Thermodynamic and near-surface correlations in uranium monophosphide

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Inelastic neutron-scattering measurements of the antiferromagnetic fluctuations in uranium monophosphide above, and in the vicinity of the Néel temperature T_N are reported. At the elastic position, with sufficiently relaxed energy resolution to integrate over the low-frequency dynamics, in the immediate neighborhood of T_N a two component wave-vector profile is observed. From measurements of the *inelastic* linewidth as a function of temperature, it is concluded that the ''broad'' component in the scattered wave-vector profile represents the response of conventional bulk thermodynamic fluctuations. These observations, taken in conjunction with an earlier magnetic x-ray-scattering study over a similar temperature interval, strongly suggest that the ''broad'' component observed in the x-ray-scattering experiments has a distinct origin from that observed here. [S0163-1829(98)02830-6]

I. INTRODUCTION

Uranium monophosphide belongs to the family of uranium monopnictides, has a simple NaCl crystal structure (lattice parameter 5.58 Å), and transforms in an apparently discontinuous manner from the disordered paramagnetic state to a simple (commensurate) type-I antiferromagnetic state[1,2] at a temperature T_N close to 121 K. Despite much theoretical effort, the nature of the phase transition from the paramagnetic to antiferromagnetic state remains unclear in this class of materials.[3–6] The understanding of the approach to the ordered state has been further clouded in recent years by the discovery of *two component* line-shape diffraction profiles in a host of different materials undergoing various types of phase transition.[7] Among these are UP and members of the uranium monopnictide family.

UP has been chosen for this study in preference to the other monopnictides since, despite the difficulty in preparing single-crystal samples, it gives no evidence, neither in its bulk properties nor in magnetic diffraction data, for an incommensurate precursor magnetic phase above T_N.[2,8] The type-I antiferromagnetic order, which occurs in the three domains consistent with the cubic symmetry of the NaCl structure, has a propagation vector along equivalent [001] directions with the magnetic sublattice moments parallel to the propagation vector. That is, the antiferromagnetic state consists of alternate sheets of ferromagnetically aligned moments, wherein the moment direction is perpendicular to the sheet and parallel to one of the original cubic axes. We note parenthetically that, although the phase transition must be accompanied by a tetragonal distortion, in practice it is so weak that one may continue to use cubic indexing in discussion.

In our previous resonant magnetic x-ray-scattering experiments[8,9] (Refs. 8 and 9, hereafter referred to as I) at the uranium M_4 edge, anomalous, domain-orientation-dependent, antiferromagnetic correlations were found up to temperatures as high as 130 K within the near-surface skin depth probed by the low-energy x-ray beam (typically to a depth of 1500–2000 Å). This work revealed the importance of near-surface magnetization density fluctuations in the approach to the antiferromagnetic phase transition in this material and established its role as a model system to examine the two length scale phenomenon in this class of material.

In the light of these x-ray studies, to further our understanding of the nature of the phase transition and the significance of the two length scale diffraction profiles observed in (I), it became important to establish the detailed spectral form of the *bulk*, dynamic, antiferromagnetic correlations over a similar temperature interval. To this end we report on both elastic and inelastic neutron-scattering measurements undertaken on this material. The experiments were carried out on the same single crystal as used in the magnetization and x-ray-scattering studies (50 mg), which is important since several authors have indicated a sample dependence associated with the observation of the two length scale phenomenon.[10,11]

The summary of the paper is as follows. In Secs. II A and II B the wave-vector dependence and energy dependence of the scattered neutron spectra are discussed, respectively. Above T_N, we find a response consistent with that anticipated from thermodynamic, bulk fluctuations. This is in sharp contrast with the observations by magnetic resonant x-ray scattering reported in (I) where *only* that domain with magnetic sublattice polarization parallel/antiparallel to the sample surface normal was seen to give a signal above T_N. Parenthetically, we note that below T_N the magnetic x-ray scattering (I), in common with the neutron investigations re-

