Magnetic properties of Pd–2.9 at. % Fe fine particles

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Magnetization and small-angle-polarized neutron-scattering measurements have been performed on Pd–2.9 at. % Fe fine particles prepared by the conventional gas evaporation method. It was found that decreasing the particle size reduces the saturation magnetization at 5 K. This reduction can be explained in terms of a nonmagnetic surface shell whose thickness is estimated to be ~12 Å in the sample, with a 162-Å median radius based on the small-angle-polarized neutron-scattering experiments. The saturation magnetization of the core is estimated to be enhanced by a factor of 1.3 compared with that of the bulk PdFe. This probably indicates that the Pd host in the PdFe particles is more magnetically enhanced compared with that in the bulk PdFe, which is consistent with our previous report on pure Pd fine particles. [S0163-1829(97)06601-0]

I. INTRODUCTION

During the last few years investigations on the magnetic properties of 4*d*-confined systems such as thin layers and clusters have attracted much attention.[1–16] In a confined system the distinct electronic structure of surface atoms can determine the main magnetic characters of the system, and lead to diverse magnetic features.

Pd shows the unique size dependence of the magnetic properties in 4*d* transition metals. Very recently, our direct magnetization measurements showed evidence of ferromagnetism in pure Pd fine particles.[11,17,18] The appearance of ferromagnetism probably originates from electrons at the surface layer, where the high peak in the local density of state (LDOS) is located around the Fermi energy. Such an interpretation is consistent with the theoretical prediction concerning the Pd thin layer[3] and cluster.[4] Theoretical calculation has shown that the Pd bilayers on an Ag(001) substrate show ferromagnetism with magnetic moments of $0.17\mu_B$ per atom, while the monolayers are nonmagnetic. In the monolayers the LDOS peak is located below the Fermi energy, while in the bilayers the *d*-*d* hybridization between the surface and second Pd layers brings back the peak of the LDOS closer to the Fermi energy, which is favorable to ferromagnetism. The theoretical calculation of the Pd_{13} cluster has shown that the magnetic moment $(0.43\mu_B)$ of the central site is larger than that of the outer site $(0.12\mu_B)$.[4] This also originates partly from the larger LDOS around the Fermi energy at the central site due to the *d*-*d* hybridization. This interpretation can explain the difference between the ferromagnetism in Pd fine particles and the nonmagnetic cluster.[16]

It is well known that the magnetic properties of Pd are very sensitive to the mixing of 3*d* transition-metal impurities, e.g., the Fe atom induces a strong polarization of the Pd matrix in a PdFe alloy, which results in the giant magnetic moment of $\sim 10\mu_B$ per Fe atom.[19] So far, however, there has been insufficient information about the magnetic behavior in the fine particle of such Pd-based dilute alloys. Thus we wish to pay attention to the fine particles of PdFe, because the Fe atom brings about the most significant change in the magnetic nature of Pd in the bulk state. Bulk $Pd_{1-x}Fe_x$, with a concentration between $x=2.2\times10^{-3}$ at. % Fe and $x=0.1$ at. % Fe exhibits spin-glass properties owing to the Ruderman-Kittel-Kasuya-Yoshida interaction between the local giant magnetic moments via conduction electrons, and the ferromagnetism appears above this percolation threshold ($x=0.1$ at. % Fe).[20] Thus we may expect the more magnetically enhanced surface region of PdFe particles to accompany the strongly magnetic Pd host in the confined geometry. Alternatively, the doping of Fe atoms may break down ferromagnetic ordering at the surface, as opposed to the situation of the pure Pd particle, because of the decrease in the mean free path of conduction 4*d* electrons; this plays an important role for ferromagnetic ordering in this material. Therefore, we intend to clarify the Fe doping effect in the Pd particle by paying attention to the magnetic behavior of its surface.

In this study, we prepare the Pd–2.9 at. % Fe fine particles by the gas evaporation technique. The Fe concentration is selected according to the following criteria. The electrical resistivity measurements of the PdFe alloy showed that the homogeneous ferromagnetic state occurs at Fe concentrations above 2 at. %.[21] Provided that we select the less concentrated Fe sample, there may be some contribution inherent in the inhomogeneous ferromagnet. Furthermore, a recent *ab initio* band-structure calculation of the $Pd_{31}Fe$ supercell revealed that it is scarcely different from that of pure Pd.[22] This would demonstrate that a degree of magnetic localization on the Pd site is hardly changed by doping Fe atoms at the present Fe concentration. Thus we select the 2.9 at. % Fe sample to discuss the magnetic properties of PdFe in com-

parison with pure Pd without considering such ambiguous contributions.

