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Neutron diffraction study of PuSb: The critical regime

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Neutron diffraction measurements on a large single crystal of ^{242}PuSb have been performed near $T_N = 85.3$ K to measure the development of long-range magnetic order ($\beta = 0.31 \pm 0.02$) below T_N and the anisotropy and temperature dependence of the short-range magnetic correlations ($\nu = 0.58 \pm 0.05$, $\kappa_\parallel / \kappa_\perp = 1.8 \pm 0.2$) above T_N. Comparisons are made to other Ce and U compounds and to recent theoretical calculations of Kioussis and Cooper.

I. INTRODUCTION

The extraordinarily high magnetic anisotropy present in many actinide compounds was first demonstrated by Gardner and Smith[1] in 1968 when they performed magnetization experiments on single crystals of US. Since that time a large body of experimental and theoretical work has addressed this aspect of actinide physics. Similar, although smaller, anisotropic behavior has been found for a number of cerium compounds, and has been treated as a consequence of strong electron hybridization.[2] The consequences of the anisotropic behavior can be best observed in bulk measurements such as magnetization, resistivity, and magnetoresistance.[3] These effects are generally at least an order of magnitude greater than anisotropies found in "conventional," i.e., localized, rare-earth materials. Of the microscopic probes available one of the most useful has been diffuse critical neutron scattering (DCNS), which can study the spatial and temporal extent of the short-range magnetic fluctuations as a function of both direction and temperature. These magnetic fluctuations appear close to the magnetic ordering temperature, and were first studied in the antiferromagnet USb.[4] Since that time studies have been made on UAs,[5] UN,[6] and extended to CeSb, CeBi, and CeAs.[7] In all these antiferromagnets the structure can be visualized as a series of (001) planes of ferromagnetic moments. The stacking of these (001) planes varies from $+-+-$ for a type-I structure, $++--$ for type-IA, and even more complex sequences, some incommensurate, have been discovered. What characterizes these arrangements is that the interactions *within* the (001) sheets are clearly much stronger than those between such sheets. It is this aspect of the correlation behavior that can be probed so well by DCNS. Fluctuations within the plane have a mean correlation length of $\xi_\perp$ (the $\perp$ sign is to note that these correlations are perpendicular to the wave-vector direction $\mathbf{q}$) and in reciprocal space we measure the inverse correlation range $\kappa_\perp$ where $\kappa_\perp = 2\pi/\xi_\perp$. Since the correlations in the (001) plane are strong we expect $\xi_\perp$ to be large, and $\kappa_\perp$ small. Between the sheets $\xi_\parallel$ (parallel to $\mathbf{q}$) is small, so $\kappa_\parallel$ large. A useful measure of this anisotropy is then

$$R = \kappa_\parallel / \kappa_\perp , \tag{1}$$

which we expect to be greater than one. In fact R values of 5.0 in USb, 3.8 in UAs, 2.8 in UN, 2.5 in CeBi, 1.8 in CeSb, and 0.6 in CeAs have been found.[7]

A phenomenological approach to the anisotropy has been adopted by Sinha *et al.*[5] and by Halg and Furrer.[7] These approaches correspond to the introduction of anisotropic bilinear exchange, with isotropic quadrupolar interactions added in Ref. 7. A microscopic theory to understand these effects has been proposed by Kioussis and Cooper.[8] This involves band-f electron anisotropic exchange and the observed anisotropic behavior arises from the different angular dependencies of the two-ion interactions in the lattice. For Ce-based compounds Kioussis and Cooper[8,9] have obtained good agreement between their theory and experiment; for U-based systems the theory still requires the input of the crystal-field parameters (V_4 and V_6), which are unknown, but qualitatively they obtain R ($=\kappa_\parallel/\kappa_\perp$) > 1 for all U based systems, in agreement with experiment; and for $Pu^{3+}(5f^5)$ systems they have found that $R > 1$ if the electrons are treated in j-j coupling, and $R < 1$ for L-S intermediate coupling schemes.

In this paper we report experiments to measure the DCNS in PuSb, the nature of the incommensurate phase below T_N in PuSb, and the critical exponents near T_N. The extension of this work to Pu systems represents not only an experimental challenge, but also an extremely important test for theories.

