Evidence of finite-size effect on the Néel temperature in ultrathin layers of CoO nanograins

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A significant reduction in the Néel temperature of CoO ultrathin films is revealed by highly sensitive specific heat measurements. It is found that the films consist of weakly coupled antiferromagnetic (AF) grains. The $T_N$ reduction from large to small grain samples scales with the grain size reduction, according to the Binder theory of critical phenomena in systems of reduced dimensions. In these finite AF nanosystems, the intergrain exchange interaction is reduced by the presence of surface Co spins, weakly coupled to Co moments inside the grains.

During the last 20 years, the progressive availability of experimental techniques permitting the controlled fabrication of nanoscale samples has opened the way to studies of critical phenomena in reduced dimension systems. In nanograins, as the grain dimensions become smaller than the relevant physical characteristic length and one approaches the zero-dimensional (0D) limit, a number of characteristic behaviors emerge. This includes the occurrence of strong fluctuations of the order parameter, the weakening of the interactions involved, and the onset of a competition between surface and volume effects. This type of effect was studied in particular in superconductors, multilayered antiferromagnets, ferromagnetic systems, and glassy systems.

As a result of the weakness of the magnetic signal, the critical phenomena in antiferromagnetic (AF) systems have been little studied by magnetic measurements despite its crucial importance in various effects like in exchange-bias systems for instance. The recent availability of ultrahigh sensitivity specific heat equipment provides an alternative experimental technique to study the critical properties of these systems. The present study focuses on cobalt oxide, CoO, one of the most studied AF compounds. CoO can be seen as the archetype of antiferromagnetic oxides. Below the Néel temperature, $T_N = 293$ K, the Co moments are coupled by superexchange interactions mediated by the oxygen atoms. Further, CoO thin films or nanograins often constitute the antiferromagnetic element of exchange-biased systems.

In addition to the weakness of the magnetic signal, characterizing any antiferromagnet, a number of other reasons justify the use of specific heat measurements to study the critical behavior of CoO. In oxide nanocrystals, uncompensated loosely coupled surface spins are often present. Although they represent a small fraction of the total number of magnetic moments in the sample, their magnetic signal dominates in magnetic susceptibility measurements and it may hide the weak magnetic signal characterizing the order-disorder transition at $T_N$.

Early specific heat measurements on CoO were undertaken on sample made of a stacking of thin CoO layers, each layer being separated from the other by SiO$_2$ and MgO layers. In this Rapid Communication, we report the first highly sensitive specific heat measurement performed on single ultrathin layers ($\approx 1.5$ to 20 nm) of antiferromagnetic CoO nanograins. The measurements of the thermodynamic properties of such small size samples (the sample total mass is less than 10 ng) has been made possible by the use of a cutting edge nanocalorimetry technique, providing ultrahigh sensitivity in a broad temperature range from 100 K to 350 K. From these measurements, the Néel temperature is extracted. Its dependence on the CoO grain mean size is discussed within the framework of the Binder theory of phase transitions.

The CoO thin films were deposited onto the SiNx membrane of the nanocalorimeters by continuous e-gun evaporation of metallic Co. In-flight oxidation of the Co atoms was ensured by letting the atoms pass through a reactive oxygen-enriched atmosphere, at an oxygen partial pressure of $10^{-4}$ Torr. During deposition, the growth rate was maintained at 0.1 nm/s and the temperature of the SiNx membrane was held constant at 525 K. Note that the sample was maintained under ultrahigh vacuum conditions from the moment of its preparation to the conclusion of the measurements.

The thermodynamic properties of the samples were characterized from 100 to 350 K by in situ fast scanning nanocalorimetry. For this purpose, a dedicated cryogenic holder was developed. The self-standing 180-nm-thick SiNx membrane is equipped on the front side with a heater/sensor element adjacent to the sample deposited on the back side. This trilayer stack conforms a calorimetric cell with a heat capacity addendum limited to around 1 $\mu$J/(K mm$^2$) at room temperature. It ensures as well good thermal contact between the sample and heater/sensor element permitting adiabatic heat capacity analysis at ultrafast heating rates, typically $6 \times 10^4$ K/s. Such extremely high heating rates are needed to reach the ultimate detection sensitivity of a few pJ/K, permitting the specific heat of ultrathin films to be quantitatively measured. Further, the measurements are realized in differential mode, i.e., following a current pulse, the temperature excursion difference between the sample and a reference idle membrane without sample is measured.

