Coherent acoustic oscillations in metallic nanoparticles generated with femtosecond optical pulses

M. Nisoli and S. De Silvestri

Centro di Elettronica Quantistica e Strumentazione Elettronica CNR, Dipartimento di Fisica,
Politecnico, Piazza L. Da Vinci 32, Milano, Italy

A. Cavalleri and A. M. Malvezzi

Istituto Nazionale per la Fisica della Materia, Dipartimento di Elettronica, Università di Pavia, Via Ferrata 1, I27100 Pavia, Italy

A. Stella

Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica ''A. Volta,'' Università di Pavia, Via A. Bassi 6,
I27100 Pavia, Italy

G. Lanzani

Istituto di Matematica e Fisica, Università di Sassari, Via Vienna 2, I07100 Sassari, Italy

P. Cheyssac and R. Kofman

Laboratoire de Physique de la Matiere Condensée, URA 190, Université de Nice Sophia Antipolis, Nice Cedex, France
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Nonthermal generation of coherent-acoustic phonons is observed in metallic nanoparticles of tin and gallium, which are solid and liquid, respectively, at room temperature, by applying femtosecond pump-and-probe spectroscopy. Oscillations in the photo-induced differential reflection are clearly detected in the picosecond time domain. The measured period increases approximately linearly with size over a wide range and extracted sound velocities are consistent with those of bulk. Transition to ballistic regime in carrier excitation is also discussed on the basis of the disappearance of oscillations for particle sizes below hot-carrier mean free paths. [S0163-1829(97)51020-4]

In the last few years, considerable attention has been devoted to both semiconducting and metallic clusters in the nanometer size range. The main motivation for this effort resides in the possibility of tailoring, by controlling cluster sizes, physical properties which lie somewhat in between those of bulk materials and of molecules. Size affects for instance, electronic confinement in semiconductor quantum dots[1] as well as nonlinear optical response of metallic clusters[2,3] and basic thermodynamic properties, such as melting temperature.[4,5] In this frame, femtosecond optical spectroscopy can be successfully applied to study the dynamical response of metallic thin films and nanoparticles after excitation with an ultrashort optical pulse.[6,7] A previous investigation of the ultrafast optical response of tin nanocrystals provided clear evidence of size dependence in the cooling of excited electrons for mean particle radii below 60 Å.[8] The generation of strain waves in metals has been previously observed in thin films of nickel,[9,10] copper, and aluminum[9] with picosecond transient thermoreflectance. Thermoelastic deformation of the surface due to nonuniform absorption of light is generally considered to be responsible for launching into the sample a compression pulse which propagates and experiences several reflections by the surfaces of the film. Such waves in metals are generally detected as modulations in reflection, due to a change in the surface optical properties occurring when the compression pulses are being reflected at the interface.

In this work, we report on pump-and-probe experiments in tin and gallium nanoparticles with average radii between 300 and 20 Å. We have detected in these systems picosecond (ps) acoustic oscillations. In this experiment, the optical response of the system can be considered as coherent, i.e., there are well-defined phase relations among the contributions of the individual particles. This is due to the single-layer arrangement of the nanospheres, as well as their shape uniformity and relatively low size dispersion, as specified below. The coherent waves are observed in our experiment for cluster sizes larger than the optical skin depth of the pump pulse. Moreover, the experimental conditions differ from those of thin films[9,10] in several respects.[11]

First, the geometry of the particles is responsible for somewhat more complicated absorption and stress profiles. Several acoustic modes of the nanosphere can be excited, and simple one-dimensional modeling is not adequate. Second, when the skin depth of the probe pulse is comparable to the cluster size, both reflectivity and transmission dynamics are sensitive to the average behavior of the whole particle. Third, the reduced size is responsible for higher thermal gradients which lead to marked size dependence in the damping of acoustic waves. Finally, the capability of growing nanocrystals over a very wide size range allows one to detect and investigate the transition from bulklike behavior to a strong confinement regime. The ability to excite and detect such oscillations with ultrashort optical pulses is a new diagnostic tool for studies of the acoustic properties of nanostructures.

