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Vibration Dynamics of Supra-Crystals of Cobalt Nanocrystals Studied With Femtosecond Laser Pulses**

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Self-assembly of nanometer-sized species in 2D or 3D supra-structures is a fundamental process in nature. A well-known example of such ordering are opals, where the crystalline arrangement of silica spheres gives rise to a wavelength-dependent diffraction, generating their iridescent colors.^[1] We are interested in self-assembled metallic nanocrystals, which are known to form so-called supra-crystals. Their intrinsic physical properties (mechanical, optical, magnetic) display specific behaviors revealing a collective response to external perturbations.^[2–4] Indeed, self-organized silver-nanocrystal supra-crystals display collective breathing modes.^[5,6] Here, the real-time observation of coherent motion in cobalt nanocrystals in supra-crystals excited by ultrashort laser pulses is reported. This motion is observed in the time-dependent reflectivity measured with a time-resolved confocal microscope designed to provide 150 fs temporal resolution and 300 nm spatial accuracy simultaneously.^[7]

Time-resolved pump-probe spectroscopy of metallic nanoparticles^[8,9] using femtosecond laser pulses is a powerful technique, which allows the unravelling of physical processes occurring from a few tens of femtoseconds up to ~1 ns, such as Coulomb interactions between electrons,^[10–12] their coupling to vibrational degrees of freedom of atoms,^[13–15] as well as heat diffusion to the environment.^[16,17] As previously reported,^[18,19] it is possible to produce both face-centered cubic (fcc) supra-crystals and disordered aggregates from the same batch of cobalt nanocrystals by controlling the evaporation process. This procedure was performed for cobalt nanocrystals of two different diameters, 6.3 ± 0.4 and 7.3 ± 0.4 nm. As the 2D and 3D mesostructures are similar for both sizes, we only show here the complete characterization of the 6.3-nm nanocrystal population. As shown in the transmission electron microscopy (TEM) image in the left inset of Figure 1A, the nanocrystals, once deposited on highly

oriented pyrolytic graphite (HOPG), form a compact 2D hexagonal network spontaneously. The long-range ordering of the nanocrystals is due to the sufficiently low size distribution (less than 13%),^[20] combined with a size segregation process.^[5] When the colloidal solution containing these particles is quickly evaporated under vacuum,^[21] the grazing-incidence small-angle X-ray scattering (GISAXS) pattern (inset of Fig. 1B) shows a very diffuse and low-intensity ring, typical of amorphous materials. In the case of slow evaporation, the diffraction pattern displays several reflections that are typical to fcc structures^[19] (right inset of Fig. 1A). The two spots labeled 3 and 4 correspond to the (111) and (222) reflections of fcc structures, respectively. The first-order reflection is very narrow and nearly resolution limited (0.0045 nm^{-1}), indicating an out-of-plane long-range ordering of the magnetic nanocrystals. This gives us the minimum value for the coherence length, 140 nm. From the position of the (111) reflection, we deduce a stacking periodicity of 7.6 ± 0.1 and 8.5 ± 0.1 nm for the 6.3 and 7.3 nm particles, respectively.^[19] The interparticle gaps (D_{i-p}) and the center-to-center interparticle distance (D_{c-c}) are 3.0 ± 0.5 , 3.1 ± 0.5 nm and 9.3 ± 0.1 , 10.4 ± 0.1 nm, respectively. These gaps are the result of the alkyl-chain interdigitation of ~6 C–C bond distances, i.e., ~0.9 nm. The other spots, labeled 1, 2, and 5, are indexed as (1,1,–1), (2,0,0), and (–1,3,1) for fcc, and reveal a 3D in-plane long-range ordering in the sample. The 3D assemblies of cobalt nanocrystals coated with dodecanoic acid chains, ordered or not, form an inhomogeneous film, as shown in the scanning electron microscopy (SEM) images (Figure 1). The film thickness varies from a few micrometers at the border to tens of nanometers in the center. Samples exposed to air for several days do not oxidize as previously reported,^[3] and no coalescence of Co nanocrystals is observed in the long term.

