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Magnetoresistance and magnetic properties of Fe_3O_4 nanoparticle compacts*

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In this paper, we report on the magnetic properties of Fe_3O_4 nanoparticles with different grain sizes under different pressures. In all the samples, the saturated magnetization M_s shows a linear decrease with increasing pressure. The thickness of the magnetic dead layer on the nanoparticle surface under different pressures was roughly estimated, which also increases with increasing pressure. The transport measurements of the nanoparticle Fe_3O_4 compacts show that the low-field magnetoresistance (MR) value is insensitive to the grain size in a wide temperature range; however, the high-field MR value is dependent on grain size, especially at low temperatures. These experimental results can be attributed to the different surface states of the nanoparticles.

Keywords: nanoparticle, saturated magnetization, magnetoresistance
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Magnetic nanoparticle assembly has been a subject of intense research due to its unique magnetic property.[1] By decreasing the particle size, some novel phenomena are observed, such as superparamagnetic relaxation for particle dimensions below a critical size,[2] surface effect on magnetic properties because of the large ratio of surface to volume,[3] quantum tunnelling of magnetization[4] and unusual large coercivities.[5] The general question is what happens to the bulk properties of a macroscopic body as one or more of its dimensions are reduced to an atomic size. One of the fundamental problems in magnetic nanoparticles is the observed reduction of the saturated magnetization M_s, which was pointed out in the late 1960s by Berkowitz *et al.*[6] Since then, the problem has been revisited several times with arguments in favour of a surface origin and in favour of a finite size effect.[7–9] More recently, the experimental results on polarized neutron scattering in $CoFe_2O_4$ [10] and Mössbauer and magnetic experiments in $NiFe_2O_4$ [11] have indicated that the surface spin disorder could be the origin of this reduction. Based on these results, a model of a ferrimagnetic core surrounded by a surface layer of canted spins has been proposed for $NiFe_2O_4$ particles, and its implications on the macroscopic quantum tunnelling have also been carefully analysed.[11]

During past ten years, the transport properties of an oxide nanoparticle assembly have attracted much attention since the discovery of colossal magnetoresistance (CMR)[12,13] and powder magnetoresistance (PMR).[14] For the latter, the thin grain surface plays a role of barrier when the spin-polarized electrons cross one particle to another. The change of the relative magnetic moment alignment of adjacent particles, caused by an applied field, results in the change of the powder resistivity. However, up to now, there has been relatively little knowledge about the transport properties of PMR in nanoparticle compacts. In this paper, as a basic study, we investigate the transport and magnetic properties of magnetite nanoparticles with different grain sizes under different pressures.

Ultra-fine Fe_3O_4 powders have been prepared by a wet method. The powders are composed of single-

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phase nanoparticles with different particle sizes. X-ray diffraction (XRD, Cu$K\alpha_1$ radiation λ=0.15405 nm) was carried out for all pellets, showing identical lattice parameters and indicating that the samples are single phase and have a cubic structure. The Scherrer formula has been used to determine the mean size of the particles from the width of XRD (311) line. Discs with a diameter of 3 mm and a thickness of about 1 mm were cold pressed at different pressures by a quasi-hydrostatic pressure method. For each compression, the pressure was kept for 45 min to stabilize the volume change. Magnetic hysteresis loops and temperature-dependent magnetization measurements were carried out by using a commercial quantum design superconducting quantum interference device (SQUID) magnetometer in the temperature range from 5–320K, and the applied magnetic fields were up to 754Am^{-1}. The MR measurements were carried out for samples at temperatures from 130–350 K in a field from −5–5T by a four-point method. Ohmic contacts were made with gold metal foil.