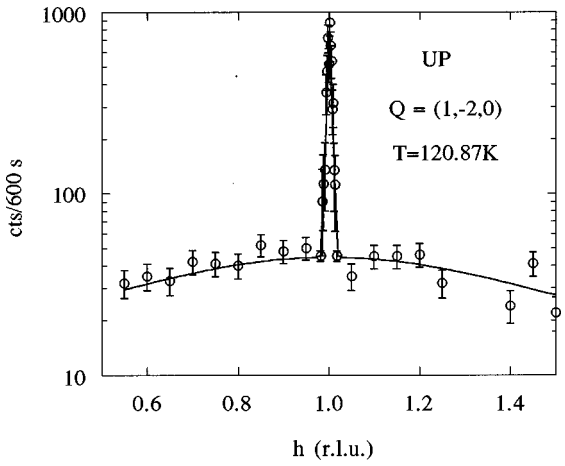

FIG. 1. An example of the two-component line shape (in wave vector) at the (120) position seen in the vicinity of T_N. Data is the difference of the elastic scattering at 120.87 K and 200 K (background) taken with incident neutrons having $k_i = 1.55$ Å^{-1}.

ported here, gave magnetic reflections from domains with propagation vectors both parallel to the sample surface normal and domains where the propagation vectors lie perpendicular to the sample surface normal. Furthermore, in common with the x-ray studies (I), a region of complex behavior is found in the vicinity of T_N. For the sake of discussion, we define a low-temperature regime $T < 120.8$ K, a transition regime around the nominal T_N of 121 ± 0.2 K, and a high-temperature regime $T > 121.2$ K.

In Secs. III and IV we bring together information gathered from bulk magnetization and the neutron and the x-ray techniques. There prove to be *three* characteristic length scales. The sharp component, seen both in x-ray and neutron scattering, is related to bulk antiferromagnetic order; the broad component, observed by neutrons (this paper), arises from thermodynamic fluctuations, and the near-surface, domain sensitive, broad component, characterized previously in resonant x-ray-diffraction experiments, appears to be driven by the break in translational symmetry associated with the sample surface [see also the discussion in (I)]. As derived in (I), there may exist a relationship between the value of the near-surface driven correlation length and the thermodynamic correlation length.

II. EXPERIMENTAL TECHNIQUE AND SUMMARY OF RESULTS

A. Wave-vector dependence of the elastic neutron scattering

Two sets of neutron-scattering experiments were performed on two different triple axis crystal spectrometers, the DN1 spectrometer at the Siloe reactor of the Centre d'Etudes Atomique (CEA), Grenoble, and the IN14 spectrometer at the Institut Laue Langevin (ILL), Grenoble, France.

First, using a well-filtered incident beam of wave vector 2.662 Å^{-1} with the spectrometer centered at the elastic position [energy resolution full width half maximum (FWHM) 0.56 meV] at low temperature in the antiferromagnetic phase, we established the presence of the three type-I antiferromagnetic domains of the NaCl structure. The domains were found to be approximately equally populated and the

