Surface Ferromagnetism of Pd Fine Particles

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We report clear evidence of the ferromagnetism of gas-evaporated Pd fine particles with a clean surface. The clean Pd particle is found to have a magnetic heterostructure: the surface of the particle is ferromagnetic and the rest is paramagnetic. The size dependence of the magnetic saturation component reveals that the ferromagnetic ordering occurs only on (100) facets of the particle and that the topmost two to five layers from the surface contribute to the ferromagnetism with a magnetic moment of $(0.75 \pm 0.31)\mu_B$/atom.

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The physical property of a fine particle is relevant to the contrasting nature of a bulk and a surface since the size of the fine particle is located in between the bulk and the atom. In particular, an effect having its origin in the surface — surface effect — is significant in the particle due to a large surface ratio to the total volume. A fine particle with a polyhedron structure, which has been observed experimentally, also shows two-dimensional (2D) character on the facet similar to ultrathin films, allowing us to study the surface-related properties with an approach applicable to 2D systems.

In a magnetic system, the low dimensionality brings about very exotic features, for example, an enhancement in the magnetization [1] or the appearance of perpendicular magnetic anisotropy [2,3]. One of the most attractive issues of a low dimensional magnetic system is ferromagnetism, which occurs in normally nonmagnetic materials. Several theoretical calculations have predicted the ferromagnetism of 4*d* transition metals in the low dimensional systems, such as clusters or ultrathin films [4–13]. Although a few experiments have *indirectly* observed a signature of ferromagnetism in 4*d* elements [14–16], there is no report *directly* evidencing the ferromagnetism of 4*d* elements, presumably due to difficulty preparing high quality samples. We previously reported a pioneering finding of the ferromagnetism of Pd fine particles [17]. The ferromagnetic ordering was assumed to lie only in the topmost layer of the particle surface. However, the detailed mechanism of the ferromagnetism is still elusive, because a possible effect of gas adsorption on the surface was not excluded due to insufficient vacuum level during sample preparation.

In this Letter, we report clear evidence of the ferromagnetism of Pd fine particles prepared in a sufficiently clean condition with a vacuum pressure lower than 2×10^{-9} Torr. The surface magnetic properties are examined by adsorbing O_2 atoms on the surface, showing that the ferromagnetic ordering of the Pd fine particle lies in the surface region and is very sensitive to the surface condition. Most significantly, the size dependence of the magnetization indicates that the ferromagnetism is likely to appear only on (100) facets of the particle.

We selected a gas-evaporation method in a high purity Ar gas atmosphere to prepare Pd fine particle samples. As the vapor phase process needs neither substrate nor surroundings, being different from other chemical processes, fine particles can be collected in a freestanding condition and with no adsorbate on the surface. The method is appropriate for investigating surface-related magnetic properties. We emphasize that a new preparation system with an ultrahigh vacuum chamber and gas purifying equipment in the gas feeding port was built to ensure a cleaner sample preparation condition than a conventional gas-evaporation method. With these improvements, the base pressure in the chamber is below 2×10^{-9} Torr and the concentration of impurities in the Ar gas such as O_2, N_2, H_2O, and H_2 is now lower than 1 ppb.

High purity Pd powder (Johnson Matthey Co., Ltd., 99.998%) was thermally evaporated from an electrically heated tungsten boat (purity 99.99%). The particles grown in an Ar atmosphere (1–12 Torr) were deposited on the inner wall of the vacuum chamber and were cooled with water or liquid nitrogen from outside of the chamber in order to prevent the particles melting or fusing by radiation heat. The deposited particles were scraped off the wall using Teflon brushes and were sealed in a quartz sample tube attached to the bottom of the chamber. All collecting processes were done in vacuum (below 1×10^{-8} Torr) after evacuating the Ar gas. The fine particle sample was never exposed to the air during these processes until magnetic measurements were finished. Thus, a possible magnetic contribution of gas adsorption on the particle surface is negligible.

The samples were characterized using x-ray diffraction measurements and high-resolution transmission electron microscope (TEM) observations. The crystal

structure of the Pd fine particle is the face centered cubic (fcc) structure with a lattice constant of 3.90 Å, which is larger than the bulk value by a factor of 0.25%. A TEM image of a typical Pd fine particle sample is shown in Fig. 1. The shape of the particle is a beautiful polyhedron with sharp edges and flat surface planes. The average radius of the particle sample was determined by fitting a log-normal distribution function to the size distribution [inset in Fig. 1(c)] [17]. The quantity of impurities was evaluated using inductively coupled plasma atomic emission spectroscopy. A small amount of Fe impurity (10 ppm) was detected but other probable impurities were at background level (lower than 1 ppm for Ni and 2 ppm for W). This is almost the same content as an evaporation source we use. Therefore, we can rule out possible effects of impurities and a change in the lattice constant on the magnetic properties of the Pd fine particles. Magnetic measurements were performed using a superconducting quantum interference device magnetometer (Quantum Design MPMS-5).