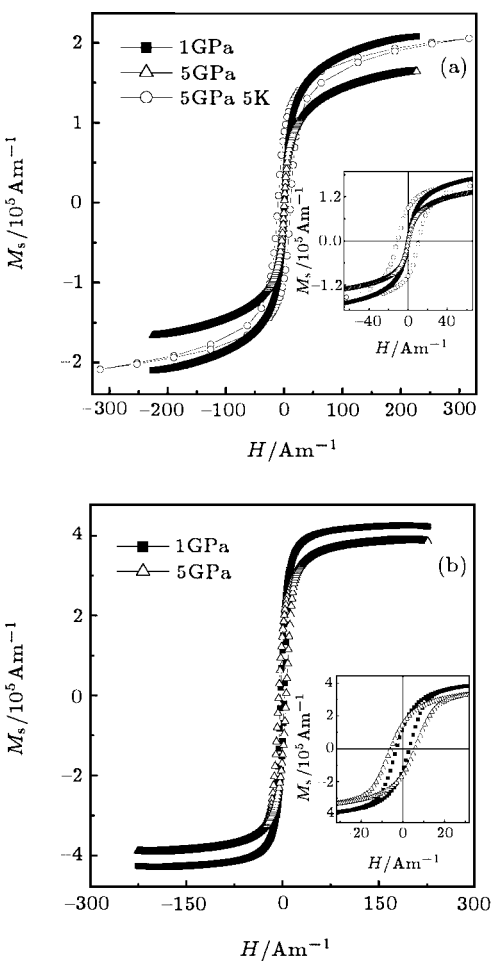


Fig.1. The magnetic hysteresis loops of samples under different conditions: (a) S20; (b) S200.

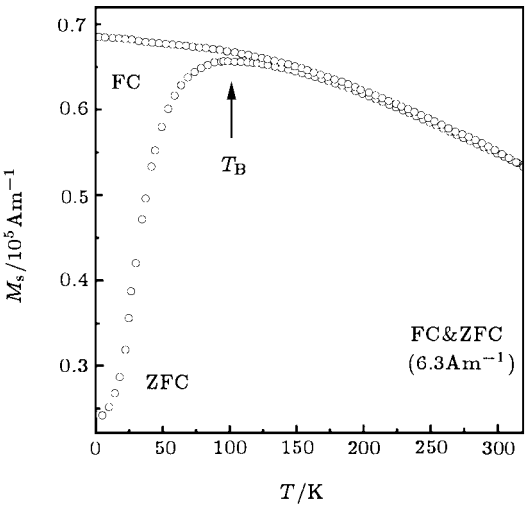


Fig.2. Zero-field-cooled–field-cooled (ZFC–FC) magnetization curves of S20.

Figures 1 (a) and 1(b) show the magnetic hysteresis loops of samples with 20 nm (S20) and 200 nm (S200) grain sizes under different conditions. At 5K, S20 is ferrimagnetic with σ_s=2.08×10^{5}Am^{-1} and the coercivity H_c ≈8.7Am^{-1}. But it becomes superparamagnetic when the temperature reaches 300K. The largely enhanced H_c can be understood by using the model proposed by Du *et al.*[15] Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of S20 are shown in Fig.2. Namely, in the case of ZFC operation, the sample was cooled first from 300 to 5K without H, then measured with H with the increase of temperature. For FC operation, the measurement was made with the increase of temperature after the sample was cooled from 300 to 5K in H. The ZFC and FC magnetization curves exhibit the typical blocking process of an assembly of superparamagnetic particles with a distribution of blocking temperature. The sample S200 is ferrimagnetic both at low and room temperatures. σ_s=4.25×10^{5}Am^{-1} at room temperature is much lower than the bulk value (4.80×10^{5}Am^{-1}). The reduced saturation magnetization of Fe_3O_4 particles has also been found by other researchers.[16,17] It has been explained by the existence of a magnetic dead layer on the surface of particles. Assuming that the thickness of the dead layer (t) is constant, the magnetization of the particles can be expressed as

$$\sigma_s = \sigma_s(\infty)\left(1 - \frac{6t}{d}\right), \qquad (1)$$

where $\sigma_s(\infty)$=4.80×10^{5}Am^{-1} corresponding to the bulk value at room temperature. Fitting the data with