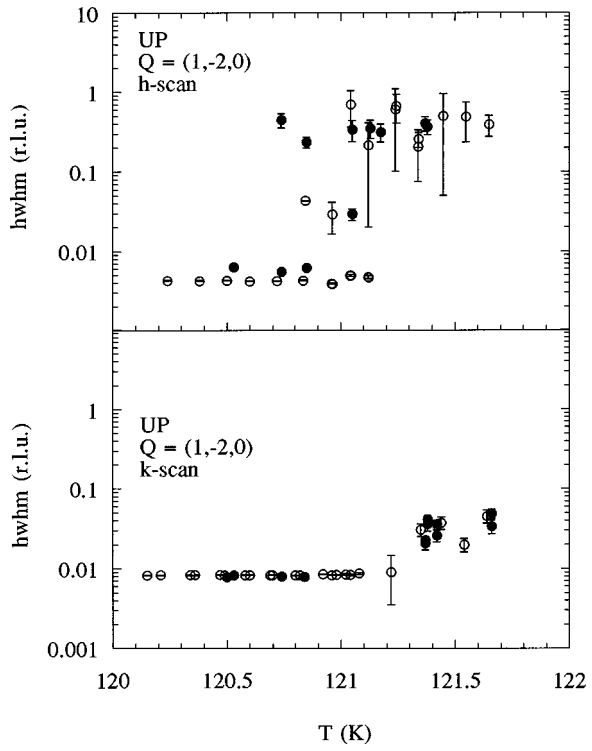

FIG. 2. The widths in reciprocal lattice units (r.l.u.) of the wave-vector dependence of scattered intensity at the (120) reflection as a function of temperature (T) obtained on two separate spectrometers at two different incident wave vectors. The filled and open symbols refer to data from DN1 at Siloe, CEA, Grenoble ($k_i = 2.662$ Å^{-1}), and IN14 at ILL, Grenoble ($k_i = 1.55$ Å^{-1}), respectively. In the upper panel the experimental widths are shown for **Q** parallel to the antiferromagnetic propagation vector. For temperatures in the vicinity of T_N (121 K), the widths of both of the two components to the line shape are given. In the lower panel, widths are given as measured in the direction perpendicular to the sublattice moment and in the scattering plane.

phase transition to the paramagnetic state took place without observable hysteresis over the temperature scale of our measurements (temperature resolution and reproducibility estimated at 0.1 K around 120 K).

The magnetic response in the transition regime about T_N was then measured. As anticipated, the intensity was centered around those points in reciprocal space that were, at low temperatures, the antiferromagnetic zone centers. In this interval one has a two-component line shape in wave vector, Fig. 1. The sharper and more intense component of which, within the resolution of the spectrometer (estimated reciprocal space resolution FWHM$\approx$0.007 Å^{-1}), has no change in linewidth from lower temperatures, appears to correspond with regions of long-range order. The weaker broad component in turn merges smoothly with the quasielastic magnetic scattering at high temperatures (the energy dependence is discussed below) and is identified with the thermodynamic fluctuations. The widths in the wave vector of the broad, quasielastic component, extracted from the data in the vicinity of T_N, are shown in Fig. 2 for the two directions, one parallel and one orthogonal to the direction of the sublattice magnetization of the low-temperature domain. The measurements, made on the two spectrometers at two different incident wave vectors, 2.662 Å^{-1} and 1.55 Å^{-1} (energy

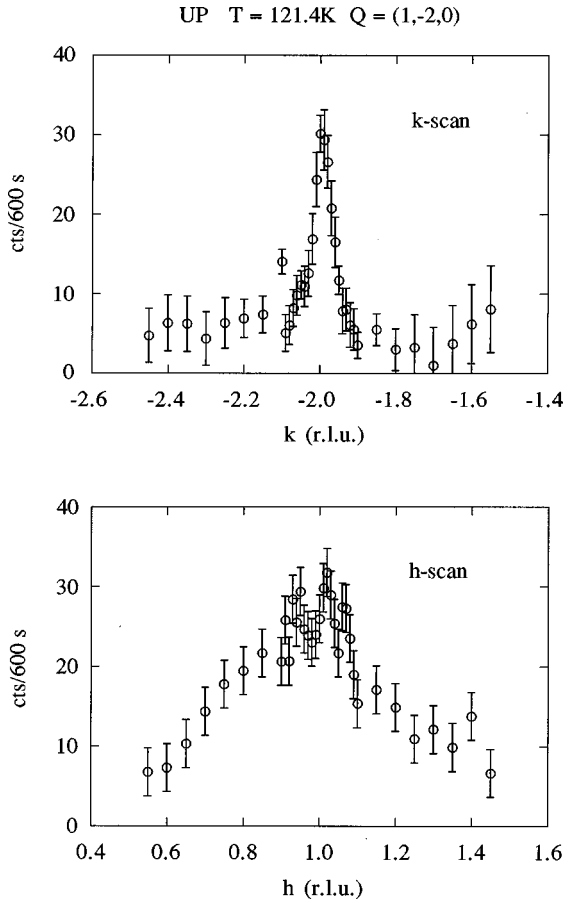

FIG. 3. The highly anisotropic line shape in wave-vector space at the (120) position seen at $T=121.4$ K (above T_N) in UP. The direction h lies parallel, antiparallel to the low-temperature sublattice magnetization directions. The direction k lies in the scattering plane and is orthogonal to the direction h.

resolution FWHM 0.11 meV and reciprocal space resolution ≈ 0.004 Å^{-1}), are represented by the filled and open circles, respectively. The agreement is good and confirms that the neutron spectrometer energy resolution is sufficient to integrate over the fluctuations, at least up to 121.5 K. At higher temperatures our energy resolved studies (below) indicate that the fluctuations have an energy spread substantially beyond that of the resolution at $k_i=1.55$ Å^{-1}, and under these conditions the integration technique would fail to extract reliable q widths. However, for $k_i=2.662$ Å^{-1}, the integration technique should be reliable up to approximately 130 K.

