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# Surface spin polarization induced ferromagnetic Ag nanoparticles

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ABSTRACT

We report on the observation of ferromagnetic spin polarized moments in 4.5 nm Ag nanoparticles. Both ferromagnetic and diamagnetic responses to an applied magnetic field were detected. The spin polarized moments shown under non-linear thermoinduced magnetization appeared on the surface atoms, rather than on all the atoms in particles. The saturation magnetization departed substantially from the Bloch $T^{3/2}$-law, showing the existence of magnetic anisotropy. The Heisenberg ferromagnetic spin wave model for $H_a$-aligned moments was then employed to identify the magnetic anisotropic energy gap of ~0.12 meV. Our results may be understood by assuming the surface magnetism model, in which the surface atoms give rise to polarized moments while the core atoms produce diamagnetic responses.



## 1. Introduction

The magnetic properties of metal nanoparticles, such as Pd, Au and Cu, have recently been the subject of numerous studies [1–9]. It is known that finite-size effects can lead to unusual ferromagnetic and diamagnetic properties and the spin behaviors in the nanostructures can be quite different from those observed in the bulk systems. Lattice rearrangement, crystalline imperfections, an enlarged degree of localization and a narrowed valence band frequently occur in the nanostructures. As a result, the spin behaviors in the nanostructures can be quite different from those observed in the bulk systems. It has also recently been observed that Pd and Au nanoparticles can acquire ferromagnetic moments at low temperature [2,4]. Pastor et al. [8] predicted that a non-uniform magnetization profile, with a larger moment near the surface, would originate from the finite size effect and this was observed by Jing et al. [10]. The appearance of ferromagnetic spin polarization in nanoparticles that have filled d shells is currently understood as based on the development of surface magnetism, arising from the giant magnetic anisotropy [11] and the Fermi hole effect [12]. The thermal excitation of Heisenberg spin waves [13,14] is presently believed to be the main mechanism giving rise to the thermoinduced magnetization observed in magnetic nanoparticles [15–18]. It is predicted that noticeably enhanced 4d localization, resulting from the charge transfer processes, will appear in nanoscale systems [19,20]. This d-electron localization helps in out understanding [21] of the ferromagnetic spin polarizations observed in Pd nanoparticles. Charge transfers from the outer atoms to the inner ones have also been found [22] to be energetically favorable for Ag clusters. As a result, the number of uncompensated spins increases noticeably nears the surface, which in turn gives rise to a non-zero average magnetic moment for Ag clusters. Bulk Ag has a closed 4d shell and an unfilled 5s subshell. The material displays a weak diamagnetic characteristic, with a magnetic susceptibility of $\chi_{bulk} = -1.9 \times 10^{-7}$ emu/g-Oe [19]. In this research we report on the results of studies of the spin polarization and thermoinduced magnetic moment of 4.5 nm Ag nanoparticles. We found there to be substantial deviation from the Langevin behavior at low temperatures and a nonlinear thermoinduced magnetic behavior. These observations may be understood by assuming that ferromagnetic spins exist near the surface with the diamagnetic contribution coming from the spins in the core.

## 2. Sample characterization

The Ag nanoparticle powder was fabricated by employing the thermal evaporation method. High-purity silver ingots (99.999%) were evaporated in an Ar atmosphere at a pressure of 1 Torr, using an evaporation rate of 0.1 Å/s. A stainless steel plate, maintained at the temperature of liquid nitrogen, was used to collect the evaporated particles. After restoration to room temperature, the

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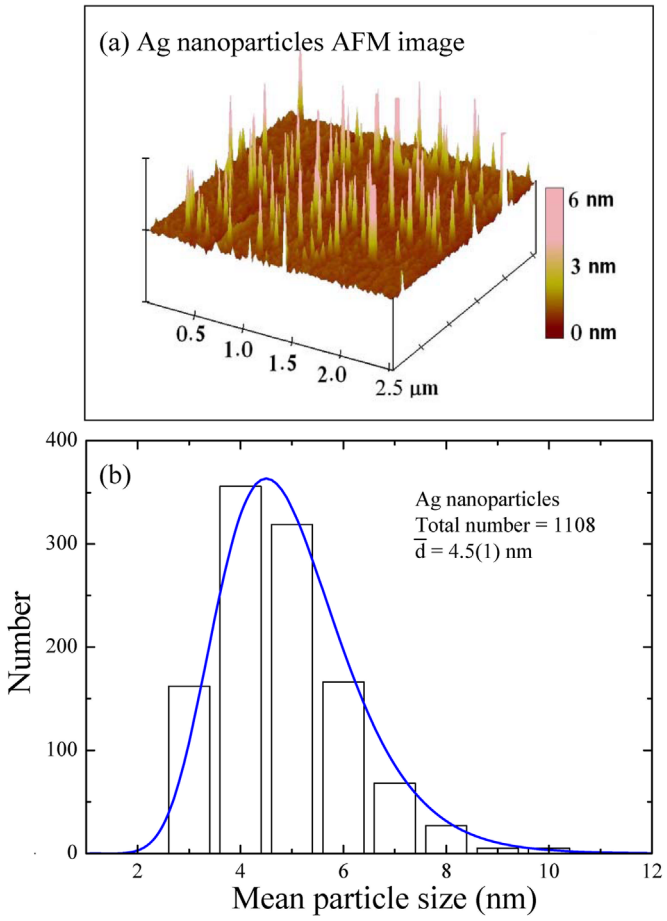


**Fig. 1.** (a) Portion of the AFM images of the Ag nanoparticles, and the size distribution obtained from the images. (b) The size distribution may be described by a log-normal distribution function (solid curve), with a mean diameter of 4.5(1) nm and a deviation width of 0.264 nm.