Figure 2(a) shows the magnetization curves of a Pd fine particle sample with an average radius of 115 Å, which clearly demonstrates a saturation behavior together with a linearly increasing magnetic component. The remanent magnetization of ~ 0.1 emu/g and the coercivity of ~ 40 Oe are also seen in the hysteresis loop even at 400 K [Fig. 2(b)]. These combined results reveal that the Pd particles are ferromagnetic rather than superparamagnetic. We express the magnetization as a simple sum of the saturation component M_S and the paramagnetic component χH, which linearly depends on magnetic field, and plot them as a function of temperature (Fig. 3). A remarkable feature is the thermal stability of M_S, which remains even at 400 K. The Curie temperature T_C of the Pd fine particle is estimated to be higher than 590 K for all samples by fitting a Brillouin function to the temperature dependent M_S (inset in Fig. 3) [18]. The angular momentum J and g factor were fixed to be $1/2$ and 2, respectively, assuming that only the spin magnetic moment contributes to the ferromagnetism. In contrast, the temperature dependence of χ has a peak at a temperature between 50 and 100 K, compatible with the Pauli paramagnetic susceptibility of Pd bulk.

In order to estimate a magnetic contribution due to gas adsorption, we exposed the particles to O_2 gas in a pressure of 3×10^{-5} Torr for 30 min. The detailed experimental procedures and the results are described in Ref. [19]. The field dependent magnetization of the O_2 adsorbed Pd fine particle shows a significant reduction in M_S in Fig. 2. The reduction in M_S is more significant when a large amount of O_2 gas is inserted in the chamber. This test shows that the ferromagnetism of the Pd fine particle is very sensitive to the surface condition and is unstable against adsorption of O_2 atoms — a convincing signature of the surface ferromagnetism of our clean samples. In this view, a simple intraparticle magnetic

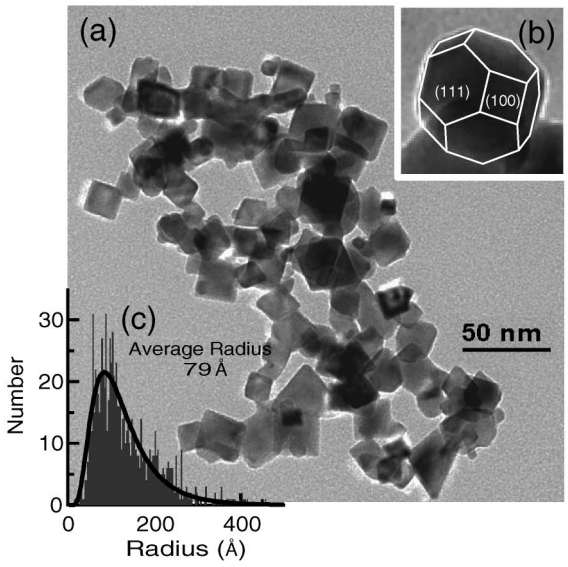

FIG. 1. (a) A TEM image of a typical Pd fine particle sample with an average radius of 79 Å. Inset (b) is an enlarged TEM image of a truncated octahedral particle, in which the contour is emphasized by white lines. Inset (c) shows the size distribution of the same sample.

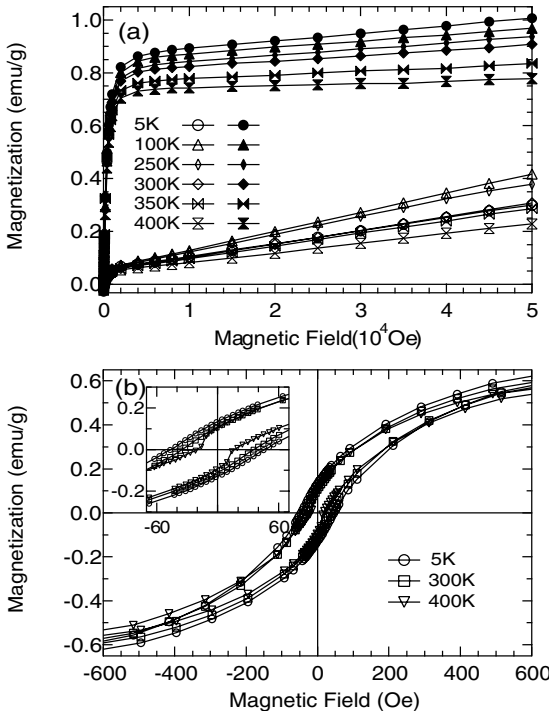

FIG. 2. (a) The field dependence of the magnetization of Pd fine particles with a clean surface (solid symbols, average radius of 115 Å) and after adsorption with O_2 atoms (open symbols, average radius of 108 Å) at various temperatures. (b) The hysteresis loops of Pd fine particle samples. The inset is the enlarged figure around zero field.

