

Nanocriticality in the magnetic phase transition of CoO nanoparticles

Machteld E. Kamminga^{1,*},† Jonas Okkels Birk,^{1,*}‡ Jari í Hjöllum^{1,2,3,§} Henrik Jacobsen¹, Jakob Lass^{1,2}, Thorbjørn L. Koch^{1,||} Niels B. Christensen⁴ Christof Niedermayer,² Lukas Keller² Luise Theil Kuhn⁵, Elisabeth T. Ulrikkeholm^{1,¶} Erik Brok^{4,#} Cathrine Frandsen⁴ and Kim Lefmann^{1,**}

¹*Nanoscience Center, Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen Ø, Denmark*

²*Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen, Switzerland*

³*Materials Research Department, National Laboratory for Sustainable Energy, Technical University of Denmark, 4000 Roskilde, Denmark*

⁴*Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark*

⁵*Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kongens Lyngby, Denmark*



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The universal theory of critical phase transitions describes the critical behavior at second-order phase transitions in infinitely large systems. With the increased contemporary interest in nanoscale materials, we investigated CoO nanoparticles by means of neutron scattering and found how the theory of critical phenomena breaks down in the nanoscale regime. Using CoO as a model system, we have identified a size-dependent nanocritical temperature region close to the antiferromagnetic phase transition where the magnetic correlation length of the nanoparticles converges to a constant value, which is significantly smaller than that of the saturated state found at low temperatures. This is in clear contrast to the divergence around T_N observed for bulk systems. Our finding of nanocriticality in the magnetic phase transition is of great importance for the understanding of phase transitions at the nanoscale.

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I. INTRODUCTION

A key achievement of statistical mechanics in the last half of the twentieth century is the description of phase transitions and critical phenomena, a universal behavior associated with second-order phase transitions which led to the development of a universal theory of critical phase transitions [1,2]. When a system is brought to a critical phase transition, many of its properties exhibit singular behavior [3]. In materials with magnetic phase transitions, the order parameter is the (sublattice) magnetization, and for anti-

ferromagnets this spontaneous magnetization disappears at the Néel temperature T_N . While spins do not spontaneously (anti)align on the macroscopic scale at temperatures well above T_N , the fluctuating spins remain correlated over a length scale ξ (the correlation length) which grows as T_N is approached.

The degree of singularity or divergence of physical quantities near the critical point is described by critical exponents [4]. The system can be described by the *reduced temperature*, $t = (T - T_c)/T_c$, with T_c being the critical temperature, i.e., T_N for antiferromagnets, and the order parameter follows power laws of t . For example, the antiferromagnetic order parameter, M_{AFM} , obeys $M_{AFM} \propto (-t)^\beta$ in the close vicinity of T_N , where β is the *critical exponent* related to the magnetization. Above the critical temperature, the correlation length of the magnetic order follows a similar behavior, $\xi \propto t^{-\nu}$, where ν is the critical exponent of the correlation length. Similarly, the correlation length of the disordered domains in the ordered phase also follows a power law. Both correlation lengths diverge at the phase transition, indicating that both ordered and disordered phases percolate at T_N , which is a key attribute of critical behavior.

Neutron scattering is well suited to studying critical magnetic behavior, because it provides direct access to the values of the order parameter and correlation length. For example, antiferromagnetic order will lead to additional Bragg reflections in a neutron diffractogram with intensity $I \propto M_{AFM}^2 = (-t)^{2\beta}$, and the magnetic correlation length can be deduced from the width of the reflection. Recent examples of critical magnetic scattering experiments include studies of the magnetic structure of $MnBi_2Te_4$ [5] and the magnetic phase transition of an artificial square ice system [6].

*These authors contributed equally to this work.

†Present address: Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, 3508 TA Utrecht, The Netherlands

‡Present address: Danish Technological Institute, Gregersensvej, 2630 Taastrup, Denmark.