The ultrafast reflectivity dynamics $\Delta R(t)/R$ of the amorphous assemblies and fcc supra-crystals of Co nanoparticles described above have been investigated using the femtosecond pump-probe technique (see Experimental Section). The maximum excitation density of the pump was 40 mJ cm^{-2} . Dynamic measurements were performed on similar individual pavements of both ordered and amorphous samples. As it is well known, after the pump-pulse excitation the femtosecond electron dynamics of metals can be described by an initial athermal distribution, which thermalizes within a few hundred femtoseconds into a hot-electron distribution via electron–electron scattering. The electrons then relax to the lattice via electron–phonon interaction, with characteristic time τ_{e-l} . This

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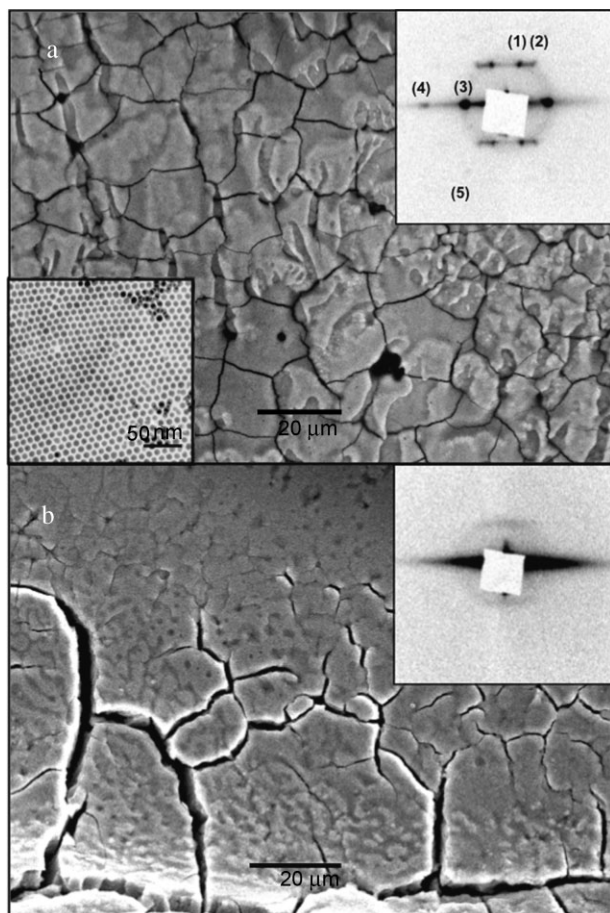


Figure 1. SEM images of assemblies of 6.3 nm cobalt nanocrystals. a) fcc supra-crystals and b) amorphous assemblies. Insets: corresponding GISAXS patterns. The right inset in (a) shows a 2D superlattice prepared using the same Co nanocrystals.

process is observed for the disordered aggregates and fcc supra-crystals of cobalt nanocrystals with a diameter of 6.3 nm in the temporal behavior of $\Delta R(t)/R$, represented during the first 15 ps in Figure 2a. The τ_{e-1} relaxation times are $\tau_{e-1}^{\text{amorp}} = 3$ ps and $\tau_{e-1}^{\text{fcc}} = 7$ ps for amorphous and fcc samples, respectively. This is consistent with the time scale of the electron-lattice relaxation in polydispersed cobalt nanocrystals implanted in a dielectric matrix,^[22] as well as with that obtained for copper and silver nanocrystals.^[8,23] On the picosecond to nanosecond time scales, the energy deposited by a pump pulse dissipates to the environment of the nanocrystals. This can be described by a thermal-diffusion mechanism. Figure 2b shows the corresponding reflectivity dynamics for the amorphous aggregates and fcc supra-crystals. For the amorphous sample, a monotonous decay is observed. For the fcc supra-crystals, conversely, large, region-independent oscillations are observed. Table 1 gives the characteristic oscillation periods observed on the explored region, which varies between 120 and 128 ps. As the average accuracy of the measurement is 2 ps, the variation in period reflects the size-segregation process occurring during the 3D supra-crystal growth. Thus