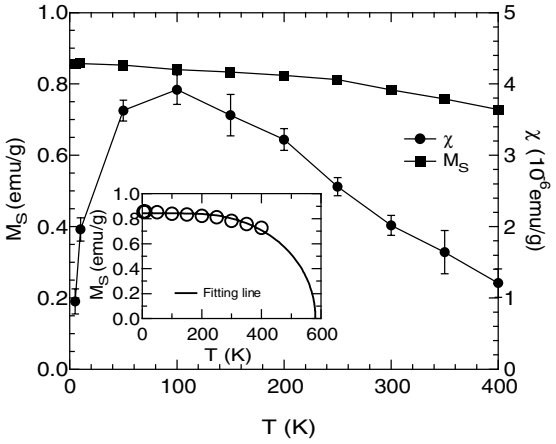

FIG. 3. The temperature dependence of M_S and χ of Pd fine particles with an average radius of 115 Å. The inset shows a fitting curve to M_S data using the Brillouin function.

structure, in which the ferromagnetic ordering occurs in the surface and the rest of the particle is paramagnetic, is most likely.

The size dependence of M_S is shown in the inset in Fig. 4. The M_S appears for samples with an average radius smaller than 144 Å and drastically decreases for samples with ~60 Å. The maximum magnetization of (1.40 ± 0.03) emu/g is obtained at 5 K for a sample with 80 Å. We now interpret the characteristic size dependence on the assumption that the ferromagnetism appears only on (100) facets of the surface of the particle. Since the Pd particle has a polyhedron structure, such as octahedral (O_h) or multiply twinned (MT) structures, the facets are (111) plane [20,21]. However, (100) facets can also appear if the crests of the O_h particle or the edges of the MT particle are truncated [see Fig. 1(b)]. That is, our samples have four different shaped particles, i.e., O_h structured particles, truncated O_h structured particles, MT structured particles, and truncated MT structured particles.

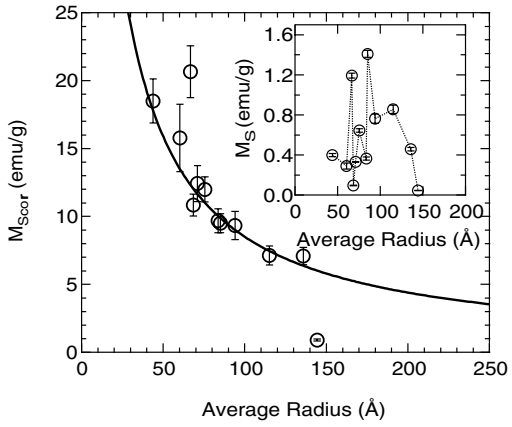

FIG. 4. The size dependence of $M_{S\mathrm{corr}}$. The solid line represents a fit using Eq. (1). The inset is the size dependence of the measured M_S.

Furthermore, the fine particle can be composed of several pyramids whose apexes are located at the center of the particle and the bases of the pyramid are the particle facets, e.g., a truncated O_h particle is composed of six quadrangular pyramids with a base of (100) facet and eight hexagonal pyramids with that of (111) facet. Here we attribute the ferromagnetism to a local magnetization at the (100) facet of the pyramids. The magnetization of the (100) pyramid ($M_{S\mathrm{corr}}$) is estimated by dividing the saturation magnetization M_S by the ratio of the volume of the (100) base pyramids to the total volume. The ratio was estimated using the following procedure. We first examined about 2000 particles in a TEM image for each sample to evaluate the truncation position. Then the area of the (100) facet (A_{100}) and the volume of the (100) base pyramid (V_{100}) were estimated for four different geometries of the particle (see Table I). Also, we took into account both the probability of O_h and MT particles to exist in the sample and the size distribution of the particles. From these evaluations, we obtained a dividing factor for calculating $M_{S\mathrm{corr}}$. For example, the dividing factor for a sample with an average radius of 68 Å is 0.034 ± 0.005.