§Present address: Faculty of Science and Technology, University of the Faroe Islands, 100 Tórshavn, Faroe Islands.

||Present address: BK Medical, Mileparken 34, 2730 Herlev, Denmark.

¶Present address: FOSS Analytical, Nils Foss Allé 1, 3400 Hillerød, Denmark.

#Present address: FORCE Technology, Park Allé 345, 2605 Brøndby, Denmark.

**Corresponding author: lefmann@nbi.ku.dk

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While the theory of critical phenomena is, strictly speaking, only valid for infinite systems, micrometer-sized systems are sufficiently large to behave like an infinite system for all practical purposes. However, it is unclear to what degree nanoscale systems can be described by this theory, as the finite size of nanoparticles naturally prevents the correlation length from diverging. Nanoparticles have received increased attention in the last decade for a large variety of both medical and industrial applications [7,8]. These applications include, but are not limited to, batteries [9–13], capacitors [14,15], catalysis [16–23], and gas sensing [24].

In this paper, we investigate the critical behavior in nanoparticles and study how the description of critical phenomena must be adjusted for phase transitions in the nanoscale regime. We use CoO as our model system, as CoO is a structurally simple Ising system and a relatively well-studied material in nanoparticle form [9–29]. Moreover, despite the frustration inherent to its face-centered cubic structure, bulk CoO has a second-order antiferromagnetic phase transition near room temperature (with a critical temperature $T_N \approx 289$ K) [30]. As T_N is close to room temperature, nanoparticles of CoO can be studied in the temperature region near T_N without the samples being destroyed by heating. In the antiferromagnetic phase, the magnetic structure is given by alternating planes of ferromagnetically aligned spins that align antiferromagnetically along the (111) direction, similar to MnO, FeO, and NiO [31]. Moreover, critical magnetic neutron scattering experiments on bulk single crystals of CoO were performed about half a century ago [32,33].

By means of neutron scattering, we show that in contrast to micrometer-sized CoO, the theory of critical phenomena breaks down for CoO nanoparticles. Furthermore, we qualitatively support our experimental observation of this nanocritical behavior by Monte Carlo simulations. Our findings provide an additional branch to the theory of critical phenomena, which is important to the understanding of magnetic phase transitions in nanosized or confined systems.

II. EXPERIMENT

The CoO nanoparticles were prepared by a method similar to one previously reported [34]. Here, $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$ was suspended in ethanol, baked at 100 °C, and consecutively annealed at a temperature between 325 and 425 °C under constant argon flow to remove acetic acid and water. By increasing the temperature and annealing time, the particles were allowed to grow together, resulting in larger-sized particles. The samples produced with this method are approximately spherical [34]. Three CoO nanoparticle samples were obtained with nominal diameters of 20, 30, and 40 nm. The samples were characterized by x-ray diffraction on a Rigaku rotating anode using Cu-K α radiation with a wavelength $\lambda = 1.54$ Å. As shown in the Supplemental Material (SM) [35], the crystalline size of the nanoparticles was determined to be 21.3(8), 29.3(4), and 41.7(5) nm, respectively. For comparison, a sample of micrometer-sized CoO particles was commercially purchased (95%; Sigma-Aldrich).

Neutron diffraction was carried out at the Paul Scherrer Institute (Villigen, Switzerland) [36], using the RITA-2 cold-neutron spectrometer [37] in two-axis mode with a wave-

