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MAGNETIC PROPERTIES OF NANOMETRIC NICKEL PARTICLES

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We have prepared nickel metal fine particles with mean diameters as low as 4 nanometers and we have studied their magnetic properties. A superparamagnetic behaviour is found for the smallest particles even at helium temperature.

1. INTRODUCTION

OVER THE last few years the magnetic properties of fine ferromagnetic particles (Fe, Co, Ni) have been widely studied, as they present an interest both for fundamental physics and for applications. We will first list some typical results.

For particles of a few ten nanometers the ferromagnetic behaviour was investigated [1]: it was shown that the saturation magnetization decreases with cluster size. For finer grains (few nanometers) a superparamagnetic behaviour was generally observed [2–5]. Concerning the theoretical interpretation of the magnetic moment of the surface atoms, the situation remains unclear [5–7]. In this paper we report very high field magnetization measurements on Ni fine particles (4–30 nm) obtained by a novel chemical method.

2. PREPARATION

Generally, fine particles are prepared by evaporating metals in vacuum or in an inert atmosphere onto a solid or liquid substrate. More sophisticated techniques were recently investigated to obtain cold and stable cluster beams using a laser vaporization source [8, 9].

In our case the particles are prepared under an inert atmosphere (N_2 or Ar) by treating a well stirred suspension (or solution) of anhydrous nickel halide with magnesium [10, 12]. The speed of reaction depends principally on the thermal conditions, the solvent used, and the state of division of the reducing metal.

When the reaction is complete, the fine black precipitate is washed first with water then with ethanol.

Two nickel salts were examined (bromide and chloride) and we have employed two solvents, tetrahydrofuran (THF) and ethanol. The change in halide does not induce an important difference in the development of the reaction, but the change of solvent is of great importance.

First, we investigated the reduction in THF. When the mixture was heated under reflux, the reaction was relatively fast (from 2 to 5 h). We have verified that the reaction was quantitative. At the end point of the reaction, all the nickel is in a zero state of oxidation; one fraction is attracted by the magnetic stirring bar at the bottom of reactor, the other part is made up of a fine precipitate with a very slow sedimentation speed. When the reduction is allowed to proceed under boiling, almost all the nickel is gathered around the magnetic bar. On the other hand at low temperatures almost all of the metal is in the form of a very fine precipitate. It would appear that the lower temperature, the smaller the size of nickel particles.

Secondly, we investigated the halide reduction in ethanol. At room temperature, whatever halide is used the reaction proceeds in two steps. In the first place, hydrogen is released during attack by the magnesium. Volumetric measurements of the gas released show that as many moles of hydrogen are formed as there were moles of nickel halide initially in the solution. At this step, aqueous hydrolysis of the solution directly yields a nickel hydroxide precipitate [$Ni(OH)_2$]. If the experiment is pursued further, black metallic nickel slowly appears; however, the metal yield can reach 100% only if the initial concentration of reactants becomes very low (halide/solvent mole ratio less than 10^{-2}).

On the other hand, if we heat the reaction mixture

under reflux when the gas evolution ceases, nickel is produced quickly, and ethanol formation can be detected (yield 70% in comparison with nickel). If heat is applied from the start, the reaction becomes too rapid to be able to distinguish the two reaction steps.

Figure 1 shows electron microscope pictures and the size distribution of the grains prepared with the two solvents. The size distribution is quite sharp around 30 nm for grains prepared in ethanol and around 4 nm in the case of THF.

3. MAGNETIZATION MEASUREMENTS

Magnetization measurements were performed using the high magnetic field facilities in Toulouse. The field is produced by the discharge of a capacitor bank in a resistive copper coil. The maximum field (43T) is reached within 80 ms and the decreasing time is about 1 s. In order to measure the magnetization two pick-up coils are mounted to give zero induced voltage in the absence of a sample. The signal in the presence of a sample is proportional to the derivative of its magnetization.

The two types of particles were studied. For these measurements the grains are coated with paraffin. The sample containing the larger grains exhibits a classical ferromagnetic behaviour as shown in Fig. 2.

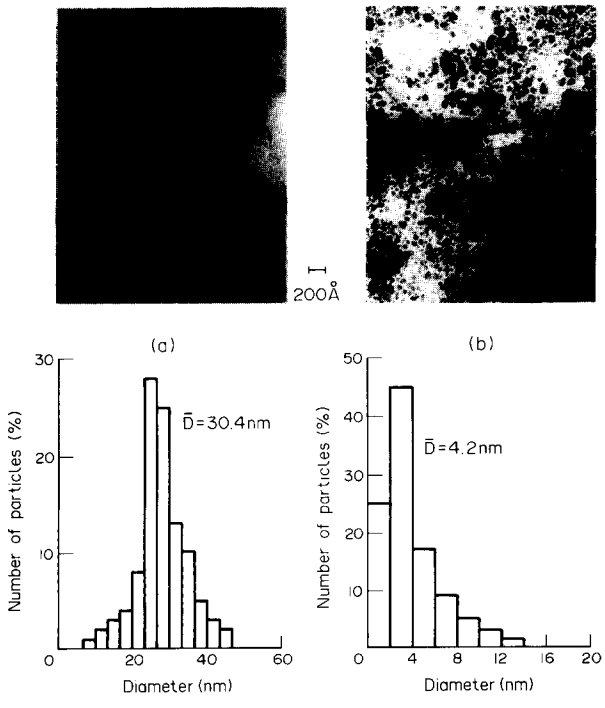

Fig. 1. Electron microscope pictures and size distribution of particles prepared with the two solvents: (a) ethanol, (b) THF.

