

Time-Resolved Study of Surface Spin Effect on Spin–Lattice Relaxation in Fe₃O₄ Nanocrystals

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Investigation of the flow of energy and momentum in spin degrees of freedom in magnetic materials is now an important field of research since the electron spin is actively exploited as a new information carrier in addition to the electron charge.^{1,2} In ferromagnetic materials, the dynamics of spin excitation and relaxation has been actively investigated.³ The relaxation of the spins requires the exchange of energy and angular momentum between the spin and lattice degrees of freedom, which is mediated by spin–orbit coupling. The effective strength of spin–orbit interaction in ferromagnetic solids is determined not only by the intrinsic atomic spin–orbit coupling strength but also by the ligand field that depends on the details of the local lattice structure and symmetry.^{4,5} In nanoscale magnetic materials, there are many surface spins under different ligand fields from those of the interior spins due to the structural discontinuity on the surface. Therefore, one would expect that the rate of energy and momentum transfer in spin degrees of freedom in nanoscale magnetic materials be significantly influenced by the surface spins.

In this communication, we report the real-time measurement of the rate of spin–lattice relaxation in photoexcited colloidal Fe₃O₄ nanocrystals to obtain insight into the role of the surface spins in the equilibration dynamics of the photoexcited spins. While the effect of surface spins on superparamagnetic relaxation dynamics involving the directional fluctuation of the magnetization was investigated in earlier studies,^{6–8} we address the dynamics of energy flow between the spin and lattice resulting in the time-dependent magnitude of the magnetization. From the analysis of the spin–lattice relaxation rates of the nanocrystals of various sizes using a simple model, we estimated the relative efficiency of the spin–lattice relaxation on the surface with respect to the interior in Fe₃O₄ nanocrystals.

To investigate the dynamics of spin relaxation in magnetic nanocrystals directly in the time domain, we employed a time-resolved Faraday rotation technique. Due to its high temporal resolution (<100 fs), time-resolved Faraday rotation is particularly useful for observing fast dynamics in spin degrees of freedom, although it probes only the relative change in magnetization via magneto-optic effect.⁹ A colloidal solution of organically passivated Fe₃O₄ nanocrystals was chosen as the model system for this study. Systematic variation of the size and surface coordination readily achievable in Fe₃O₄ nanocrystals makes it particularly suitable for investigating the role of surface spins on the energy flow in the spin degrees freedom.¹⁰ In our recent report,¹¹ size-dependent magnetization dynamics in photoexcited Fe₃O₄ nanocrystals were discussed with an emphasis on the magnitudes of the demagnetization and its recovery. In this study, we focus on the *rate* of equilibration of the magnetization following the photoinduced demagnetization, which will be correlated with the average strength of spin–orbit interaction of the nanocrystals.

Figure 1 shows the time-dependent Faraday rotation data obtained from the colloidal Fe₃O₄ nanocrystals 5–15 nm in diameter. The samples were photoexcited with 780 nm, 60 fs pulses at a fluence of 20–40 mJ/cm² while being continuously refreshed to avoid sample damage by the repeated excitation. In this measurement, the same

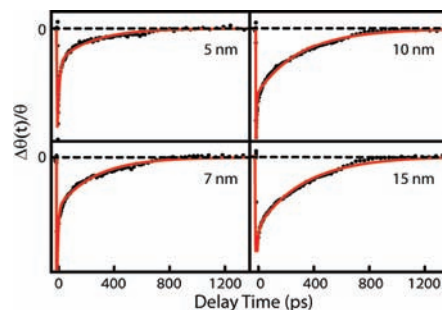


Figure 1. Time-dependent $\Delta\theta(t)/\theta$ of photoexcited Fe₃O₄ nanocrystals. Solid curves are the biexponential fit of the data.

excitation density was maintained for all the samples. Fractional change in Faraday rotation, $\Delta\theta(t)/\theta$, represents the time-dependent magnetization of the photoexcited nanocrystals. General dynamic features of the data in Figure 1 are (i) sub-ps demagnetization following the excitation, (ii) recovery on ~ 10 ps scale, (iii) recovery on $\sim 10^2$ ps scale. Time scales of the recovery of $\Delta\theta(t)/\theta$ extracted from biexponential fitting of the data are summarized in Table 1.

Table 1. Time Constants Obtained from Biexponential Fit of $\Delta\theta(t)/\theta$

size (nm)	5	7	9	10	15
τ_a (ps)	22	29	32	24	12
τ_b (ps)	255 ± 10	275 ± 10	295 ± 10	325 ± 10	345 ± 10

The feature (i) has been previously observed in many metallic ferromagnets.^{12–14} Such ultrafast demagnetization has been a topic of active research recently, which resulted in the discovery of a number of ultrafast spin–orbit coupling pathways. We will not discuss this process since it is beyond the scope of our discussion. Here, we focus on the dynamic feature (iii), occurring on the time scale $\tau_b = 250$ – 350 ps. Justifications for relating τ_b to the time scale of spin equilibration via usual spin–lattice relaxation pathway are the following. First, τ_b has the correct order of magnitude for the spin–lattice relaxation time of $\sim 10^2$ ps expected for the ferromagnetic materials of transition metals.⁴ In addition, τ_b in Co_xFe_{3-x}O₄ nanocrystals decreased with increasing content of Co that has a stronger spin–orbit interaction than Fe in a separate experiment.¹⁵ This strongly indicates that τ_b reflects the spin–lattice relaxation determined ultimately by the strength of the spin–orbit interaction. The origin of the faster dynamics (ii), an order of magnitude faster than the slower dynamics, is not entirely clear, although it may still reflect part of spin relaxation.

