Observation of Two Length Scales in the Magnetic Critical Fluctuations of Holmium

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The short-ranged correlations associated with magnetic ordering in the rare earth antiferromagnet holmium have been characterized in high-resolution x-ray and neutron scattering studies. We find that within about 2 K of T_c, the magnetic fluctuations exhibit two length scales, instead of one as expected in an ideal system. This result is reminiscent of behavior observed at the cubic-to-tetragonal structural phase transitions of the perovskites.

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A central feature of our understanding of second-order phase transitions is the appearance near the transition temperature T_c of large scale, coherent fluctuations. As the temperature T approaches T_c, the average size of the fluctuating domains diverges as $\xi \sim |T-T_c|^{-\nu}$, where ξ is the correlation length and the exponent ν is determined by the universality class of the transition. In this paper we report the results of high-resolution x-ray and neutron scattering studies of the critical fluctuations in the spiral antiferromagnet holmium. Holmium was chosen, in part, because the intensity of the x-ray resonant magnetic scattering is large and well understood [1]. In addition, the critical behavior of this material remains controversial, as we shall discuss below. The main result of this work is that within about 2 K above T_c the magnetic critical scattering exhibits two components, one broad and the other narrow. Thus, instead of the single length scale predicted for a second-order phase transition in an ideal system, there are two length scales. These surprising results are reminiscent of the two-component line shapes observed in the structural transitions of the perovskites [2]. There, the second length scale is thought to originate from random defects, and it may be related to the observation of two time scales in the "central" peak problem [3]. However, it is also possible that the second length scale observed in holmium is induced by surface-related effects. Magnetic correlations with two length scales have been observed [4] in x-ray scattering studies of the random-field Ising antiferromagnet $Mn_{1-x}Zn_xF_2$, and in this case the longer length correlations have been directly related to surface preparation.

We first summarize current knowledge of the behavior of holmium. The crystal structure is hexagonal close packed with lattice constants $a=3.58$ Å and $c=5.62$ Å at room temperature. Below the transition temperature, $T_c \sim 131.2$ K, the magnetic moments are confined to the basal planes and exhibit spiral magnetic order [5], propagating along the c-axis direction. The magnetic diffraction pattern consists of pairs of satellites offset from each of the chemical Bragg reflections by $\Delta\mathbf{Q}=(0,0,\pm\tau)$, where τ is proportional to the turn angle per atomic plane. The transition at 131.2 K has previously been investigated by a number of techniques, including neutron diffraction [6], specific heat [7], and high-resolution dilatometry [8]. Most of these experiments have indicated that the transition is second order; however, the dilatometry experiments suggest that it is weakly first order. Assuming a second-order transition, neutron scattering experiments [6] have determined the values of the critical exponents to be $\nu=0.57\pm0.04$, $\gamma=1.14\pm0.1$, and $\beta=0.39\pm0.04$. In early measurements of the specific heat, Jayasuriya, Campbell, and Stewart [7] deduced $\alpha=0.27$ near T_c, and suggested a crossover to a different universality class at reduced temperatures $(T-T_c)/T_c<10^{-3}$. Wang, Belanger, and Gaulin [7] have recently questioned the existence of a crossover and concluded that α lies between 0.1 and 0.2. It is worth noting that the complete set of experimental values for the exponents is not consistent with the scaling relations $\alpha+2\beta+\gamma=2$ and $d\nu=2-\alpha$. Theoretically, Bak and Mukamel [9] calculated the critical exponents $\nu=0.7$, $\beta=0.39$, $\gamma=1.39$, and $\alpha=-0.17$ on the basis of a symmetric $O(n)$ model with $n=4$. More recently, Kawamura [9] considered a more general Ginzburg-Landau-Wilson free energy and proposed a new fixed point of chiral symmetry with exponents $\nu=0.53$, $\beta=0.25$, $\gamma=1.1$, and $\alpha=0.4$. In contrast, Barak and Walker [10] have proposed that the transformation is driven first order by fluctuations, and Azaria, Delamotte, and Jolicouer [10] have suggested that the critical behavior of the spiral rare earths is controlled by tricritical points in their phase diagrams.