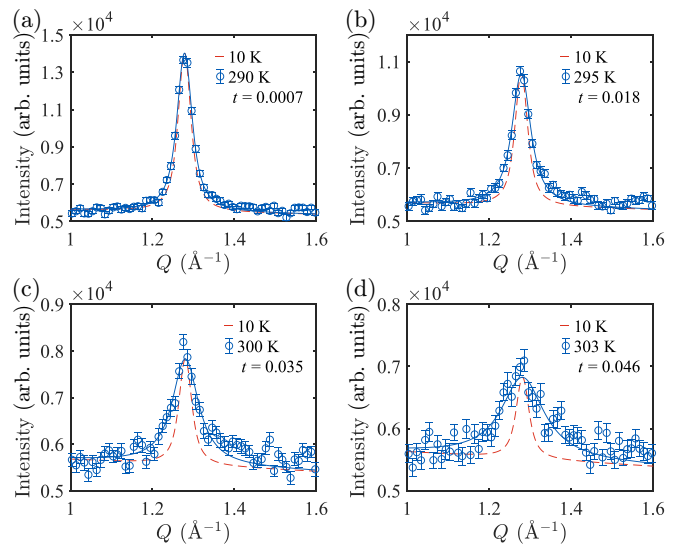


FIG. 1. Development of critical scattering near the antiferromagnetic phase transition in 30-nm CoO particles, at (a) 290 K, (b) 295 K, (c) 300 K, and (d) 303 K. The measured neutron diffraction intensities as a function of momentum transfer are depicted in blue (the error bars represent one standard deviation), the fit to the data is given by the solid blue curve (Voigt), and the red dashed curve represents the fit to the long-range ordered signal measured at 10 K, as given in Fig. S3 of the SM [35], but rescaled to match the intensity of each peak.

length of 4.7 Å, taking advantage of the large area of the position-sensitive detector. Additional diffraction data were taken at the cold-neutron powder diffractometer DMC at the Paul Scherrer Institute, using a wavelength of 4.2 Å and the full detector bank covering 80° of scattering angles. We fitted the magnetic peaks using a Voigt function, where the Lorentzian half width at half maximum Γ is the broadening caused by the finite size of correlated domains, and the Gaussian width is the resolution of the instrument, determined by fitting the data obtained on the micrometer-sized particles at 10 K. We also allowed for a sloping background in the fitting.

Unfortunately, the 20-nm data appeared to be of insufficient quality to perform proper data fitting and are therefore excluded from further analysis in this paper (see Fig. S2 in the SM for an example of insufficient data quality [35]). We also note that the work of Ghosh *et al.* demonstrated that very small CoO nanoparticles (<16 nm) contain different magnetic behavior (ferromagnetic interactions) than their larger counterparts, putting a lower limit to the size of antiferromagnetic CoO nanoparticles [27].

III. RESULTS AND DISCUSSION

In our neutron experiment, we observed the critical magnetic scattering around the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ peak. Typical results of the development of this critical scattering in the 30-nm sample for four temperatures above T_N are shown in Fig. 1. The 40-nm sample shows very similar behavior, as will become apparent below. It was not possible to measure the critical scattering at temperatures below T_N , as the very strong signal from the

magnetic Bragg peak overshadows the signal of the critical scattering at lower temperatures. This is in contrast to the work by Rehtin and Averbach, who could easily separate the magnetic Bragg-scattering component in their study on a single crystal with sharp collimation [33]. The fact that we use nanoparticle samples in our study significantly enhances the complexity of our data analysis. However, we were able to investigate the temperature dependence of the magnetic correlation length, and its critical exponent ν , at the phase transition as approached from the high-temperature side.

The magnetic correlation length ξ is inversely proportional to the width of the magnetic diffraction peak: $\xi = 1/\Gamma$, where Γ is the half width at half maximum (HWHM). As shown in Fig. 1, the width of the critical scattering increases with temperature. This means that the size of magnetic domains, measured as magnetic correlation length, is largest at T_N and decreases for increasing temperature, in agreement with the theory of critical phenomena as established for infinitely large systems. However, we observe that the critical scattering as measured very close to T_N [see Fig. 1(a)] is slightly broader than the Bragg scattering measured at 10 K. These low-temperature data correspond to the completely ordered magnetic structure, and the width of the peak is given by the resolution of the instrument and the finite size of the magnetic structure of the nanoparticles. Thus, as expected, the magnetic correlation length appears to not diverge at T_N for CoO nanoparticles, as it does for infinite systems.

