SUPERPARAMAGNETIC-PARAMAGNETIC TRANSITION IN SMALL PARTICLES

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Abstract. — The paramagnetic state and the superparamagnetic regime of small particles of the granular system $\text{Fe}_{64}\text{Cr}_{16}\text{B}_{20}-\text{Al}_2\text{O}_3$ have been studied by mean of magnetization and susceptibility and compared to the properties of the corresponding bulk metal. The evolution of the magnetic structure near and above T_c is the same for both compounds. Deductions upon the particle size have been attempted.

Introduction

It is well known that the value of the susceptibility of small particles with the approximation of the Langevin fonction at low field obeys a Curie type law above the blocking temperature T_B [1]. For ferromagnetic particles the ratio $(\delta(1/\chi_{sp}/\delta T)/(\delta(1/\chi_p)/\delta T))$ is equal to the number n of magnetic atoms, χ_{sp} and χ_p being respectively the superparamagnetic and the paramagnetic susceptibilities, if the effective moment μ_{eff} per magnetic atom in the magnetic state at low temperature is equal to the moment μ per magnetic atom in the pure paramagnetic state. However no pertinent verification upon the temperature limits has been performed probably because the high Curie temperature of the usually studied small particles. On the other hand, the thermal variation of the small particle susceptibility near T_c has never been studied. It could show interesting features as the magnetic state is generally more disordered in small particles and the development of the magnetic structure near T_c can be modified owing to the fact that the particles have a limited volume.

Experiment

A medium T_c value for the particle was necessary to study easily the paramagnetic state. We have chosen $\text{Fe}_{64}\text{Cr}_{16}\text{B}_{20}$ metallic glass as particle composition. Ribbons of this material prepared by melt-spinning technique have been cosputtered with alumina as a thin film of $\sim 1 \mu\text{m}$. The target composition has been chosen in order to get a T_B value of about 30 K. Therefore the spreading of the temperature range where superparamagnetic regime occurred was sufficiently large. The composition of the granular compound in agreement with that of the ribbon has been checked by electron microprobe analysis. Transmission electron microscopy revealed the amorphous state of the sample. The Mössbauer spectrum at 300 K did not exhibit any Fe^{2+} neither pure Fe^{3+} but nearly 10 % of perturbed metallic iron was detected probably due to the pollution at the surface sample.

Results and discussion

The magnetic characteristics of the ribbons are consistent with the values previously given for such a composition [2]: $T_c = 230 \text{ K}$ and $\mu_{eff}/\mu_B = 1.10$ per Fe atom at 10 K (Fig. 1). These low values are due to the antiferromagnetic influence of Cr [2]. Between 295 K and 420 K, a Curie-Weiss law is observed with $\Theta_p = 247 \text{ K}$ and a Curie constant which leads to $\mu_p/\mu_B = 5.50$ per Fe atom. This too high value shows that the true paramagnetic state is not reached. The real value μ_r in the paramagnetic state is certainly higher than μ_{eff} but also lower than μ_p . Therefore short range order occurs for this range of temperature. In this case $\mu_p = \sqrt{n_p} \cdot \mu_r$, n_p being the number of spins ferromagnetically coupled.

Fig. 1. — Magnetization *versus* field at 10 K a) for the metglass small particles b) for the metglass ribbon.

In figure 1 is reported the field dependence of magnetization for the granular sample at 10 K. We can deduce $\mu_{eff}/\mu_B = 1.0$ per Fe atom after correction due to the oxydized part near the surface sample. This value is lightly lower than that of the ribbon and we can remark that saturation is reached for higher fields. Disorientations occurring at the particle surface are responsible for these features and lead to a weaker average magnetic moment per Fe atom.

In figure 2 are presented the inverse of the susceptibility χ_{sp} for the granular sample. In the superparam-

Fig. 2. - Inverse of susceptibility *versus* temperature for the metglass small particles a) experimental values b) corrected values from the thermal variation of magnetization.

agnetic regime, between T_B ($= 18$ K for $H = 350$ Oe) and T_c , we do not observe a straight line. This is not in disagreement with the model because the magnetic moment follows the thermal variation of the magnetization $M(T)$. χ_{sp} has been corrected from this variation (Fig. 2, curve b). A straight line is obtained which leads to $\Theta_{sp} \approx -50$ K and $n\mu_{eff}^2/\mu_B^2 \approx 6\,600$, n being the number of Fe atoms in each particle. Above 170 K, the correction becomes doubtful due to the vicinity of the Curie point and deviations to the superparamagnetic Curie law can appear for the same reason. The correction $M(T)/M(0)$ has been determined from the $M(T)/M(0)$ values measured for the

ribbons and checked by extrapolating at 350 Oe the $M(T)/M(0)$ values obtained for the granular sample with sufficiently high field to block the particles.

In the paramagnetic state, we observe a straight line which leads to $\mu_p/\mu_B \approx 3.90$ per Fe atom after correction due to the oxydized part near the surface sample and $\Theta_p \approx 350$ K. We find the same features than for the ribbon which can be discussed in the same way. The lightly smaller values of μ_p/μ_B can be correlated to a slightly modification of the short range order. In fact, near the particle surface, disorders must appear in the ferromagnetic short range order, lowering the μ_p value. On the other hand, from the determined value of $n\mu_{eff}^2/\mu_B^2$, we can deduce the thermal variation of the particle moment and we obtained a very similar variation to that of the ribbon. These features are consistent with the same evolution of the magnetic structure near and above T_c for the two materials.

The ratio of the $1/\chi$ curve slope in the superparamagnetic and paramagnetic states cannot be used to determine n because n_p (or μ_r) is unknown. This method will be available only if pure paramagnetic state is reached and if $\mu_r = \mu_{eff}$. These conditions reduce the field of application. Nevertheless we can evaluate n from the μ_{eff} value of the small particles determined at low temperature. This leads to $n \approx 6\,600$, and a particle volume ≈ 60 Å³.

In conclusion, we have shown that the evolution of the magnetic structure near and above T_c is the same for bulk material and small particles. This feature requires of course that the crystalline structure and the magnetic state at low temperature of the small particles are not too perturbed with regard to the corresponding bulk material.

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