Dynamics of coherent phonons in bismuth generated by ultrashort laser pulses

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Coherent phonon spectra of bismuth measured at temperatures from 10 to 295 K by a femtosecond pump-probe reflectivity technique were compared with the corresponding Raman-scattering spectra. The decay rate and frequency show almost the same behavior for the coherent and incoherent phonons. This result indicates that the decay process of the coherent optical phonons is dominated by the anharmonic decay (energy relaxation) and that the contribution of the pure dephasing is negligibly small. [S0163-1829(98)01034-0]

I. INTRODUCTION

Recently, there have been a lot of reports on coherent phonons generated by ultrashort laser pulses. These reports have covered the observation of high-frequency phonons and the dephasing of phonons and have discussed the mechanisms by which these phonons are generated. The studies on dephasing are especially important for understanding of the nature of coherent phonons, and the decay process of coherent phonons excited by picosecond pulses has been examined using time-resolved coherent anti-Stokes Raman scattering (CARS).[1–3] The phonon dephasing rate can be generally described as a sum of the anharmonic decay rate and the pure dephasing rate.[4] The main channels for the relaxation of incoherent optical phonons in semiconductors are thought to be the dephasing originating from the phonon-phonon interaction caused by anharmonicity of the lattice potential and the decay of the excited optical phonons into acoustic phonons.[5] Direct comparison has been made between the results obtained by time-resolved CARS and Raman scattering spectroscopies.[4,6] Liu *et al.* have measured frequency and decay rate of the E_g phonon in $LaAlO_3$ by impulsive Raman- and incoherent Raman-scattering at various temperatures, and have compared these parameters.[7] A direct comparison between the ultrafast Kerr effect and high-resolution light-scattering spectroscopy has been made by Kinoshita *et al.*[8] However, no systematic study of the relaxation of optical phonons excited coherently by femtosecond laser pulses has been carried out.

Several mechanisms have been proposed for the coherent phonon generation. The coherent phonons are in general represented by exponentially damped sinusoidal waves in the time domain, and the phase of their oscillations is thought to be related to the generation mechanism. For semimetals (Bi, Sb, and Ti_2O_3), the so-called displacive excitation of coherent phonons (DECP mechanism) has been proposed.[9,10] In this mechanism, photoexcited carriers create a nonequilibrium electron distribution, and as a result, the crystal lattice begins to oscillate around the new equilibrium position and the phonon oscillation shows a cosine dependence. For molecular crystals, impulsive stimulated Raman scattering (ISRS) is considered as the main mechanism of the generation of coherent phonons.[11] This mechanism does not require photogenerated carriers, and the phonon oscillation shows a sine dependence. The phases of the coherent phonons at zero delay time have been measured for a few materials.[12–14] However, the reported values of the phase are widely scattered because the pulse durations used were not sufficiently smaller than the period of the oscillation and because they differed in different experiments.

Coherent phonons generated by femtosecond pulses are in phase, and are in a nonequilibrium state. The amplitude of the coherent phonons depends strongly on the excitation power densities. For incoherent phonons, the expectation value of the amplitude vanishes because of the randomness in the phase of the atomic displacements. The intensity of Raman scattering by incoherent phonons is related to the number of thermal equilibrium phonons, and is proportional to the Bose-Einstein thermal factor depending on the temperature. The temperature dependence of the behaviors of coherent phonons has not yet been examined, but if we are to understand coherent phonons we must investigate their properties over a wide range of temperatures.

In this paper the relaxation process of coherent optical phonons in bismuth films has been studied by comparing results obtained by femtosecond pump-probe reflectivity measurements with the results obtained from Raman (frequency domain) measurements. The amplitude and phase of the coherent phonons have been evaluated precisely by femtosecond reflectivity measurement at temperatures below 300 K, and the initial phase of the coherent A_{1g} mode has been determined by using ultrashort (20 fs) pulses.

