Distinct Magnetic Phase Transition at the Surface of an Antiferromagnet

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In the majority of magnetic systems the surface is required to order at the same temperature as the bulk. In the present Letter, we report a distinct and unexpected surface magnetic phase transition at a lower temperature than the Néel temperature. Employing grazing incidence x-ray resonant magnetic scattering, we have observed the near-surface behavior of uranium dioxide. UO_2 is a noncollinear, triple-**q**, antiferromagnet with the U ions on a face-centered cubic lattice. Theoretical investigations establish that at the surface the energy increase—due to the lost bonds—is reduced when the spins near the surface rotate, gradually losing their component normal to the surface. At the surface the lowest-energy spin configuration has a double-**q** (planar) structure. With increasing temperature, thermal fluctuations saturate the in-plane crystal field anisotropy at the surface, leading to soft excitations that have ferromagnetic *XY* character and are decoupled from the bulk. The structure factor of a finite two-dimensional *XY* model fits the experimental data well for several orders of magnitude of the scattered intensity. Our results support a distinct magnetic transition at the surface in the Kosterlitz-Thouless universality class.

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An interesting question is how the magnetism at the surface of a magnet differs from its bulk magnetism. Understanding the role of the breaking of translational and inversion symmetry and how the bulk structure and order terminate at the surface of materials is the subject of the rich field of electronic reconstruction [1]. The experimental control of such symmetries leads to emergent behavior with charge, orbital, and spin orders not present in the bulk [2]. Moreover, for the case of antiferromagnets, it has recently been shown that spintronic effects can be realized, affording new opportunities for device applications [3].

In magnets, the onset of bulk magnetic order usually coincides with that at the surface having the same transition temperature: the bulk ordering acts as an effective field for the surface [4–6]. Nevertheless, there are extraordinary magnets with stronger magnetic interactions on the surface, which can promote order at a higher temperature than the bulk [7,8]. However, given the coupling between the bulk and the surface, surface antiferromagnetic (AFM) ordering at a critical temperature below the Néel temperature of the bulk has not been reported or predicted yet. Our study provides the first observation of this situation, as well as a theoretical description.

Although surface magnetism has been investigated theoretically for many years [9], there are still relatively few experimental scattering studies. This is in contrast to structural studies, which are well developed. The emphasis on structural transitions is not surprising given the difficulty in studying the magnetic order from effectively hundreds of picograms of material. Only with the photon brightness of a third generation x-ray source and the amplified sensitivity to magnetism afforded by resonant x-ray scattering (RXS) [10] is this feasible. In this work, we utilize both of these developments, together with the enhancement in surface sensitivity arising from grazing incidence. Furthermore, we exploit the large resonant enhancement in the magnetic scattering cross section at the uranium M_{IV} absorption edge [11] to study the magnetism at the surface of antiferromagnetic UO_2.

This dramatic resonant enhancement makes UO_2 the best candidate to observe surface magnetism. In addition, its magnetism gives rise to unexpected behavior close to the surface. For example, at the surface of UO_2, the bulk first-order magnetic transition becomes continuous [12]. UO_2 has the CaF_2 crystal structure, where the uranium (U^{4+}) cations reside on an face-centred cubic (fcc) lattice with eight nearest-neighbor oxygen (O^{2-}) anions forming a cube. Below the Néel temperature T_N, the magnetic dipole and the electric quadrupole moments [13,14] of the two $5f$ electrons on the U^{4+} cations adopt long-range AFM order of the transverse triple-**q** type.

The triple-**q** AFM order results from the balancing of three single-**q** components of AFM order: (001)-type

planes with ferromagnetic and electric ferro-quadrupolar order are stacked antiferromagnetically along the three equivalent $\langle 001 \rangle$ directions. At the same time, the oxygen anion cage that surrounds each U^{4+} cation distorts in such a way that cubic symmetry is preserved. At $T_N \sim 30.2$ K, there is a discontinuous order-disorder transition and for $T > T_N$ the long-range magnetic order, the electric quadrupole order, and the Jahn-Teller distortion of the oxygen cage all disappear [13].

A key technique to provide atomic resolution information on surface ordering is grazing incidence x-ray scattering [15]. The abrupt termination of a crystal at its surface gives rise to rods of diffuse scattering, the so-called structural or charge truncation rods (CTRs), which are parallel to the surface normal and connect the charge Bragg reflections [12]. The variation of the scattered intensity along the CTRs gives information about the electronic charge density near the surface. Analogously, the abrupt truncation of magnetic order at the sample surface gives rise to magnetic truncation rods (MTRs), as shown in Fig. 1. In this Letter we report measurements of MTR scattering that allows us to obtain information about the magnetic configuration near the surface of UO_2.