II. EXPERIMENTAL DETAILS

The preparation and growth of single crystals of this and similar transuranium compounds is performed at the European Institute for Transuranium Elements, Karlsruhe. Full details are given elsewhere.[10,11] Briefly,

compressed pellets of the materials are kept in vacuum in tungsten crucibles for long periods (~ 10 days) at temperatures some 20 to 50 °C below their melting points. For PuSb this is 1680 °C. Crystals form by the mineralization process. The most common isotope of plutonium is 239. Unfortunately, this has a high-capture (269 b) and fission (743 b) cross section at thermal neutron energies (25 meV). Early experiments on the magnetization,[12] phase diagram,[13] and form factor of the Pu ion,[14] all used small crystals (<5 mm^3) made with ^{239}Pu. A much more favorable isotope both for low temperature (because of the self-heating of the ^{239}Pu nucleus) and difficult neutron experiments is ^{242}Pu. We have obtained a supply of this isotope from the U.S. Department of Energy and fabricated a number of large crystals, the largest of which is ~ 350 mm^3, and these were used both for this critical scattering experiment and for studies of the magnetic excitation behavior. A preliminary report of the latter has been published.[15]

Plutonium monoantimonide orders initially ($T_N = 85.3$ K) with an incommensurate structure,[13] which is longitudinal, i.e., the magnetic moments are parallel to the propagation direction, with a wave vector parallel to a cube edge. The wave vector $|\mathbf{k}| = k$ varies from 0.131 at T_N to ~ 0.100 at 67 K, where a first-order transition to ferromagnetism, $k = 0$, takes place. Figure 1 illustrates the [001] projection of the reciprocal lattice in which our measurements take place. (200) is a nuclear zone center and is the point at which ferromagnetic ordering ($k = 0$) occurs. At T_N peaks appear at $(2, \pm k, 0)$ and $(2, 0, \pm k)$ corresponding to two domains of the sinusoidally modulated $\langle 001 \rangle$ planes of magnetic moment. The domain with $\mathbf{k} = (\pm k, 0, 0)$ does not give rise to satellites at $(2 \pm k, 0, 0)$ because the moment is parallel to the scattering vector $\mathbf{Q}$. This domain can, of course, be observed around points such as (0,2,0). Within the plane we shall concentrate on the satellite at $(2, k, 0)$. Above T_N magnetic fluctuations will give rise to diffuse critical neutron scattering (DCNS). Correlations between (010) sheets, $\mathbf{k} = (0, k, 0)$, can be determined by performing scans $\mathbf{q}_\parallel$ parallel to $\mathbf{k}$, and correlations within the sheets can be determined by scanning $\mathbf{q}_\perp$ perpendicular to $\mathbf{k}$. Anticipating one of the results of our study we have drawn in Fig. 1 an ellipse to illustrate contours of equal intensity at the satellite position. As drawn $R \simeq 2$, where R is defined in Eq. (1).

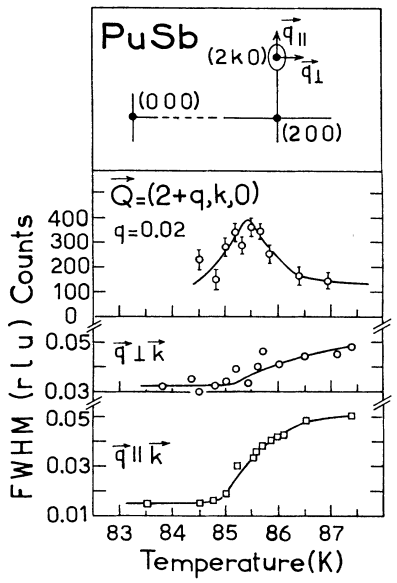

FIG. 1. Top figure shows the portion of reciprocal space in which the measurements were performed. Note that at T_N, $k = 0.131$. The second panel down shows the intensity at a position just away from the Bragg point as a function of temperature. This gives $T_N \sim 85.4$ K. The two lower panels show the full width at half maximum (FWHM) as a function of temperature in the two different directions about the ordering wave vector $(2, k, 0)$. Note the offset from zero in both these FWHM values.