A series of CoO thin films, with thickness ranging from 1.5 to 20 nm, were prepared. After the heat capacity measurements each sample was extensively characterized by TEM (transmission electron microscopy). For this purpose, the membranes were cut into thin slices by ultramicrotomy. In-plane and cross-section TEM micrographs of thinned slices were obtained using a 200 kV JEOL JEM-2011 microscope (see Fig. 1).
FIG. 1. (Color online) Microstructural study by ex situ TEM on samples grown on the SiN_x membranes and characterized by nanocalorimetry. (a) Cross-section TEM micrograph of the 2-nm-thick CoO layer, showing its continuity and amorphous structure. (b) Cross-section TEM micrograph of the 20-nm-thick CoO layer showing the columnar growth of the nanograins. In-plane TEM micrograph of the 3-nm-thick CoO layer (c) where crystalline grains are already evident and of the 20-nm-thick CoO film (d) showing the narrow grain size distribution. (e) In-plane and out-of-plane grain size as a function of the nominal thickness of the CoO sample deposited on the SiN_x membrane of the nanocalorimeters. The inset shows the schematics of grain growth.

Down to the thinnest sample, CoO forms a continuous layer that is found to wet perfectly on the SiN_x substrate. Films above 2 nm are characterized by the occurrence of clear electron diffraction (ED) rings revealing their (nano)crystalline nature. The thinnest films below 2-nm film are essentially amorphous. However, even in this case, shallow ED rings indicate an incipient crystallinity. The TEM images reveal the granular nature of the prepared films. Quantitative analysis of the grain’s shape and size was obtained by image analysis and digital counting of more than 100 grains per TEM micrograph. The results are gathered in Fig. 1. The average grain size increases with the layer thickness, t. In the 3-nm sample, the grains are approximately isotropic, and the grain mean diameter d ≈ t. However, for t > 3 nm, the grains take the shape of columns, of which length equals the film thickness. The formation of elongated columnar grains is a common feature of granular films in which the in-plane growth is limited by nature whereas the out-plane growth is essentially free.

The specific heat data recorded on all samples are shown in Fig. 2. The specific heat increases monotonously with temperature, as expected for a dominant lattice contribution. An additional contribution develops as one goes from thin to thick films, which represents the sample magnetic specific heat. The Neél temperature was taken as the temperature at which the inflexion of the C_p curve occurs (see Fig. 2). The T_N value and the specific heat jump occurring at T_N decrease with decreasing sample thickness. Further, a progressive rounding of the curve representing the temperature dependence of the magnetic specific heat is found as one goes toward thinner films. This rounding cannot be due to sample temperature inhomogeneities since it would be identical in all samples. Rather it can be attributed to the existence of a certain size distribution of the CoO nanograins, which tends to be relatively larger in smaller grain size samples. Alternatively, an intrinsic broadening of the specific heat anomaly may exist in nanosize granular systems.13

In view of identifying the link between the magnetic specific heat and the film nanostructure, the measured specific heat signatures of two CoO films, 6-nm and 8-nm thick, respectively, deposited according to a procedure different from normal continuous evaporation, were examined. In this procedure, the films were deposited in steps of 1 nm, separated by latent periods of 5 minutes during which the deposition was stopped. TEM observations showed that the CoO grain size in these samples was similar to the grain size obtained in 2-nm-thick samples prepared by continuous evaporation. The specific heat measured on these two different films is compared in Fig. 3 to the specific heat measured on films of the same...
essentially exchange-decoupled nanograins. For an assembly of AF grains, weak intergrain interaction is expected since there is no a priori reason that good lattice matching exists between neighboring grains. Several recent studies of exchange bias in nanosystems reached the same conclusions.\textsuperscript{17,18}

Considering that the environment of surface atoms differs from bulk, the magnetic properties of the atoms at the grain surface should differ from those of the atoms in the core of the grains. In principle, the existence of weakly coupled magnetic moments should show up as an upturn in $\chi$, the susceptibility, in magnetic measurement. Such measurements were attempted using highly sensitive SQUID magnetometry. Unfortunately, the weakness of the magnetic moment precludes any conclusions from these measurements.