We measured the magnetization and small-angle-polarized neutron scattering of PdFe fine particles. It was found that decreasing a particle size results in the reduction of saturation magnetization at 5 K. This indicates a nonmagnetic surface shell in PdFe fine particles. We estimated the thickness of the surface shell by the small-angle-polarized neutron scattering experiment. On the basis of both results, we discuss the surface magnetism in the PdFe particle.

II. EXPERIMENT

PdFe fine particles were prepared by the conventional gas evaporation method under an Ar gas (purity 99.9995%) atmosphere. The arc-melted $Pd_{95}Fe_5$ ingot was annealed for 50 h at 900 °C and then quenched in ice water. This homogenized $Pd_{95}Fe_5$ ingot was used for the gas evaporation. PdFe fine particles evaporated on the inner wall of the chamber were collected in vacuum by Teflon brushes into the quartz tube attached to the bottom of the chamber. To seal the quartz tube in vacuum prevents the adsorbtion of active gases on the surface of particles. The size of the particles can be controlled by changing the pressure of the Ar gas in the chamber from 2 to 12 Torr. The compositions of evaporated PdFe particles, determined by means of electron probe microanalysis, were 2.9 at. % Fe in all the samples. The bulk $Pd_{97.1}Fe_{2.9}$ sample was also prepared by the same method as used for preparing the $Pd_{95}Fe_5$ ingot.

Transmission electron microscope (TEM) was used to determine the size of the particles. The dc magnetization measurements were performed from 5 to 300 K and under fields up to 55 kOe using a Quantum Design MPMS2 superconducting quantum interference device magnetometer. Small-angle-polarized neutron-scattering (SAPNS) experiments were performed using the time of flight spectrometer with optical polarizer (TOP) spectrometer at the National Laboratory for High Energy Physics. The neutron-scattering intensities $I_{\perp}^{+}(Q)$ and $I_{\perp}^{-}(Q)$ were counted separately for incident neutrons whose spins are parallel and antiparallel to the magnetic field at 8.0 K. A magnetic field of 9 kOe was applied perpendicular to the momentum transfer vector Q.

III. RESULTS

A. Characterization of the PdFe fine particle

A typical size distribution of PdFe particle samples is shown in Fig. 1. As shown by the solid line in Fig. 1, the size distribution follows the log-normal distribution function well:

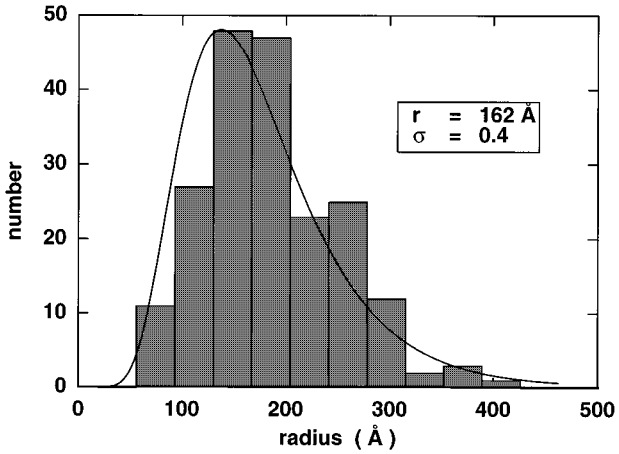

FIG. 1. Typical size distribution of PdFe fine particles prepared by the gas evaporation method.

$$f(r)=\frac{1}{\sqrt{2\pi}\sigma r}\exp\left(-\frac{(\ln r-\ln r_0)^2}{2\sigma^2}\right), \tag{1}$$

where r_0 (median radius) and σ are parameters of the distribution function. The average radius of the PdFe particle is defined using the expression[23]

$$\overline{r}=\left\{\sum_i^n r_i^3/n\right\}^{1/3}, \tag{2}$$

where r_i is the radius of the ith particle, and n is the number of particles contained in each sample. We analyze the magnetic data using the average radius defined in Eq. (2). The average radii of the samples are listed in Table I.

