Neutron scattering investigation of the phase transitions in uranium arsenide

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A number of neutron elastic scattering experiments are reported on single crystals of the compound UAs. This has the NaCl crystal structure, orders antiferromagnetically with the type-I structure (AF-I) at $T_N \sim 126$ K, and exhibits a first-order phase transition to the type-IA structure at 63.5 K. The most interesting behavior can be studied via the critical (diffuse) scattering near T_N. Above T_N the critical scattering is anisotropic and centered about a wave vector that suggests a tendency to order with an incommensurate structure, but then at T_N suddenly orders with the commensurate type-I ordering. We present a detailed analysis by writing down a Hamiltonian in which the strong cubic anisotropy is included, and then obtain the $\vec{q}$-dependent susceptibility via a mean-field calculation. The resulting parameters show that the z-z exchange interaction within the (001) planes is ~ 40 as strong as the x-x or y-y coupling between the spins. Moreover, the competition within the interactions leads to the system experiencing "frustration" in deciding between AF-I or a sinusoidal spin arrangement, so that the system is in the vicinity of a Lifshitz point. The strong cubic anisotropy is interpreted as arising from bonding effects between the $5f$ wave functions and the anion p orbitals.

I. INTRODUCTION

The uranium monopnictides UX (X = N, P, As, Sb, and Bi) with the NaCl crystal structure form a family of antiferromagnetic compounds in which the Néel temperatures and ordered moments steadily increase from UN (53 K and $0.75\mu_B$) to UBi (285 K and $3.0\mu_B$). In their ordered states all compounds exhibit the type-I antiferromagnetic structure in which ferromagnetic (001) planes are stacked antiferromagnetically, i.e., in the sequence $+-+-$. The moment direction is along the propagation axis and therefore perpendicular to the planes so that for the c domains $\vec{\mu} \| [001]$. Normally, the populations of the a, b, and c domains are equal. In UAs an additional transition occurs to the so-called type-IA structure[1,2] at approximately $0.5T_N$. In this structure the moment direction remains the same, but the stacking of sheets changes to $++--$, so the repeat distance in real space is two unit cells, as opposed to the type-I structure which has the same magnetic and chemical unit cells. The transition in UAs is also accompanied by an increase in the ordered magnetic moment per uranium.[2]

Recently, with the availability of single crystals, many of these compounds have been reexamined. Of particular interest has been the discovery of strong cubic anisotropy in the magnetic interactions. This is seen most clearly by experiments measuring the critical scattering (i.e., the correlations between moments close to the ordering temperature) in UN (Ref. 3) and USb.[4]

In this paper we report a series of neutron investigations on single crystals of UAs. In the first part we describe Bragg scattering experiments characterizing the paramagnetic to type-I structure at T_N, the I-IA phase transition at lower temperature, the shape of the magnetic moment distribution in UAs, and the (unsuccessful) searches for both external and internal distortions in UAs in the ordered state. In the second part we describe the investigations of diffuse scattering above T_N, the Néel temperature. To analyze these results we invoke a Hamiltonian which explicitly incorporates the cubic anisotropy and then use a mean-field approach to calculate the susceptibility. Fitting to the observed diffuse scattering allows us to evaluate numerically the extent of the anisotropy. The results show that UAs at high temperature is in fact near a so-called Lifshitz point[5] at which commensurate and incommensurate phases are in equili-

brium with the paramagnetic phase. The critical behavior of such systems is of considerable theoretical interest at this time.[6]

II. EXPERIMENTAL

The crystals for these investigations were grown in a similar way to that described[7] for USb, i.e., by a recrystallization process when the material is kept ~50 °C below the melting temperature of 2540 °C.

Experiments were performed at both the Argonne CP-5 and Brookhaven High Flux Beam reactors. The initial studies at ANL were done on crystal (I) with a volume of 19.4 mm^3 and with a low-temperature four-circle arrangement capable of examining large portions of reciprocal space.[8] The incident neutron beam of 1.03 Å was obtained from a Ge(311) monochromator, which is essentially free of $\lambda/2$ contamination. No energy analysis of the scattered beam was performed. For the experiments on the critical scattering at BNL a second larger crystal (II) of volume 34 mm^3 was used. A three-axis neutron spectrometer was used with an incident neutron energy of 13.5 meV ($\lambda = 2.46$ Å). Both monochromator and analyzer crystals were graphite (002) and a pyrolitic graphite filter was used to reduce higher-order contamination. The collimation was 20′ throughout the spectrometer. The study of the diffuse scattering was carried out both as a function of momentum and energy transfer, but in the latter case no inelasticity was detected within the instrumental resolution ($\Delta E = 0.4$ meV). A similar lack of inelasticity was observed in the diffuse scattering from USb.[4] At ANL the crystal was placed in a small vanadium can in good thermal contact with a copper block containing the heater and calibrated resistors. The temperature was controlled to ±0.1 K. At BNL the sample was contained in a Al can, filled with He gas at room temperature, and attached to the cold block of a standard CT-14 Cryogenic Associate Cryostat.

III. RESULTS

A. Para-I transition

The results of our neutron study of the 110 type-I magnetic reflection are shown in Fig. 1. Previous studies[1,2,9,10] give $T_N \sim 127$ K and crystal I has a T_N in agreement with this. As we shall see, this value is apparently sample dependent, since crystal II has $T_N = 123.5$ K, very close to the value recently found in heat-capacity studies.[11] Such a variation of T_N, possibly as a function of stoichiometry, has also been observed for USb.[7]

The unusual behavior of the 110 magnetic peak in Fig. 1 shows that the phase transition cannot be

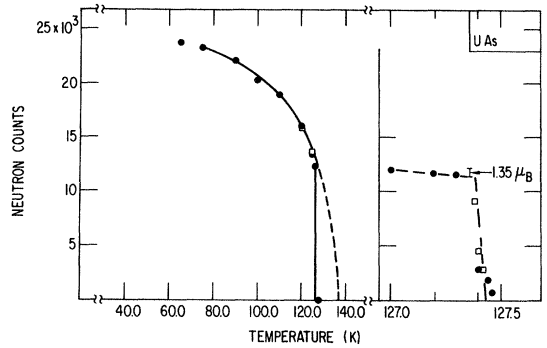

FIG. 1. Integrated intensity of the 110 magnetic reflection from crystal I as a function of temperature. Closed points are taken in cooling, open in heating. Note the expanded temperature scale on the right-hand side figures.

second order. On the other hand, the steady decrease in intensity as the temperature is increased from 80 to 120 K precludes a simple first-order description as well. For want of a better definition we call this a "weakly first-order transition," and its implications are discussed further below. The ordered moment in the type-I phase at 78 K is $1.93\mu_B$/(U atom). The results in Fig. 1 show that 70% ($1.35\mu_B$) of this total moment is ordered by $T_N - 0.1$ K. No hysteresis is observed in this phase transition. The diffuse scattering associated with the type-I transition is discussed in Sec. IV.

