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Morin temperature of annealed submicronic α-F$_2$O$_3$ particles

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The Morin temperature (T_M^0) of annealed, monodispersed, nearly spherical particles having diameters (d) between (0.07–0.62) μm have been investigated. A plot of T_M^0 versus $1/d$ is linear. The extrapolation of this plot between 230 and 262 K to $d=\infty$ gives $T_M^0 = 264 \pm 2$ K, the Morin temperature of the bulk α-Fe$_2$O$_3$. Furthermore, $T_M^0 = 0$ implies $d = 83 \pm 5$ Å, which is the size limit for the onset of superparamagnetism in this system.

I. INTRODUCTION

Bulk α-Fe$_2$O$_3$ possesses the corundum-type crystal structure with an antiferromagnetic spin ordering. This material exhibits a first-order magnetic transition at 263 K, known as the Morin temperature T_M^0. The superscript 0 implies that the general Morin temperature, T_M^H, which depends on the magnetic field, H, has been extrapolated to the zero-field case. Between this transition and the normal Néel temperature, $T_N = 961$ K, α-Fe$_2$O$_3$ has a weak ferromagnetism due to slight spin canting out from the basal plane. Between T_M^0 the spins are aligned antiferromagnetically along the c axis. Specific details of the nature of the Morin transition has been given by Artmann *et al.*[1]

It can be expected that when a particular magnetic material is prepared in the form of small particles, certain magnetic properties will become size dependent. Earlier experimental studies[2] have shown that T_M^0 decreases with decreasing particle size. Yamamoto[3] demonstrated that T_M^0 shifts downwards as the crystal lattice expands both along the a and c axis. He proposed that the shift in T_M^0 is related to the change of the dipolar magnetic field due to this lattice dilation. Kundig *et al.*[4] regarded the surface of a fine particle as a defect capable of pinning the spins and thus influencing the value of T_M^0. Recently, the role of strain defects and particle size were reported by Muench *et al.*[5]

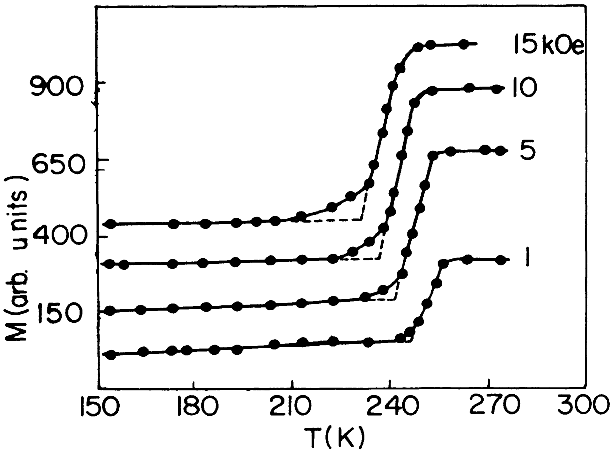

FIG. 1. Volume magnetization, M, of as-prepared particles having the diameter 0.17 μm as a function of the absolute temperature, T, in the neighborhood of the Morin transition.

It is well known that the methods of particle preparation and their relation to the morphology, surface condition and strains are important factors which determine the particle physical properties. In this work, submicronic, nearly spherical particles of uniform size and well-defined chemical characteristics were prepared from metal hydrous oxid sols. The Morin temperature of these particles was studied using as prepared and also annealed (at 573 K for 24 h) samples.

II. EXPERIMENTAL CONSIDERATIONS

The samples of α-Fe$_2$O$_3$ were prepared using techniques described elsewhere.[6] The particle sizes were determined by methods of electron microscopy. The mean particle diameters ranged from 0.07 to 0.62 μm with a standard deviation less than 0.02 μm. All the particles prepared by this method were nearly spherical except for the smallest (0.07 μm) and largest (0.62 μm) particles which were cubical.

Magnetization measurements were made using a vibrating sample magnetometer with the magnetic field, H, ranging from 1000 to 15 000 Oe. The temperature T_M^H was observed from the rapid increase in the magnetization as the sample was warmed up through the transition region. Specifically, T_M^H was chosen to be the temperature at which the straight line through the magnetization data before the transition intersected the straight line through the steepest part of the transition. Figure 1 shows such typical plots of volume magnetization, M, as a function of

TABLE I. Diameters and Morin temperatures of α-Fe$_2$O$_3$.