For the experimental geometry, the RXS signal is sensitive to the component of the uranium magnetic moment parallel to the scattered wave vector ($\mathbf{k}_f$), which lies primarily in the surface (see inset in Fig. 1). The chosen position on the MTR for our measurements is correlated to the depth accessed by our probe; giving a near-surface sensitivity of about 10 nm, measurements at Bragg spots are essentially bulk, whereas away from the Bragg spots the measurements are dominated by surface scattering. A characterization of the temperature dependence of the MTR will therefore allow us to quantify the change of magnetic behavior at the surface.

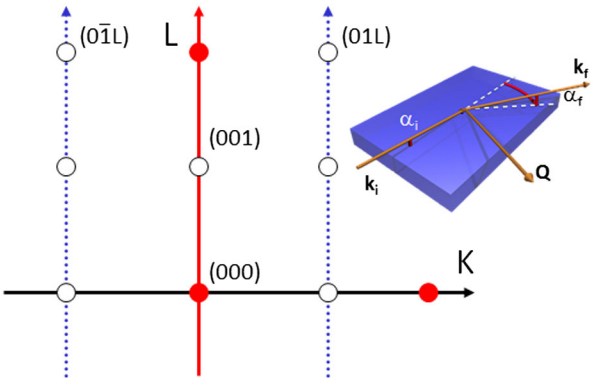

FIG. 1 (color online). fcc allowed structural Bragg reflections in the $(001) \times (010)$ plane: H, K, L are all even or all odd. The structural or charge bulk Bragg spots are solid red. The magnetic Bragg spots are open. The red solid lines show TRs that are both structural and magnetic. The blue dotted lines are pure MTRs. The inset schematically depicts the grazing incidence scattering geometry employed in the experiment. $\alpha_{i(f)}$, $\mathbf{k}_{i(f)}$ are the incident (final) angle and wave vector, respectively. $\mathbf{Q}$ is the wave-vector transfer, which is mainly contained within the surface.

A transverse cut through the bulk magnetic (011) Bragg reflection (open symbols) is shown in Fig. 2 (lower curves) for two temperatures below T_N. There is no change in the observed line shape, which is empirically well described by a Lorentzian function raised to the power of 1.75. Below the bulk ordering transition (T_N), we expect the bulk Bragg reflection line shape to be temperature independent, as observed. In contrast, the magnetic scattering (Fig. 2, upper curves) across the (0 Q_K 0.97) MTR (purely magnetic rod) exhibits a pronounced change in line shape with changing temperature.

The initial working hypothesis is two-dimensional (2D) behavior at the surface region. Indeed, phenomenologically the best fit of the MTR scattering line shape is provided by the structure factor $S(\mathbf{Q})$ derived for a 2D XY model, with a Lorentzian-square distribution of domain sizes. To obtain this structure factor, we followed the derivation by Dutta and Sinha [16] but used the static spin-spin correlation function $\langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(0) \rangle$ [17] in place of the atomic form factor. For large distances the 2D correlation function decays with distance r as $(r/\xi)^{-\eta}$, where ξ is the size of the system, here the in-plane, domain size. The surface domain size, ξ below T_N, where bulk magnetic order is present, is expected to be independent of temperature.

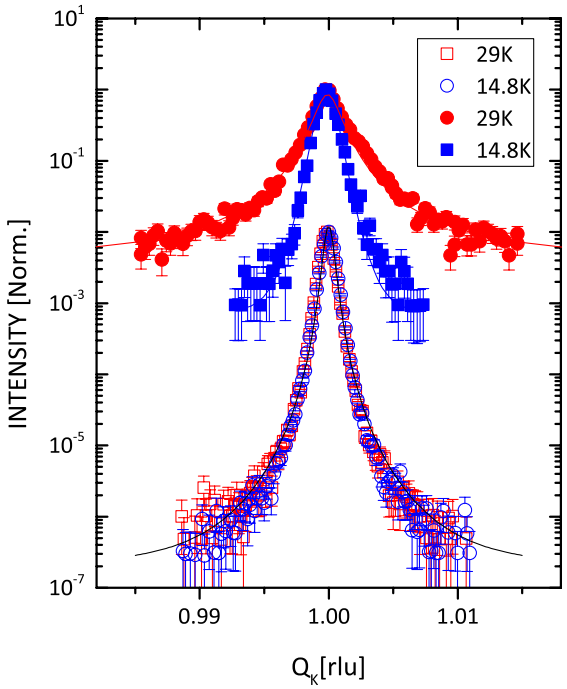

FIG. 2 (color online). Upper curves: The observed normalized intensity (closed symbols) at the magnetic truncation rod (0 Q_K 0.97) for two temperatures below the bulk Néel temperature. Lower curves: The equivalent data (open symbols) for the bulk magnetic Bragg peak (011). The respective data are normalized and offset for clarity. The solid lines are best fits to the model described in the text.

