \( \gamma_e \) has been deduced in thermal expansion measurements at very low sample temperature (\( T \ll \theta_D \), \( \theta_D \) is the Debye temperature). Under this condition, the lattice and electronic contributions to thermal expansion exhibit distinct temperature dependences. Consequently, they can be separated and both lattice Grüneisen parameter \( \gamma_l \) and electronic Grüneisen parameter \( \gamma_e \) can be directly obtained. At such low temperatures, however, the magnetic contribution to thermal expansion sets in for most magnetic metals, and it displays the same or similar temperature dependence as the electronic contribution. This makes it virtually impossible to separate the electronic and magnetic contributions from each other.

Here, we report the accurate measurement of \( \gamma_e \) in paramagnetic state nickel using a recently demonstrated method. Unlike the conventional low temperature measurements, we create a nonequilibrium condition by ultrafast heating the conduction electrons of a sample to a temperature much higher than that of lattice using femtosecond laser pulses. By tracing the following thermal and coherent lattice motions in real time with femtosecond electron diffraction (FED), we are able to differentiate the contributions of electrons and lattice to thermal expansion in the time domain, and make an accurate measurement of \( \gamma_e \).

The experiments are conducted on the FED instrument, which is described in more detail elsewhere. To achieve sufficient signal-to-noise ratio for accurate determination of \( \gamma_e \) in nickel, a third generation electron gun and a more efficient electron detector were developed. The detective quantum efficiency of the detector, which is consisted of a phosphor screen in series with an image intensifier and a charge coupled device camera, is close to four times that of our previous direct-bombard microchannel plate imager. The electron gun’s output beam energy up to 100 keV represents a significant step forward from our second generation 60 kV electron gun in generating femtosecond electron pulses with a high electron density. Higher beam energy shortens the pulse propagation time to the sample location and lengthens the longitudinal beam dimension in the traveling reference frame. It also leads to a larger compression ratio in Lorentz transformation due to the relativistic effect. All these factors contribute to the shortening of electron pulses durations at a given electron density. At 80 keV beam energy and for a subpicosecond temporal resolution, the diffraction signal recorded by the third FED instrument is close to an order of magnitude larger than that of our second generation machine. This is crucial for an accurate measurement of \( \gamma_e \), since the diffraction signal of nickel is more than four times weaker than that of aluminum under our experimental conditions.

The polycrystalline thin-film nickel samples, with thickness of 22 ± 4.0 nm characterized with atomic force microscopy, are prepared by sputtering 99.99% purity nickel target in high vacuum on freshly cleaved NaCl single-crystal substrates. The films on NaCl substrates are subsequently detached in a solvent and transferred to transmission electron microscopy (TEM) grids as freestanding films. The TEM grids are mounted on a heating/cooling sample holder and placed inside the main chamber with a base pressure better than \( 3 \times 10^{-10} \) torr. In the current measurement, the sample temperature was set at \( T = 680 \) K, well above its Curie point of 627 K.

To maintain the optimal time resolution, the electron beam intensity is set to contain on the average, less than 1200 electrons/pulse. The overall temporal resolution, convoluting the excitation laser pulse width (~50 fs), probe electron pulse width, and the temporal degradation, is esti-
The temporal evolution of lattice temperature (structural dynamics) is obtained by capturing diffraction patterns at various pump-probe delay times. To obtain a quantitative measurement of structural dynamics, we convert the recorded two-dimensional diffraction pattern to a function of sample temperature normalized to data at $T=0$. 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 the peak width.

The temporal evolution of lattice temperature (thermal lattice motions) is shown in the right panel of Fig. 2. It was constructed from the intensity attenuation data of Bragg peak (left panel of Fig. 2) using the Debye–Waller factor. To minimize the effect of probe electron density fluctuations, we use the normalized peak intensity ($I_{311}/I_{111}$) of each diffraction curve recorded at a given time delay. According to the Debye–Waller effect, the temperature dependence of $I_{311}/I_{111}$ is given by

$$\frac{I_{311}(T)}{I_{111}} = \frac{I_{311}(T=0)}{I_{111}} \exp\left(-\frac{1}{2}(S_{311}^2 - S_{111}^2)\Delta B(T(t) - B(T=0))\right),$$

where $S=2 \sin \theta/\lambda$ and $B$ is the Debye–Waller parameter. The lattice temperature $T(t)$ was then determined using the $I_{311}/I_{111}$ curve obtained in the static diffraction measurement by varying the sample temperature (inset of left panel of Fig. 2). The obtained film temperature rise of 12 K at long delay times is in good agreement with the value of 14 K obtained by dividing the bulk value of nickel heat capacity with the absorbed optical energy. By fitting the data with a single exponential function, $\delta T(t) = T_i (1 - e^{-t/\tau_{e-ph}})$ (solid line in the right panel of Fig. 2), we extract the time-zero uncertainty of 60 fs and a time constant $\tau_{e-ph} = 740\pm 90$ fs for lattice thermalization. This lattice heating time constant is in good agreement with the values obtained by recent time-resolved femtosecond optical measurements.