B. Magnetization measurements

First, we will briefly review the magnetic behavior of pure Pd fine particles. The susceptibility of Pd fine particles enhances a great deal with decreasing particle size, and ferromagnetic ordering appears in samples with a median radius below 64 Å. Figure 2 shows definitive evidence of the ferromagnetic ordering observed in Pd particles with 59 Å in median radius. The ferromagnetic ordering is retained stably even at room temperature. Further, we deduced the magnetic moment of $0.23\mu_B \pm 0.19\mu_B$ per atom in the most magnetically enhanced Pd sample, on the assumption that only the surface monolayer of the particle is magnetic. The present magnitude of the magnetic moment is comparable to the

TABLE I. Characteristic parameters of the PdFe fine particles for magnetization measurements.

Sample No.	Average radius (Å)	Curie temperature (K)	Saturation magnetization (emu/g)
1	155	109	8.8
2	191	118	9.7
3	212	118	11.4
4	305	119	12.5
5	bulk	107	12.7

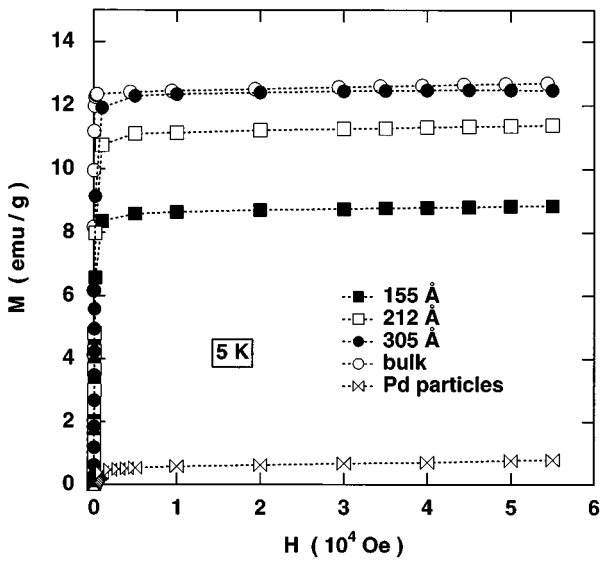

FIG. 2. Field-dependent magnetization of various samples of PdFe fine particles at 5 K, and Pd fine particles 59 Å in median radius at 1.8 K.

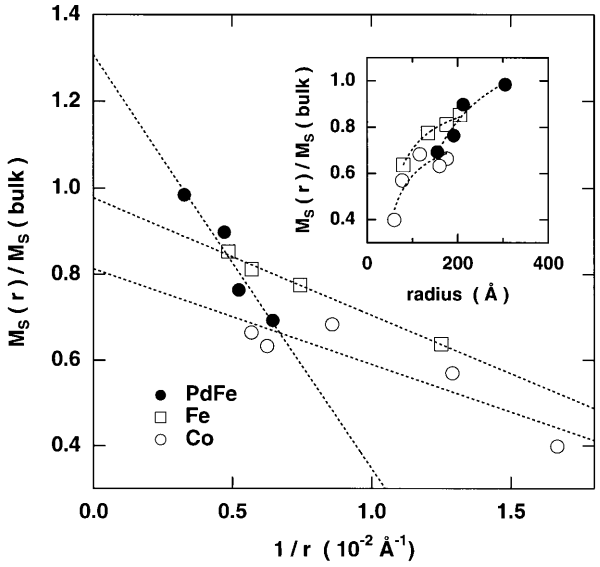

FIG. 4. Size dependence of saturation magnetization at 5 K: data for Fe and Co fine particles were measured by Du *et al.* (Ref. 28) and by Gangopandhyay *et al.* (Ref. 29), respectively.

theoretically predicted value: $0.12\mu_B$ per atom for the Pd cluster,[4] or $0.17\mu_B$ per atom for the Pd bilayer.[3]

Next, we show magnetization data for PdFe fine particle samples with different average sizes listed in Table I. Figure 2 shows the field-dependent magnetization at 5 K. The samples were cooled in zero magnetic field from room temperature to a measuring temperature, and then the magnetization curve was recorded. The saturation magnetization is reduced by decreasing the average particle size. Figure 3 shows the M^2 versus H/M plots (Arrott plots) of sample 3, where a change in the curvature is observed at a temperature between 110 and 120 K. A similar change in the curvature was observed in amorphous ferromagnetic materials,[24] and the Curie temperature was identified with a temperature at which the extrapolation of M^2 at large H/M down to