The high sensitivity of the quasiadiabatic method permits the measurement of $T_N$ for ultrathin single layers with grain sizes down to 1.5 nm. The variation of the Néel temperature as a function of the grain mean diameters ($d$) is plotted in the inset to Fig. 4, and in Fig. 4 a log-log plot of the same quantities as a function of $d$ is shown. The linear behavior revealed by this last plot implies that the Néel temperature follows a grain diameter power law dependence. This is in agreement with the Binder theory of critical phenomena in reduced dimension systems.\textsuperscript{13} The Néel temperature is expected to obey the following relation:

$$\frac{T_N^b - T_N^{\text{grain}}}{T_N^b} = \left( \frac{d}{\xi_0} \right)^{-(1/\nu)},$$

where $T_N^b$ is the Néel temperature in the bulk, $T_N^{\text{grain}}$ the Néel temperature extracted from the measurement of nanograin films, $\xi_0$ the magnetic correlation length at $T = 0$ K, and $\nu$ the critical exponent related to $\xi_0$ [note that $\xi(T) = \xi_0 (1 - T/T_N^b)^{-\nu}$].

The best adjustment between Eq. (1) and our data (solid line in Fig. 4) is obtained for $\xi_0 = 1 \pm 0.1$ nm and $\nu = 0.48 \pm 0.02$. The short value of the correlation length is consistent with the fact that superexchange coupling is short-ranged and the value of the critical exponent for the correlation length, close to one-half, is in agreement with the expected value within the theory of critical phenomena.\textsuperscript{13-15} We also did try to adjust our data within the framework of the model of Lang \textit{et al}. based on spin exchange interactions, however no correct fitting was obtained (see Ref. 16).

The full consistency of the present analysis leads us to conclude that the CoO films are made of an assembly of essentially exchange-decoupled nanograins. For an assembly of AF grains, weak intergrain interaction is expected since there is no a priori reason that good lattice matching exists between neighboring grains. Several recent studies of exchange bias in nanosystems reached the same conclusions.\textsuperscript{17,18}

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The fact that the surface moments are not coupled to the moments in the bulk of the grains provide an explanation for the decrease in the magnetic specific heat per unit mass from large grain size to small grain size samples. Although within the Landau theory of second-order phase transition, the ratio \( \Delta C_p / T_N \) should be approximately the same in all samples, it is actually smaller in small grain size samples than in large grain size ones. This implies that the number of spins involved in the magnetic transition is less in the former than in the latter. For each sample, the magnetic entropy \((J / gK)\) was obtained by integrating the magnetic specific heat anomaly in the entire temperature range, between 120 K and 330 K. The entropy deficit normalized to the bulk entropy is plotted in Fig. 5 as a function of the nominal sample thickness. The curve obtained mimics the curve, also shown in Fig. 5, representing the ratio of the number of surface to volume atoms (number of surface atoms/number of total atoms) and calculated by using the TEM-derived grain size values.

Using highly sensitive specific heat measurements, we have shown that it is possible to measure the thermodynamic signatures of an antiferromagnetic second-order phase transition in a system that is close to the 0D limit. Actually, the observed scaling of the Néel temperature with the nanograin diameter down to 1.5 nm is characteristic of phase transition in finite 3D systems. The presence of loosely coupled Co spins at the grain surface was derived from the analysis of the magnetic entropy, which decreases very significantly as the size of the nanograins is reduced. This observation has very special importance for exchange-bias nanosystems where antiferromagnetic CoO layers are often studied in conjunction with ferromagnetic ones.

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