TIME-RESOLVED OBSERVATION OF COHERENT PHONONS IN GRAPHITE

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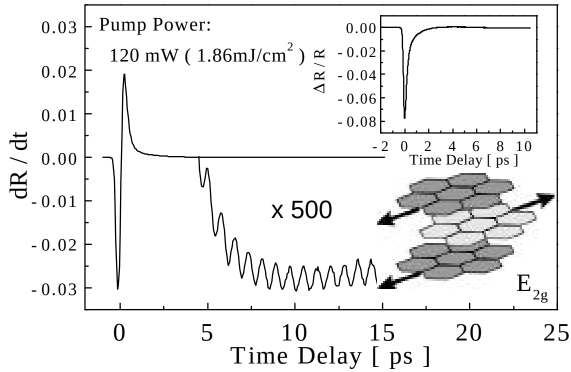
We report on the observation of the coherent phonons in graphite by the femtosecond pump-probe experiment. The transient reflectivity measurement with time-delay modulation technique gives the coherent phonon signal of interplanar shearing mode whose vibrational energy and symmetry are 42 cm^{-1} and E_{2g}, respectively. We have examined the polarization dependence of the coherent phonon signal in detail. The result indicates that the coherent phonon is generated by ISRS (Impulsive stimulated Raman scattering) process and that the signal is detected as an interference between Rayleigh and Raman components of the reflected probe beam. The polarization dependence gives the clear and direct information about the symmetry of the Raman tensor.

Owing to its simple two-dimensional structure, graphite is one of the most important and standard system in solid-state physics. Therefore, much work has been done on the various properties of graphite in both experimental and theoretical aspects [1-6]. Femtosecond carrier dynamics of graphite has been comprehensively studied [4]. The static lattice properties of graphite are well studied by Raman scattering experiment [5]. Although there are many reports on the observations of coherent phonons in various materials [7,8], there is no report on the observation of the coherent phonon in graphite.

In this work, we have measured the coherent phonon oscillation in highly ordered pyrolytic graphite (HOPG). The Raman spectrum of graphite shows two zone-center optic phonons whose vibrational energies are 1581 cm^{-1} and 42 cm^{-1}. They correspond to the in-plane carbon-carbon bond stretching and interplanar shearing motion, respectively. The transient reflectivity measurement gives the coherent phonon signal of interplanar shearing motion.

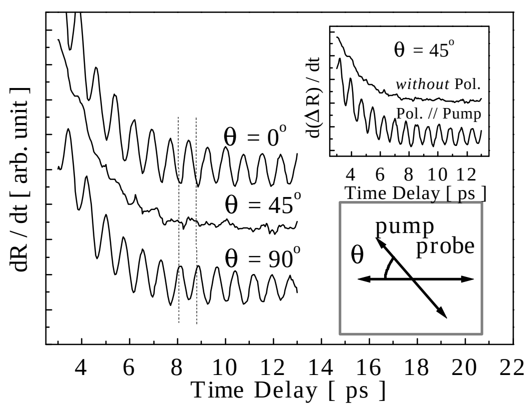
The time-resolved pump-probe experiments were performed at room temperature with a mode-locked titanium-sapphire laser which produces 130 fs pulses at a repetition rate of 82 MHz. The time delay between pump and probe pulses was scanned by two retroreflectors. They were mounted on a shaker in the pump beam line and a stepping motor stage in the probe beam line, respectively. The time delay was modulated by the shaker and the time derivative of the reflectivity *dR/dt* was detected by a lock-in amplifier as a function of time delay scanned by the stepping motor stage. The time-delay modulation technique enables the observation of very weak oscillation signal. Although, we measured several grades of HOPG and a natural graphite samples, no significant difference was observed. The following experimental results were obtained using a ZYA grade HOPG sample. The inset of Fig.1 shows the normal pump probe signal in reflection geometry and the large peak at the time delay of 0 ps corresponds to the absorption saturation of the π-π^* optical transition [4]. The time derivative signal is shown in Fig.1 with the schematic diagram of the lattice displacement for the interplanar mode. The 500 times expanded time trace clearly shows the coherent phonon oscillation. The frequency and the amplitude of the shaker modulation were 80 Hz and 0.2 ps. The pump and probe polarizations were parallel, and the excitation density and the center wavelength of the laser pulse were 1.86mJ/cm^2 and 790nm, respectively. The observed change of the reflectivity ΔR caused by coherent phonon is expressed as