B. I-I*A* phase transition

The intensity of the 110 type-I and $11\frac{1}{2}$ type-I*A* reflections have been reduced to moment per U atom and shown in Fig. 2. Note that *no* coexistence of phases occurs; either the magnetic structure is type I or I*A*. A thermal hysteresis of 0.25 K occurs at this transition. In the original work on a polycrystalline sample[2] a large hysteresis of ~10 K was observed, in addition to the coexistence of both I and I*A* phases. These results are clearly a consequence of working with highly strained polycrystalline samples. The single-crystal results of Fig. 2 show unambiguously that the I-I*A* transition is first order and this is supported by x-ray measurements[12,13] showing a volume discontinuity of $(V_{65\,K} - V_{5\,K})/V_{5\,K} = -4 \times 10^{-4}$ at the I-I*A* transition. No observable distortion of the lattice, $|c/a - 1| < 2 \times 10^{-4}$, occurs in the low-temperature phase.[13]

We have also made a number of other searches for effects in the I*A* phase suggested by previous work. Although these are negative results we report them here for completeness.

i. Critical scattering. Searches around both the 110 and $11\frac{1}{2}$ peaks at temperatures very close (0.1 K) to the transition temperature revealed no observable

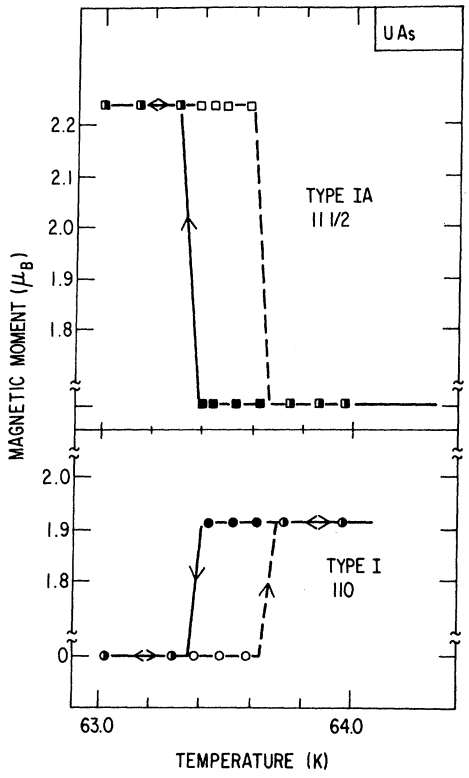

FIG. 2. Magnetic moment in the type-IA and I phases as deduced from the intensities of the $11\frac{1}{2}$ and 110 reflections, respectively. Closed points are taken in cooling, open points in heating.

critical scattering. The absence of such scattering is a further indication of the first-order nature of the transition.

ii. Determination of wave vector. Accurate measurements of the distance between the 111 nuclear and $11\frac{1}{2}$ magnetic peaks showed the wave vector $\vec{q}_{IA} = 0.500 \pm 0.001\,\vec{c}^*$ (i.e., the true type-IA structure in which the repeat distance in real space is given by $1/q = 2$ unit cells).

iii. Anomaly at 41 K. In certain samples, depending on the heat treatment, a discontinuity was found[14] in the susceptibility curves at ~41 K. No evidence of any discontinuity in the intensity or position of the $11\frac{1}{2}$ IA peak were found near this temperature. In fact the intensities of the IA magnetic peaks increase by only 3% in cooling from 60 to 4.2 K.

iv. External distortion. One of the unusual properties of these uranium monopnictides is that they show very little, if any, distortion when ordering magnetically.[13] The symmetry of both the type-I and -IA structures is tetragonal so we should expect a distortion such that $c/a \neq 1$. X rays have a very small penetration depth (~5 μm) for normal Cu $K\alpha$ radiation and uranium compounds so that some doubt exists as to whether they are really measuring bulk effects.[15] The resolution with neutrons is considerably poorer than that obtainable with a back reflection Bond technique, but scans over the 008, 00 10, and 551 peak also show no change in peak width in the IA phase and we conclude from our neutron experiment that $|c/a - 1| < 5 \times 10^{-4}$. (The very small peak broadening seen in our x-ray study,[13] and ascribed to strain effects, is too small to be seen in the neutron experiment.) The value from the x-ray experiment[13] is less than 2×10^{-4}.

v. Internal distortion. Using the results found[16] for UO_2, Cooper[17] proposed that the I-IA transition was driven by the condensation of a longitudinal-optic phonon, resulting in a small displacement of the As ions from their regular lattice sites. If this occurs, one would expect small nuclear reflections to occur at positions $hk\,l \pm \frac{1}{2}$ and the other positions corresponding to a permutation of h, k, and l. This is analogous to what happens in UO_2.[16] These peaks would *increase* as a function of $|\vec{Q}|$, the momentum transfer, as opposed to the magnetic peaks which *decrease* with $|\vec{Q}|$ because of the magnetic form factor. Accordingly, we have made careful scans from 008 to 00 10 and from 550 to 552, but found nothing unexpected. One cannot, of course, totally eliminate the possibility of the formation of a superlattice without exhaustive scans in $\vec{Q}$ space, but for the mechanism proposed by Cooper we can say the amplitude of the displacement must be less than 0.01 Å. In UO_2 the oxygen displacement is 0.014 Å.

C. Magnetic form factor

Measurements of the magnetic form factor yield information about the spatial extent of the unpaired electrons. We reported a detailed study[7] of USb in 1976. The main conclusions of this, and other work on ordered uranium systems,[18] are as follows: (i) It is extremely difficult to tell from these studies if the f electron occupation is $5f^2$ or $5f^3$ (or intermediate) whereas $5f^4$ and $5f^5$ form factors have quite distinctive shapes and can be eliminated. Uranium will thus be in either the $5f^2(U^{4+})$ or $5f^3(U^{3+})$ state, or some intermediate one. (ii) The most useful information can be obtained by studying the anisotropy of the form factor as a function of $\vec{Q}$. For an antiferromagnetic system, in which we cannot make use of the nuclear-magnetic interference term to effectively enhance the magnetic signal, this measurement is limited in practice to measuring the anisotropy of the quadrupole magnetic moment. The quadrupole moment can have two shapes, both of which have cylindrical symmetry about the quantization axis $\vec{J}$. The first is prolate—the shape of an American football, the second is oblate—the shape of a pumpkin or