The $M_{S\mathrm{corr}}$ clearly shows a monotonic increase with decreasing particle size as shown in Fig. 4. Assuming that the ferromagnetic ordering appears in the topmost several layers of the (100) facet surface and the magnetization is uniform in the layer, $M_{S\mathrm{corr}}$ can be expressed as

$$M_{S\mathrm{corr}} = \left(\frac{3\Delta r}{r} - \frac{3\Delta r^2}{r^2} + \frac{\Delta r^3}{r^3}\right) M_{\mathrm{surf}}, \qquad (1)$$

where Δr is the thickness of the ferromagnetic surface layer and M_{surf} is the magnetization of the ferromagnetic surface layer. The thickness of the ferromagnetic surface layer and the surface magnetization can be estimated to be (7.8 ± 3.0) Å and (39.5 ± 16.6) emu/g by fitting Eq. (1) to $M_{S\mathrm{corr}}$ in Fig. 4, respectively. The estimated surface thickness is comparable to two to five layers of (100) planes and the magnetic moment per Pd atom is $(0.75 \pm 0.31)\mu_B$/atom. The estimate of the surface thickness is consistent with previously reported theoretical predictions: magnetic moments appear only in a Pd bilayer, although the magnetic moment is slightly larger

TABLE I. Typical parameters used for the calculation of $M_{S\mathrm{corr}}$ for a Pd fine particle sample (average radius of 68 Å), where N is the number of particles measured from a TEM image, $A_{100}/A_{\mathrm{total}}$ is the ratio of A_{100} to the total surface area for each particle, and $V_{100}/V_{\mathrm{total}}$ is the ratio of V_{100} to the total volume.

	O_h	Truncated O_h	MT	Truncated MT
N	976	256	226	423
$A_{100}/A_{\mathrm{total}}$	0	0.044 ± 0.010	0	0.177 ± 0.009
$V_{100}/V_{\mathrm{total}}$	0	0.077 ± 0.017	0	0.612 ± 0.031

than the values obtained by theoretical calculations; $0.12\mu_B$/atom for a Pd cluster [11] and $0.17\mu_B$/atom for a Pd bilayer [12]. In our previous study, the magnetic moment per Pd atom in a Pd fine particle was estimated to be $(0.23 \pm 0.19)\mu_B$/atom, which is smaller than the value we obtained here [17]. The discrepancy can be understood if gas adsorption was significant during the sample preparation in the previous study, resulting in a reduction in the Pd magnetic moment. In addition, the Curie temperature of 740 K calculated using the observed magnetic moment of $0.75\mu_B$/atom and an exchange correlation integral I [22] broadly agrees with the value estimated from fitting of the temperature dependent M_S.

Theoretical studies have reported that the ferromagnetism of a $4d$ ultrathin film occurs mostly on (100) oriented planes [4–10,12] while a few reports suggest a possible ferromagnetism on (111) planes [23–26]. The feature of the $4d$ ferromagnetism is compatible with our experimental results that show the advantage of the (100) plane for $4d$ ferromagnetism rather than the (111) plane. Within the Stoner's theory, ferromagnetism is expected to occur when the Stoner criterion $N_{\mathrm{loc}}(E_F)I > 1$ is satisfied, where I is the exchange integral and $N_{\mathrm{loc}}(E_F)$ is the local density of states at the Fermi energy. In an fcc crystal structure, the d band width of the (100) plane is substantially narrower and hence N_{loc} is larger than that of the (111) plane because of the smaller coordination number of the atoms in the (100) plane. In this context, the surface effect promises an additional band narrowing in the (100) oriented plane, resulting in the ferromagnetism in our samples. Therefore, our assumption that only (100) facets of a Pd fine particle contribute to the ferromagnetism is consistent with the conventional theoretical understandings. From these connected experimental and theoretical considerations, we believe that the ferromagnetism of our Pd particle is closely associated with the two-dimensional character and the ferromagnetism has its origin in the intrinsic change of the electronic structure at the surface of the particle.

In conclusion, we have directly observed ferromagnetism of freestanding Pd particles with a clean surface prepared by using a newly built gas-evaporation system. The ferromagnetic ordering occurs only in a few topmost surface layers of the (100) facets and the rest of the particle remains paramagnetic, similar to Pd bulk. The magnetic moment per Pd atom is estimated to be $(0.75 \pm 0.31)\mu_B$/atom and the Curie temperature higher than 590 K is consistently obtained. The origin of the ferromagnetism of the Pd fine particles can be understood within existing theoretical models and the ferromagnetism should be associated with the two-dimensional character of the particle surface.

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