The Néel Temperatures of Nanocrystalline Chromium*

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The Néel Temperatures of Nanocrystalline Chromium

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Abstract— Wide-angle neutron diffraction measurements at temperatures from 6 to 250 K indicate that the major portion of a nanocrystalline chromium sample with a mean grain size of 73 nm becomes antiferromagnetically ordered at 119 ± 10 K. The remainder of the sample has a Néel temperature above 250 K, as would be expected for coarse-grained chromium. No evidence for antiferromagnetic order in a second sample with a mean grain size of 11 nm was observed, even to temperatures as low as 6 K.

A number of previous studies have reported the suppression of long-range magnetic (ferromagnetic or antiferromagnetic) order in several nanocrystalline materials. These studies report large reductions in the Curie temperatures, T_C , of nanocrystalline iron [1], nickel [2], and α -Fe₂O₃ [3], which become ferromagnetic below T_C . Large reductions in the Néel temperatures, T_N , have been reported for other nanocrystalline materials, including chromium [4,5], CoO [6], and FeF₂ [7], which become antiferromagnetically ordered below T_N .

The next generation of magnetic recording devices with storage capabilities exceeding 60 Gbytes per square centimeter will require miniaturization of the magnetic particles used in recording media to the nanometer-size regime. Since the loss of magnetic order would be catastrophic in magnetic recording devices, the effects on the magnetic properties of materials whose microstructures are limited to nanometer dimensions are of interest. This letter describes the temperature dependence of the magnetic moment per atom of nanocrystalline chromium with an average grain size of 73 ± 4 nm. The detailed temperature dependence of the transition to antiferromagnetic order has not previously been reported for nanocrystalline chromium.

In our previous studies [4,5] we identified two instances where nanocrystalline chromium samples were not antiferromagnetically ordered even at temperatures as low as 20 K, indicating that the Néel temperatures of these samples are suppressed drastically below that of strain-free single crystal chromium (311 K [8]). These samples had grain-sizes less than 16 nm; however, samples with grain-sizes larger than 19 nm were found to be antiferromagnetically ordered at 20 K. One of the larger-grain-sized samples

was examined at room temperature and found not to be antiferromagnetically ordered; thus, the Néel temperature of this sample was known to be between 20 and 300 K. It was concluded in the previous study that the suppression of antiferromagnetic order in body-centered-cubic (bcc) nanocrystalline chromium is most strongly correlated with decreasing grain-size, while the influence of microstrain, point defects and light-element impurities is at most of secondary importance.

Two samples of nanocrystalline chromium were examined in this study and they are identified in this report using the nomenclature of Ref. 5. The first sample, Sample A, consisted of loose powder (0.98g) with an average grain size measured previously to be 73 ± 4 nm [5]. The powder was protected from air exposure prior to and during the neutron diffraction measurements. The second sample, Sample E (about 0.2g) had a mean grain-size previously measured to be 11 ± 1 nm [4]. It had been compacted into 9 mm diameter disks with thicknesses ranging from 0.1 to 0.5 mm. Besides the smaller average grain size of Sample E compared to Sample A, a second distinction between these samples is that the particles in Sample A will have primarily free surfaces, while for Sample E there is a preponderance of grain boundaries.

Neutron-powder-diffraction data were acquired using the BT-9 neutron diffractometer in low-resolution/high-intensity mode at the National Institute of Standards and Technology. The samples were enclosed in He-filled vanadium cans and placed in a liquid-He cryostat. The data were taken at 17 temperatures ranging from 6 to 250 K using constant wavelength neutrons ($\lambda=2.352\text{\AA}$) selected by a pyrolytic graphite monochromator and a pyrolytic graphite filter to suppress contamination from higher order

wavelengths. Initially, the temperatures of the samples were held fixed and the detector was scanned across the 100 magnetic Bragg reflection of bcc chromium. These so-called 2θ scans were used to identify the position of the intensity maximum and width of the Bragg reflection. After completing the 2θ scan, the detector was moved to the position of the Bragg reflection maximum and its intensity was recorded. The intensity due to sources of background scattering was estimated from measurements of the background measured $\pm 3^\circ$ on either side of the Bragg reflection maximum where no reflection is observed. In this way the magnetic signal could be determined.

Since the magnetic moment per chromium atom is proportional to the square root of the integrated intensity of the 100 Bragg reflection [9], the integrated intensity measurements can be used to determine the temperature dependence of magnetic order in the sample, from which the Néel temperature, T_N , and order parameter of the material can be deduced. The measurements of the magnetic moment for chromium atoms in Sample A can be placed on an absolute scale ($\bullet$'s in Fig. 1), since the magnetic moment of this sample at 20 K was determined to be $0.38 \pm 0.05 \mu_B$ per chromium atom from our earlier study [5]. These data can be fitted to a simple model to determine the Néel temperature of the portion of Sample A that transformed in the measured temperature interval.

The model for the temperature dependence of the sublattice magnetization of the sample includes a Brillouin function for a spin $\frac{1}{2}$ particle [10], which is a mean-field representation of the ordered magnetic moment of the chromium atoms in the ultrafine-grain portion of the sample. The Brillouin function is given by

$$\mu'(T) = \begin{cases} \phi \tanh\left(\frac{\mu' T_N}{\phi T}\right) & \text{for } T \leq T_N \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

and Eq. 1 is solved numerically to obtain μ' . In order to account for any residual magnetic order, which may be due to coarser-grained material, the function used to represent the data, $\mu(T) = \mu'(T) + C$, includes the constant C . The parameters ϕ , T_N and C were optimized to produce the best-fit curve shown in Fig. 1. From this fit a Néel temperature $T_N = 119 \pm 10$ K was deduced for the nanocrystalline portion of the 73 nm grain-sized sample, Sample A.