TABLE I. Analysis of the form factor of UAs at 80 K in type-I phase ($a = 5.768$ Å), q^2 is the square of the magnetic interaction vector, Δf_{obs} is the difference between the f_{obs} values at the same $|\vec{Q}|$ but different directions. $f_{calc}^{USb}(\vec{Q})$ is the calculated form factor for USb ($a = 6.190$ Å at 80 K) taken from Ref. 7. Δf_{calc} is derived from $f_{calc}^{USb}(\vec{Q})$ the same way as Δf_{obs}.

hkl	$\sin\theta/\lambda$ (Å^{-1})	q^2	$f_{obs}(\vec{Q})$	Δf_{obs}	$F_{calc}^{USb}(\vec{Q})$	Δf_{calc}
201	0.194	0.800	0.82(4)		0.846	
112	0.212	0.333	0.82(4)		0.839	
221	0.260	0.889	0.73(2)		0.729	
223	0.357	0.471	0.56(2)		0.585	
401		0.941	0.49(2)	0.07(3)	0.537	0.048
114	0.368	0.111	0.57(5)		0.545	
330		1.000	0.43(3)	0.14(6)	0.507	0.038
314	0.442	0.385	0.40(3)		0.439	
510		1.000	0.35(3)	0.05(4)	0.371	0.068

in its extreme case of a disk. A detailed discussion of the calculation of magnetic form factors is given in Ref. 7, in which we show that for the free-ion $5f^2$ and $5f^3$ states the shapes are prolate. However, in USb the experiment clearly shows the spatial extent of the $5f$ electrons is *oblate*. To demonstrate this directly we define a quantity $\Delta f = f(\vec{Q}_1) - f(\vec{Q}_2)$ where $|\vec{Q}_1| = |\vec{Q}_2|$ and $\vec{Q}_1$ makes a smaller angle with the magnetic moment $\vec{\mu}$ than $\vec{Q}_2$. For a series of reflection pairs $Q_1(hkl)$ and $Q_2(hkl)$ we then plot Δf against $\sin\theta/\lambda[= Q/(4\pi)]$. With an oblate distribution $\Delta f > 0$ whereas for a prolate one $\Delta f < 0$ and the observation of an oblate distribution for USb led us to suggest a rather unusual ground state.

In view of the complex situation existing in understanding the dynamic properties of these materials,[19] we can no longer have confidence in the *exact* ground-state wave function derived in Ref. 7. However, the presence of an oblate quadrupole moment is an experimental fact that is quite independent of the crystal-field–type analysis presented in Ref. 7. As we shall see, this shape plays an important role in understanding the strong cubic anisotropy discussed below. For UAs, therefore, we have examined the form factor specifically for this shape function. To do so we measured a series of integrated intensities at 80 K (type-I phase), averaged the equivalent reflections (usually at least 4) and reduced the structure factors to an effective form factor $f_{obs}(\vec{Q})$. The results are presented in Table I. For pairs of reflections at the same $|\vec{Q}|$ we deduce Δf_{obs} defined as above. Note for three cases $\Delta f > 0$. In Table I we also tabulate the calculated form factor from the USb study and Δf_{calc}. The agreement is quite good and, in particular, the sign of Δf is predicted correctly. Table I should not be construed as a complete form-factor analysis of the uranium moment in UAs, but it does show the similarity between the form factors of UAs and USb. We note in passing that this oblate shape for UAs eliminates the ground-state wave function discussed by Troc and Lam,[10] since this function gives a quadrupole moment which is prolate. We shall return to the shape of the magnetic-moment distribution later.

IV. DIFFUSE SCATTERING ASSOCIATED WITH MAGNETIC ORDERING

A. Experimental

In this section we shall describe the form of the diffuse scattering, a full analysis of which is presented in Sec. IV B. First, partly as a historical note, we present in Fig. 3 the data obtained on a polycrystalline sample of UAs at ANL almost 10 years ago in the course of our studies on the UAs-US solid solutions.[2] Here the diffuse scattering near T_N is clearly not peaked at the 110 position, but at a slightly longer scattering vector. This was not understood at that time and Fig. 3 does not appear in Ref. 2, but after the results on USb,[4] it seemed likely that diffuse scattering occurred in UAs, the first-order phase transition notwithstanding.

More of the nature of the diffuse critical scattering is revealed in studies of single crystals of UAs. A first result, which is also known from studies of polycrystalline samples, was that scans about $\vec{Q}$

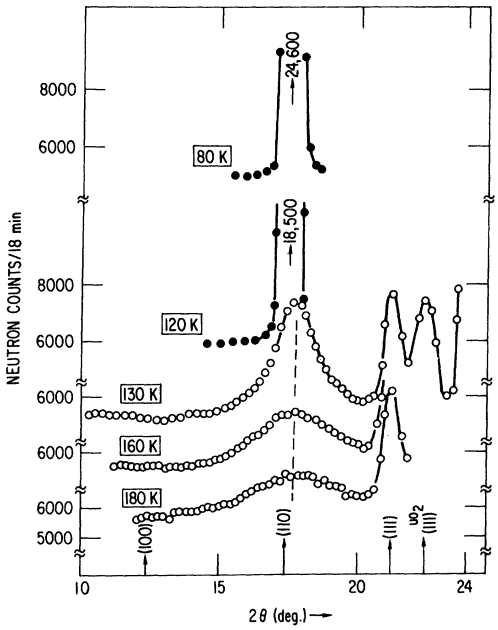

FIG. 3. Data obtained on polycrystalline UAs at several temperatures. T_N was estimated as 126 K. Note the large amount of diffuse scattering, extending up to T_N+50 K, and which near T_N is clearly peaked at a scattering vector longer than $|\vec{Q}(110)|$.

