

LETTER TO THE EDITOR

Magnetization studies in quasi two-dimensional palladium nanoparticles encapsulated in a graphite hostD Mendoza[†], F Morales[†], R Escudero^{†§} and J Walter[‡][†] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, México Distrito Federal, 04510, Mexico[‡] Osaka National Research Institute, AIST, MITI 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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Abstract. In this work, magnetization studies on quasi bi-dimensional nanoparticles of Pd encapsulated in a graphite host as a function of magnetic field and temperature are presented. We found that an important magnetic signal can be attributed to the Pd nanoparticles. The obtained magnetic behaviour is interpreted in view of theoretical studies which predict ferromagnetism in slabs of Pd with some monolayers of thickness.

Bulk palladium is not magnetic but theoretical studies indicate the existence of magnetism in multilayers [1] and monolayers [2], as well as in small clusters [3–5]. In addition, the appearance of quantum size effects in very small clusters of Pd has been established experimentally and is reflected in their thermodynamical properties depending on whether they have an odd or even number of electrons [6]. Due to the fact that bulk Pd has a narrow d band, it is considered as an enhanced paramagnet having a Stoner factor of around 10 [7], but never fulfilling the Stoner criterion for the onset of ferromagnetism. Nevertheless, the situation may change in systems with reduced dimensionality, such as in two dimensions, where the coordination number is reduced compared to the three-dimensional case. Theoretical calculations predict effective magnetic moments ranging from $0.42 \mu_B$ (μ_B is the Bohr magneton) to $0.45 \mu_B$ for a monolayer [2], and up to $0.5 \mu_B$ for the middle layer of a trilayer [1]. More specifically Bouarab *et al* have predicted ferromagnetism, for Pd slabs with 2–5 layers, and zero magnetic moment, for a monolayer and for slabs with more than 5 layers [1].

In this work we present our results on magnetization studies in quasi two-dimensional nanoparticles of palladium intercalated into a graphite host (Pd-GIC in short).

Quasi two-dimensional palladium nanoparticles have been prepared by hydrogen reduction of a PdCl₂ graphite intercalation compound flakes precursor at 400 °C [8]. A typical transmission electron microscopy (TEM) picture of such particles is shown in figure 1. The TEM study showed hexagonal, cubic and intermediate bodies of palladium encapsulated in graphite. The lateral dimension of these particles ranged from 2 to 200 nm, with an average size of (53 ± 34) nm. The thickness of the particles was not estimated exactly. However, it was observed that hexagonal Pd platelets change via intermediate shapes to common cubic bodies [8]. The occurrence of hexagonal platelets for a cubic metal is only possible if ultra thin particles of a thickness of a few layers grow slowly [9]. This gives evidence that the

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Figure 1. Bright field transmission electron microscope (TEM) photograph of a typical sample of palladium nanoparticle encapsulated in graphite host. The picture was taken with a Hitachi H-9000 TEM operated at 300 kV.

lateral dimension of the particles is much larger than their thickness, and their shape can be interpreted as quasi two-dimensional.

Although the natural graphite used as the host may have the following magnetic impurities (data from Graphitwerke Kropfmühl): Fe (30 ppm), Co (5 ppm) and Ni (5 ppm); an analysis by energy dispersive spectroscopy (EDS) on Pd-GIC samples showed no magnetic impurities in the range of the detection limit of this technique (100 ppm).

Magnetization measurements on a specimen of 3 mg of randomly oriented flakes were performed using a SQUID magnetometer in the DC mode. In figure 2, we show curves of magnetization versus field at different temperatures for the Pd-GIC sample, and at two temperatures for graphite are shown in the inset. Note that, although an hysteretic behaviour for the graphite is present, the magnetization signal per unit mass is very small compared to that of Pd-GIC. An estimation of the Pd content indicates that $\sim 37\%$ of the total weight of the Pd-GIC sample corresponds to Pd. Notice the characteristic form of the M versus H curves tending to saturation which progressively increase as the temperature is lowered. This behaviour is not observed in graphite. Detail of the M versus H curve around zero field is shown in figure 3 for $T = 2$ K.