In order to analyze the critical scattering data as a function of temperature, it is crucial to precisely determine the critical temperature for each sample, as T_N might depend on the particle size. For single-crystal or micrometer-sized samples, T_N is usually determined by following the sharp magnetic Bragg peak below T_N , fitting the peak intensity in the approximate range $0.1 < -t < 0.01$, with $t = (T - T_N)/T_N$, where we expect the peak intensity to scale as $\propto (-t)^{2\beta}$. However, for the nanoparticles this procedure proved unreliable due to the relatively higher background levels and finite-size broadening of the Bragg peak, giving unacceptable uncertainties of T_N of the order 3–4 K. Instead, we found that for nanoparticles, a much better method was to determine T_N from the high-temperature data. Here, we expect a power-law behavior of the form $\xi \propto t^{-\nu}$, and T_N was defined as the value where the high-temperature data best follow this equation, using a simple χ^2 fit.

For the CoO bulk sample, i.e., the commercially bought micrometer-sized CoO, we performed this power-law analysis of the correlation length, resulting in a T_N of 286.2(4) K and a critical exponent of $\nu = 1.6(4)$. As our obtained value of ν is higher than 0.63, expected for a three-dimensional (3D) Ising system [38], we argue that the CoO system appears to be more complex and cannot be described by such a simple model. In fact, previous work has shown that the critical exponent β (see SM [35]) does not follow the simple 3D Ising model either as it is severely affected by a tetragonal lattice contraction below T_N [39]. We note, however, that in this paper we report experimental values of ν for bulk CoO and further assessment of the origin of this variation in critical exponents is beyond the scope of this work. We also note that with our powder sample we can only investigate the critical scattering above

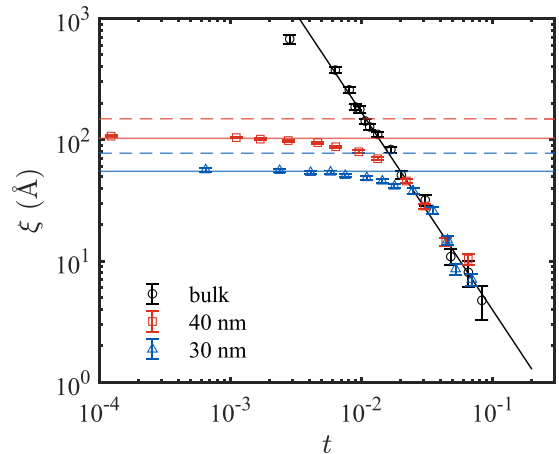


FIG. 2. Correlation length of short-range order for 30- and 40-nm CoO particles as a function of reduced temperature, $t = (T - T_N)/T_N$. The black line corresponds to the power-law fit to the bulk CoO data. The solid blue and red lines correspond to the converged values of the correlation lengths close to T_N for the 30- and 40-nm particles, respectively. The dashed lines denote the correlation length of the corresponding long-range ordered state, measured at 10 K.

T_N , whereas a single crystal would allow for access to the critical scattering also below T_N [33].

The value of T_N is in agreement with the value found by fitting the peak intensity as explained above. Note, however, that this deviates a bit from the expected value of $T_N \approx 289$ K [30]. The reason for this deviation is that the cryostats are calibrated for low temperatures and not for high temperatures, leading to a small offset in the apparent temperature near room temperature. In addition, the samples were not all measured in the same cryostat, and so the offset might be different for different samples. However, as we are mainly concerned with temperature differences, this slight miscalibration cancels out to first order and therefore has minimal impact on our results. For the 30- and 40-nm samples, T_N was determined by fitting the highest-temperature data to the same model as described for the bulk data, using the least-squares method. We argue that this method is accurate, because in the limit of the smallest domain sizes, the size of the particle itself does not matter, and all data should therefore lie on the same line (i.e., the black line shown in Fig. 2). This method yielded a T_N of 289.8(5) and 290.2(4) K for the 30- and 40-nm samples, respectively. Additionally, these Néel temperatures were used to determine the critical exponent, β , of the magnetic order parameter, as shown in Fig. S4 of the SM [35]. We note that the critical exponents to first order do not depend on any uncertainty in T_N .