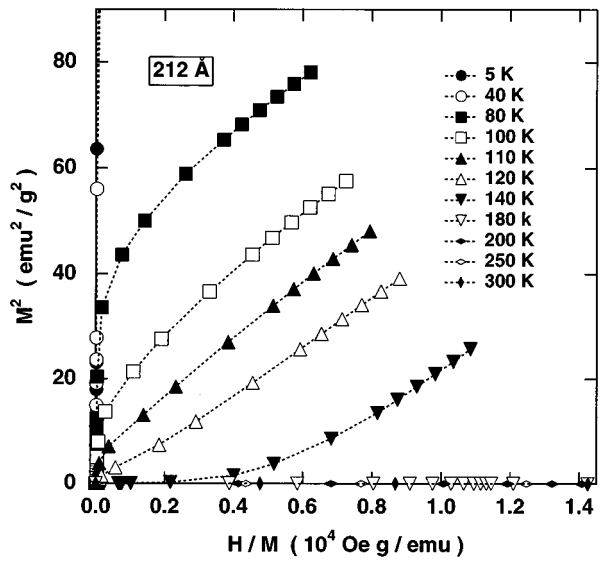

FIG. 3. M^2 vs H/M plot of sample 3.

$H/M=0$ intersects the origin. Therefore, we wish to determine the Curie temperature in the same manner. The determined Curie temperatures are listed in Table I, which are almost independent of the particles size within the experimental error. The Curie temperature of thin films is typically reduced at a thickness less than 100 Å according to the finite-size effect.[25,26] The present PdFe particles (average size $\geqslant 300$ Å) may be too large to detect the finite-size effect on the Curie temperature. Recently Tang, Sorensen, and Klabunde[27] analyzed the size-dependent saturation magnetization of ferrite nanoparticles by plotting them as a function of the inverse radius of the particle, and were led to a core-shell magnetic structure in which the shell magnetization is lower than the bulk. In this model the saturation magnetization should vary linearly with inverse radius r^{-1} as follows:

$$M_S(r)=M_S(\infty)-\frac{3\Delta r}{r}\Delta M_S, \tag{3}$$

where $M_S(\infty)$ is the core magnetization, Δr is the thickness of the surface shell, and ΔM_S is the difference between magnetizations of the core and shell. Thus we plot the saturation magnetization of PdFe at 5 K versus the inverse average radius in Fig. 4. The data of Fe[28] and Co[29] are also shown in Fig. 4 for comparison. A shell thickness of 24 Å is obtained based on Eq. (3), assuming a nonmagnetic shell of the particle, which will be compared with the intraparticle magnetic structure estimated from the neutron-scattering experiment. The core magnetism $M_S(\infty)$ estimated from the linear extrapolation of $M_S(r)$ to $r^{-1}=0$ is larger by a factor of 1.3 ± 0.1 than the bulk value of 12.7 emu/g. This suggests a magnetic enhancement of the core in the PdFe fine particles. Finally, we present the temperature, dependence of M/H obtained in various magnetic fields in Fig. 5. The M/H of the particle samples are field dependent even above the Curie temperature, in contrast to the field-independent susceptibility of the bulk. Such a field dependence is more significant in

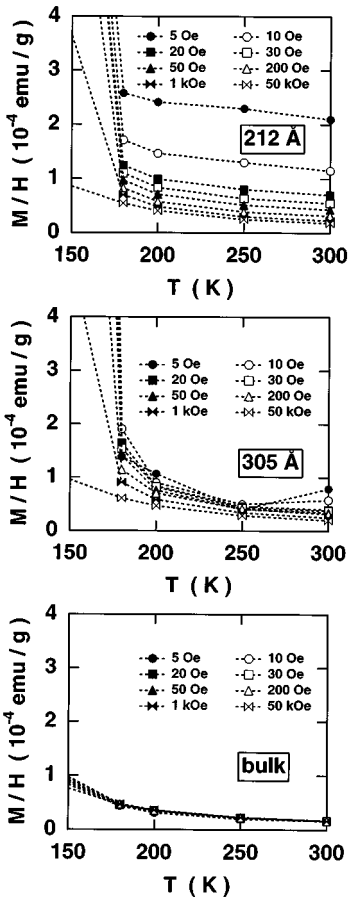

FIG. 5. Temperature-dependent M/H in various magnetic fields of the PdFe samples.

the smaller particle sample. This indicates that there exists a ferromagnetic contribution due to particles smaller than the average size even above the Curie temperature determined by the Arrott plot. Thus we mention that the Curie temperature of the smaller particle may become higher in contrast to the other magnetic particles except for the ferrite nanoparticle.[27] This result is very stimulating, but now remains an open question.