The samples were prepared by evaporation condensation in ultrahigh vacuum on sapphire substrates. Sn and Ga vapor was condensed on a previously evaporated thin film (<500
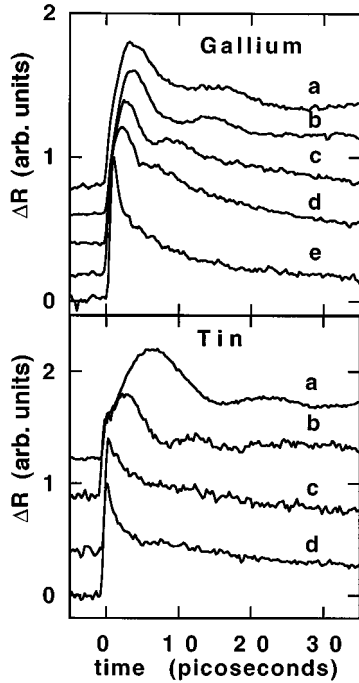
FIG. 1. Differential reflection measurements ΔR on a 35 ps timescale for gallium nanoparticles with radii of 310 Å (a), 220 Å (b), 120 Å (c), 105 Å (d), and 70 Å (e) in the upper part and for tin nanoparticles of 250 Å (a), 140 Å (b), 60 Å (c), and 40 Å (d) in the lower part of the figure. Plots have been shifted vertically for clarity.

FIG. 2. Oscillation period as a function of particle size in gallium (dots) and tin (squares).

Å) of an amorphous dielectric. The metallic clusters were then covered by an additional layer of the same amorphous dielectric. Interesting and important details of the growth technique are (a) the use of an amorphous embedding matrix so that no preferential orientation is induced and no restriction to lattice mismatch is produced as well; (b) a deposit which does not wet (or only partially wets) the substrate, so that the formation of islands is favored (Volmer-Weber mode); (c) the temperature of the substrate is set so as to deposit the film in the liquid phase thus allowing surface tension to play a dominant role in determining the shape of the droplets; (d) by subsequently lowering the temperature, nanodroplets are frozen in the solid state before being covered by a protection layer. In the case of gallium, the nanodroplets are in the liquid phase at room temperature.[4] Ultrafast-optical response was measured in a two color pump-probe experiment. Pulses 180 fs in duration at 390 nm were used as a pump, whereas probing was performed with 150 fs, 780 nm pulses. The experimental set up is the same as that described in Ref. 8.

Figure 1 shows the reflectivity time response for, respectively, gallium and tin nanoparticles of several average sizes on a 35 picosecond time scale. Damped oscillations with a size-dependent period are observed superimposed to the transient-optical response. Moreover, one observes that for larger particles the oscillations are more pronounced, whereas they are less evident when the size is reduced. Similar curves were also obtained in transient transmission.

We attribute the impulsive generation of stress waves to the nonuniform absorption of pump radiation inside the nanoparticle.[9] The skin depth at 390 nm is in fact, respec-
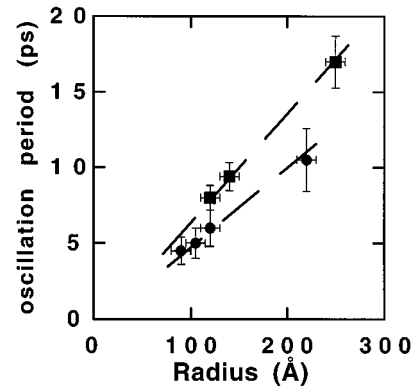
tively, 140 Å for tin and 120 Å for gallium. Such strain waves induce variations of the local optical constants due to compression/expansion of the metal lattice and can, therefore, be detected by either reflectivity or transmission measurements. An expression for the time and space dependence of the strain normal modes of an ideal spherical particle[13] can be written as

$$\eta(r,t) = \sum \ (A_{l,n}\sin\Omega_{l,n}t + B_{l,n}\cos\Omega_{l,n}t)$$
$$\times j_l(\alpha_{l,n}r/R)Y_{l,0}(\vartheta,\varphi), \qquad (1)$$