d=20 nm in Eq.(1), we have obtained the thickness of the dead layer, which is about 1.87 nm for the sample compressed at 5GPa. The obtained dead layer values are close to those of Chen *et al.*[17] So our data give further support to the dead layer theory. Moreover, the fit with Eq.(1) gives the 1.16 nm dead layer for sample S20 pressed at 1GPa. The increase of the dead layer on nanoparticle surfaces gives further evidence of the reduction of saturated magnetization. The increase of the dead layer thickness with increasing pressure means that the surface structure is strongly influenced by the applied pressure. However, while increasing the particle size, M_s increases to $3.88\times10^5\mathrm{Am}^{-1}$ in S200. M_s also shows a decreasing trend with increasing pressure (from 4.25 to 3.88 $\times10^5\mathrm{Am}^{-1}$ corresponding to the dead layer thicknesses of 0.18 and 0.31 nm, respectively).

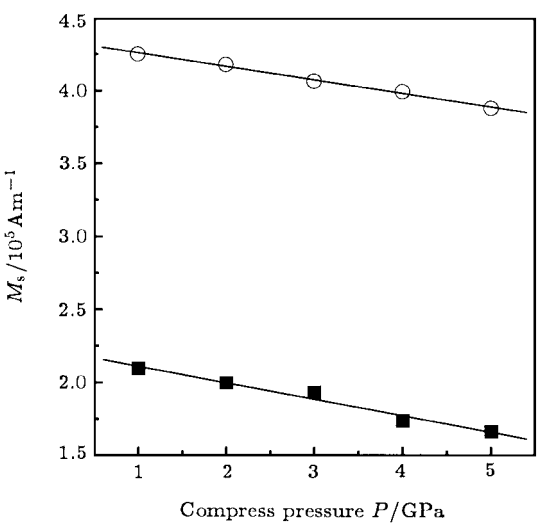


Fig.3. Variation of M_s with the applied pressure in S20 (■) and S200 (○).

In all the samples, M_s varies linearly with the applied pressure in the measuring range of our experiment. Two typical curves are shown in Fig.3. Although there is a large difference of absolute M_s values between S20 and S200, the decreasing trend of M_s is similar in both samples. The relationship could be well fitted by

$$M_s = aP + b, \tag{2}$$

where P represents the pressure, a is about -1.79 for both samples, and b is 83.66 for S20 and 42.51 for S200. Obviously, b represents the M_s of powder samples without applied pressure. Here, the values of b are also significantly smaller than the bulk value due to the surface spin disorder. Also, a should be a parameter that represents the distortion degree of grain surfaces with pressure.

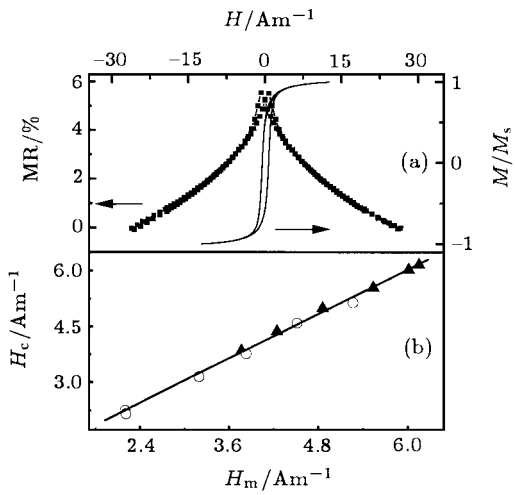


Fig.4. (a) MR as a function of magnetic field measured at 130K. The magnetic hysteresis loop for the sample obtained at the same temperature using a SQUID magnetometer is also plotted. (b) Relation between the coercivity and the field for the maximum resistance for S100 (▲) and S200 (○).