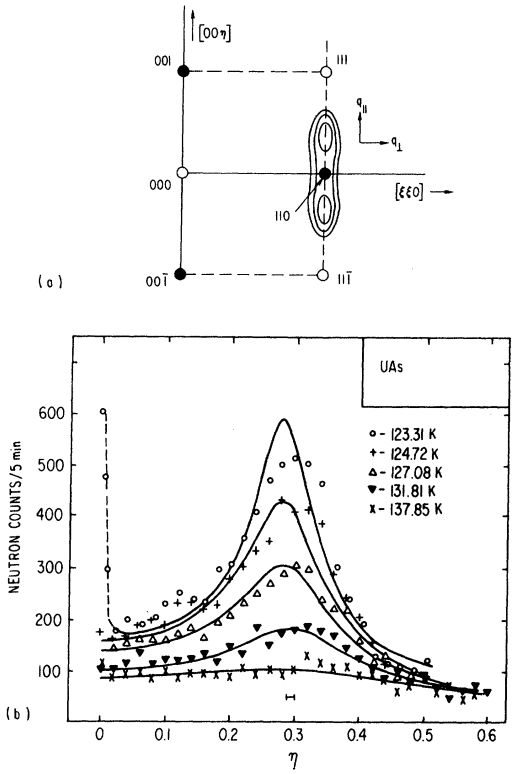

FIG. 4. (a) Upper portion shows the region of the reciprocal space of interest and a schematic of the diffuse scattering intensity around 110. The vectors $\vec{q}_{\parallel}$ and $\vec{q}_{\perp}$ are taken from the 110 point. (b) The open points are nuclear Bragg positions, the solid are magnetic Bragg positions. The lower section shows the intensity of the scattering along $[00\eta]$ from 110 as a function of temperature. The resolution function is shown by the horizontal bar. The solid lines are fits to the data described in the text.

$=(2\pi/a)(0,0,1)$ revealed no magnetic Bragg reflection below T_N. This implies that in the AF-I ordering the spins are aligned along the [001] direction. Also, no critical scattering was observed about (0,0,1) above T_N. Since neutrons couple only to transverse fluctuations of the magnetization, this scattering would involve the transverse components $\chi^{xx}(\vec{q})$, $\chi^{yy}(\vec{q})$ of the susceptibility, and we conclude that for $\vec{q}$ along [001] only $\chi^{zz}(\vec{q})$ shows critical behavior. {By cubic symmetry, critical behavior for $\chi^{xx}(\vec{q})$ for $\vec{q}$ along [100] and $\chi^{yy}(\vec{q})$ for $\vec{q}$ along [010] would be observed around the points $\vec{Q}=(2\pi/a)(0,1,1)$ and $\vec{Q}=(2\pi/a)(1,0,1)$, respectively.} This behavior is similar to that of the critical scattering observed in UN, (Ref. 3) and USb.[4] The scattering at $\vec{Q}=(2\pi/a)(1,1,0)$ will sample fluctuations both parallel and perpendicular to [001], but, as mentioned, the transverse components of the susceptibility are very small so that we measure directly $\chi^{zz}(\vec{q})$ at (1,1,0). Figure 4 shows a study of $\chi^{zz}(\vec{q})$ as measured about (1,1,0). Let us denote deviations from the antiferromagnetic superlattice point $(2\pi/a)$ (1,1,0) by $q_{\parallel}$ and $q_{\perp}$, depending on whether the component is parallel to or perpendicular to [001], respectively. Scans along $q_{\parallel}$, the $[00\eta]$ direction in Fig. 4, reveal the most interesting feature of the diffuse scattering. The point at the origin, $\vec{Q}=(2\pi/a)$ (1,1,0), is the superlattice point of the AF-I structure as measured along [001] from the recriprocal-lattice point $\vec{Q}=(2\pi/a)(1,1,1)$. As the temperature is lowered toward $T_N=123.5$ K, the scattering becomes more intense and peaks at the incommensurate position $\vec{Q}=(2\pi/a)(1,1,0.3)$ corresponding to $\vec{q}=(2\pi/a)$ (0,0,0.7) as measured from (1,1,1). This increase in intensity corresponds to a divergence of $\chi^{zz}(\vec{q})$ at $\vec{q}=(2\pi/a)(0,0,0.7)$, and thus implies a tendency towards sinusoidal ordering of the ferromagnetically correlated (001) sheets of spins. Figure 5 shows the temperature dependence of the peak intensity at $Q=(2\pi/a)(1,1,0.3)$, and $(2\pi/a)(1,1,0)$, the AF-I Bragg peak position. The intensity at (1,1,0.3) is diverging over a large temperature range, but a first-order phase transition to the type-I structure preempts the development of long-range incommensurate order. Below T_N, the incommensurate fluctuations disappear, and the system possesses long-range order of the AF-I type.

Another important feature of the diffuse scattering is the anisotropic q dependence. Scans along $\vec{q}_{\parallel}$ in

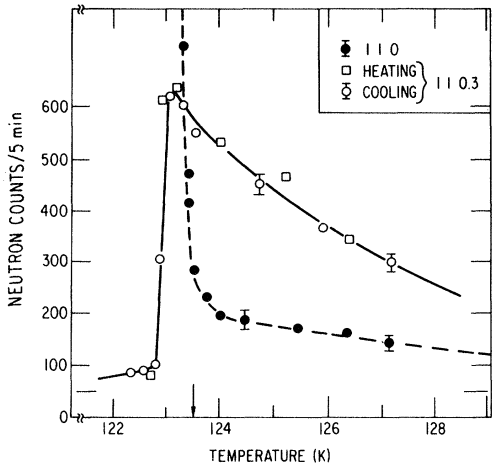

FIG. 5. Intensity as a function of temperature for the 110 ($\eta=0$) and 11 0.3 ($\eta=0.3$) positions in UAs. The background level is ~50 counts and the lines are guides to the eye.

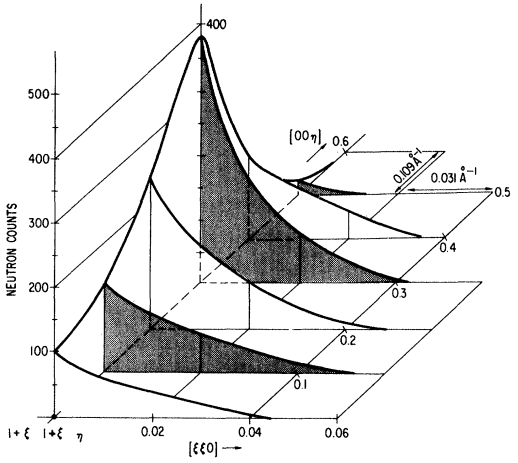

FIG. 7. Schematic representation of the diffuse scattering at $T_N+1.2$ K around the 110 point. The reciprocal-lattice projection is $1\bar{1}0$. Note the difference in scale in the $[\xi\xi 0]$ and $[00\eta]$ directions. The instrumental resolution functions are $\Delta\xi=0.012$ and $\Delta\eta=0.005$ in appropriate reciprocal-lattice units.

the $[00\eta]$ direction reveal that the full width at half maximum (FWHM) is about 20–30 times the instrumental resolution (Fig. 4 and upper portion of Fig. 6). However, for scans along $q_\perp$ in the $[\xi\xi 0]$ direction (Fig. 6) the q width is much narrower, being only twice the instrumental resolution. Thus the