The broad wave-vector component that continues above T_N has typical q widths, respectively, one and two orders of magnitude larger than the q resolution for directions parallel and perpendicular to the domain propagation vector, Fig. 3. This broad response has been measured for points related to all three domains and yields similar results. This observation alone is in stark contrast to the results of (I) where *only* that domain with magnetic moment polarization parallel to the sample surface normal was seen above T_N. Thus, in the temperature interval where the near-surface antiferromagnetic correlations as measured by x-ray scattering are domain orientation sensitive, the bulk (thermodynamic) correlations measured by neutron scattering occur equally for all three domain polarizations. This is a primary result of this investigation and supports the interpretation in (I) that *neither* of the ''two length scale'' components observed in magnetic x-ray-scattering diffraction profiles may be directly identified with the thermodynamic fluctuations.

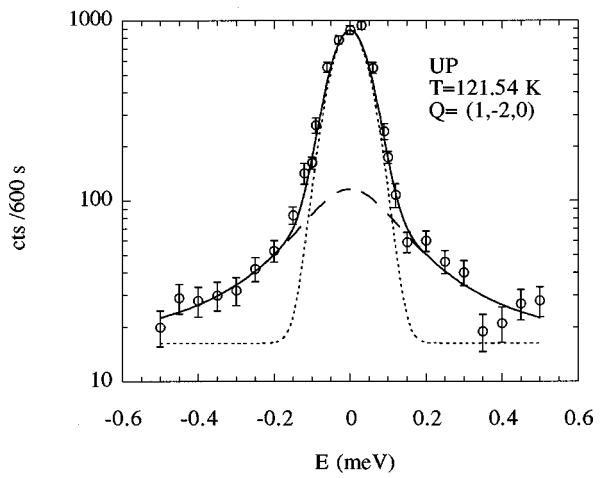

FIG. 4. Inelastic scan taken at $\mathbf{Q}=(1\bar{2}0)$ in the paramagnetic phase of UP. A clear quasielastic peak is seen in addition to the incoherent (elastic resolution limited) scattering. Counting time was 600 s per point.

As in the interpretation of the x-ray-scattering data, it is convenient to discuss the reciprocal of q widths in terms of the number of antiferromagnetic layers, one unit antiferromagnetic layer being taken to have the chemical cell spacing and consisting of one sheet of up-spin moments coupled to one sheet of down-spin moments. The inverse widths of the h scans at (120) correspond with the number of correlated layers in the direction parallel to that of the low-temperature sublattice moment. This number is approximately two antiferromagnetic layers in the temperature range above T_N. That is to say the antiferromagnetic fluctuations consist primarily of bilayers and trilayers even in the immediate vicinity of T_N. No evidence for diverging bulk antiferromagnetic correlations has been found, in agreement with the discontinuous nature of the transition. In the orthogonal direction, that is, lying within a ferromagnetic sheet, the neutrons sense bulk thermodynamic correlations with a typical spatial extent of some 30 cells.

B. Energy widths of paramagnetic excitations

Experiments were also undertaken to examine the energy dependence of the neutron-scattering intensity by antiferromagnetic fluctuations above T_N. A weak signal was observed in addition to the intensity coming from incoherent elastic scattering. This weak scattering is within the resolution centered at zero energy and of Lorentzian line shape in the energy transfer; see Fig. 4. The inelastic response was measured at the wave vector corresponding with that of the low-temperature antiferromagnetic zone center and followed up in temperature to 130 K (Fig. 5). Above this temperature the scattering was very weak, although some signal persisted to around 150 K where it became indistinguishable from the high-temperature background scattering (data taken at 200 and 300 K show no measurable difference).