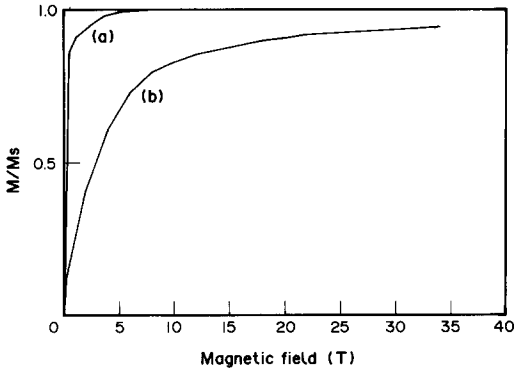

Fig. 2. Magnetization measurement at 4.2 K for the two types of particles: (a) prepared with ethanol, (b) prepared with THF.

Between 4.2 K and 77 K, the temperature dependence of the magnetization is similar to that of bulk nickel. It is not easy to discuss the exact value of the saturation moment M_S as the concentration of nickel in paraffin cannot be known with a very good accuracy. In [1] the authors report a small decrease of M_S for many particle sizes which they explain by a surface oxidation which is avoided in our case.

More exciting are the properties of the finest particles. We can observe on Fig. 2 a paramagnetic-like behaviour after a magnetization step at very low field due to the presence of a small amount of ferromagnetic larger grains as observed by electron microscopy.

We performed measurements at various temperatures between liquid helium and liquid nitrogen temperatures in fields up to 35 Tesla. Even such high magnetic fields are not enough to saturate the magnetization. As suggested by various authors, mentioned above, we try to analyse the data in terms of superparamagnetism. First we subtract the small parasitic ferromagnetic contribution. As we performed very high field measurements, we can then test the agreement between the experimental data and a Langevin law over a wide H/T even at high temperature. Thus the temperature dependence in the low field region of the slope of the magnetization is not crucial for us. Agreement with the model is clearly shown in Fig. 3. Let us recall that the Langevin equation can be written:

$$M/M_S - \coth \mu B/kT - kT/\mu B,$$

where μ is the mean magnetic moment of each grain. In order to obtain a good agreement we have found that it is necessary to replace T by an effective temperature $T_{\text{eff}} = T + T_0$. The presence of the T_0 term shows that the grain magnetization is not completely free to orient itself in the magnetic field.

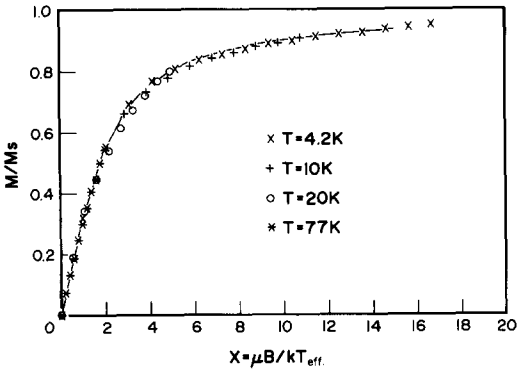

Fig. 3. Best fit between magnetization data (points) and several temperatures and Langevin law (line).

One possible cause is dipolar interactions between grains. Alternatively each grain may be submitted to an effective pinning because the surface atoms (which for these very small particles form a large fraction of the total) are in an anisotropic environment. This will lead to an effective crystal field acting on the particle. Stresses due to the differential contraction on cooling will also play a role. Moreover, uncertainties on the value of T_0 can arise from subtracting the small ferromagnetic contribution at low temperature, as we assume it is saturated in very low fields. Then, we only consider T_0 as a fit parameter and we don't try, at the moment as the concentration is not measured, to attribute it a defined physical meaning. The best fit in Fig. 3 corresponds to $T_0 = 6$ K. The system clearly exhibits a superparamagnetic behaviour. In this regime, we can determine μ which was obtained as a temperature independent fit parameter. We obtain $\mu = 11\,\mu_B$ corresponding to approximately 20 magnetic nickel ions per grain. As was already observed in thin film studies [12] we find a dead magnetic layer around the grains whose thickness is about 15 A.

Our chemical process of preparation shows that the presence of such dead layer, observed by various authors, is not due to a surface oxidation. The absence of oxidized nickel at the surfaces is insured by X-ray diffraction and electronic diffraction. The most convincing argument is given by the high catalytic activity of this particle. Indeed the catalytic properties very quickly disappear with oxidation [13]. It is noticeable that the superparamagnetic behaviour remains down to low temperatures.

4. CONCLUSION

We succeeded in synthesis very fine Ni particles by a chemical route. The very high field magnetization measurements confirmed the ferromagnetism of particles of 30 nm diameter; a superparamagnetic behaviour is clearly observed for the finest grains ($d = 4$ nm) in the whole temperature range (4–77 K).

Further work is in progress to investigate the origin of T_0 by varying the grain concentration in the samples. Finer particles will be available in the near future. They will allow us to improve the estimate of the thickness of the dead magnetic layer which is not due to oxidation.

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