C. Small-angle-polarized neutron scattering

Neutron-scattering intensities $I_{\perp}^{+}(Q)$ and $I_{\perp}^{-}(Q)$ in a large saturating magnetic field are expressed as follows:

$$I_{\perp}^{\pm}(Q)=\langle(F_n(Q)\pm F_m(Q))^2\rangle S_{\perp}(Q)+I_{\text{incoh}}, \tag{4}$$

where $F_n(Q)$ and $F_m(Q)$ are the nuclear and magnetic scattering form factors of particles, respectively, $S_{\perp}(Q)$ is the interparticle correlation, I_{incoh} is the incoherent scattering intensity, and $\langle\rangle$ denotes the average over the particle's size distribution. Since the incoherent scattering intensity is not negligible in the present SAPNS experiments, we thus analyzed the Q-dependent subtracted intensity.

$$I_{\perp}^{+}(Q)-I_{\perp}^{-}(Q)=4\langle F_N(Q)F_M(Q)\rangle S_{\perp}(Q). \tag{5}$$

In such a manner the incoherent scattering intensity is automatically canceled using the polarized neutrons. Figure 6 shows the subtracted intensity recorded in the Q range of 0.02–0.1 Å^{-1} under a magnetic field of 9 kOe at 8.0 K. This can be analyzed by assuming an intraparticle magnetic structure and interparticle correlation.

We suppose that the particle consists of a magnetic core and a nonmagnetic surface shell, consistent with the magnetic data (Fig. 7). Assuming the shape of particle is spherical, the magnetic and nuclear form factors are expressed as follows:

$$F_n(Q)=\frac{4}{3}\pi r^3 b\frac{3j_1(Qr)}{Qr}, \tag{6}$$

$$F_m(Q)=\frac{4}{3}\pi r_0^3 p\frac{3j_1(Qr_0)}{Qr_0}, \tag{7}$$

$$j_1(x)=(\sin x-x\cos x)/x^2, \tag{8}$$

where b and p are the nuclear and magnetic scattering length density, r and r_0 are the radii of the particle and magnetic core, and $j_1(x)$ is the first-order spherical Bessel function.

The present PdFe sample has a size distribution with $r=162$ Å and $\sigma=0.4$, and a magnetic scattering density of 0.37×10^{10} cm^{-2} as determined from TEM micrograph and magnetic data, respectively. Only the nonmagnetic surface shell thickness is unknown for analyzing the neutron data. Based on the subtracted intensity calculated by parametrizing nonmagnetic shell thickness (Fig. 6), we obtain a best-fitted shell thickness of 12 Å. In addition, we should mention that the magnetic enhancement of the surface, as predicted for the Pd particle, cannot be determined based on the neutron data. In this analysis we intentionally neglected the interparticle correlation $S_{\perp}(Q)$, because it is almost unity in the experimental Q range of $Q>0.04$ Å^{-1} in the case of the present particle size $r=162$ Å.

IV. DISCUSSION

First we discuss the origin of the nonmagnetic surface shell validated by both the magnetization and neutron-scattering data. We pay close attention to the possible localization of conduction electrons at the surface, owing to the surface effects. Such electron localization leads to the depletion of conduction electrons, via which local magnetic Fe moments ferromagnetically interact in PdFe. This brings about the breakdown of the ferromagnetic coupling between Fe atoms, so that the Fe moment at the surface should behave as paramagnetic. Thus the nonmagnetic surface region of the PdFe particle can be formed by a mechanism specific to the magnetic origin, so that conduction electrons play an important role in the ferromagnetic ordering. This situation is very different from the case of the ferrite particles, in which

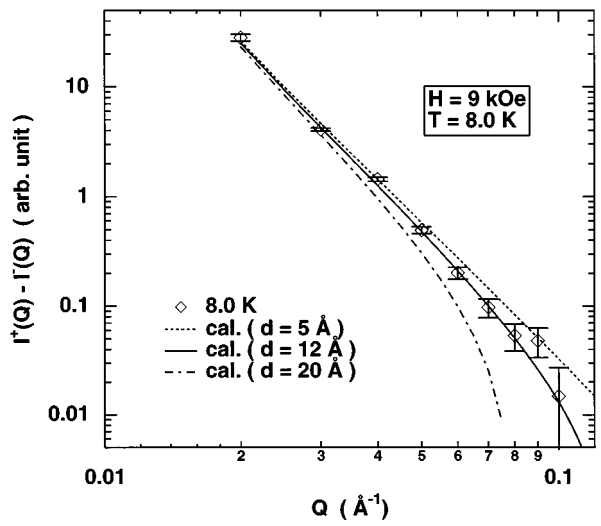

FIG. 6. Q-dependent $I_{\perp}^{+}(Q)-I_{\perp}^{-}(Q)$ counted at 8.0 K; the lines are calculated curves based on the core-shell model.