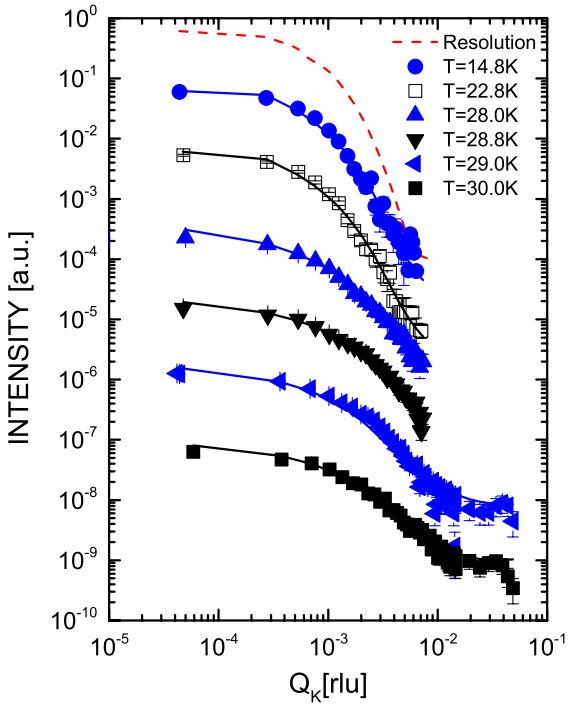

FIG. 3 (color online). Intensities vs wave vector as a function of temperature. One can observe that for temperatures above 22.8 K the reduction in intensity as a function of Q_K is much more gradual (linear) than for lower temperatures, as shown explicitly for two temperatures in Fig. 2. This is a key signature of magnetic roughening. The data are offset for clarity.

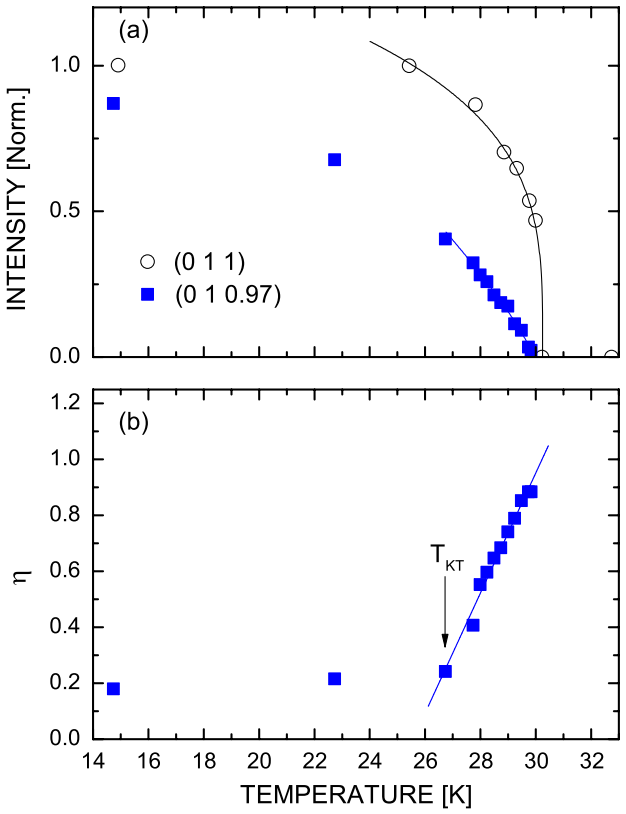

FIG. 4 (color online). (a) Open circles show the integrated intensity of the (011) magnetic Bragg reflection as a function of temperature. The transition is first order (discontinuous). The line connecting the points is a fit to the expression $I_0(1-(T/T_N))^{2\beta}$ with $\beta = 0.3$. The blue squares show the integrated intensity at the MTR (0 1 0.97) near the (011) Bragg spot. The transition at the surface appears continuous. (b) The variation of η as a function of temperature. A discontinuity is identified at a temperature, T_{KT}.

The strength of $\eta \geq 0$ controls how fast spin correlations decay with distance, and thus it is a measure of the disorder of the magnetism at the surface: $\eta = 0$ corresponds to perfect order, while finite values of $\eta > 0$ correspond to quasi–long range order. The explicit form of $S(\mathbf{Q})$ is given in the Supplemental Material [18]. The in-plane domain size at base temperature (15 K) is found to be $\xi = 250 \pm 1$ nm and is consistent with that found in Ref. [12].