Our experiments were performed at Brookhaven National Laboratory in the National Synchrotron Light Source on beamlines X22C and X25, and in the high flux beam reactor on spectrometer H7. In the x-ray scattering experiments, the incident photon energy was tuned to $\sim$8070 eV, which corresponds to the dipole maximum of the resonant magnetic scattering at the L_{III} absorption edge. The highest resolution in these experiments [obtained at the $(0,0,2-\tau)$ reflection] had half-width at half maxima (HWHM) of 0.00029 Å^{-1}, 0.00045 Å^{-1}, and 0.0043 Å^{-1} in the transverse, longitudinal, and out-of-scattering-plane directions, respectively. The neutron spectrometer was configured in an energy integrating double-axis mode (no analyzer) with an incident neutron

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energy of 14.7 meV and collimation 10′-5′-SAMPLE-10′-open. Two magnetic peaks were studied in the neutron scattering experiments. In the low resolution experiments at the $(0,0,2-\tau)$ reflection, the half-widths in the transverse, longitudinal, and out-of-scattering-plane directions were 0.0029 Å^{-1}, 0.0046 Å^{-1}, and 0.042 Å^{-1}, respectively. In the high-resolution measurements performed at the magnetic satellite of the origin $(0,0,\tau)$, the half-widths in the transverse, longitudinal, and out-of-scattering-plane directions were 0.00030 Å^{-1}, 0.0041 Å^{-1}, and 0.033 Å^{-1}, respectively. The c axis face of the sample was prepared by first mechanical polishing and then electropolishing in a passivating methanol-perchloric acid solution. Scanning ion fluorescence measurements yielded no unusual chemical impurities. Structural defects, such as pits, were evident in scanning electron microscopy measurements at micron length scales. The mean-square roughness, as determined by x-ray reflectivity measurements in air, was 20 Å or greater. The sample mosaic determined from x-ray scattering was 0.008° HWHM. In all the experiments, the sample was mounted in a closed-cycle helium refrigerator (different for the x-ray and neutron experiments) with temperature stability of 0.01 K over several hours. For each data set the temperature dependence of the magnetic peak intensity within ~ 1 K below T_c was fitted to a power law $I \sim (T_c - T)^{2\beta}$. These fits revealed variations in T_c from cycle to cycle which were typically a tenth of a degree Kelvin. It is not known whether these deviations reflect the accuracy of the thermometry, the uncertainty in the determination of β, or possible hysteresis near T_c. The average values for β extracted from the fits were $\beta = 0.3 \pm 0.1$ for neutrons and $\beta = 0.37 \pm 0.1$ for x rays. The differences between our x-ray and neutron results may arise from extinction effects in the neutron scattering experiments. We note that the x-ray results for β agree with the neutron results [6] of Brits and de V. du Plessis and Eckert and Shirane.

The main results of our work are presented in Fig. 1, where transverse scans are plotted for several temperatures and three experimental configurations. High-resolution x-ray scattering results are shown in the left-hand column, low-resolution neutron scattering results in the middle column, and high-resolution neutron scattering results in the right-hand column. The top row shows scans taken below T_c which illustrate the resolution limits for the respective experimental conditions. The center and bottom panels show scans taken at temperatures increasing above the transition. The most striking feature of the data is the existence of two components in the magnetic scattering above T_c. Comparison of the scans in the middle row indicates that the narrow component is preferentially detected by x-ray scattering, while the broad component is dominant in the low-resolution neu-