Before any analysis of the experimental curves is made, it is important to mention that a simple addition of the experimental magnetization signal of graphite plus a model curve for Pd does not reproduce the total signal of the Pd-GIC system. We tried a linear M versus H dependence (such as should be in pure paramagnetic Pd) and an 'S' shape curve modelled with a Langevin function. None of the two models reproduce the experimental curves for the Pd-GIC system. In the case of the 'S' shape model for Pd, an approximate form for the experimental results can be achieved with a very small hysteresis (this hysteretic behaviour arises from graphite, see inset of figure 2), but the complete experimental form of the M versus H hysteretic behaviour is not reproduced. In addition, the trend in the M versus H curves as a function of temperature is only observed in the Pd-GIC sample and not observed in graphite alone. Then, we consider that the important magnetization signal in the Pd-GIC system comes from the Pd nanoparticles.

On the other hand, it is known that magnetic properties of small ferromagnetic particles

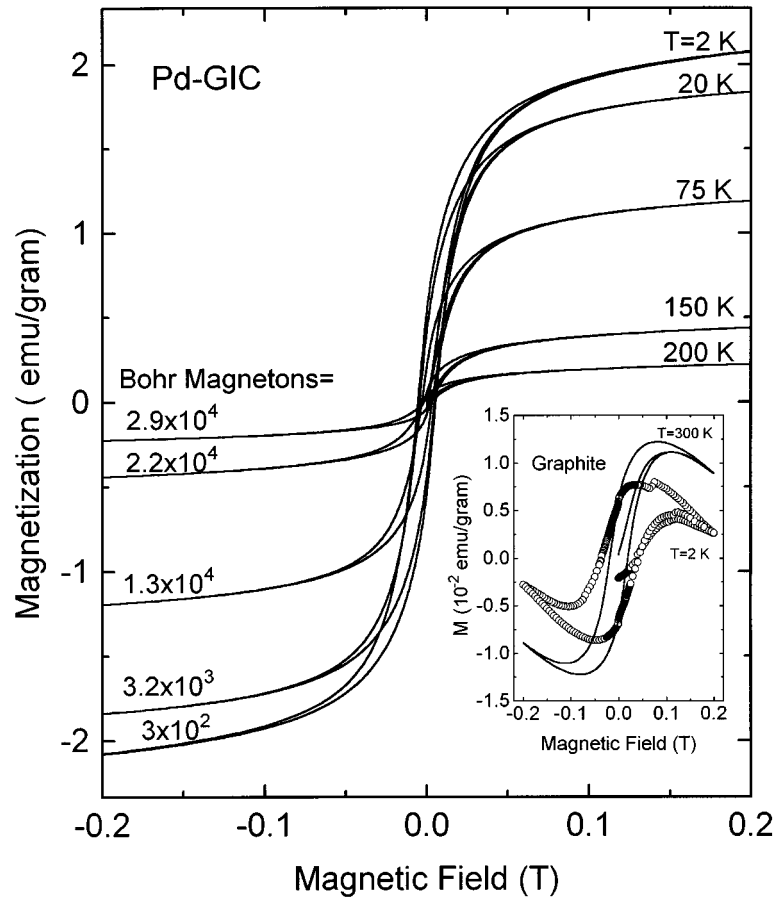


Figure 2. Magnetization (M) against magnetic field (H) measurements in the Pd-GIC system taken at different temperatures. The effective magnetic moment in units of the Bohr magneton (μ_B) obtained by fitting a Langevin function is shown at the corresponding temperature. M is given per unit mass, where 3 mg of the Pd-GIC sample was taken, although only $\sim 37\%$ of the total weight corresponds to Pd. In the inset, M versus H graphs at two temperatures for graphite (used as the host) are shown.

may present different characteristics when the size of the system is smaller than the exchange correlation length. One of these properties is the so-called phenomenon of superparamagnetism for the clusters of magnetic particles [10]. The coercivity field H_C of such an assembly of magnetic particles should obey the relationship $H_C = H_{Ci}[1 - (T/T_B)^{1/2}]$, where T_B is the blocking temperature, above which the ensemble of single-domain particles behaves as paramagnetic molecules with giant magnetic moment [10, 11]. In the inset of figure 3 the temperature dependence of the coercivity field is presented. A least squares fit of H_C versus $T^{1/2}$ data gives a blocking temperature around 452 K, which indicates a Curie temperature for the system higher than this temperature.