II. COMPARISON BETWEEN TIME-DOMAIN AND RAMAN MEASUREMENTS

Based on the well established theory of vibrational dynamics,[4] we will briefly describe the frequency-domain and time-domain spectra. The equation of a damped harmonic oscillator is given by

$$\frac{d^2Q}{dt^2}+\frac{2}{\tau}\frac{dQ}{dt}+\omega_0^2Q=\frac{1}{m}f(t), \tag{1}$$

where Q is the displacement, ω_0 is the natural frequency of the oscillator, $f(t)$ is the impulsive driving force, $\tau=1/\gamma$ is the decay time of the oscillation amplitude (here γ is the decay rate of phonons), and m is the mass of the oscillator. The solution of Eq. (1) can be written

$$Q(\omega)=\frac{1}{m(\omega_0^2-\omega^2-2i\omega/\tau)}F(\omega), \tag{2}$$

where $Q(\omega)$ and $F(\omega)$ are, respectively the Fourier-transformed displacement and the Fourier-transformed impulsive driving force. From Eq. (2) we obtain the response function

$$\chi(\omega)=\frac{1}{m(\omega_0^2-\omega^2-2i\omega/\tau)} \tag{3}$$

and its imaginary part

$$\frac{\mathrm{Im}[\chi(\omega)]}{\omega}=\frac{1}{m\tau}\frac{1}{(\omega^2-\omega_0^2)^2+(2\omega/\tau)^2}. \tag{4}$$

According to the fluctuation-dissipation theorem, the spectral intensity for Raman scattering $I_{\mathrm{RS}}(\omega)$ is given by $\mathrm{Im}[\chi(\omega)]/\omega$. The phonons measured by Raman scattering are incoherent phonons at a thermal equilibrium. Using Eq. (4), we obtain $I_{\mathrm{RS}}(\omega)$ for frequencies ω near the resonance frequency ω_0:

$$I_{RS}(\omega)=\mathrm{const}\frac{1/\tau}{(\omega-\omega_0)^2+(1/\tau)^2}. \tag{5}$$

In Eq. (5) the full width at half maximum of the Raman band, $\Gamma[\mathrm{cm}^{-1}]$, is related to the decay time τ (in the units of ps) by the relation of $\Gamma[\mathrm{cm}^{-1}]=2/\tau=1/(\pi\tau c)$, and the decay rate of phonons is given by $\Gamma(=2\gamma)$.[4,6] Here c is the speed of the light. The time correlation function of the displacement Q is given by the Fourier transform of $\mathrm{Im}[\chi(\omega)]/\omega$:

$$\phi(t)=\langle Q(0)Q(t)\rangle=\frac{\hbar\omega_0}{2\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Im}[\chi(\omega)]}{\omega}e^{i\omega t}d\omega. \tag{6}$$

Equation (6) indicates that the spectral intensity distribution $I_{\mathrm{RS}}(\omega)$ is connected to a vibrational correlation function $\phi(t)$ by Fourier transformation. The time correlation function of the displacement $\phi(t)$ can readily be calculated from Eqs. (5) and (6):

$$\phi(t)=A\ \exp\left(-\frac{t}{\tau}\right)\cos[\omega_0 t], \tag{7}$$

where A is the amplitude of a vibrational correlation function. We have assumed here that the coherent oscillation observed by time-resolved reflectivity (or transmissivity) measurement is given by the time correlation function of displacement Q. For transport phenomena, Kubo related the expectation value of a current J to the time correlation function $\langle J(0)J(t)\rangle$.[15] The reflectivity change is expressed as