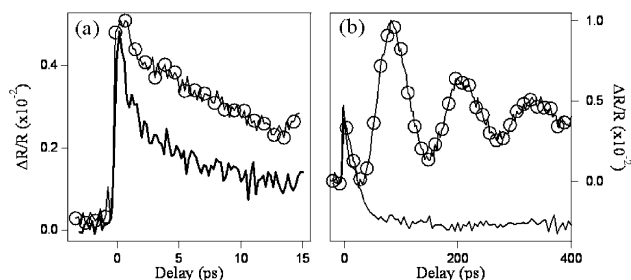


Figure 2. Differential reflectivity dynamics of assemblies of 6.3-nm cobalt nanocrystals. a) Short time range and b) long time range (solid line: amorphous assembly; open circles: fcc supra-crystal).

the average characteristic period of the ordered sample, τ_{osc} , is found to be 125 ± 5 ps, which corresponds to a low frequency mode of 1.7 cm^{-1} . The reflectivity dynamics on a bare HOPG substrate does not show any modulation, and the oscillations do not depend on the polarization of the incident light, excluding the possibility of a birefringence effect. Clearly, this modulation of $\Delta R(t)/R$ is present only for the cobalt nanocrystals ordered in fcc supra-crystals. It results from the Van der Waals interactions between the dodecanoic acid chains coating the nanocrystal, strong enough to establish a correlation between vibrating nanocrystals, so that they vibrate coherently in the supra-crystal. The excitation of this mode occurs due to the heating of the supra-crystal, associated with the relaxation energy of the pump pulses, which occurs in two steps. First, the relaxation energy is released within each particle (short-time behavior in Fig. 2a). Then it is dissipated to the environment, via the interdigitated aliphatic chains. This modulation is therefore caused by the coherent motion of the entire supra-crystal of cobalt nanocrystals linked dodecanoic acid chains. This result is consistent with recent static measurements of silver nanocrystals coated by aliphatic chains on 3D fcc supra-crystals, where an internanocrystal coherent vibration was observed using Raman spectroscopy.^[5,6] The oscillations dampen faster than the heat-diffusion time, due to the presence of structural defects in the supra-crystal, as revealed by the coherence length (>140 nm) when the spot size of the probe is 300 nm. A simple model description consists of spheres (cobalt nanocrystals) of mass m , interconnected by

Table 1. Experimental values of the oscillation period τ_{osc} for different regions of the 3D superlattices.

Average diameter (nm)	Zone	τ_{osc} (ps)
6.3	1	123
6.3	2	125
6.3	3	125
6.3	4	120
6.3	5	125
6.3	6	128
7.3	1	130
7.3	2	129
7.3	3	128
7.3	4	131

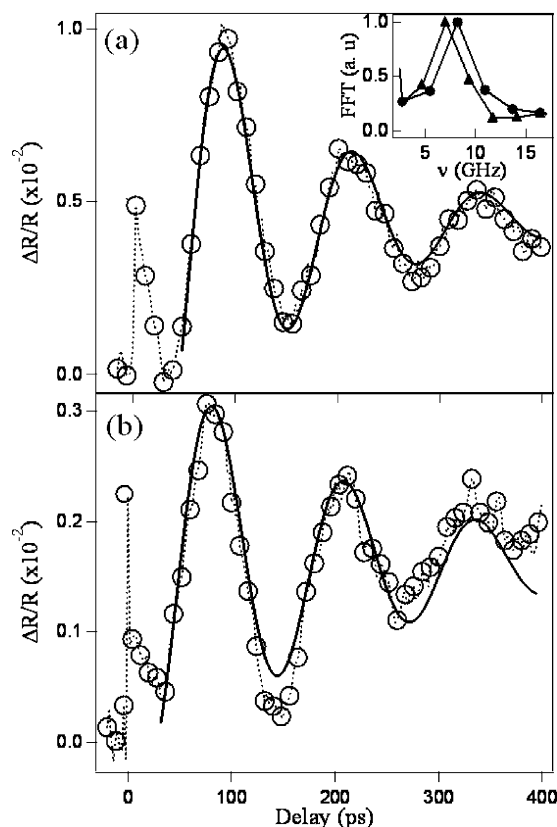


Figure 3. Differential reflectivity dynamics (open circles) and corresponding damped oscillator fit (solid lines) for a) fcc supra-crystals of 6.3-nm cobalt nanocrystals and b) fcc supra-crystals of 7.3-nm cobalt nanocrystals. Inset: fast Fourier transform corresponding to a) (full circles) and b) (full triangles).