In order to have a further insight into the magnetic nature of the Pd particles, we performed a fit of the M versus H data to a Langevin function $M(x) = M_0[\coth(x) - 1/x]$ at different temperatures. Here $x \equiv \mu H/k_B T$, and μ is the effective magnetic moment of the particles [11]. The fit at $T = 2$ K in the cycle from $H = 0$ T to higher positive fields is shown as a continuous

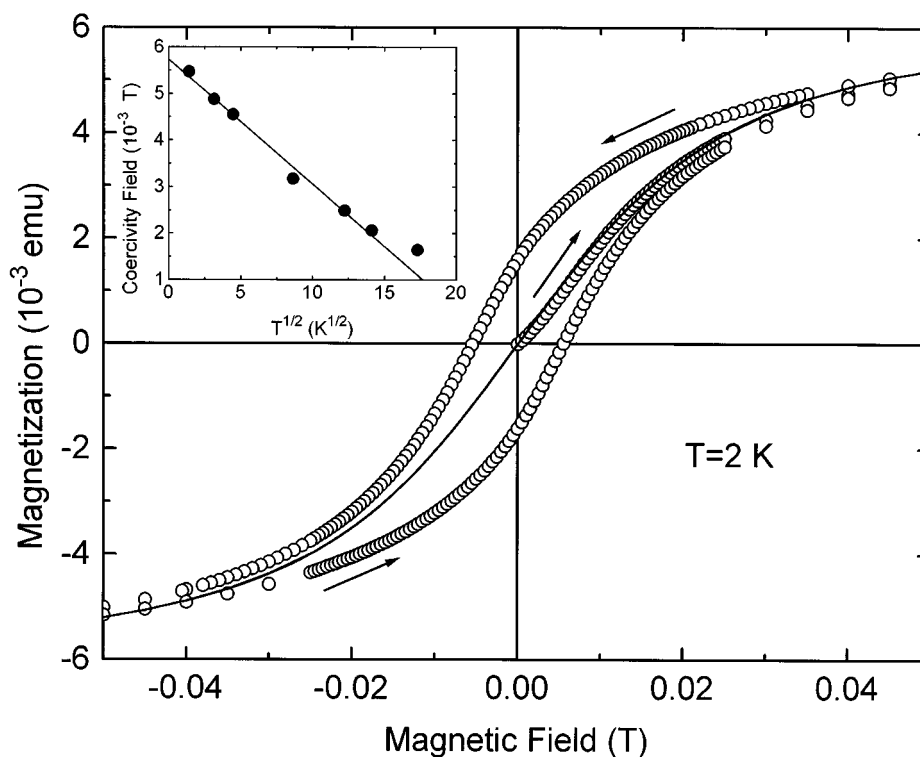


Figure 3. Enlarged M versus H curve taken at $T = 2$ K for the Pd-GIC system; the arrows indicate the direction of the measurement cycle. The continuous line corresponds to the fit using a Langevin function. In the inset a plot of the coercivity field (H_C) as a function of temperature is shown. H_C was taken as an average of the positive and negative values of H where M is equal to zero. The continuous straight line in the inset is a fit of the experimental values of H_C versus $T^{1/2}$ (see text) for temperatures from 2 to 200 K.

line in figure 3. The effective magnetic moment obtained from the fit, in terms of Bohr magnetons, is shown in figure 2 for the corresponding temperature. The apparent temperature dependence of the effective magnetic moment can be explained in terms of the temperature dependence of the relaxation time of the magnetic clusters. At high temperatures, larger clusters are able to respond in the experimental time used in the measurements [12]. In our case we know that the Pd nanoparticles have a broad distribution of sizes [8].

Since the thickness of the Pd nanoparticles is, to date, unknown, it is difficult to know the exact number of Pd atoms per particle. However, if we model the Pd particles as cylindrical platelets having an average radius of ~ 26.5 nm (see above) and a thickness of 2–5 monolayers of Pd atoms, it is possible to estimate the number of Pd atoms in the platelets taking $r_0 \approx 1.48$ Å as the radius of each Pd atom [7]. In this way we have a rough estimation of the effective magnetic moment per Pd atom at $T = 200$ K: 0.3, 0.2, 0.15, and 0.12 Bohr magnetons assuming 2, 3, 4, and 5 monolayers of thickness, respectively. The maximum value estimated in this way is in fair agreement with those calculated theoretically for Pd slabs with 2–5 monolayers for which ferromagnetism is predicted [1]. We should recall that the preceding estimations were made at $T = 200$ K, but higher effective magnetic moments per Pd atom are expected at higher temperatures. The maximum available experimental temperature attained in the present work

is $T = 300$ K, but some care should be taken since the effect of the magnetization signal arising from graphite may be important at this temperature.

In the numerical estimations we supposed that the magnetic signal arising from the ferromagnetic Pd nanoparticles (slabs from 2 to 5 monolayers, after reference [1]) is predominant, and the magnetic signal of the other particles is negligible. In the present situation we are not able to separate both magnetic signals, but we believe that the magnetic behaviour of the non-ferromagnetic Pd nanoparticles should be paramagnetic, as in the bulk palladium.