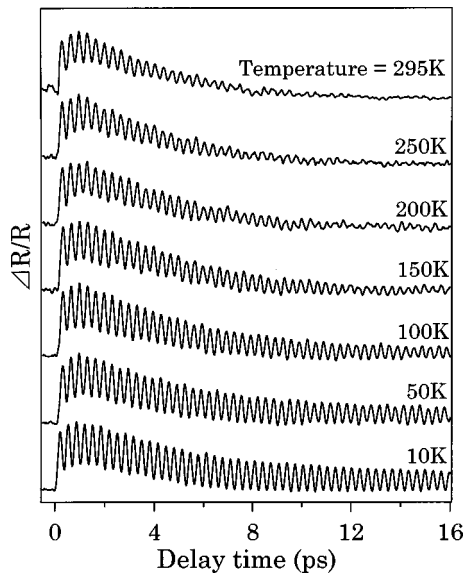

FIG. 1. The time-resolved reflectivity changes for bismuth films at temperatures between 10 and 295 K.

$$\frac{\Delta R}{R}=\frac{1}{R}\left[\left(\frac{\partial R}{\partial\varepsilon}\right)\left(\frac{\partial\varepsilon}{\partial Q}\right)\right]\Delta Q$$
$$\sim\frac{A}{R}\left[\left(\frac{\partial R}{\partial\varepsilon}\right)\left(\frac{\partial\varepsilon}{\partial Q}\right)\right]\exp\left(-\frac{t}{\tau}\right)\cos[\omega_0 t], \tag{8}$$

where ε is the dielectric constant and ΔQ is the expectation value of the microscopic displacement Q. Thus we can obtain the decay rate of the coherent phonons by a time-domain measurement and that of incoherent phonons by a Raman-scattering measurement.

III. EXPERIMENTS

The bismuth films studied in this work were prepared by evaporation on polished silicon substrates at room temperature. They were about 1000 Å thick, and x-ray-diffraction measurements showed that they were polycrystalline. The short pulse laser used was a mode-locked Ti:sapphire laser with a central wavelength of 800 nm and pulse width of 80 fs. A standard reflection-type pump-probe configuration was employed. Pump and probe beams were polarized orthogonal to each other to avoid the scattered pump beam, and were focused to a diameter of about 50 μm on the samples. The reflectivity change $\Delta R/R$ was measured as a function of the delay time by scanning the optical path length of the probe beam. In order to determine the initial phase of coherent phonons precisely, we also used pulses with a duration of 20 fs. Figure 1 shows the coherent oscillations of the fully symmetric A_{1g} mode (97.7 $\mathrm{cm}^{-1}=2.93$ THz at 295 K) measured at temperatures between 10 and 295 K. As the temperature is lowered, both the decay time and the amplitude of the coherent A_{1g} mode become larger. The E_g mode (71 cm^{-1}) has also been observed using an EO sampling technique.[16] For Bi single crystals with the (111) surface, the amplitude of the E_g phonon oscillation is large at low temperatures when the polarization of the pump beam is parallel to the c axis. In Sb crystals the E_g mode was measured with a specific polarization setup at low temperature (8 K) by Garrett *et al.*[17] The

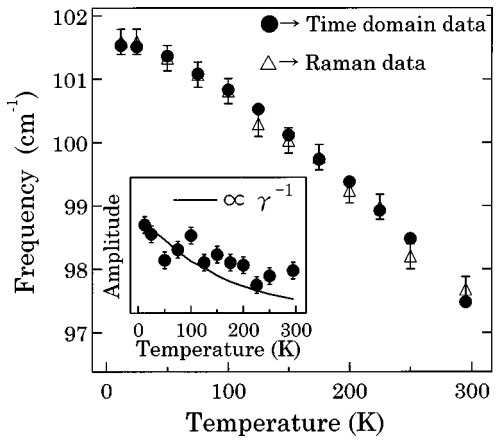

FIG. 2. A comparison of the frequencies of A_{1g} mode between time-domain and Raman-scattering spectroscopies. The closed circles and open triangles represent time-domain data and Raman data, respectively. The inset shows the amplitude of the coherent A_{1g} mode. The closed circles are experimental data, the solid line is the curve predicted from the correlation function.