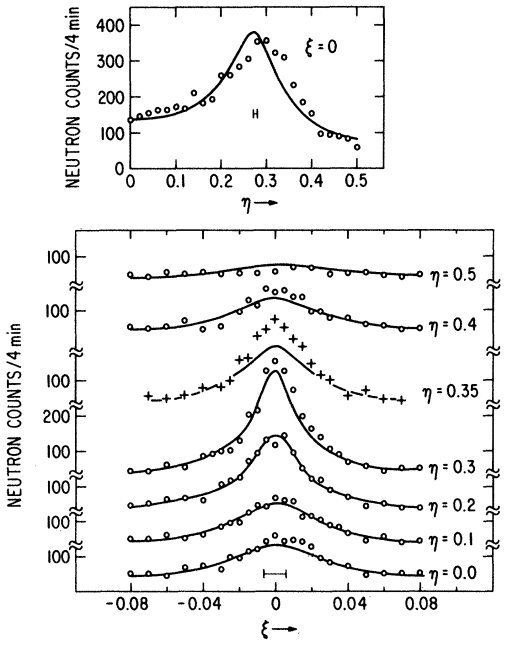

FIG. 6. Observed (points) and calculated (full lines) diffuse intensity in different directions around the 110 at 124.75 ($T_N+1.25$ K). The horizontal bars indicate the width of the resolution function.

scattering appears as a cigar in reciprocal space, elongated along $[00\eta]$ as shown in the top part of Fig. 4. Physically this anisotropy in the diffuse scattering implies that the spin correlations are very long range within the (001) sheets, but short range between the sheets. This is similar to the situations in UN (Ref. 3) and USb.[4]

Figure 7 gives a schematic representation of the scattering and reveals some other features which are predicted by the theory to be presented below. The curves are for $T=T_N+1.2$ K and are calculated from Eq. (6) below. First notice that along the $[00\eta]$ direction the peak at $\eta=0.3$ is asymmetric and has a long tail extending to $\eta=0$, see also upper portion of Fig. 6. In the $[\xi\xi 0]$ direction the width depends upon η and has the smallest FWHM when the intensity is a maximum along η (i.e., at $\eta=0.3$). This is shown more quantitatively in lower portion of Fig. 6. All of these features are produced by the mean-field theory we use to describe the phase transition.

B. Analysis of diffuse scattering

To understand the behavior we adopt a mean-field approach and introduce an effective spin Hamiltonian

$$\mathcal{H}=-\sum{}' J^{\alpha\alpha}(\vec{R}_{ij})S_i^\alpha S_j^\alpha - v\sum(S_i^\alpha)^4 \ , \qquad (1)$$

where the anisotropic exchange interaction $J^{\alpha\alpha}(\vec{R}_{ij})$ is assumed to be diagonal and transforms with $\vec{R}_{ij}$ according to full cubic symmetry, S_i^α is the α component of the spin operator for the ith ion, and v is a constant associated with the single-ion anisotropy. If

$v > 0$ then the effect of the single-ion anisotropy terms will favor $\vec{S} \| \langle 100 \rangle$ whereas for $v < 0$ then the term favors $\vec{S} \| \langle 111 \rangle$. As we shall see, the present system is consistent with $J^{zz}(\vec{R})$ being $>> J^{xx}(\vec{R})$ and $J^{yy}(\vec{R})$ for $\vec{R}$ lying in the xy plane, etc. We assume interactions between first- and second-neighbor uranium moments on the NaCl lattice, given by

$$J^{zz}(\vec{R}_1) = J_0, \quad J^{xx}(\vec{R}_1) = J^{yy}(\vec{R}_1) = J_1 \quad [\vec{R}_1 = (a/2, a/2, 0)] \ ;$$

$$J^{zz}(\vec{R}_2) = J_2, \quad J^{xx}(\vec{R}_2) = J^{yy}(\vec{R}_2) = J_3 \quad [\vec{R}_2 = (0, 0, a)] \ .$$

To preserve symmetry, the tensor components of the interactions must be permuted in an appropriate fashion as $\vec{R}_1$ and $\vec{R}_2$ are taken over the first and second sets of neighbors, respectively. For example, for $\vec{R}_1 = (a/2, 0, a/2)$, $J^{yy}(\vec{R}_1) = J_0$ and $J^{xx}(\vec{R}_1) = J^{zz}(\vec{R}_1) = J_1$. For $\vec{R}_2 = (a, 0, 0)$, $J^{xx}(\vec{R}_2) = J_2$ and $J^{yy}(\vec{R}_2) = J^{zz}(\vec{R}_2) = J_3$. Then a mean-field treatment for the paramagnetic phase yields

$$\chi^{zz}(\vec{q}) = C[T - J^{zz}_{\text{eff}}(\vec{q}) CV/(g^2 \mu_B^2)]^{-1} \ , \tag{2}$$

where g is the Landé factor for the U ions, V the crystal volume, C is the Curie constant, and

$$J^{zz}_{\text{eff}}(q) = \tfrac{1}{3} v S(S+1) + 2\left[J_0 \left(\cos(q_x + q_y)\frac{a}{2} + \cos(q_x - q_y)\frac{a}{2} \right) + J_1 \left(\cos(q_x + q_z)\frac{a}{2} + \cos(q_x - q_z)\frac{a}{2} + \cos(q_y + q_z)\frac{a}{2} + \cos(q_y - q_z)\frac{a}{2} \right) + J_2 \cos q_z a + J_3 (\cos q_x a + \cos q_y a) \right] \ . \tag{3}$$

We assume that $J_0 > 0$, and $J_1, J_2 < 0$ yielding a maximum for $J^{zz}_{\text{eff}}(\vec{q})$ in the vicinity of $\vec{q}_0 = (2\pi/a)(0,0,1)$. Note that $J^{xx}_{\text{eff}}(\vec{q})$ would be given by Eq. (3) with an appropriate permutation of q_x, q_y, q_z, etc. Evaluation of this expression shows that at q_0, $J^{xx}_{\text{eff}}(\vec{q})$ and $J^{yy}_{\text{eff}}(\vec{q})$ are very much smaller than $J^{zz}_{\text{eff}}(\vec{q})$, provided that J_0 is the dominant interaction. This explains why critical scattering is seen only from $\chi^{zz}(\vec{q})$ for $\vec{q}$ along [001], although cubic symmetry would, of course, require $\chi^{xx}(\vec{q})$ and $\chi^{yy}(\vec{q})$ to diverge along [100] and [010], respectively. Since the critical scattering is well localized around q_0 in the $q_\perp$ direction, we may expand to $O(q_\perp^2)$ and obtain