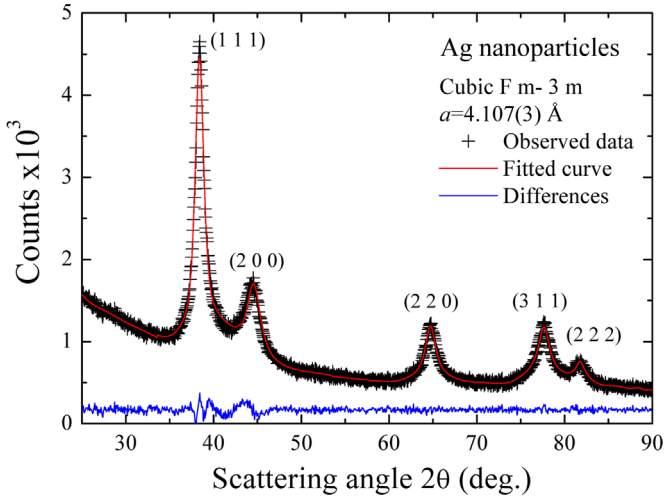


**Fig. 2.** X-ray diffraction pattern of the Ag nanoparticle powder, taken at room temperature, showing a face-centered cubic structure with a lattice constant of $a=4.107(3)$ Å that is about 1% larger than that of bulk Ag.

nanoparticles, which were only loosely attached to the collector, were stripped off. The resultant samples were in the form of a dry powder, and consisted of a collection of a macroscopic amount of individual Ag nanoparticles. The sample was kept in vacuum to avoid possible surface oxidization. X-ray diffraction and atomic force microscopy (AFM) were used to characterize the sample. A portion of the AFM images and the size distribution, obtained from a $2.5 \times 2.5\ \mu m^2$ image, are shown in Fig. 1(a) and (b). The results reveal a size distribution that can be described (solid curve in Fig. 1 (b)) using a log-normal distribution function [23]. The parameters obtained from the fits are $\bar{d}=4.5(1)$ nm and $\sigma=0.264$ nm. The mean particle diameter is also determined from the X-ray diffraction profiles. Fig. 2 displays the X-ray powder diffraction pattern of the Ag nanoparticles, taken at room temperature. The analysis was performed using the program package of the General Structure Analysis System (GSAS) [24], following the Rietveld method [25]. All the diffraction peaks can be associated with a face-centered cubic (fcc) Ag structure, with a lattice constant of $a=4.107(3)$ Å, that is about 1% larger than that of bulk Ag. No traces of impurities or oxidation phases were found within the 3% X-ray resolution limitation. The widths of the diffraction peaks were much broader than the instrumental resolution, reflecting the appearance of the finite size effect. For a particle of diameter $\bar{d}$ that crystallizes into an fcc structure with lattice constant $a$, the number of layers of atoms, $n$, in the particle and the number of atoms in the $n$th layer, $N_n$, may be calculated [26] as follows: $n = \frac{1}{2}\left\{\frac{\bar{d}}{a}\sqrt{2}+1\right\}$ and $N_n = 10n^2 - 20n + 12$. Accordingly, there are $n=8$ layers of Ag atoms in a 4.5 nm Ag particle and there are $N_8=492$ Ag atoms on the surface.

## 3. Ferromagnetic spin polarization

### 3.1. Thickness of the spin correlated shell

The magnetizations were measured employing the conventional setup. To reduce the coupling that could arise among the Ag nanoparticles, the powder was loosely packed into a cylindrical holder; the mass density was ~6% that of bulk Ag. We estimated the average spatial separation between two neighboring Ag nanoparticles to be ~11 nm. Fig. 3 shows the variations of the magnetization with the applied magnetic field, $M(H_a)$, taken at several temperatures. It can be seen that at low $H_a$, the magnetization increases rapidly with increasing $H_a$, reflecting the existence of ferromagnetic spin correlations. Diamagnetic signals dominate at high $H_a$, where magnetization decreases linearly with increasing $H_a$. No noticeable differences in the magnetization curves were found between the measurements made with a field-increasing loop and a field-decreasing loop. There were two

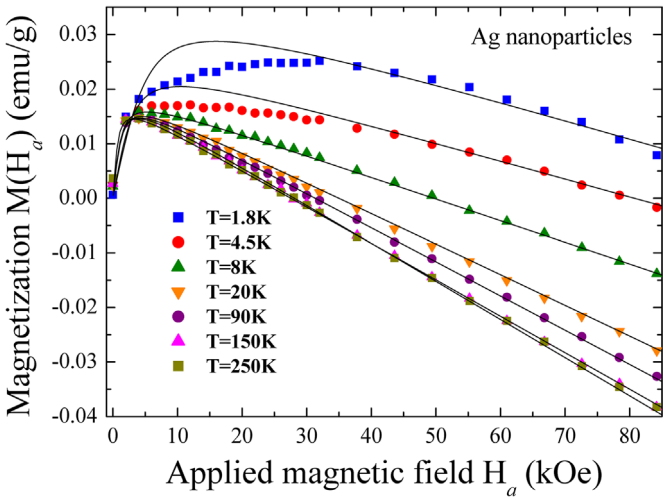


**Fig. 3.** Magnetization curves of the Ag nanoparticle powder, measured at several temperatures. The solid curves indicate the fits of the data to a Langevin profile plus a linear diamagnetic response.