springs (aliphatic chains) with a rigidity constant k . A similar model is often used for modeling the vibrations of an atomic crystal.^[24] The frequency of this harmonic oscillator is $\omega_{\text{osc}} = 2\sqrt{k/m}$. Figure 3 presents the oscillations of the supra-crystal for the 6.3-nm (Fig. 3a) and 7.3-nm (Fig. 3b) diameter nanocrystals. The inset in Fig. 3a displays their Fourier transforms, showing a slight change in the oscillation frequency, f_{osc} ($d = 6.3$ nm) = 8.2 GHz and f_{osc} ($d = 7.3$ nm) = 7.1 GHz. Figure 3 also shows the best fit obtained assuming a damped oscillator model, $\Delta R(t)/R = Ae^{-t/\tau} \cos[\omega_{\text{osc}}(t - t_0)]$, where A is an arbitrary constant, t the time, and τ the damping characteristic time. For the 6.3-nm nanocrystals ($m = 2.28 \times 10^{-21}$ kg), the rigidity constant k can be deduced from ω_{osc} , and was found to be 1.4 N m^{-1} . This is the rigidity of the bundles of interdigitated dodecanoic acid chains linking two nanocrystals, and can be compared to the one estimated from the compressibility modulus of such a chain, $K_m = 10^8 \text{ N m}^{-2}$.^[25] Considering that the surface of a polar head group of the coating agent is $\sim 0.5 \text{ nm}^2$, and that the coverage ratio for a 6.3 nm cobalt nanocrystal is $\sim 75\%$,^[26] then the number of decanoic acid chains can be estimated to be 190, contributing to 12 connections with

neighboring nanocrystals in the fcc supra-crystal. Hence, there are 16 chains per connection, corresponding to an area $A = 8 \text{ nm}^2$, and the strength of the connection is therefore $K_m A = 8 \pm 1 \times 10^{-10} \text{ N}$. This leads to a compressibility of connection of $0.9 \pm 0.1 \text{ N m}^{-1}$, if we consider the spring is only in the interdigitation zone (~ 0.9 nm long), and $0.3 \pm 0.1 \text{ N m}^{-1}$, if we consider that all the chains between the two nanocrystals act as springs (~ 3 nm long). These rigidity values are in good agreement with those deduced from our experimental results ($1.4 \pm 0.2 \text{ N m}^{-1}$). For the 7.3-nm-diameter nanoparticle supra-crystal, a similar modulation of $\Delta R(t)/R$ is observed, with a characteristic period $t_{\text{osc}} = 131 \pm 5$ ps. This allows us to check the validity of our model, knowing that the period depends both on k ($1.8 \pm 0.2 \text{ N m}^{-1}$ deduced from ω_{osc}) and m ($\tau_{\text{osc}} \propto \sqrt{m/k}$). A variation of diameter induces a variation of m , which varies with the volume $\sim d^3$, whereas k depends on the surface $\sim d^2$ (number of chains in the connection). Therefore, $\Delta \tau_{\text{osc}}/\tau_{\text{osc}} = 1/2(\Delta d/d)$. A variation of 1 nm in the diameter d corresponds to a change of 7% in the oscillation period τ_{osc} , which is in very good agreement with the experimental values (133 ps vs. 131 ps).

In conclusion, we report the first real-time observation of the collective motion of nanocrystals self-assembled in a 3D supra-crystal. The long-range ordering in the fcc cobalt supra-crystals studied here is ideal to launch coherent vibrations of the nanocrystals when suddenly heated by femtosecond laser pulses. The interdigitated aliphatic chains linking the particles act as mechanical nanosprings, which can be resonantly excited by ultrashort laser perturbations. This macroscopic supra-molecular motion finds its origin at the microscopic level where, similarly, the cobalt atoms in each nanocrystal have their own dynamics, including their electron and lattice relaxation energies.