$$\chi^{zz}(\vec{q}) = a_1 \left[1 + \left(a_2 - a_3 \cos\frac{a q_\parallel}{2} \right) \frac{a^2 q_\perp^2}{4} + a_4 (1 - \cos a q_\parallel) - 4 a_3 \left(1 - \cos\frac{a q_\parallel}{2} \right) \right]^{-1} \ , \tag{4}$$

where the mean-field predictions for the temperature dependence of the coefficients are

$$a_1 = \frac{C}{T - T_0}, \quad a_2 = \frac{2CV}{g^2 \mu_B^2} \frac{J_0 + 2J_3}{T - T_0} \ ,$$
$$a_3 = \frac{2CV}{g^2 \mu_B^2} \frac{J_1}{T - T_0}, \quad a_4 = \frac{2CV}{g^2 \mu_B^2} \frac{J_2}{T - T_0} \ , \tag{5}$$

and T_0 is the mean-field ordering temperature. Note that if $a_4 \simeq a_3$ (implying $J_1 \simeq J_2$), the denominator of $\chi^{zz}(\vec{q})$ would have a vanishing coefficient of $q_\parallel^2$ around $\vec{q}_0$. This would correspond to a generalized Lifshitz point where there is a balance between competing antiferromagnetic interactions between first- and second-neighbor (001) sheets of spins and thus a balance between tendencies to sinusoidal and commensurate AF-I ordering. The energy-integrated neutron diffuse scattering at $\vec{Q} = (2\pi/a)(1,1,0)$ is related to the susceptibility by[20]

$$\frac{d\sigma}{d\Omega} = A f^2(\vec{Q}) \chi^{zz}(\vec{q}) T \ , \tag{6}$$

where A is a constant and $f(\vec{Q})$ is the magnetic form factor of the U ion. We have assumed that only $\chi^{zz}(\vec{q})$ goes critical around $\vec{Q} = (2\pi/a)(1,1,0)$, and that $\hbar\omega << k_B T$ where ω is an excitation frequency of the system. Using the full mean-field expression for $\chi^{zz}(\vec{q})$ in Eq. (4), the expression (6) was folded with the experimental instrumental resolution in momentum space and fitted to the data using a_1, a_2, a_3, and a_4 in Eq. (4) and a constant background as fitting parameters. Figures 4, 6, and 8 show the quality of the fits obtained using the mean-field theory at various temperatures. Note that the observed behavior is reproduced semiquantitatively, but that the poor fit along the η axis at low temperatures indicates a need for interactions between further neighbor (001) sheets to be included. Of particular importance are the fits in Fig. 6. This figure, which shows the ξ half-width as a function of η, indicates very dramatically that the diffuse scattering is narrowest in ξ where it is most intense, and this feature

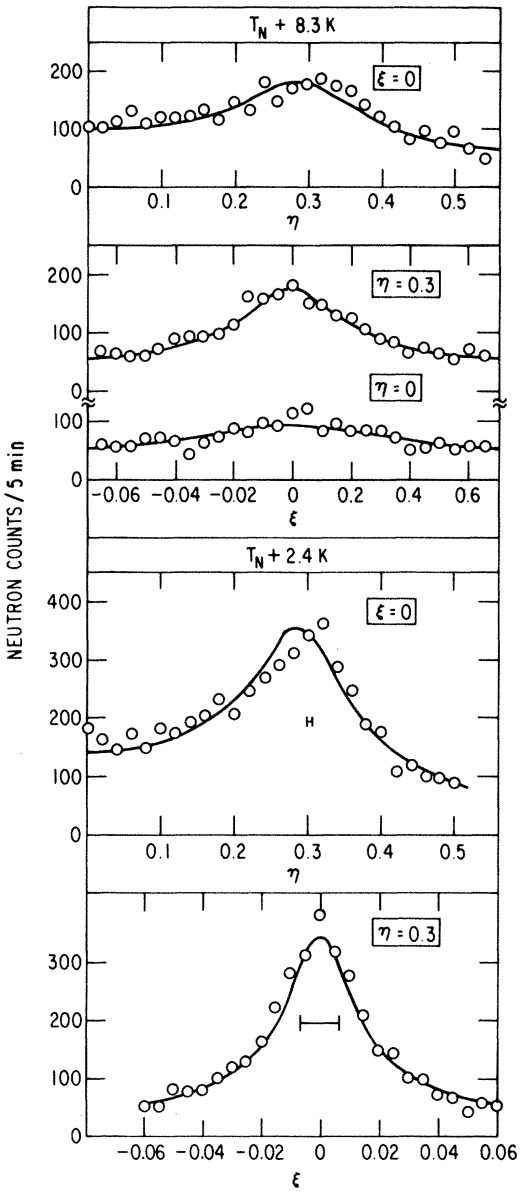

FIG. 8. Observed (points) and calculated (full lines) diffuse intensity for UAs in different directions for $T_N+8.3$ K and $T_N+2.4$ K. The horizontal bars indicate the resolution function.

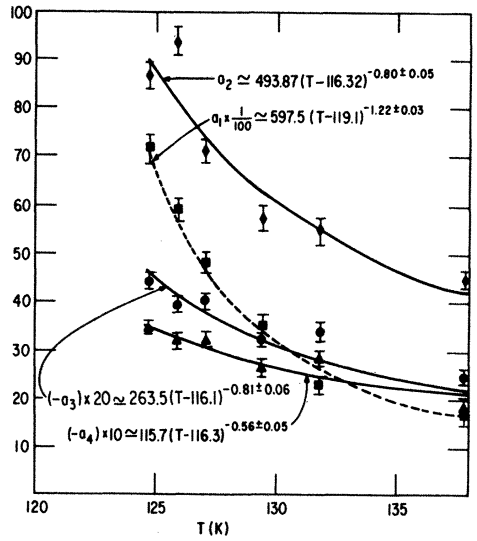

FIG. 9. Variation of the parameters a_1, a_2, a_3, and a_4 as a function of temperature. The individual values are obtained by using Eqs. (6) and (5) to fit the experimental data, some of which is shown in Figs. 4, 6, and 8, together with the calculated fits.