Figure 2 shows the measured correlation length as a function of reduced temperature for the CoO nanoparticles in comparison to the bulk data. These data clearly show a divergence of the correlation length near T_N , as expected by the universal theory of critical phase transitions [1,2]. However, two different regions are apparent for the nanoparticle data: (1) the region above $t = 0.03$, where the nanoparticle data follow the bulk data, and (2) a converging correlation length below reduced temperatures of $t = 0.01$, corresponding to temperatures between T_N and ~ 292 K. Thus, as expected, no

divergence of the correlation length near T_N is observed for the nanoparticle samples. In fact, the value of the converged correlation length depends on the size of the nanoparticles: 55(2) and 103(2) Å for the 30- and 40-nm particles, respectively. These converged values correspond to roughly 2/3 of those of the long-range ordered state measured at 10 K [77(2) and 149(2) Å for the 30- and 40-nm particles, respectively].

Note that the correlation length of the magnetic domains determined as $\xi = 1/\Gamma$ is not the same entity as the diameter D of the ordered magnetic regions in the nanoparticles at low temperatures. The latter can be calculated using the Scherrer equation, $D = \pi K/\Gamma$, where K is a dimensionless shape factor. Using Scherrer's value of $K = 0.94$ [40], we find $D = 21.3(5)$ nm and $D = 44.0(5)$ nm at 10 K for the 30- and 40-nm particles, respectively. These values indicate that there are magnetic dead layers on the surface of the 30-nm particles, as seen in other nanoparticles [41], while the 40-nm particles are fully ordered. We now focus on the correlation length of the magnetic domains near T_N .

It is logical that no infinitely large correlation lengths can be observed in finite systems; the size of the nanoparticles already provides an upper limit. However, for both sizes of nanoparticles, the converged value of the correlation length only corresponds to about 2/3 of that of the long-range ordered state as measured at 10 K, which is the longest correlation length observed in the particles. This means that no true long-range order exists in the nanoparticles near the phase transition. We therefore conclude that magnetically ordered and disordered domains coexist over a region of a few kelvins around T_N , in what appears to be a semistable equilibrium.

To investigate the behavior of magnetic nanoparticles near T_N in more detail, we carried out classical Monte Carlo simulations using a simple nearest-neighbor Ising model on a cubic lattice with a lattice constant equal to the Co-Co distance in CoO, $a = 4.2615/\sqrt{2}$ Å. To capture the physics of spherical, monodisperse nanoparticles, we used open boundary conditions and included only spins within a sphere of diameter D . We used the Metropolis-Hastings algorithm [42,43], where spin flips that reduce the energy were always kept, and spin flips that increase the energy were kept with a probability of $\exp[-\Delta E/T_s]$, where ΔE is the change in energy and T_s is the simulated temperature of the system. The phase transition was found at $T_s \approx 4.5$. The simulations were carried out on the Quantum Wolf Cluster at the Laboratory for Quantum Magnetism, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland. More details regarding the simulations are given in the SM [35].

For consistency, we analyzed the simulated data using the same approach as for the experimental data. At the lowest temperatures, the intensity is well approximated by a Gaussian, which captures the finite size of the particles. At higher temperatures, the signal broadens and can be described by a Voigt function, in which the Lorentzian part accounts for the additional broadening. Examples of the simulated signal of a 36-nm particle below and above the phase transition are shown in Fig. 3.