In Fig. 3 we show MTR intensities vs Q_K collected at several temperatures below T_N. We also show their fits, with η and the amplitude as the only parameters, using the 2D structure factor $S(\mathbf{Q})$. The quality of the fit is excellent over several orders of magnitude in intensity and all temperatures measured. The dotted (red) line corresponds to $\eta = 0$ and gives the convolution of the delta function $\delta(Q)$ with the experimental resolution.

Finally, in Fig. 4(a) we confirm, with new data, a striking observation first reported in Ref. [12]: the bulk first-order transition at the surface appears continuous. In Fig. 4(b) we show the fitted values of η as a function of temperature. A discontinuity is observed at a new characteristic temperature $T_{KT} = 26.8$ K. Looking forward we shall discuss this transition in the context of the Kosterlitz-Thouless (KT) transition [19,20]. For temperatures below T_{KT} the exponent $\eta(T)$ is almost constant, while above T_{KT}, the exponent η increases rapidly. The critical value, $\eta(T_{KT}) = 0.25$, is consistent with a Kosterlitz-Thouless transition at the surface [19,20].

The KT transition, in two dimensions, is characterized by the appearance of algebraic order in the system; it is associated with vortex unbinding in the original theoretical treatment of the XY model [19,20]. This type of transition is observed in structural surface roughening, which we now briefly discuss, although our magnetic transition corresponds directly to the original theoretical formulation.

The surface roughening transitions and the KT transition are in the same universality class. Below the roughening transition temperature the surface is smooth, while above the surface height is no longer well defined. In a scattering experiment, below the critical temperature, a measurement of the transverse line shape of the CTR should yield a δ function (ignoring resolution effects). Above the critical temperature, the scattering is described by a power-law line shape characterized by the same exponent, η, and giving rise to power-law singularities: $S(q) \propto q^{\eta-2}$. This exponent η is then a measure of the surface roughness.

Surface-induced order-disorder transitions [21] have been observed in a range of systems, including the chemical surfaces of Ag(001) [22] and Cu_3Au [23]. In addition, KT transitions have been also observed recently in trapped atomic gases [24], in exciton-polariton condensates [25], and in a photonic lattice [26]. Even though it was suggested as the archetypal example, an observation in a purely magnetic system is extremely rare and this is the first time that it has been seen at the surface of a three-dimensional magnet.

For a KT transition the basic ingredients are the two spatial dimensions and an XY behavior of the magnetic moments. Therefore the main questions to address the explanation of the present results are (i) whether the surface of UO_2 is decoupled from the bulk, demonstrating 2D behavior, and (ii) whether the surface of UO_2 is then described by an XY Hamiltonian.

In UO_2 and for temperatures below T_N there is simultaneously magnetic [13,14] and electric quadrupolar triple-**q** AFM order, and a Jahn-Teller distortion of the oxygen cage surrounding the U^{4+} cations, which retains its cubic symmetry following the triple-**q** bulk order of the U^{4+} cations. In the following analysis we subsume into a generic anisotropy a potentially essential ingredient, namely the Jahn-Teller distortion of the oxygen cage.

The unusual and sophisticated transverse triple-**q** magnetic order only occurs in geometrically frustrated geometries, such as UO_2, with the uranium atoms sitting on a fcc lattice [14]. The main sophistication is that there are three styles of long-range order, and each of these states are simultaneously present in equal amounts in a triple-**q** magnet.

The triple-**q** states have several unusual characteristics. Firstly, due to the noncollinear spins, there is a huge magnetoelastic coupling which leads to hybridization between phonons and spin waves [14,27]. Secondly, and more pertinent, the spins can heal disorder [28]: neighboring noncollinear spins can rotate a component parallel to each other locally and the ordering can be subtly altered in such a way that usual magnets cannot. Indeed, the low-energy spin wave corresponds to precisely such distortions, which are energetically the lowest-energy fluctuations of the magnet.

The relevant Hamiltonian of a triple-**q** magnetic structure has been discussed previously [29]. It includes a Heisenberg term as well as some anisotropic ones. The small spin-wave gap, observed in UO_2, at the magnetic reciprocal lattice points [30] demonstrates that the Heisenberg energy dominates and indicates that multiple-**q** deformations are the lowest-energy magnetic excitations. However, the anisotropic terms lead to the stability of a triple-**q** structure.