As seen in Fig. 5, the measured energy linewidth, or inverse relaxation time, decreases as the temperature is

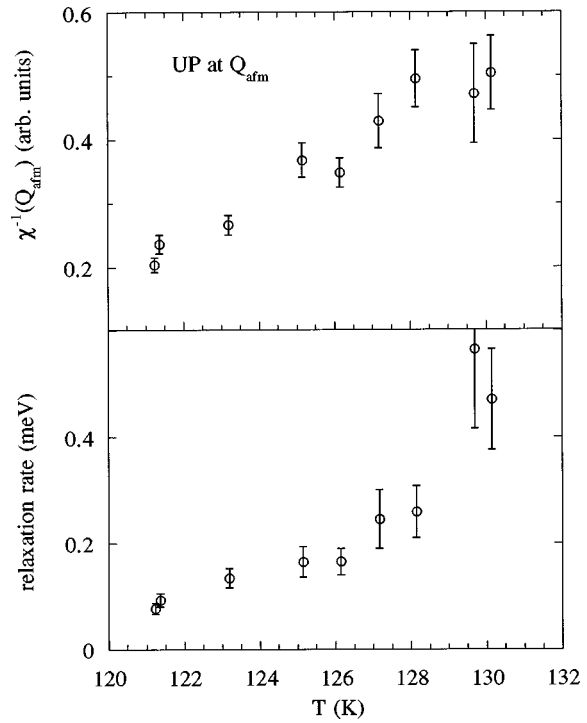

FIG. 5. The temperature dependence of Lorentzian energy half-widths and inverse magnetic susceptibility at Q_{afm}, measured on IN14 at ILL, Grenoble ($k_i = 1.55$ Å^{-1}).

lowered, extrapolating to a finite limit at T_N. In a similar manner the inverse of the intensity of the scattering falls to a finite value at T_N when proper account is taken of the detailed balance and kinematic factors in the cross section. Thus, the behavior of the inelastic component is just that anticipated for thermodynamic fluctuations on approaching a discontinuous phase transition where both the susceptibility and correlation length saturate on approaching T_N.

This inelastic response was seen at those reciprocal lattice points that would eventually become antiferromagnetic zone centers below T_N, having a magnetic propagation vector **q** *not* parallel to $\mathbf{k}_f - \mathbf{k}_i = \mathbf{Q}$, where $\mathbf{k}_i$, $\mathbf{k}_f$ are, respectively, the incident and scattered wave vectors. In contrast, for a reciprocal lattice point where **q** *would* lie parallel to **Q**, no quasielastic intensity was observed. Given that in the ordered state the time-averaged moments lie parallel/antiparallel to the magnetic propagation vector **q**, and that the cross section is sensitive to the transverse component of the magnetization, as expressed through the vector product **M^Q**, it would appear that the fluctuating moments in the paramagnetic phase have no significant transverse components.

III. DISCUSSION

The combination of the wave-vector-dependent and energy resolved studies indicate the presence of strongly polarized, longitudinal, fluctuations that exhibit the characteristic response of bulk thermodynamic modes. Given the antiferromagnetic structure, such longitudinal fluctuations in the paramagnetic state, as inferred from the measured scattering amplitude, may arise either from fluctuations in the local magnitude of **M** or from a fluctuating correlation length in the ferromagnetically aligned sheets of moments. We are unable to distinguish the two effects in these experiments.

From the wave-vector-dependent studies (Figs. 2 and 3) one knows that the magnetic fluctuations of the paramagnetic phase in the vicinity of T_N have condensed to form spatially extended sheets of ferromagnetically aligned moments that are coupled together in magnetic bilayers and trilayers. The relative values of the intraplane to interplane coupling associated with these layers may be estimated with a simple mean-field model.