Figure 4 shows the correlation length for three nanoparticle diameters as a function of reduced temperature. As for the

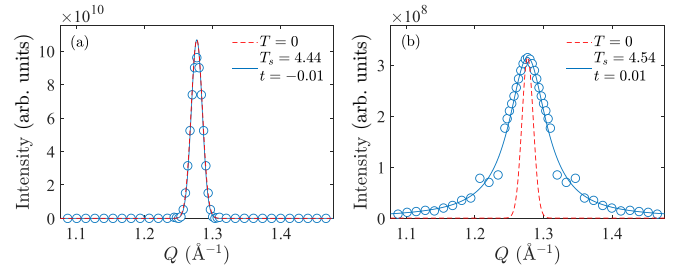


FIG. 3. Simulated scattering (a) below ($t = -0.01$) and (b) above ($t = 0.01$) the magnetic phase transition in a magnetic nanoparticle with a diameter of 36 nm. The fit to the data is shown by the solid blue curve, and the red dashed curve represents the fit to the long-range ordered signal at base temperature, but rescaled to match the intensity of each peak.

experimental data, we calculated the correlation length using $\xi = 1/\Gamma$, where Γ is the HWHM of the signal. There is a clear qualitative agreement between our experimental data and simulations. The simulations show two different regions, one where the correlation length follows the expected bulk behavior and one where it converges to a constant value, indicating a lack of divergence of the correlation length near the critical temperature in the nanoscale regime. Moreover, this value of the converged correlation length depends on the size of the nanoparticles and only reaches a fraction of that of the long-range ordered state obtained at $T = 0$. This is in close agreement with the experimental data. These results indicate that at T_N , the center of the particles orders, while the surface is still mostly disordered. As the particles are cooled further, the size of the ordered region expands.

Note that a quantitative comparison between the experimental and simulated data is compromised by the simplified simple cubic lattice used in the simulations, which does not include the magnetic frustration present in the CoO lattice. For example, the critical exponent of the simulated bulk be-

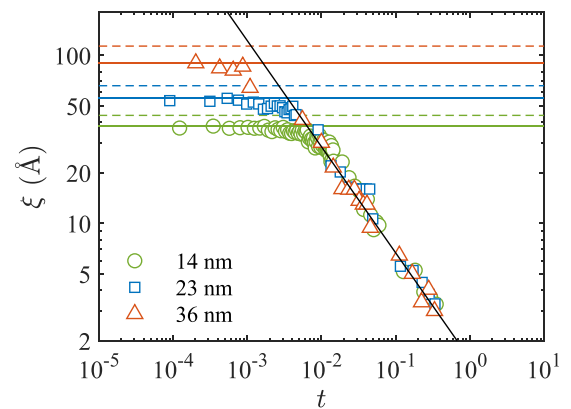


FIG. 4. Correlation length of short-range order for simulated magnetic nanoparticles of different sizes as a function of reduced temperature. The black line corresponds to the expected bulk behavior with $\nu = 0.63$. The solid colored lines correspond to the converged values of the correlation lengths close to T_N for nanoparticles of different sizes. The dashed lines denote the correlation length of the corresponding long-range ordered state, obtained at $T = 0$.

havior ($\nu = 0.63(3)$), corresponding to a 3D Ising system [38]) deviates from that of the experimental data [$\nu = 1.6(4)$], as discussed above.

IV. CONCLUSIONS

In conclusion, we used neutron scattering to measure the critical magnetic scattering near the antiferromagnetic phase transition in CoO at the nanoscale. Our results show that nanoparticles of CoO exhibit a different critical scattering behavior at temperatures close to T_N , as compared with their bulk counterpart. In contrast to the divergence in correlation length observed for larger systems, a converged value of the correlation length close to the phase transition is observed at the nanoscale. Notably, the converged value is significantly smaller than that of the saturated state observed at low temperatures. Moreover, the size of the maximum correlation length depends on the size of the nanoparticles. Our Monte Carlo simulations support our findings of such a converged correlation length near the phase transition. We hereby show that the theory of critical phenomena, developed for macroscopic systems displaying continuous phase transitions, requires modifications when applied to a nanoscale system

in which geometrical constraints on the correlation need to be taken into account. We emphasize that while our study deals with magnetic nanoparticles, such modifications would be required for any nanoscale system.

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