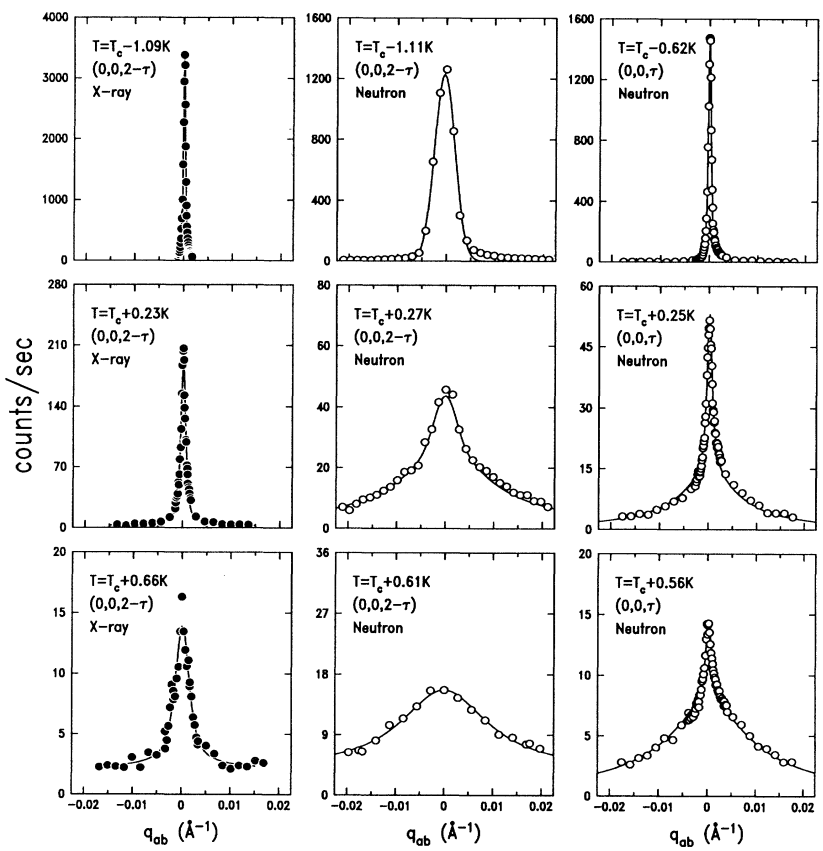

FIG. 1. Transverse x-ray and neutron scattering scans taken at the $(0,0,2-\tau)$ and $(0,0,\tau)$ magnetic peak positions. The scans in the top row of the figure were taken at temperatures below the transition, and represent the resolution of the different experimental configurations. The center and bottom rows show critical scattering observed at temperatures above the transition. The solid lines represent fits to the Lorentzian plus squared-Lorentzian line shape discussed in the text.

tron scattering data. Both components are visible in the high-resolution neutron scattering scan. We have confirmed by direct simulation that these differences in sensitivity to the broad and narrow components can be accounted for by differences in the three-dimensional resolution functions. The low-resolution neutron scattering scans above T_c show little indication of a narrow component. This agrees with previous neutron scattering experiments which were all performed in a low-resolution configuration, and explains why the narrow component has remained undetected until now. The high-resolution neutron scattering scans in the right-hand column suggest that the intensity of the narrow component decreases more rapidly with temperature than the broad component. In fact, the narrow component was not visible for temperatures above ~ 2 K in either the x-ray or high-resolution neutron scattering data, while the broad component was still visible 10 K above the transition.

The lines through the data in Fig. 1 represent fits to the following expression convolved with the appropriate resolution function [11]

$$I(\mathbf{q}) \sim \chi \Big/ \left[1 + \frac{q_a^2 + q_b^2}{\kappa_{ab}^2} + \frac{q_c^2}{\kappa_c^2}\right] + \chi_2 \Big/ \left[1 + \frac{q_a^2 + q_b^2}{\sigma_{ab}^2} + \frac{q_c^2}{\sigma_c^2}\right]^2 .$$

Here χ is the susceptibility, κ_{ab} and σ_{ab} are inverse correlation lengths within the basal plane, κ_c and σ_c are inverse correlation lengths along the c axis, and $\mathbf{q} = (q_a, q_b, q_c)$ is the deviation from a magnetic Bragg reflection. The use of a squared-Lorentzian line shape to fit the narrow component was motivated by previous work on structural phase transitions [2]. The solid lines through the x-ray data represent fits to the above equation with the width of the Lorentzian term determined by the neutron scattering results at the same temperature. The Lorentzian plus squared-Lorentzian line shape provided a satisfactory description of the data (with an uncertainty of 0.1 K in the determination of T_c), but this description is not unique. For example, the x-ray scattering data were also well described by a single component Lorentzian line shape. A detailed discussion of our analysis will be given elsewhere.

The half-width at half maximum (HWHM) of the broad and narrow components (κ_{ab} and $0.64\sigma_{ab}$) are plotted against the reduced temperature $t = (T - T_c)/T_c$ in Fig. 2. These data were extracted from fits to the Lorentzian plus squared-Lorentzian line shape described above. Fits to alternative two-component line shapes gave qualitatively similar results. Open and closed symbols give the results of neutron and x-ray scattering experiments, respectively. The temperature at which the narrow component diverted was used for T_c in calculating the reduced temperature t. The results in Fig. 2 show that the broad and narrow components detected by neutron scattering differ by a factor of ~ 10 in magnitude at comparable reduced temperatures. The narrow component detected by x-ray scattering also has a width ~ 3 times larger than the narrow component detected by neutron scattering. While the width of the narrow com-

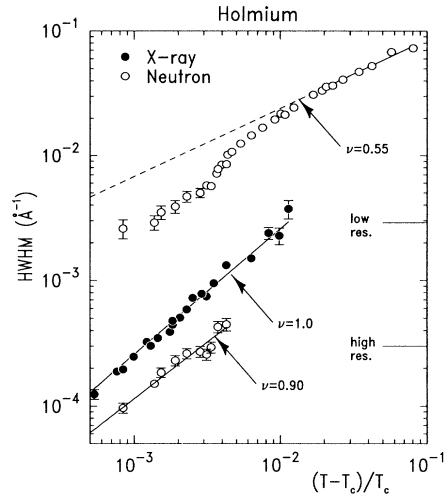

FIG. 2. Half-width at half maxima (HWHM) of the broad and narrow components for scans taken within the basal plane. The solid lines through the data represent fits to a power law HWHM $= \kappa_0[(T - T_c)/T_c]^\nu$. The resolution limits for the various configurations are shown to the right of the data. The low-resolution neutron scattering limit is identified by "low res.," while the x-ray and high-resolution neutron scattering limits are identified by "high res."