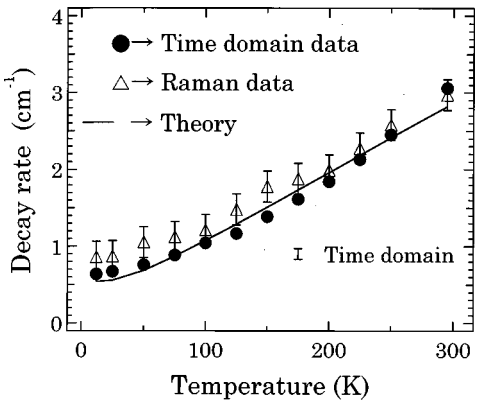

FIG. 3. The decay rates of the A_{1g} mode obtained by time-domain and Raman-scattering spectroscopies. The closed circles and open triangles represent time-domain data, and Raman data, respectively. The solid line is a fitting curve with Eq. (10).

decay time of the E_g mode also became longer at lower temperatures. The temperature dependence of the decay rate and frequency for the A_{1g} and E_g modes in Bi films is almost the same as in single crystals. The frequencies, amplitudes, and decay times of the coherent A_{1g} mode at various temperatures were determined in the present study by fitting the time-domain data to a harmonic oscillation with a single exponential decay:

$$\frac{\Delta R}{R} = A\ \exp\left(-\frac{t}{\tau}\right)\cos(\omega t) + B\left[\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right], \tag{9}$$

where A is the amplitude, ω is the frequency, and τ is the decay time of the coherent phonon. The second term arises from the photoexcited carriers. Here B is the amplitude, and τ_1 and τ_2 are the relaxation time, and the rising time of the electric component, respectively.

The excitation power dependence of the amplitude, of the decay time, and of the frequency was studied for coherent phonons in Bi at room temperature. The amplitude increased linearly with increasing excitation power at weak excitation when the spot size of laser beams was 50 μm. However, the amplitude saturates at high excitation for a spot size of about 5 μm. Both the oscillation frequency and decay time decrease with increasing excitation power. Such a behavior can be explained in terms of sample heating at high excitation.

In order to compare the decay rates of the incoherent and coherent phonons, we measured the Raman spectra by using a cw Ti:sapphire laser operating at the same wavelength. The Raman bandwidth was corrected for a slit function of the spectrometer by a deconvolution.[18,19] In Fig. 2 the frequencies of the A_{1g} mode at different temperatures obtained by the time-domain measurement are compared with those obtained from the Raman data. The amplitude of the coherent A_{1g} mode is plotted in the inset. The frequency of the A_{1g} mode shifts from 101.5 to 97.7 cm^{-1} when the temperature increases from 10 to 295 K. The A_{1g}-mode frequencies obtained from the two different measurements are consistent over a wide temperature range. As shown in the inset, the amplitude of the coherent A_{1g} mode increases with decreasing temperature. The ratio of the amplitude of the coherent A_{1g} mode obtained at 10 K to that obtained at 295 K is about 1.7. In Fig. 3 the decay rates for the A_{1g} mode obtained by the two measurements are plotted as a function of temperature. Although the temperature dependences of these decay rates are in agreement within experimental errors (0.2 cm^{-1}), there is a slight but systematic discrepancy at lower temperatures. This discrepancy might partly result from the difference in a laser heating of the sample by the femtosecond pulse laser and the cw laser. Another cause may be a difference in pure dephasing. The incoherent phonons generated in Raman process are the same in frequency but have different wave vectors, whereas the coherent phonons generated by femtosecond pulses have the same frequency and wave vector. For the incoherent phonons a momentum relaxation by phonon-phonon scattering contributes to the pure dephasing of phonons, but for the coherent phonons this contribution may be small. This explanation is consistent with the fact that the decay rates of the incoherent phonons is slightly greater than those of the coherent phonons. Another possible explanation for this discrepancy is a contribution of the self-energy effect due to anharmonic interaction on the Raman-allowed optical mode. Menendez and Cardona have reported that the linewidth measured experimentally arises from not only the imaginary part but also the real part of the phonon self-energy, and one should calculate the spectral dependence of real part of the self-energy at each temperature in order to obtain the corresponding corrections.[5] It seems, however, difficult to attribute the discrepancy to the self-energy effect because the self-energy would affect the decay rate of both the incoherent phonons and the coherent phonons. Even if the pure dephasing contributes to the decay process, the decay of the coherent optical phonons in bismuth seems to be dominated by anharmonic decay (energy relaxation) because of the similarity of the decay rates derived from the two different methods. A possible decay channel for the A_{1g} mode in bismuth is the decay into two acoustic phonons at the Λ point whose frequency is half of the A_{1g}-mode frequency.[20] The corresponding temperature dependence of the decay rate of the A_{1g} mode is given, according to Ref. 6, by