One imagines the ''up''- and ''down''-spin sheets as two sub-systems with magnetizations of $\mathbf{M}_1$ and $\mathbf{M}_2$, respectively. For an interplane coupling J, one has

$$\mathbf{M}_1 = \chi_1(\mathbf{H} + J\mathbf{M}_2)$$

and

$$\mathbf{M}_2 = \chi_2(\mathbf{H} + J\mathbf{M}_1),$$

where J (positive) augments $J\,\mathbf{M}_2$ and decreases the effective field on $\mathbf{M}_1$. For the $\mathbf{M}_2$ sublattice, $J\,\mathbf{M}_1$ acts in a similar way. Since the two subsystems are identical, this gives the bulk susceptibility $\chi(0)$ and antiferromagnetic susceptibility $\chi(Q_{afm})$ as

$$\chi(0) = \frac{2\chi_i}{1 - J\chi_i} \quad \text{and} \quad \chi(Q_{afm}) = \frac{\chi_i}{1 + J\chi_i},$$

respectively. χ_i is the susceptibility of one of the subsystems. One sees that the divergence of χ_i may drive the antiferromagnetic susceptibility critical before χ_i itself for an appropriate value of J (negative). In a mean field picture χ_i may be represented in Curie-Weiss form

$$\chi_i = \frac{\chi_0}{1 - J_0\chi_0},$$

where J_0 gives a measure of the Curie-Weiss divergence. From the bulk susceptibility, Fig. 6, one estimates the divergence of $\chi(0)$ around $20\ \mathrm{K} = \Theta$ while $\chi(Q_{afm})$ diverges at $121\ \mathrm{K} = T_N$. The condition of divergence of the staggered susceptibility at T_N and the unfulfilled divergence of the bulk Curie-Weiss susceptibility yields an estimated ratio of coupling constants of

$$\frac{-J}{J_0} = \frac{T_N - \Theta}{T_N + \Theta} \approx 0.57,$$

indicating the relatively stronger internal sublattice coupling associated with the ferromagnetic sheets.

We consider now the difference between the broad component of scattering observed in the vicinity of T_N in the previous x-ray experiments, and the scattering from bulk thermodynamic fluctuations identified here. We return to the Ginzburg-Landau model developed in (I), which takes into account both the discontinuous nature of the phase transition and the surface perturbation. This model demonstrates that, although physically distinct, there should exist a numerical relationship between the value of the near-surface driven correlation length perpendicular to the surface, and hence perpendicular to the sheets of ferromagnetic order, and the corresponding thermodynamic correlation length. Explicitly, one has for the model considered in (I) a free energy of the form

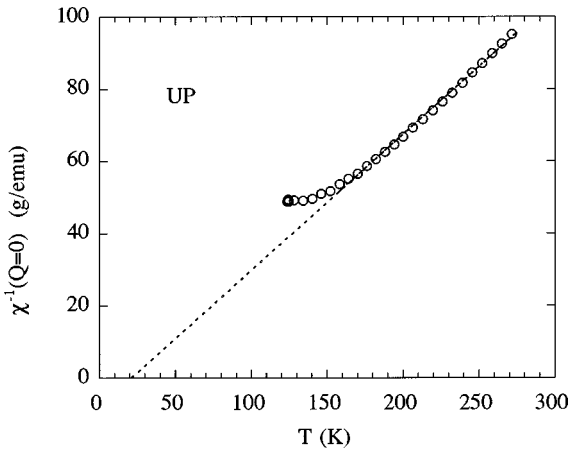

FIG. 6. The temperature dependence of bulk magnetic susceptibility measured on the sample used in these experiments. The data were taken in a commercial squid magnetometer of the ''Quantum'' design at the CEA, Grenoble. The applied field of 500 G used in these measurements was approximately parallel to a fourfold axis of the crystal. From the high-temperature behavior, one extracts a Curie-Weiss moment of $3.4\mu_B$ per uranium atom and a Curie-Weiss temperature of 20 K. The estimated error in a given data point is approximately represented by the size of the symbol.

$$F=\int_0^\infty dz(f_b+f_s),$$

where f_b is a bulk contribution chosen to yield a first-order transition and f_s is the surface induced contribution. This leads to a spatial dependence of the near-surface magnetization (z is the distance down from the surface into the bulk)

$$m(z)^2=m^{*2}\left(\frac{T-T_c}{T^*-T_c}\right)\left[1+\sqrt{\frac{T-T^*}{T^*-T_c}}\sinh(2z\kappa+AS)\right]^{-1},$$

where T^* and T_c are the critical temperatures of the model. T^* corresponds with the temperature at which the free energy passes with its minimum at finite sublattice magnetization through zero. T_c is the point at which the stable state is one of finite sublattice polarization. The scaling parameter m^* is the value to which the sublattice magnetization jumps at T^* in those regions that transform and κ is the inverse thermodynamic correlation length (that may be estimated from the top panel of Fig. 2).