where r is the radial coordinate in the frame of the particle and t stands for time. $j_l(\alpha_{l,n}r/R)$ is the Bessel function of order l, $Y_{l,m}$ is the spherical harmonic of order l,m and $\alpha_{l,n}$ is the nth root of the Bessel function of lth order. In Eq. (1), for 780 nm probing, we assume all the spatial variations are averaged out over the skin depth and we take into account only the oscillatory time dependence with relative frequency $\Omega_{l,n} = v_s\alpha_{l,n}/R$, where v_s and R stand, respectively, for the sound velocity and the particle radius.

In Fig. 2 we have plotted the oscillation period as a function of radius. An approximately linear dependence is observed. The horizontal error bars shown in this plot refer to the average dispersion in particle size ($<20\%$ over the whole size range). From such results we extract sound velocities of 3.2×10^5 ($\pm20\%$) cm/sec for tin. The measured value for Ga, 4.9×10^5 ($\pm20\%$) cm/sec turns out to be substantially in excess of the liquid data found in the literature (2.7×10^5 cm/sec).[14] For what concerns the increased damping for smaller particles, we note that the expected time constant for heat diffusion from a metallic nanoparticle into the glass matrix is proportional to the cluster-surface area,[15] whereas the oscillation period scales linearly with the particle radius. Calculated damping times show that, for tin particles with a radius of 50 Å (±10 Å), heat diffusion time is comparable with one acoustic period, meaning that for smaller particles, strain waves are expected to be over damped. Therefore, as far as the timescale of thermal diffusion the over damping of acoustic oscillations may be satisfactorily explained.

In order to gain some insight into the stress generation process, we have further investigated in some detail the optical response at short-time delays. Experimental results for the first 4 picoseconds after excitation are shown in Fig. 3.
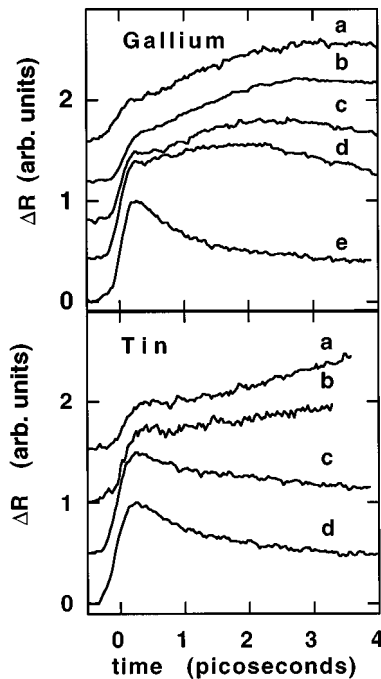
FIG. 3. Differential reflection measurements ΔR on a 4 ps timescale for gallium nanoparticles with radii of 310 Å (a), 220 Å (b), 120 Å (c), 105 Å (d), and 70 Å (e), in the upper part and for tin nanoparticles of 250 Å (a), 140 Å (b), 60 Å (c), and 40 Å (d) (lower part). Plots have been shifted vertically for clarity.

These measurements show that the stress wave, identified by an increase in reflectivity, starts well before electron-phonon thermalization has occurred ($t \approx 1$ ps) and no reflectivity decay is observed at early times as one would expect for thermalization of the hot-electron distribution with lattice. A significant nonthermal contribution in the generation of the acoustic oscillations comes therefore from the excited electron plasma, as pointed out by Thomsen *et al.*[9] Nonthermal stress generation, which could not be observed in any of the preceding picosecond experiments,[9–12] becomes important for excitation with femtosecond pulses, where electrons and phonons are initially out of equilibrium and contribute separately to lattice expansion. A more general formalism for strain generation in absorbing solids excited with ultrashort optical pulses[9] expresses stress σ as