is totally reproduced by our mean-field theory. Figure 9 shows the parameters a_1, a_2, a_3, and a_4 plotted as a function of temperature. The curves represent individual power-law fits of the form $A\,(T-T_0)^{-r}$ to the parameters, where T_0 is the mean-field ordering temperature. T_0 depends on the parameter being fit but is between 116 and 119 K, so that the range of reduced temperature over which the observations extend is in all cases quite small. Thus one cannot determine true critical exponents here. It is interesting to note that both the parameters a_2 and a_3 have $T_0 \sim 116.2$ K and the exponent $r=0.8\pm0.1$. An examination of Eq. (4) shows the square of the correlation length in the (001) sheets; i.e., ξ_1^2 is given by $(a_2-a_3)a^2/4$, so that we should equate r with 2ν, where ν describes the decay of the correlation length. This would then point to the same power law for growth of correlations in these sheets ($\nu \sim 0.4$) as was obtained in USb.[4] Because of the competing antiferromagnetic and sinusoidal correlations along [001] no correlation length in this direction can be simply defined. The maximum value which $\xi_\perp$ reaches just above the first-order transition is $5.6a$. The ratio $|J_1/J_2|$ obtained from a_3 and a_4 varies between 0.62 and 0.69, as compared to the value 1.0 as the condition for a Lifshitz point. If we assume the same value α for the ratio of $|J_0/J_1|$ and $|J_2/J_3|$, then the average value obtained for α is 37.4. This shows that an extremely large cubic anisotropy exists, so that the diffuse scattering would be elongated along $q_\parallel$ even if the competition between J_1 and J_2 did not occur.

V. NATURE OF THE PHASE TRANSITION

The Hamiltonian invoked for this system has many close analogies with the Ising model studied recently by Bak and van Boehm[21] and by Selke and Fisher.[22] These authors also considered a situation where a competition between adjacent and next-nearest (XY) layers led to paramagnetic, sinusoidal, and commen-

surate antiferromagnetic (or ferromagnetic, depending on the sign of J_1) phases coexisting at a multicritical point, the Lifshitz point. Their results indicate that away from this point, the transition from paramagnetic to sinusoidal or from paramagnetic to commensurate AF-I is a second-order transition, but the transition between the sinusoidal and commensurate phases is first order. Interestingly, they do observe a AF-I*A* structure as the lowest temperature periodicity in the sinusoidal phase. In addition, the periodicity of their sinusoidal structure "locks" into various commensurate values as the temperature is lowered.

The present system, which shows sinusoidal *fluctuations* then enters the commensurate AF-I phase from the paramagnetic phase in a first-order manner, can be accounted for phenomenologically by assuming a free energy of the form

$$G = G_0 + \sum_{\vec{q},\alpha} \tfrac{1}{2}[\chi^{\alpha\alpha}(\vec{q})]^{-1} S_{\vec{q}}^{\alpha} S_{\vec{q}}^{\alpha} + \sum_{\substack{\alpha\beta\gamma\delta \\ \vec{q}_1 \cdots \vec{q}_4}} A_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4}^{\alpha\beta\gamma\delta} S_{\vec{q}_1}^{\alpha} S_{\vec{q}_2}^{\beta} S_{\vec{q}_3}^{\gamma} S_{\vec{q}_4}^{\delta} + \sum_{\substack{\alpha\beta\gamma\delta\epsilon\nu \\ \vec{q}_1 \cdots \vec{q}_6}} B_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4\vec{q}_5\vec{q}_6}^{\alpha\beta\gamma\delta\epsilon\nu} \times S_{\vec{q}_1}^{\alpha} S_{\vec{q}_2}^{\beta} S_{\vec{q}_3}^{\gamma} S_{\vec{q}_4}^{\delta} S_{\vec{q}_5}^{\epsilon} S_{\vec{q}_6}^{\nu} + \cdots , \quad (7)$$

where $S_{\vec{q}}^{\alpha}$ is the α component of the amplitude of a sinusoidal spin structure of wave vector $\vec{q}$. We assume we are in the region of $\vec{q}_0$, where only S_q^z can exist, and now consider a Landau-type expansion of the free energy in power of $q_{\parallel}$, $q_{\perp}$, and S, using Eq. (4). We obtain

$$G = G_0 + \alpha_1 S^2 + \alpha_2 q_{\parallel}^2 S^2 + \alpha_3 q_{\parallel}^4 S^2 + \alpha_2' q_{\perp}^2 S^2 + \beta_1 S^4 + \beta_2 q_{\parallel}^2 S^4 + \beta_2' q_{\perp}^2 S^4 + \gamma_1 S^6 + \cdots , \quad (8)$$

where

$$\begin{aligned} \alpha_1 &= (T - T_0)/2C , \\ \alpha_2 &= \frac{V}{2}\frac{a^2}{g^2\mu_B^2}(J_2 - J_1) , \\ \alpha_3 &= \frac{(T - T_0)}{2C}\frac{a^6}{24}\left(\frac{a_3}{4} - a_4\right) \\ &= \frac{V}{24}\frac{a^4}{g^2\mu_B^2}\left(\frac{J_1}{4} - J_2\right) , \\ \alpha_2' &= \frac{V}{g^2\mu_B^2}\frac{a^2}{4}(J_0 + 2J_3 - J_1) , \end{aligned} \quad (9)$$

and the higher-order constants β and γ cannot be defined *a priori*. From the previous analysis, we know that in the vicinity of the first-order transition T_N, $\alpha_1, \alpha_2', \alpha_3 > 0$ and $\alpha_2 < 0$. Stability requires $\gamma_1 > 0$. Whereas the fluctuations in the paramagnetic phase are a maximum around $q_{\parallel} = [\frac{1}{2}(|\alpha_2|/\alpha_3)]^{1/2}$, $q_{\perp} = 0$, as in the previous analysis, a *first-order* transition will occur at $q_{\parallel} = q_{\perp} = 0$ provided the following conditions are satisfied at some temperature $T_N > T_0$: (a) $\partial G/\partial q_{\perp}$, $\partial G/\partial q_{\parallel} = 0$ has only a solution at $q_{\parallel} = q_{\perp} = 0$; (b) $\partial G/\partial S = 0$ has a solution for finite $S = S_0$, $q_{\parallel} = q_{\perp} = 0$; (c) $G(S = S_0, q_{\parallel} = q_{\perp} = 0) = G_0$; and (d) all second drivatives of G are positive at this point. Condition (a) is satisfied if $\beta_2 S_0^2 > |\alpha_2|$ and $\alpha_2' \geq \beta_2' S_0^2$ so that $\beta_2 > 0$. Conditions (b) and (c) yield $\beta_1 < 0$; $|\beta_1|^2 = 4\alpha_1\gamma_1$; $S_0^2 = \frac{1}{2}|\beta_1|/\gamma_1$. Condition (d) is automatically satisfied if these conditions are satisfied. Summarizing, if the coefficients $\beta_1, \beta_2, \gamma_1$ are such that

$$\beta_1 < 0, \quad \beta_2, \gamma_1 > 0, \quad |\beta_1|\beta_2 > 2|\alpha_2|\gamma_1 ,$$

then a first-order transition will take place to the AF-I structure at a temperature

$$T_N = T_0 + \frac{C|\beta_1|^2}{2\gamma_1} \quad (10)$$

with a spontaneous staggered magnetization given by

$$S_0 = \left(\frac{1}{2}\frac{|\beta_1|}{\gamma_1}\right)^{1/2} . \quad (11)$$

Since $\gamma_1 > 0$, Eq. (10) shows that $T_N > T_0$, as observed experimentally.