It is essential to understand how this Hamiltonian is optimized in the presence of a surface. The surface severely affects one of the three equivalent triple- **q** magnetic structures. Starting from the triple-**q** state in the bulk it seems natural to eliminate this third component and leave a double-**q** state at the surface which tolerates the loss of bonding. The energetic expense is the anisotropy energy and the balance between these two energy scales determines how the angle ψ, between the moments and the cube axes, changes smoothly between the bulk value $\psi_\infty = 35.26°$ ($\psi_\infty = \arcsin(1/\sqrt{3})$) for the triple-**q** state and the surface value $\psi_0 = 0°$ for the double-**q** state. This picture has been confirmed by classical Monte Carlo simulations of finite clusters with periodic boundary conditions in the xy plane of the fcc lattice (with area $L_x \times L_y$) and open boundary conditions in the z direction (which extends from $-L_z/2$ to $+L_z/2$ so that the plane perpendicular to the z axis at $z = 0$ represents the bulk of the crystal). Finite-size scaling then confirms that the triple-**q** antiferromagnetism becomes double-**q** as the surface is approached. These calculations clearly establish the XY character of the magnetic structure and the absence of a moment perpendicular to the surface. The details of these calculations, which partly contribute to the explanation of a KT transition, are beyond the scope of the present Letter and will appear elsewhere.

In UO_2, in-plane deviations from the double-**q** surface state are only weakly coupled to the bulk and with nearly isotropic, plane-rotor character. There is a weak residual crystal-field potential, which at low enough temperatures destroys the isotropy in the xy plane. Because the surface-bulk coupling does not vanish, thermodynamically no order that exists in the bulk can disappear sharply below the surface. Given that all three triple-**q** order parameters are present up to the first-order transition in the bulk, in principle none of these orders can control a surface transition. However, the analogy with similar unusual behavior in the bulk helps to explain our findings.

In Sr_2YRuO_6, a partial long-range ordered state with coupled alternate AFM $YRuO_4$ square layers coexisting with the short-range correlations is developed below $T_{N1} = 32$ K and a second transition to a fully ordered AFM state is developed below $T_{N2} = 24$ K [31]. The reduced dimensionality of the spin correlations is arguably due to a cancelation of the magnetic coupling between consecutive AFM square layers in fcc antiferromagnets. In UO_2 a similar behavior with more spectacular results comes from the near independence of the surface and the bulk, which are weakly coupled.

The puzzle of understanding the two bulk phase transitions in these type-I antiferromagnets is the same: at intermediate temperatures between the two transitions, the existing order of the higher-temperature phase is expected to influence and keep the lower-temperature phase ordered too. The way out is that the symmetries of the two phases are different. Theoretical studies of the planar rotor model in the presence of a p-fold crystal-field anisotropy establish [32] that above a critical temperature thermal fluctuations saturate the anisotropy field, when $p \geq 4$, and reduce the model to an effectively isotropic planar rotor. At the surface of UO_2, the energy scale of the anisotropy field is the same as the coupling with the bulk, and the excitations of the double-**q** surface state also thermally decouple from the

bulk. Hence, the surface magnetic transition of the UO_2 can be interpreted as the broken-symmetry, double-**q** surface layer pointing along the anisotropy directions, destabilizing into an isotropic, spatially varying, power-law controlled double-**q** state.

The angle that characterizes the style of double-**q** state is the variable that loses its algebraic order, thus providing the second crucial theoretical ingredient of XY model behavior. When in-plane excitations of the surface state become thermodynamically isotropic, they also effectively decouple from the bulk. In the experiment, this is the region where the power-law exponent η increases rapidly with increasing temperature.

As a consequence, the physical picture of the distinct surface behavior of the triple-**q** magnetism in UO_2 now emerges. The bulk has a triple-**q** state with a spin-wave gap that softens close to T_N. The expected bulk transition to a spatially varying multiple-**q** magnetism is very well characterized as a first-order transition. At the surface, the spins flatten, providing a local double-**q** state with weakened anisotropy. This state does indeed suffer a continuous transition to a 2D, spatially varying double-**q** state at a different characteristic temperature.

The observed remarkable effect of the surface, seemingly acting differently from the bulk, is a consequence of the magnetic frustration; this can lead to a two-step process towards final order, both in the bulk and independently on the surface. This phenomenon has been revealed as a result of the advancement of the x-ray magnetic scattering technique at third generation synchrotron sources. By producing epitaxial nanoscale thin films of UO_2 it should be possible to induce finite-thickness effects, thereby stabilizing uniquely the double-**q** state which would then be accessible by the methodology outlined in this work. The sharp changes in the correlation functions and the subsequent analysis is consistent with the scenario of a surface phase transition in the universality class of Kosterlitz-Thouless, the ramifications of which should be further investigated theoretically.

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