The sizable error bar on this measurement is due to at least two reasons. Firstly, a lack of data points in the vicinity of the Néel temperature leads to uncertainty in determining its value. Secondly, this mean-field model is oversimplified. In particular, since the Néel temperature depends upon grain-size and since Sample A is composed of grains with a variety of sizes (whose mean is 73 nm), we expect the distribution in grain-sizes to produce a distribution in transition temperatures. A more sophisticated model might replace the single value for T_N in Eq. 1 with a distribution of values reflecting the distribution of grain sizes in Sample A. To a limited extent this was done in the present model, since the residual magnetic order above 119 K was represented by a magnetic moment that was constant over the measured temperature interval.

If the grain-size distribution of Sample A were unimodal, and the suppression of the Néel temperature continuous with grain-size, then a

decrease in the residual magnetic moment above 119 K would be anticipated as temperature is increased; however, the residual moment appears to be constant above T_N . Either the grain-size distribution is not unimodal, or the suppression of the Néel temperature varies rapidly or becomes discontinuous at a critical grain-size, γ_c . In the former instance, the distribution of grain-sizes in Sample A might be bimodal with a large fraction of the material having particle sizes centered about 73 nm, while the remainder may be micron-sized. In this situation, the coarse-grained component would remain antiferromagnetic to 311 K— the Néel temperature of strain-free chromium (the Néel temperature of strained chromium can be as high as 475 K [8]) , and contribute to a measured residual magnetic moment that would be essentially constant in the temperature interval from 6 to 250 K. Evidence for such bimodal grain-size distributions has been observed in nanocrystalline palladium [11]. To date, the resolutions of the neutron powder diffraction experiments have not been adequate to determine whether or not the grain-size distribution of Sample A is bimodal.

Alternatively, the distribution of grain-sizes may be unimodal. For example, many nanocrystalline materials exhibit a log-normal grain-size distribution [12]. The measured moment is related to the product of the grain-size distribution and the magnetic moment per particle, which is proportional to its size or volume (assuming the densities of all particles are the same). In order that the magnetic moment be constant with temperature above 119 K, the Néel temperature of particles greater than a critical size, γ_c , must not depend strongly upon grain-size. In other words, the magnetic properties of particles with sizes greater than γ_c should be no different from bulk chromium.

A value of γ_c can be estimated, since the residual moment above 119 K is about 38% of the total moment, and the mean of the log-normal distribution is 73 nm for Sample A. If the geometric standard deviation of the distribution has a value of 1.5, which is typical of nanocrystalline powders made using the gas-condensation-technique [12], then a value of $\gamma_c=160$ nm is obtained. If this explanation for the residual magnetic moment above 119 K is correct, then particles greater than 160 nm will remain antiferromagnetically ordered until the bulk Néel temperature, while the Néel temperature for smaller particles would depend upon their grain-size.

A Néel temperature could not be deduced for Sample E— the 11 nm grain-sized compacted nanocrystalline chromium sample, since the magnetic 100 Bragg reflection from this sample was not observed even at a temperature as low as 6 K. If this finer-grained sample were to become antiferromagnetically ordered, either it does so at a temperature lower than 6 K, only a fraction of the sample is ordered antiferromagnetically at 6 K and this fraction is too small to produce a detectable signal. Alternatively, it might be possible that the magnetic structure differs for small grain sizes, e.g. for sizes smaller than 20 nm. The spin density wave magnetic structure for bulk chromium originates from a nested Fermi surface, and the electronic properties will be strongly affected as the particle size is reduced and quantum effects become important. However, no experimental evidence of an alternate magnetic structure has been obtained yet.

If the tendency to suppress long-range magnetic order in nanocrystalline chromium is typical of other nanocrystalline materials, then difficulties may

be encountered in the development of new magnetic recording devices that rely on nanometer-sized magnetic particles for high density information storage. On the other hand, the ability to suppress long-range magnetic order by tailoring the microstructure, e.g. grain-size, of the material, may be a useful tool in the development of other future magnetic technologies. For example, magneto-resistive (MR) multilayers are being considered for use as magnetic read-heads. These materials are composed of alternating layers of ferromagnetic and non-ferromagnetic materials, e.g. Fe-Cr or Co-Cu. It may be possible to fashion a different type of MR multilayered material by alternating coarse-grained and nanocrystalline layers of a single material that is ferromagnetic in coarse-grained form, but not ferromagnetic in the nanocrystalline form. Such a device would circumvent chemical incompatibility problems that could arise when more than one chemical species is used. Alternatively, the amount of roughness between adjacent layers in a MR multilayer, an important factor affecting MR, may be more controllable when the multilayer is synthesized from a single chemical species rather than two. Potential cost savings might also be realized by the processing of a single material.

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Figure Caption

FIG. 1 The temperature dependence of the ordered magnetic moment per chromium atom ($\bullet$) obtained from the integrated intensity measurements of the magnetic 100 Bragg reflection from Sample A plotted versus temperature. The solid curve was obtained from a model where the magnetic moment for the sample is the sum of the moment for the smallest grain-sized component, represented by a Brillouin function, and a residual moment (attributable to a coarser-grained component), which is treated as a constant in the measured temperature interval.

Fig. 1