While the Landau theory presented here provides a phenomenological "explanation" of the nature of the observed transition, a more satisfactory approach must be sought within the applications of renormalization-group theory. The Hamiltonian with cubic anisotropy has been discussed by Aharony,[23] and Bruce.[24] Such a Hamiltonian is relevant also for many structural phase transitions. It appears that for $n = 3$, the transition can be second order with Heisenberg-like critical behavior, although the "irrelevant" cubic anisotropy terms are believed to represent very slowly decaying corrections to the leading scaling behavior. For strongly cubic anisotropy, the fluctuations can drive the transition first order, even though mean-field theory would predict a second-order transition. It whould, however, be pointed out that the renormalization-group calculations have only been done for cubically isotropic *ferromagnetic* systems and not in the vicinity of the point $(2\pi/a)(0,0,1)$ in the NaCl reciprocal lattice. USb and UN do exhibit a second-order paramagnetic-AF-I transition and appear to display anisotropy comparable to the present case. A corresponding mean-field treatment for USb would yield the value 49.0 for the ratio J_0/J_1 if only first-neighbor interactions are included. Thus the first-order nature of the transition in UAs may be due to

the additional complication of being in the vicinity of a Lifshitz point,[5] where paramagnetic, sinusoidal, and AF-I phases are in coexistence.

VI. SUMMARY

In this paper we have described a series of neutron experiments on the rocksalt uranium compound UAs. The most interesting part concerns the paramagnetic to antiferromagnetic phase transition. The diffuse (critical) scattering above T_N suggests that UAs will order with an incommensurate sinusoidal modulation, but, instead, a weakly first-order phase transition occurs to the type-I antiferromagnetic state. The diffuse scattering is highly anisotropic. This anisotropy may be related microscopically to the covalent bonding of the $5f$ orbitals on the U atoms with anion p orbitals in (001) sheets. We show this schematically in Fig. 10. Note that the $5f$ electrons around the U atom are confined to oblate orbitals, i.e., they have a higher probability of being in the (001) plane than out of it, and this gives rise to the strong interaction with the four neighboring p orbitals. The experimental evidence for this oblate shape of the $5f$ wave function is the magnetic form factor (see Table I and accompanying discussion). By mixing strongly spin-orbit coupled f states with d and p states in a band picture one can show that the $\vec{q}$-dependent paramagnetic susceptibility may have the required cubic anisotropy. An alternative explanation of the anisotropic exchange in these compounds in terms of a Coqblin-Schrieffer interaction has been put forward recently by Siemann and Cooper.[25]

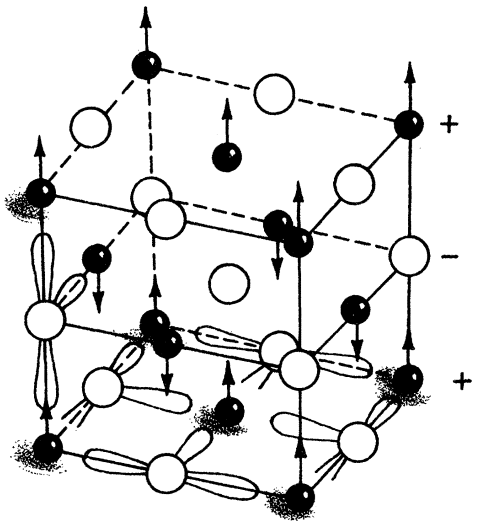

FIG. 10. Schematic of bonding arrangements in the type-I antiferromagnetic structure. The $5f$ electrons around the uranium atoms (solid points) are confined in the (001) plane perpendicular to the spin direction. They interact strongly with the anion p wave functions in the (001) plane, but relatively little with those above and below.

By adopting a mean-field approach we have shown that the z-z exchange interaction within the (001) planes is ~40 as strong as the x-x or y-y coupling between the spins. Moreover, the tendency to antiferromagnetic ordering due to the z-z coupling between adjacent (001) planes of spins is opposed by the z-z coupling between next-nearest (001) planes. This almost cancellation of effects leads in UAs to "frustration," and results in commensurate and incommensurate phases being in equilibrium with the paramagnetic phase—the definition of a Lifshitz point.[5]

The parameters derived in Sec. IV from an analysis of the diffuse scattering have been used in Sec. V to show how a Landau expansion can provide a phenomenological explanation of why UAs experiences a first-order phase transition to the type-I state. The process of magnetic ordering in UAs is closely analogous to the case of some first-order structural phase transitions in some Perovskite structure compounds.[26,27] Aharony and Bruce[6] have shown that a uniaxial stress can cause such a transition to become second order and thus pass through a tricritical Lifshitz point, for which they have calculated critical exponents. These seem to be confirmed by EPR measurements on stressed $RbCaF_3$.[27]

Interestingly enough, similar diffuse critical scattering has been observed in a study of magnetite (Fe_3O_4) near the Vervey transition.[28] Cigarlike features peaking up at an incommensurate wave vector were observed and increased over a large temperature range as the transition temperature was approached. However, a first-order transition occurred into a commensurate structure which preempted the development of long-range order at the incommensurate wave vector. The results were interpreted as due to a competition between 3D (three-dimensional) and 1D correlations, but it would be interesting to reevaluate the results in light of the present experiment and theory.

A number of further experiments are suggested by our present work. Rossat-Mignod *et al.*[29] have examined single crystals of UAs under extremes of uniaxial stress and high magnetic fields in order to explore the nature of the phase transition and magnetic phase diagram. The uniaxial stress measurements show that the type-I phase is indeed a single $\vec{q}$ state as we describe it, but they claim that the low-temperature $1A$ phase is a $2\vec{q}$ structure with the resultant spin direction as $\langle 110 \rangle$. Our experiments, performed in zero field and stress, cannot give any information on this point. The phase diagram of UAs appears to resemble that of CeSb, in which a number of planar

ordering arrangements are observed.[30] Susceptibility measurements by Rossat-Mignod *et al.*[29] show that uniaxial stress enhances the first-order nature of the P-I transition, but a detailed examination of the critical scattering as a function of either magnetic field or uniaxial stress has not yet been reported.

A brief report of this work describing the relevance of this work to current discussions on Lifshitz points has been published.[31]

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