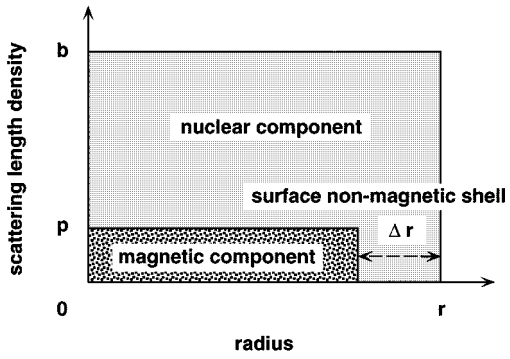

FIG. 7. Schematic drawing of the intraparticle magnetic structure of the PdFe fine particle.

the superexchange interaction is the main origin of magnetic ordering.[27] Alternatively, the magnetic moments of Fe atoms may dissolve into the 4*d* electron sea of host Pd. In other words, well-localized Fe moments may become partly itinerant owing to the change in the Fermi level of the 4*d* electron sea of host Pd at the surface. This may be supported by the itinerant nature of the Fe-rich PdFe system, e.g., $PdFe_3$.[30,31]

The oxidation can be also responsible for the nonmagnetic shell of particles, e.g., Ni particles,[32,33] Co particles,[34] and ferrite particles[27] exposed to the samples in air. However, we exclude oxidation as a candidate for the origin for the nonmagnetic shell, because we kept the particles in evacuated quartz tubes after evaporation in this study with the purpose of not exposing them to air. Further, provided that oxidation occurs during the evaporation process, the uniform magnetic structure should be recognized in the PdFe particle even if the magnetism is weakened. The neutron-scattering data, however, deny such uniformly oxidized particles. Thus we believe that the nonmagnetic surface is not a result of the oxidation process.

Next we compare the magnetic properties of the PdFe particle with that of the Pd particle. In the Pd particle, the onset of ferromagnetism is mainly interpreted on the basis of the band calculations for thin Pd layer,[3] although in a near-ferromagnet such as Pd the electron localization may be also responsible for the ferromagnetism. It is interesting to compare the nonmagnetic shell with a thickness of 12 Å in the PdFe particles with the ferromagnetic surface of Pd, since the 1-ML surface ferromagnetism is convincing in the Pd particle. First, the difference of surface magnetic states is probably attributed to a change in the itineracy of 4*d* electrons in host Pd at the surface of PdFe, which is caused by doping Fe atoms. Next, we briefly mention the different thicknesses of the ''magnetic surface region'' between Pd and PdFe, i.e., the one-layer ferromagnetism in Pd and the 12-Å-thick nonmagnetic shell in PdFe. Such differences suggest that a sufficient condition for inducing ferromagnetism in a Pd particle is more severe than that for the destruction of ferromagnetism in PdFe particles. In other words, the mechanism of the magnetic ordering of a Pd particle is effective only in the vicinity of the surface, while that for the latter works in the deeper region of the PdFe particle. Since the present comparison is beyond any existing theoretical approach, we eagerly expect a theoretical investigation of the present particle system.

Finally, we comment on the inconsistency between shell thicknesses estimated from the neutron (12 Å) and magnetic data (24 Å). This may be due to a difference in the time scales of measurement between neutron-scattering and magnetization measurements. We speculate the following situation: the magnetic moments fluctuate in the vicinity of the interface between the surface shell and core, and the time scale of the fluctuation is longer than that of the neutron measurement ($\sim 10^{-11}$ s) but shorter than that of the magnetization measurements (~ 10 s). In such a situation, the neutron-scattering experiment should detect a larger ferromagnetic region than that found from magnetization measurements.

V. CONCLUSION

The saturation magnetization of PdFe fine particles reduces with decreasing size of a particle. This suggests a nonmagnetic surface shell in the PdFe particle. Such an intraparticle structure is supported by the results of the polarized neutron-scattering experiment, and the surface shell thickness is estimated to be 12 Å. Furthermore, the saturation magnetization of the core is estimated to be larger by a factor of 1.3 than that of the bulk PdFe. This indicates a more magnetically enhanced Pd host in the PdFe particles compared with that in the bulk PdFe, which is consistent with the magnetic enhancement observed in the pure Pd fine particles.

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