$$\sigma = \sum_{\mathbf{k}} \delta n_e(\mathbf{k}) E_{\mathbf{k}} \gamma_{\mathbf{k}}^e + \sum_{\mathbf{k}} \delta n_p(\mathbf{k}) \hbar \omega_{\mathbf{k}} \gamma_{\mathbf{k}}^p, \quad (2)$$

where the two terms take into account the separate contributions of modified electron and phonon distributions [$\delta n_e(\mathbf{k})$, $\delta n_p(\mathbf{k})$]. In Eq. (2), E_k and $\hbar \omega_{\mathbf{k}}$ are the energy of an electron and of a phonon of wave-vector $\mathbf{k}$, respectively, and $\gamma^{e,p}$ are the corresponding Grüneisen factors.[16] Assuming that $\gamma^{e,p}$ do not vary significantly with $\mathbf{k}$ then Eq. (2) reduces to

$$\sigma \approx \gamma^e \sum_{\mathbf{k}} \delta n_e(\mathbf{k}) E_{\mathbf{k}} + \gamma^p \sum_{\mathbf{k}} \delta n_p(\mathbf{k}) \hbar \omega_{\mathbf{k}}$$

$$\approx \gamma^e \Delta(C^e T^e) + \gamma^p C^p \Delta T^p, \quad (3)$$

where $C^{e,p}$ is the specific heat for electrons and ions, and $\Delta T^{e,p}$ is the temperature variation for electrons and ions, respectively. When the carriers and lattice reach mutual thermal equilibrium ($t>1$ ps), i.e., when electronic and lattice temperatures are equal, Eq. (3) reduces to a simple thermal model, where the local stress is proportional to the lattice-temperature variation. In this case the oscillation would be driven solely by the nonuniform lattice-temperature profile. This is because at room temperature the electronic heat capacity C^e is about two orders of magnitude smaller than that of the lattice[16] and the phononic contribution largely dominates. At short times, before the occurrence of thermalization, however, the temperature of electrons is much higher than that of the lattice. Because the electronic heat capacity is linearly proportional to the carrier temperature, the average electron energy $\langle E^e \rangle$ (proportional to $C^e T^e$) grows quadratically with T^e. A reasonable maximum carrier temperature for UV excitation can be estimated as ≈ 0.3 eV, leading to a non-negligible nonthermal contribution. An acoustic disturbance may then be injected into the nanoparticle by nonuniform electronic excitation before the occurrence of significant lattice heating. Nevertheless, in this case, a generation of acoustic oscillation relies on a spatially nonuniform stress generation, as pointed out on speculative grounds by Thomsen *et al.*[9] but not yet experimentally evidenced.

In this respect, the rapid disappearance of acoustic oscillations in the case of nanoparticles with radii below ≈ 60 Å (Ref. 8) may be interpreted through several mechanisms. In particular, the increased homogeneity in excitation and thermal diffusion over small depths certainly favors a reduction in amplitude of oscillations. However, the effect can also be interpreted as evidence for a transition from bulklike excitation and relaxation dynamics to a regime where particle size becomes smaller than the electron mean free path (≈ 44 Å for bulk tin). When cluster size approaches a hot-carrier mean free path, electron wave functions are intrinsically delocalized and spatial homogeneity of the excitation is in itself ill defined. Therefore, the relaxation dynamics, which is mainly mediated by surface-scattering events, does not provide any inhomogeneous stress distribution and no acoustic oscillations take place.

In conclusion, we have observed the development of acoustic oscillations in metallic nanoparticles both in liquid and solid phase due to nonuniform pump absorption by means of femtosecond pump-probe measurements. The dependence of the oscillation period upon size is in reasonable agreement with bulk sound velocities. The stress generation process is identified as a nonthermal excitation of acoustic modes inside the nanosphere. For cluster sizes below the carrier mean free path disappearance of the oscillations is interpreted as a transition into nonbulk regime, where excitation of the nanoclusters occurs in a homogeneous fashion. These observations are made possible by using a self-organization growth technique of the nanoparticles which allows a variation in sizes in a wide range around the penetration depth of the radiation.

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