The quantity AS in the above equation and defined below, sets the length scale for the near-surface correlations in $m(z)$. The possibility to have a plateaulike region in $m(z)$ at a given temperature above the bulk phase transition temperature, as observed in the x-ray-scattering experiments, depends on the quantity AS being negative. The spatial extent is given in magnitude as AS times the thermodynamic correlation length. From the explicit equation for AS, one sees that the closer T approaches to T^*, the more negative AS becomes, and hence the larger the region of delocalized or near-surface magnetization. This behavior is distinct from that of the bulk fluctuations, the correlations of which saturate on approaching T_N. Explicitly, the model expression for the parameter AS is

$$AS=\operatorname{arcsinh}\left(\frac{\left(\frac{m^*}{m(0)}\right)^2\left(\frac{T-T_c}{T^*-T_c}\right)-1}{\sqrt{\frac{T-T^*}{T^*-T_c}}}\right).$$

Experimentally, the number of antiferromagnetically correlated layers perpendicular to the near surface observed by the x-ray technique is approximately 4 unit cells or 8 magnetic layers. This is a low multiple of the estimated number of thermodynamically correlated layers in the equivalent direction, the thermodynamic bilayers and trilayers identified in this neutron experiment. The temperature dependence of the thermodynamically correlated and near-surface layers are also different. Taken over the temperature range $121\text{ K}<T<130\text{ K}$, one sees that the near-surface correlations as measured by x-ray scattering arise from a correlated moment that is approximately constant over this interval (Fig. 12 in Ref. 8) while the inverse susceptibility that falls continuously on approaching T_N (top panel, Fig. 5) is indicative of continuously increasing magnetic correlations. The numerical difference in the correlation lengths observed by the two techniques, their different temperature dependencies, and the domain selectivity in the x-ray case (I) and not in the neutron measurements, suggest that there really is a difference between the two broad components. Although one may see two-component line shapes in both neutron and x-ray-scattering experiments (Fig. 1, this paper, and Fig. 5 in Ref. 8), they represent, on the one hand, the bulk thermodynamic fluctuations and, on the other, a surface stimulated correlation length.

IV. CONCLUSIONS

It has been shown that bulk antiferromagnetic fluctuations in UP occurring above T_N have the character expected for thermodynamic modes corresponding to a discontinuous phase transition. The modes have a lifetime that increases but remains finite on approaching the antiferromagnetic phase transition and, in a similar way, the real-space correlation volume associated with the dynamic fluctuations remains finite on approaching the phase transition. These behaviors are consistent with elementary pictures of discontinuous phase transitions. The lack of an observable scattering intensity for fluctuations transverse to the eventual domain sublattice moment direction, and the extreme anisotropy of the measured response in the wave vector, reflect the anisotropy between the intraplanar and interplanar coupling. In summary, it appears from the neutron-scattering work reported here that, over the measured temperature regime, the thermodynamic fluctuations in the paramagnetic state consists of finite lifetime two-dimensional sheets of ferromagnetically aligned moments coupled together in bilayers or trilayers.

The observation that the dynamic neutron-scattering response above T_N peaks, in wave vector space, in the vicinity of all three low-temperature antiferromagnetic zone centers, is significant. This is in contrast to the behavior of the antiferromagnetic near-surface correlations observed by resonant

x-ray magnetic scattering where *only* scattering from that domain with magnetic moment polarization parallel to the sample surface normal was seen above T_N. This observation, plus the saturation of the thermodynamic correlation length, reinforces the interpretation in (I) that *neither* of the two length scale components observed in magnetic x-ray-scattering experiments may be identified with the bulk thermodynamic fluctuations. Finally, through a combination of neutron (this work) and x-ray (I) scattering, we have been able to identify *two* distinct broad components representing bulk thermodynamic fluctuations and a surface stimulated correlation, respectively.

ACKNOWLEDGMENTS

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