τ_b obtained from the fitting of data was not sensitive to the wavelength of the probe light, unlike in transient absorption, as expected for $\Delta\theta(t)/\theta$ representing the magnetization dynamics.⁹ At sufficiently low excitation intensities, τ_b was also independent of the excitation intensity (Supporting Information). On the other hand, τ_b increased from 250 to 350 ps as the size of the nanocrystal increased

from 5 to 15 nm. We attribute the size dependence of τ_b mainly to the weaker average spin–orbit interaction in the larger nanocrystals as will be discussed below.

According to Fermi's golden rule, spin–lattice relaxation rate ($1/\tau_b$) is proportional to the square of the coupling Hamiltonian term ($\langle V \rangle^2$) between the spin–orbit perturbed ligand field states, where the Hamiltonian V is the fluctuating electric potential of the ligand.¹⁶ Here, we assume $\langle V \rangle^2$ of nanocrystals has contributions from the interior ($\langle V_i \rangle^2$) and the surface ($\langle V_s \rangle^2$) proportionally to the fraction of the interior (f_i) and surface (f_s) spins. A similar model incorporating the surface contribution in the energy relaxation has been used to explain exciton relaxation dynamics in quantum dots.¹⁷

$$1/\tau_b \propto \left| \langle V \rangle \right|^2 = f_i \cdot \left| \langle V_i \rangle \right|^2 + f_s \cdot \left| \langle V_s \rangle \right|^2 \quad (1)$$

Using this model, we estimated the relative efficiency of the surface in spin–lattice relaxation with respect to the interior. The values of f_i and f_s depend on the thickness (t) of the surface region, which is somewhat arbitrary. In our analysis, we chose the values of t between 3 and 5 Å that contain the outermost atomic layer. By comparing the variation of $1/\tau_b$ with the variation of $\langle V \rangle^2$ on the nanocrystal size, we obtained $\langle V_s \rangle^2 / \langle V_i \rangle^2 \approx 3$ for $t = 4$ Å. Comparison of the relative values of $1/\tau_b$ and $\langle V \rangle^2$ as a function of the nanocrystal diameter is shown in Figure 2.

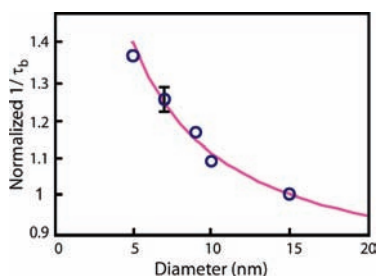


Figure 2. Relative values of $1/\tau_b$ (circle) and $\langle V \rangle^2$ (line) as a function of the diameter of nanocrystal. All the values are normalized to those of 15 nm sample. The error bar represents a typical margin of error.

This result indicates that the surface of the Fe_3O_4 nanocrystal is 3 times more efficient than the interior for spin–lattice relaxation. Considering that spin–orbit interaction is a major factor determining the spin–lattice relaxation rate, the observed size-dependence of τ_b can be interpreted as the stronger spin–orbit interaction on the surface. While the unequal vibrational baths of the surface and interior may contribute to the size dependence of τ_b , we believe it plays a less significant role in our study.¹⁸

Stronger spin–orbit coupling at the surface can be justified as follows. In magnetic crystals, the effective spin–orbit energy (E_{so}), representing the strength of spin–orbit coupling, is on the order of $\zeta^2/\Delta E$, where ζ is the atomic spin–orbit coupling parameter and ΔE is the ligand field splitting energy.⁴ In Fe_3O_4 nanocrystals, Fe ions have a smaller number of oxygen ligand on the surface than in the interior. The lacking oxygen ligand is replaced with weakly bound carboxylic group of oleic acid used as the surfactant. Therefore, the ligand field acting on the surface spins is smaller than that of the interior spins. Consequently, E_{so} of the surface spins can be larger than that of the interior spins, resulting in a decreasing average E_{so} with increasing nanocrystal size.

A stronger spin–orbit interaction of the surface spin is also corroborated by the earlier study on surface coercivity of the magnetic nanocrystals by Vestal et al.¹⁹ They observed that surface

coercivity of MnFe_2O_4 nanocrystals increased as the ligand field of the coordinating molecules decreased. This indicates that the effective spin–orbit interaction of the surface spin increases with the weaker ligand field, consistent with our results. It would be desirable to correlate the size-dependence of $1/\tau_b$ to the experimentally determined variation of E_{so} to further support our conclusion more quantitatively. However, we did not pursue such an analysis in this study. In the bulk phase, information on the variation of E_{so} is indirectly obtained from magnetocrystalline anisotropy energy E_{mca} , which is more readily measurable. For this reason, earlier studies often correlated the spin relaxation rate with magnetic anisotropy.^{20,21} We did not make a similar analysis in our study, since the size-dependent E_{mca} of the nanocrystals does not correctly reflect the size-dependent E_{so} , due to the heavily weighted contribution of the surface anisotropy to the experimentally measured total E_{mca} .²²

In summary, we have investigated the relaxation rate of the spins in colloidal Fe_3O_4 nanocrystals following the optically induced demagnetization. From the analysis of spin relaxation times of nanocrystals of different size using a simple model, we estimated the efficiency of spin–lattice relaxation at the surface relative to the interior region. This result will also be a starting point for the investigations on the effect of surface modifications on the spin–lattice relaxation in nanocrystals.

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Supporting Information Available: TEM images of the nanocrystal samples and comparison of $\Delta\theta(t)/\theta$ data at different probe wavelength and excitation fluence. This material is available free of charge via Internet at <http://pubs.acs.org>.

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