The magneto-transport measurements for Fe_3O_4 nanoparticles are carried out on two samples with different grain sizes of 200 and 100 nm, represented by S200 and S100 respectively. Fig.4(a) shows a typical negative MR and a magnetic loop of Fe_3O_4 powder compact measured at 130K. The MR is defined as $(R_H\text{-}R_{H=0})/R_{H=0}$. A "butterfly" curve, with a reversible high-field slope, is observed. The magnetic loops are normalized to M_s with coercivity being about $6.3\mathrm{Am}^{-1}$. The curves of both MR magnetic loops show a coincidence between the field of the maximum resistance H_m and the coercivity H_c. This coincident relationship is shown in Fig.4(b), where the coercivity H_c is plotted against the field H_m for temperatures ranging from 130 to 300K in both samples. These results are in agreement with those of Coey *el al.*[14]

The value of low-field MR ($25\mathrm{Am}^{-1}$) decreases while the temperature increases in both samples (see Fig.5(a)). It is noted that the value of low-field MR and the trend of temperature dependence are very similar in both samples, although they have different grain sizes. However, the high-field MR ($250\mathrm{Am}^{-1}$) shows a difference between the two samples. This difference is much larger at low temperatures. High-field MR versus temperature is shown in Fig.5(b).

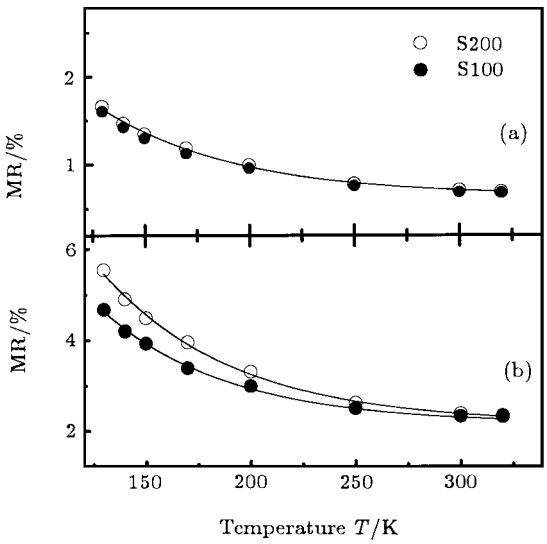


Fig.5. MR values of the two samples, taken from the MR curves measured at different magnetic fields: (a) $25 Am^{-1}$ and (b) $250 Am^{-1}$.

The MR effect in polycrystalline magnetic oxides is mainly due to a spin-dependent grain boundary tunnelling effect at low magnetic field.[18] The relative switch of magnetic moment between adjacent magnetic grains leads to different resistivity states when a magnetic field is applied. The coincidence between H_c and H_m demonstrates that the observed MR effect is a type of spin-related phenomena, which have been found in other magnetic nanostructures: metallic multilayers, granular ferrimagnets, and spin-polarized tunnelling junctions. The similarity of low-field MR values in both samples shows that there is a spin-dependent grain boundary tunnelling process unrelated to the grain size at low magnetic field.

The high-field MR, which is observed in the polycrystalline samples of the colossal magnetoresistance magnetite $La_{0.7}Ca_{0.3}MnO_3$, arises from the grain-boundary scattering.[18] The difference of high-field MR values in both samples demonstrates different states of grain boundaries, which mainly include the structural distortions, the chemical condemnation, and the spin disorders at grain boundaries. The different grain boundary states lead to a different spin scattering process in both samples. It is natural to expect that the smaller the grain size, the more disordered the states of the grain boundaries. It is noted that the difference of both high-field MRs is significant at low temperatures, indicating that the influence of grain boundary varies with the temperature. This experiment exhibits that the spin disorder may play a dominant role at the grain boundary when the temperature decreases.

In summary, we have studied the magnetotransport and magnetic properties of nanoparticle Fe_3O_4 compacts with different grain sizes under different pressures. The curve of M_s versus pressure shows a linear decrease with the increasing pressure, as brought about from the deformation of particle surfaces. A relationship between pressure and M_s is proposed. We roughly obtain the thickness of the dead layer at the nanoparticle surface, which gives further evidence of the decrease of M_s with increasing pressure. The changes of the grain sizes have almost no effect on the low-field MR, however the high-field MR is dependent on the grain size. The different spin-scattering process at grain boundaries can explain the result.

Acknowledgments

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