Finally, in figure 4 the temperature dependence of the magnetization at different fields is shown. The curve at the lower field presents a broad maximum above 50 K which is typically observed in bulk palladium [7, 13] and a small peak centred around 14 K, which disappears at higher fields. We propose that this small peak, which is not observed in bulk Pd, may be related to a weak antiferromagnetic coupling between adjacent Pd platelets stacked along the c -axis of the graphite host. Due to the fact that we do not have a perfect intercalated system, it is probable that only some of the platelets couple in this manner, and the majority of the Pd particles are not coupled. This might be the reason why the whole system behaves as a ferromagnet, because the antiferromagnetic signal is so small. It should be noted that a weak antiferromagnetic interplanar exchange interaction has been observed in other graphite intercalation compounds, which approximate quasi two-dimensional systems [14].

It is necessary to mention that the magnetic properties of Pd are very sensitive to the presence of magnetic impurities. For example, a clear up-turn of the magnetization as a function

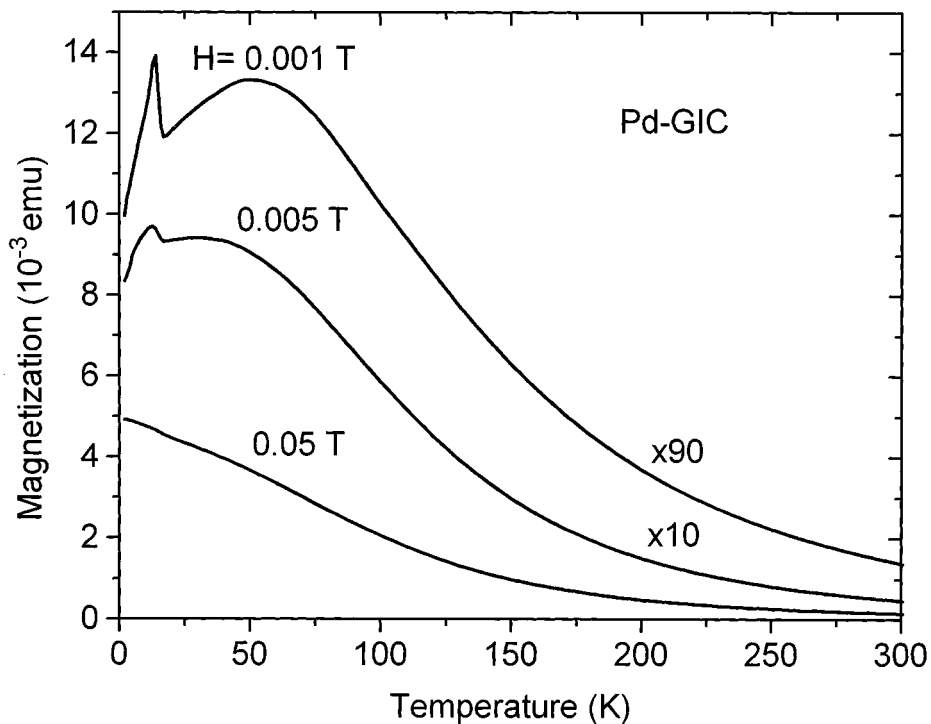


Figure 4. Magnetization as a function of temperature from $T = 2$ – 300 K at different magnetic fields. To obtain these curves, the sample was cooled to $T = 2$ K in zero field, then the respective magnetic field was applied and the measurement was made by raising the temperature to 300 K.

of temperature is observed at low temperatures [13]. Such a behaviour is not observed in our experiments, at least at low applied magnetic fields (see figure 4). Also, in alloys of Pd–Fe with 0.15 at% of Fe, a magnetic moment of around $20 \mu_B$ is observed [15]. In our case, effective magnetic moments per particle are orders of magnitude greater than that value, indicating that a higher content of magnetic impurities should be present in our samples. As indicated before, the EDS analysis indicates no presence of any ferromagnetic impurity. Then we believe that a true ferromagnetic behaviour is present in the Pd quasi bi-dimensional nanoparticles.

In conclusion, the samples consisted of isolated Pd particles encapsulated in graphite. Due to this fact, the overwhelming majority of the particles are separated from each other by graphitic sheets. These graphitic layers act as a spacer, as well as a template for the growth of the particles. The sample is a good realization of a quasi two-dimensional system of Pd particles, for which ferromagnetism is experimentally observed.

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