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MAGNETISM AND FERROELECTRICITY

The Influence of Breaking of Exchange Bonds on the Curie Temperature

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Abstract—The size effect of magnetically ordered nanoparticles on the Curie temperature is discussed. For a system of Fe_3O_4 nanoparticles with different dispersities, it is demonstrated that the smaller the size of the particles, the larger the thickness of their surface layer, which is characterized by considerable distortions of the regular structure. © *2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

In recent years, great interest has been expressed by researchers in the structure and properties of ultrafine particles. This is caused not only by the unique physicochemical properties of nanoparticle systems but also by the wide possibilities of using these properties in practice [1, 2]. In particular, nanoparticles have an anomalously large coefficient of thermal expansion, which suggests that the anharmonicity of atomic vibrations plays a significant role in the surface layers of the nanoparticles [3]. The smaller the particle size, the more noticeable the influence of different factors on the surface layers and, consequently, on the properties of the particle as a whole [4].

One of the most important problems concerning the properties of ultrafine particles is associated with the elucidation of the interrelation between the specific features of the structure of the surface layers and the macroproperties of the particle as a whole. In this work, we would like to call attention to a relatively simple way of obtaining quantitative information on the structural features of the surface layer of nanoparticles from data on the Curie temperature. The proposed approach is based on the following obvious assertion. The larger the fraction of atoms in the surface layer of the particle, the greater the number of dangling exchange bonds between the atoms (as compared to the case of a large-sized particle).

2. THEORETICAL BACKGROUND

Let us first consider the situation where the surface layers of particles have a magnetic crystal structure similar to the structure of bulk particle regions. The particles are treated as identical sphere with radius r. If the particle size is not very small (for example, $r \geq 10$ nm), approximately half the exchange bonds between the magnetically active surface atoms are dangling. It is these bonds that are responsible for magnetic ordering inside the particle below the Curie temperature $T_C(r) \equiv T'_C$.

It is assumed that, for a large-sized particle, the number of exchange bonds per unit volume is equal to n. From the aforesaid it follows that, for the magnetically active surface atoms of a nanoparticle, this number amounts to $n/2$. In the case when the Curie temperature for a nanoparticle, as in our approximation, is proportional to the mean number of exchange bonds per unit volume, it is easy to show that the ratio between the Curie temperatures for ultrafine and large-sized particles can be expressed by a simple formula

$$\frac{T'_C}{T_C} = 1 - \frac{3\Delta r}{2r}, \tag{1}$$

where Δr is the thickness of the layer that is half-depleted of exchange bonds.

The quantity Δr is a convenient averaged parameter that characterizes the features of the defect structure of nanoparticles. If Δr is independent of the particle radius r, then, according to relationship (1), the relative correction to the Curie temperature, which is caused by the decrease in the particle size, changes with varying r in accordance with the hyperbolic law

$$\frac{\Delta T'_C}{T_C} = -\frac{3\Delta r}{2r}. \tag{2}$$

3. RESULTS AND DISCUSSION

The deviation from this law would unambiguously indicate that the quantity Δr is a parameter characterizing the influence of the surface layer on the Curie temperature rather than the thickness of the layer depleted

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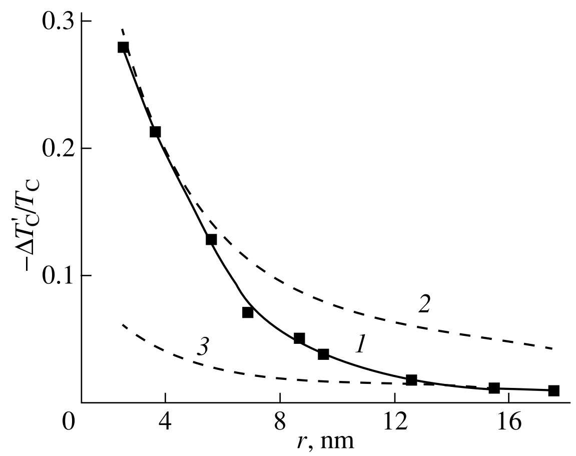

Fig. 1. Correction $\Delta T'_C/T_C$ applied to the Curie temperature (due to the decrease in the particle size) as a function of the radius r of Fe_3O_4 nanoparticles: (*1*) experimental data taken from [5] and (*2*, *3*) variants of the fitting of the experimental data with the use of formula (2) for Δr = 0.5 and 0.1 nm, respectively.

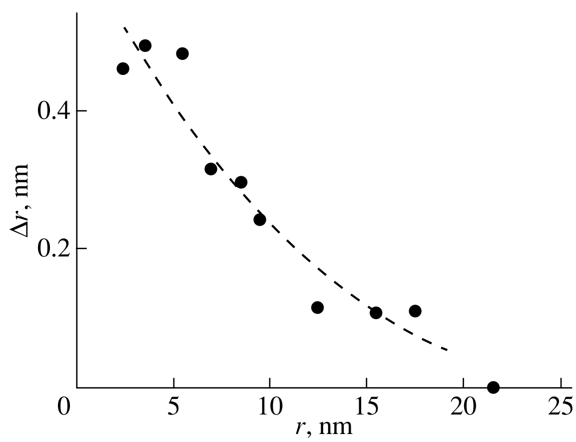

Fig. 2. Parameter of imperfection Δr for Fe_3O_4 nanoparticles as a function of the particle radius r.

of exchange bonds. In this case, an analysis of the dependence $\Delta r(r)$ for particular systems of magnetically ordered particles would permit us to trace the variation in this parameter with a decrease in the particle size.

As an example, we can use the experimental data obtained by Sadeh *et al.* [5], who measured and investigated the experimental dependence $T'_C(r)$ for nanoparticles of magnetite Fe_3O_4. As can be seen from Fig. 1, the attempts to fit theoretical curves calculated from relationship (2) at Δr = const to the experimental data taken from [5] were unsuccessful. In other words, using the quantity Δr as the fitting parameter, we failed to achieve reasonable agreement between the calculated and experimental dependences.

For a system of Fe_3O_4 nanoparticles with different dispersities, it is possible to show that the quantities Δr and r, which are related to the correction to the Curie temperature $\Delta T'_C/T_C$ through relationship (2), characterize the interrelation between the degree of imperfection of the magnetic structure and the particle size. The dependence $\Delta r(r)$ for Fe_3O_4 nanoparticles (Fig. 2) is in agreement with relationship (2) and the results obtained in [5]. This dependence suggests a progressively increasing role of the surface layer with a decrease in the particle size. To put it differently, the smaller the size of the particles, the larger the effective thickness Δr of the layer characterized by considerable distortions of the regular structure. Therefore, the quantity Δr can be actually treated as the parameter of imperfection of the magnetic structure of the nanoparticles.

An analysis of the dependence $\Delta r(r)$ shown in Fig. 2 makes it possible to refine the size corresponding to the notion of large-sized particles. In the case of magnetite, particles with $r \geq 20$ nm can be considered to be large-sized. For these particles, the parameter of imperfection Δr is approximately equal to zero.

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