$$\Delta R(t) = -A\exp(-\Gamma t)\sin(2\pi t / T)$$

Where, A, Γ, and T are 1.5x10^{-5}, 0.12ps^{-1}, 0.768ps, respectively. The corresponding wave number and width of the phonon line are 43.4cm^{-1} and 0.82cm^{-1}.

We also examined the polarization dependence of the coherent phonon signal. Although the sample rotation along c-axis gives no significant change in the coherent phonon signal, the angle between pump and probe polarizations gives drastic change. The polarization dependence of the coherent phonon signal is shown in Fig. 2. The time traces for θ = 0° and 90° show clear oscillations in opposite phases, whereas the trace for 45° shows no oscillation. The similar result has been already



observed in $LaAlO_3$ [9]. To check the disappearance of the oscillation, we insert a polarizer in front of the signal detector and set the polarization parallel to the pump. The inset of Fig. 2 shows the result. The oscillation recovers and its phase is the same as that of 0° angle data. The polarization dependence is clearly explained by the symmetry of the Raman tensor and the detection process of the coherent phonon signal. Two independent phonon fields Q_1 and Q_2 belong to E_{2g} irreducible representation and the related Raman tensor is written as

$$\frac{\partial \chi}{\partial Q_1} = \begin{pmatrix} f & 0 \\ 0 & -f \end{pmatrix}, \qquad \frac{\partial \chi}{\partial Q_2} = \begin{pmatrix} 0 & f \\ f & 0 \end{pmatrix}.$$

If we consider the ISRS (Impulsive stimulated Raman scattering) as the generation process of the coherent phonon, the symmetry of the Raman tensors explains the inversion of the coherent phonon signal since the 90° rotation of pump beam inverts the sign of the force. Therefore the main generation mechanism of the coherent phonon signal is the ISRS process. The disappearance and the recovery of the coherent phonon signal by inserting the polarizer can be explained by considering the following detection process. The reflected probe field from the sample is simply expressed as

$$\vec{E}_R(t) = \vec{E}_{Rayleigh} \cos(\omega t + \phi) + \vec{E}_{Raman} \cos\omega t \sin\Omega t$$

where, ω, ϕ and Ω are the optical frequency, the relative phase and the phonon frequency, respectively. The Rayleigh component corresponds to the background reflection and its polarization is parallel to the incident probe light. By multiplying the envelope function of the probe pulse, the equation holds for the short probe pulse. Since the intensity of the reflected light is proportional to the time average of the square of the field and the Raman component is much weaker than the Rayleigh component, the coherent phonon signal is

$$\Delta I_R(t) \propto \vec{E}_{Rayleigh} \cdot \vec{E}_{Raman} \cos\phi \sin\Omega t.$$

The 45° rotation of the pump beam exchanges the excitation mode from Q_1 to Q_2 and the Raman tensor for Q_2 is off-diagonal. Therefore the polarizations of two components are orthogonal and the signal disappears. If the polarizer is inserted, the polarizations are mixed and the signal recovers.

In this work, we have observed the coherent phonon oscillation of the interplanar shearing mode of graphite. We have examined the optical polarization dependence of the coherent phonon signal in detail. The result clearly indicates that the coherent phonon is generated by the ISRS process and that the signal is detected as the interference between Rayleigh and Raman components. Since, there is a strong π-π^* optical transition, the real carrier generation also might contribute to the coherent phonon generation process. Further experimental and theoretical works are required to fully understand the phonon generation process.

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