The coherent lattice motions, which are displayed as the oscillation of Bragg peak positions, are shown in Fig. 3. It is obtained by dividing the peak positions with the pump laser on by those with the pump beam blocked and setting the averaged value before pump laser pulses to zero. These vibrations exhibit the typical features of film breathing motion along the surface normal, with all Bragg peaks perfectly oscillating in phase and with the same vibrational period set by the standing wave condition. The Fourier transform of vibration data is shown in the inset of Fig. 3, which yields a single peak centered at 0.124 THz. The corresponding ~8 ps vibrational period agrees well with that predicted by the one-dimensional standing wave condition $T_e \approx 2L/\nu$, where $L$ is the nominal average film thickness of 22 $\pm$ 4.0 nm and the velocity of sound in the film is $6040$ m/s.

FIG. 1. (Color online) Diffraction intensity curve of polycrystalline free-standing thin-film nickel of 22 nm thickness. This curve is the radial average of diffraction pattern recorded with $\sim 2.5 \times 10^7$ probe electrons. Inset: a typical fit of (311) Bragg peak to a Gaussian profile. The peak center position is determined to be $0.940 \pm 0.0007 \text{Å}^{-1}$.

FIG. 2. (Color online) Left: the temporal evolution of Bragg peak intensity. Each data point is obtained by dividing the (311) peak intensity by that of (111) peak ($I_{311}/I_{111}$). This value is normalized with the averaged value at negative delay times. Inset: the static measurements of $\ln(I_{311}/I_{111})$ as a function of sample temperature normalized to data at $T=600$ K. A linear fit (solid curve) is used to extract the Debye–Waller factor. Right: the temporal evolution of lattice temperature. The solid line is a fit to the data using an exponential function with a time constant $\tau_{e-ph} = 740 \pm 90$ fs.

FIG. 3. (Color online) The temporal evolution of Bragg peak positions. The data are obtained by arithmetic averaging the vibration data of all Bragg peaks. The error bars represent one standard deviation. The solid curve is a fit to the experimental data using Eqs. (2) and (3) as described in the text. Inset: Fourier transform of the vibration data. The peak frequency is approximately 0.124 THz, which corresponds to an 8 ps vibrational period.
The value of $\gamma_e$ is obtained by fitting the coherent vibration data to a damped harmonic oscillator driven by both lattice and electronic heating:

$$\frac{d^2Q}{dt^2} + 2\beta \frac{dQ}{dt} + \omega_0^2 Q = A - B e^{-t/\tau_{e-ph}},$$

(2)

with $\gamma_e = \gamma(1 - B/A)$.

(3)

where $\omega_0$ is the angular vibrational frequency, $\beta$ is a phenomenological damping constant, and $A$ and $B$ are two constants related by Eq. (3). In deriving this equation, we have assumed that the electron thermalization is instantaneous after the absorption of pump laser energy ($\sim 50$ fs) and the total energy deposited into the film is conserved in the picosecond time span. The fitting results, with phonon angular frequency $\omega_0=0.82 \pm 0.01$ THz and damping constant $1/\beta=9.4 \pm 1$ ps, are plotted as a solid curve in Fig. 2, and are in very good agreement with the coherent lattice vibration data. To determine $\gamma_e$, we used $\gamma=1.9$ measured at room temperature. It is valid since this temperature is very close to the Debye temperature and $\gamma$ is almost independent of the lattice temperature. Using this $\gamma$ value and the fitted values of $A=0.018 \pm 0.001$ and $B=0.005 \pm 0.002$, 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.

The $\gamma_e$ value of Ni in paramagnetic state was calculated by Levy et al. from the density-functional theory. In the calculation, the authors applied the finite temperature linear muffin-tin orbital band structure method and used the von Barth–Hedin parametrization within local spin-density approximation (LSDA) for electron correlation potential. It has been shown that LSDA is a very effective method to treat electron correlations, especially in the transition metals such as nickel with itinerant 3d band electrons. In the calculation, the contribution of local magnetic moment (LM), which persists in the paramagnetic state of nickel, to thermal expansion was excluded. The value of $\gamma_e=1.3$ obtained in this calculation is in excellent agreement with our experimental value and supports that LM in paramagnetic state of nickel does not provide an important contribution in electronic thermal expansion. This result is also supported by the calculation of electronic thermal expansion in nickel on the basis of variational theory by Kakehashi and Samon.

It is interesting that the measured $\gamma_e$ is significantly smaller than the value of $\gamma_{em}=2.1^{13}$ obtained at low sample temperature. Measurement of $\gamma_e$ at sample temperatures below Curie point is being conducted now in our laboratory to fully understand the thermal expansion mechanism in ferromagnetic transition metals.

In summary, we have measured $\gamma_e$ in the paramagnetic state of transition metal nickel using FED, which overcomes the limitation of traditional low temperature methods. The result is in excellent agreement with the model calculation from LSDA. This congruence provides the experimental evidence that the amplitude of LM in paramagnetic state of nickel does not significantly contribute to electronic thermal expansion.

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