		T_M^0 (K)	
Sample	d (μm)	As-prepared	Annealed
1	0.07	233	233
2	0.10	212	240
3	0.13	228	248
4	0.17	241	252
5	0.33	248	257
6	0.62	206	261

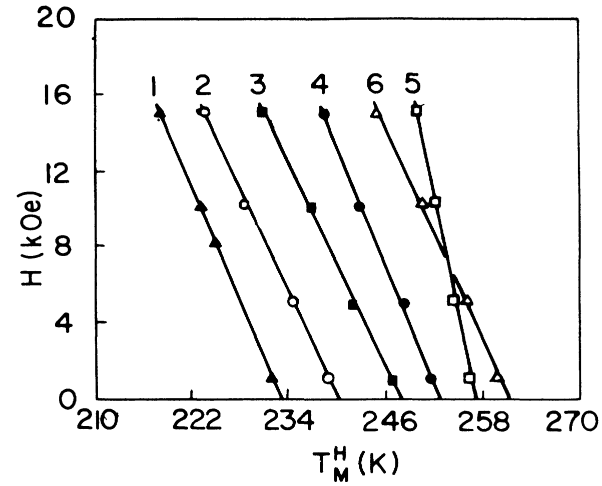

FIG. 2. Morin temperature, T^H_M, as a function of the applied magnetic field.

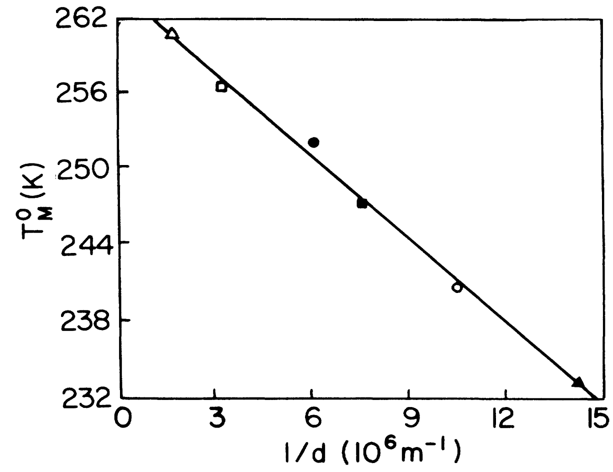

FIG. 3. Morin temperature, T^0_M, as a function of the inverse diameter, $1/d$.

absolute temperature, T, for as-prepared α-Fe_2O_3 particles having the diameter of 0.17 μm.

III. RESULTS AND DISCUSSION

The Morin transition was first explored in larger (up to 15 000 Oe) magnetic fields for the as-prepared particles of various sizes. In order to remove strains and inhomogeneities or any absorbed water in as-prepared particles, all the samples were annealed at 573 K for a period of 24 h. This temperature for annealing was chosen to avoid the sintering problem of the submicronic particles that could have caused further inhomogeneities. It was observed that annealing had a significant effect on T^0_M of these particles. As listed in Table I, annealing of sample 6 increased T_M by 55 K. For all the samples, except sample 1, T^0_M increased, indicating the removal of strains and inhomogeneities that were causing the depression of the T^0_M. Still this does not necessarily imply that the value of T^0_M should be a characteristic of the crystal structure and size of the individual particle. In fact, the results presented in Fig. 2 show that for a particular size of α-Fe_2O_3 particles, T^H_M decreases linearly with increasing H for fields used in this study. The solid straight lines (which are least square fits through the particular set of points), extrapolated to $H=0$, give the true Morin temperature T^0_M for the sample. These temperatures are presented in Table I, which show a decrease of T^0_M with the size of particles. When the values of T^0_M are plotted against $1/d$, the data fit excellently a straight line (see Fig. 3). The least squares method gives the following relation,

$$T^0_M = 264.2 - 2.194/d \ , \qquad (1)$$

where d is expressed in Å and T^0_M in K.

The linear variation of T^0_M with $1/d$ indicates the dependence of T^0_M on the surface to volume ratio. This is quite reasonable, since for small particles this ratio is large and sensitive to specific details of preparation and heat treatments. Annealing of particles should decrease the internal defects and thus enhance the importance of the surface effects. Thus the surface could act like a large defect capable of pinning magnetic moments. Also, the surface effects can change the dipolar magnetic fields. This idea was first postulated by Néel[7] to explain the anomalous magnetic behavior of Cr_2O_3 particles of about 0.2 μm in diameter.

Equation (1) predicts that $T^0_M = 264 \pm 2$ K for a bulk α-Fe_2O_3 while $T^0_M = 0$ for particles of 83 ± 5 Å. The Morin transition temperature of bulk usually quoted in literature is $T_M = 263 \pm 5$ K. Furthermore, the onset of superparamagnetism for α-Fe_2O_3 has been detected for diameters of 50–80 Å particles. Thus Eq. (1) correctly describes the size effect of T^0_M with appropriate extrapolated predictions.

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