ponents as detected by both x rays and neutrons shows power law behavior, the neutron scattering data for the broad component do not follow a single power law over the entire temperature range for which it was observed. This conclusion holds even when the transition temperature used in calculating the reduced temperature $t = (T - T_c)/T_c$ is varied. The breakdown in power law behavior of the broad component occurs when the narrow component first becomes observable, which suggests that the two phenomena are related. Fitting to a power law form for the half-widths, HWHM $= \kappa_0 t^\nu$, we have extracted the parameters ($\kappa_0 = 0.0021$ Å^{-1}, $\nu = 1.0 \pm 0.2$) for the narrow component of the x-ray scattering data and ($\kappa_0 = 0.0007$ Å^{-1}, $\nu = 0.90 \pm 0.3$) for the narrow component of the neutron scattering data. For the broad component detected by neutron scattering we have fitted only the data for temperatures larger than ~ 2.5 K above the transition; a power law fit over this temperature range gave ($\kappa_0 = 0.021$ Å^{-1}, $\nu = 0.55 \pm 0.04$). The half-widths measured along the c axis had exponents ν similar to that along the a axis, but κ_0 was 20% larger in this direction for the narrow component detected by x rays and 25% smaller for the broad component detected by neutrons. Overall, the broad component had power law behavior for temperatures well above T_c which was consistent with Kawamura's theory [9]. The narrow component exhibited power law behavior which is not predicted by any current theories.

A natural interpretation of our results is that the transition in holmium exhibits two length scales near T_c in analogy to the discontinuous cubic-to-tetragonal transitions in the perovskites. In these systems, inelastic neutron scattering experiments on strontium titanate origi-

nally revealed the presence of short-ranged structural correlations with two time scales, with the longer time scale associated with a "central peak" in an energy transfer scan [3]. Subsequently, x-ray scattering experiments also revealed the presence of structural correlations with two length scales [2]. Specifically, the diffraction line shape in momentum space had two components, a broad one originating from a soft phonon mode, and a second narrow component. While the origin of the narrow component is not understood in detail, it is generally believed that random defects or impurities nucleate domains with a second length scale [3,12]. In this interpretation the narrow component would exhibit a squared-Lorentzian line shape in momentum space, and this has been found in the perovskites [2]. From this perspective, our results suggest that a small degree of disorder can significantly alter the critical behavior of magnetic systems, with the appearance of a second length scale occurring in this particular case. Interestingly, preliminary inelastic neutron scattering experiments on holmium suggest the possibility of two time scales in the magnetic fluctuations, so a central peak may also exist in holmium. The results of these experiments will be presented elsewhere.

Finally, it is worth commenting on the possibility that the narrow component of the scattering originates in the volume near the sample surface. Because the x-ray penetration depth is $\sim \frac{1}{2}$ μm, while the neutron penetration depth is $\sim \frac{1}{2}$ cm, the x-ray measurements are especially sensitive to the near surface region. Recent studies [4] of $Mn_{1-x}Zn_xF_2$ have also shown that the surface preparation may under some conditions affect the magnetic ordering, at least within an x-ray penetration depth of the surface. To test this idea, we prepared two additional samples with mosaics of 0.014° and 0.048° HWHM and repeated the x-ray scattering experiments. For both samples, the measured x-ray inverse correlation lengths exhibited power law behavior $\kappa_0 t^{\nu}$ with widths comparable to that measured in the primary sample. While these experiments show that the behavior of the narrow component observed with x rays is affected by the gross surface morphology (probably through strain fields), they do not prove that the narrow component originates at the surface. It is interesting to note that experiments with different perovskite samples [2] also failed to show that the long length scale is wholly induced at the surface. Unfortunately, we have not been able in our analysis of the neutron integrated intensities to determine whether the narrow component originates in the "skin" near the sample surface or in the bulk.

In summary, we have measured the critical magnetic fluctuations present near the magnetic ordering transition of holmium using both x-ray and neutron scattering techniques. As a result of the high momentum-transfer resolution, we have found a second, longer length scale in the critical fluctuations near T_c. The phenomenology of this result is reminiscent of the two-length-scale behavior found in the perovskites. In our view, it seems possible that these effects could be more common in magnetic systems than was previously realized, and they may explain discrepancies between theoretical and experimental values for critical exponents in other materials, such as erbium and thulium [13].

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