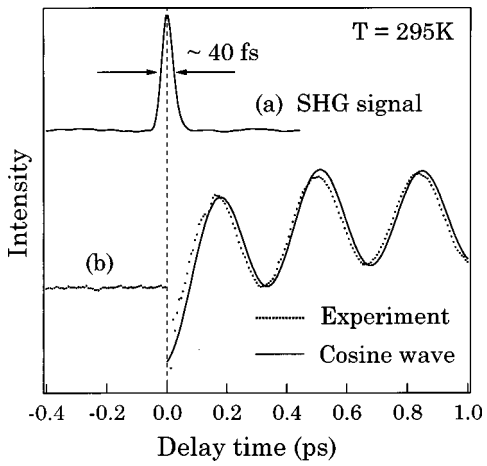

FIG. 4. The time-resolved reflectivity changes of the A_{1g} mode obtained with 20 fs ultrashort laser pulses. (a) Autocorrelation of the laser pulses. (b) Coherent phonon oscillation for the Bi film. The dotted curve corresponding to the experimental data, and the solid curve [$\propto\cos(\omega t)$] corresponds to a displacive limit.

$$\Gamma_{A_{1g}}=\Gamma_0\left[1+\frac{2}{\exp(\hbar\omega_{A_{1g}}/2/k_BT)-1}\right], \tag{10}$$

where, Γ_0 is an effective anharmonic constant, $\omega_{A_{1g}}$ is the frequency of the A_{1g} mode, and k_B is the Boltzmann constant. The fitting of the time-domain data to Eq. (10) is shown in Fig. 3, where we obtain $\Gamma_0=0.5\ \mathrm{cm}^{-1}$. The temperature dependence of the decay rate of A_{1g} mode is well described by Eq. (10).

The initial phase φ in bismuth films was determined in pump-probe experiments using 20 fs laser pulses, which are much shorter than the oscillation period (341 fs). Figure 4(a) shows the autocorrelation of the laser pulse obtained by a second-harmonic generation (SHG) at the sample position. The width of the autocorrelation function of laser pulses (40 fs) gives a pulse width of $\leqslant$25 fs. Thus the peak position of this SHG signal determines zero delay time accurately. Figure 4(b) demonstrates the coherent oscillation of the A_{1g} mode observed in the initial stage at room temperature. Fitting the damped oscillation with a single exponential decay to the experimental data gives a phonon decay time $1/\gamma=3.79$ ps, an amplitude 1.36×10^{-5}, and an initial phase $\varphi=15.4\pm1$ degrees. The calculated $\cos(\omega t)$ oscillation is also shown in Fig. 4. The observed coherent A_{1g} phonon shows $\cos(\omega t+\varphi)$ dependence. The phase shift obtained for Bi is comparable to the values reported for other semimetals: The initial phase of coherent phonons in Sb and Bi reported by Zeiger *et al.* were (3 ± 4) degrees for the A_{1g} mode in Sb and (-13 ± 13) degrees for the A_{1g} mode in Bi.[10] Garrett *et al.*, on the other hand, reported that the initial phases in Sb were (-23 ± 11) degrees for the A_{1g} mode and (43 ± 8) degrees for the E_g mode.[13] These results demonstrate that the coherent A_{1g} oscillation observed in semimetals is described approximately with a $\cos(\omega t)$ wave, whereas the E_g mode shows significant departure from the $\cos(\omega t)$ wave. Therefore, the dominant generation mechanism of the coherent A_{1g} phonons in semimetals may be the DECP. Especially for the E_g mode, however, a mixture of DECP and ISRS cannot be excluded.[13,14]