Experimental

Synthesis of Cobalt Nanocrystals: The synthesis of cobalt nanocrystals coated with dodecanoic acid is described in Ref.[20]. Reverse micelles of $5 \times 10^{-2} \text{ M Co(AOT)}_2$ form an isotropic phase. The amount of water added to solution was fixed to reach a water concentration defined as $w = [\text{H}_2\text{O}]/[\text{AOT}] = 32$. Sodium borohydride was added to the micellar solution to reduce the cobalt ions, in a concentration defined by $R = [\text{NaBH}_4]/[\text{Co(AOT)}_2] = 6$. Immediately after the addition of NaBH_4 , the color of the micellar solution changed from pink to black, indicating the formation of colloidal cobalt particles. The nanocrystals were coated and then extracted from the surfactant. The coating process was as follows. Dodecanoic acid ($\text{C}_{12}\text{H}_{25}\text{COOH}$, 0.2 M) was added to the solution containing nanocrystals, surfactants, water, and isooctane, inducing the formation of a chemical bond between the dodecanoic acid and the Co atoms located on the surface. The coated cobalt nanocrystals were then washed and centrifuged several times with ethanol to remove all the AOT surfactant, and the black powder obtained was dispersed in hexane. Since the synthesis took place in a supersaturated regime, particles of different sizes were formed. In order to eliminate the largest particles, the solution was centrifuged and only the upper phase, which contained the smallest particles, was collected. At the end of the synthesis, cobalt nanocrystals coated with dodecanoic acid and with a size distribution of 11% were produced. The reducing agent oxidized when exposed to air, causing the reduction rate to decrease with time, yielding smaller nanocrystals. Hence, the

size changed from one synthesis to another, and sizes were in the range of 6–7.5 nm.

Sample Preparation: After synthesis, the concentration of the nanocrystals dispersed in hexane was fixed at 5.5×10^{-7} M. HOPG pieces (10 mm \times 5 mm) were horizontally immersed in 200 mL of this concentrated nanocrystal solution. To form an amorphous assembly, the solvent was evaporated rapidly, under vacuum inside a dessicator. The evaporation time was very small, less than 1 min. To form an ordered assembly, solvent evaporation took place at 25 °C under a nitrogen flow, in order to prevent oxidation. Such evaporation took a few hours in total. It is important to note that both assemblies were prepared with the same batch of cobalt nanocrystals.

Sample Characterization: SEM was performed using a JMS-5510LV instrument. TEM was performed using a JEOL 1011 microscope. The X-ray experimental set-up consisted of a rotating copper-anode generator (50 kV, 30 mA) operated with a small-size focus (0.2 mm \times 0.2 mm). The optics consisted of a parabolic multilayer graded mirror coupled to a nickel-coated mirror bent at right angles. The delivered X-ray beam was well-defined, parallel, intense and monochromatic ($\lambda = 0.154$ Å). The sample was vertically placed on the sample holder, which rotated around a vertical axis (rotation 2°). The diffracted beam passed through the cell under vacuum, in order to reduce air scattering. Diffraction patterns were recorded on photo-stimulable imaging plates. GISAXS measurements probed a section several micrometers wide, from one edge of the substrate to the other, i.e., 5 mm.

Reflectivity Measurements: The time-dependent differential reflectivity signals $\Delta R/R(t)$ were measured using the ultrafast pump and probe technique. The ultrashort laser pulses were delivered by an amplified titanium:sapphire system with a repetition rate of 5 kHz. The pump beam was centered at the fundamental wavelength of the laser system, 790 nm, with pulse duration 120 fs. The probe was set at 395 nm, by frequency doubling in the β -BaB₂O₄ (BBO) crystal. The pulse duration of the probe was 150 fs. In addition to the temporal resolution of 150 fs, a spatial resolution of 300 nm was obtained with a confocal microscope optimized for femtosecond pump-probe experiments.[7] The two collinear beams were focused at normal incidence by a microscope objective lens with 0.6 numerical aperture. The beam diameters of the pump and the probe were 600 and 300 nm, respectively. The reflected probe beam was collected using a dichroic beam splitter through a 20 μ m diameter aperture, allowing for confocal resolution, and was detected with a photomultiplier. The differential reflectivity $\Delta R/R = (R_{\text{with pump}} - R_{\text{without pump}})/R_{\text{without pump}}$ was obtained using the low-frequency (215 Hz) mechanical chopping of the pump beam, and a synchronous lock-in detection scheme.

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