IV. DISCUSSION

An alternative expression of the time correlation function that includes initial phase shift was given by Kubo *et al.*, who calculated vibrational correlation function using a different form of the power spectrum for the displacement Q.[21] The calculation of the correlation function was done using Eq. (4) instead of Eq. (5), yielding

$$\phi(t)=\frac{\pi I_f}{2m^2\gamma\omega_0^2}e^{-\gamma t}\sqrt{1+\frac{\gamma^2}{\Omega^2}}\cos\left[\Omega t-\tan^{-1}\left(\frac{\gamma}{\Omega}\right)\right], \tag{11}$$

where $\Omega\equiv\sqrt{\omega_0^2-\gamma^2}$ and $\gamma=1/\tau$ is the decay rate of phonons. Here it is assumed that the impulsive driving force $f(t)$ can be expressed by a δ function, so that the power spectrum of impulsive driving force $I_f(\omega)$ is nearly constant (white spectrum): $I_f(\omega)=I_f=$const. The main difference between Eq. (11) and Eq. (7) is that the former includes the initial phase shift. The term $(1+\gamma^2/\Omega^2)^{1/2}$ in Eq. (11) is approximately equal to unity when $\gamma=3$ and $\Omega=97\ \mathrm{cm}^{-1}$. Equation (11) indicates that the amplitude increases when γ decreases. As shown in the inset of Fig. 2, the amplitude of the coherent phonon does increase with decreasing temperature. The ratio of the amplitudes at 10 and 295 K ($\gamma_{295\ \mathrm{K}}/\gamma_{10\ \mathrm{K}}$) predicted using the observed values of γ is 3.5, more than twice the experimental value 1.7. The tendency in temperature variation of the amplitude is consistent with Eq. (11) even though the magnitudes of the experimental and predicted amplitudes are not the same. A possible explanation for this difference between the predicted ratio (3.5) and the experimental value (1.7) is the self-energy effect.[5] However, it is not clear at present how the real part of the self-energy affects the temperature dependence of the decay rate and amplitude of the coherent phonons in bismuth.

The temperature dependence of the initial phase could not be measured because of the difficulty in determining the zero time delay when the sample was in the cryostat. The phase shift estimated using Eq. (11), and the measured values of γ and Ω is $\varphi=-\tan^{-1}(\gamma/\Omega)=-1.7$ degrees, and this is too small when compared with the experimental value (15.4 ± 1 degrees when we take $\Omega=2.93$ THz). A similar expression of the oscillation profile based on the DECP mechanism was obtained by Zeiger *et al.*[10,22] For the driving force decaying exponentially they calculated a response function which is proportional to the photoexcited carrier density. Their calculation shows that the amplitude varies with γ and β (β is the decay constant of photogenerated carriers), and that the initial phase has the same form as in our expression. Their calculation, however, cannot explain the temperature dependence of the amplitude observed in our experiment.

V. CONCLUSION

In conclusion, the relaxation of the coherent optical phonons in bismuth films has been studied by comparing the results of femtosecond pump-probe measurements and Raman-scattering measurements at various temperatures. The agreement of the decay rates obtained from the two

methods indicates that the decay of coherent phonons in bismuth is dominated by anharmonic decay (energy relaxation). The coherent phonon oscillation for the A_{1g} mode determined by the pump-probe measurement shows almost $\cos(\omega t)$ behavior in Bi, as has been reported by other groups. The amplitude of the coherent phonons is larger at lower temperatures, and this trend is consistent to that predicted from the time correlation function approach.

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