The neutron experiments were performed at the Siloë Reactor at the Centre d'Etudes Nucléaire de Grenoble on both a double-axis and a triple-axis (set for elastic scattering) instrument. The wavelength was 2.40 Å and a pyrolitic graphite filter was used to suppress second-order contamination. Of central importance in all studies of DCNS is the instrumental resolution. In these experiments we have used both horizontal and vertical collimators of 20′ after the sample. Unfortunately, the PuSb crystal itself has quite a wide mosaic so that the best resolution $\Delta q_\parallel = 0.014$ rlu, where this is defined as full width at half maximum, and rlu represents reciprocal lattice units, 1 rlu $= 2\pi a^{-1} = 1.0093$ Å^{-1}, with the lattice parameter $a = 6.225$ Å. This resolution is almost totally defined by the crystal quality and neutron wavelength used. In contrast Sinha *et al.*[5] achieved $\Delta q_\parallel = 0.006$ Å^{-1} with a highly perfect crystal of UAs at the same incident neutron energy. In the perpendicular direction we have $\Delta q_\perp = 0.032$ Å^{-1}. The large value of $\Delta q_\perp$, which is also related to large mosaic spread of the crystal, limits the minimum value of $\kappa_\perp$, the inverse perpendicular correlation range, that can be measured. In all cases we have performed a three-dimensional resolution convolution to determine $\kappa_\parallel$ and $\kappa_\perp$. The variation of the full widths as a function of temperature is shown in Fig. 1.

III. RESULTS

A. Below T_N

Measurements of the intensity as a function of reduced temperature $t = (T_N - T)/T_N$ give a value of 2β, where $I \propto t^{2\beta}$. Such a logarithmic plot is shown in Fig. 2 and gives the values $T_N = 85.3 \pm 0.1$ K and $\beta = 0.31 \pm 0.02$. The value of T_N from these refinements is in good agreement with that found experimentally (Fig. 1) by monitoring the magnetic intensity of the critical scattering at a point away from the ordering wave vector. This value of β is the same as that found in USb (0.32 ± 0.02) and in excellent agreement with the three-dimensional (3D) Ising solution of $\frac{5}{16} = 0.3125$. The points at small t appear to show a deviation from the linear behavior, but there may be systematic errors here due to inhomogeneity in the sample temperature across

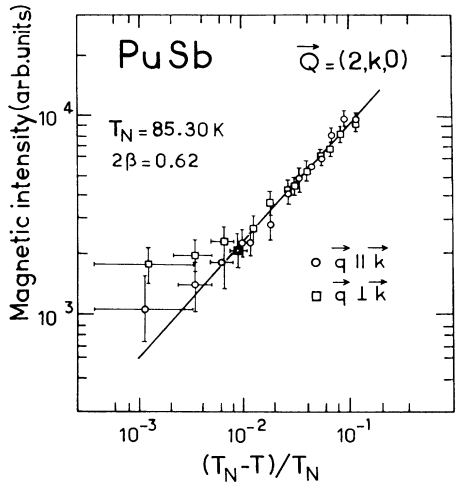

FIG. 2. Logarithmic plot of intensity vs reduced temperature below T_N in the incommensurate state.

the whole crystal.

The second measurement below T_N is of the wave vector k. In the earlier work[13] this was found to vary approximately as $k(T_N)-k(T)\propto(T_N-T)^3$, but as shown in Fig. 3, with the new larger nonabsorbing crystal we are able to accurately determine that the exponent is 2.0 ± 0.2, rather than ~ 3 in the earlier work. In agreement with Ref. 13 we find $k(T_N)=0.131\pm0.001$.

On cooling the sample between T_N and the first-order incommensurate to commensurate transition ($T_{I\text{-}C}\sim 67$ K) there appears to be no discontinuity at $k=0.125$, which corresponds to a commensurate structure of eight repeat units. This is in contrast to the behavior in a magnetic field, in which a "lock-in" phase transition at $k=\frac{1}{8}$ is found.[13] We have also searched for, but not found, third-order satellites at $(2,3k,0)$, which would signify some squaring of the sine wave modulation. Quantitatively we find at 74 K ($\sim 0.9T_N$)

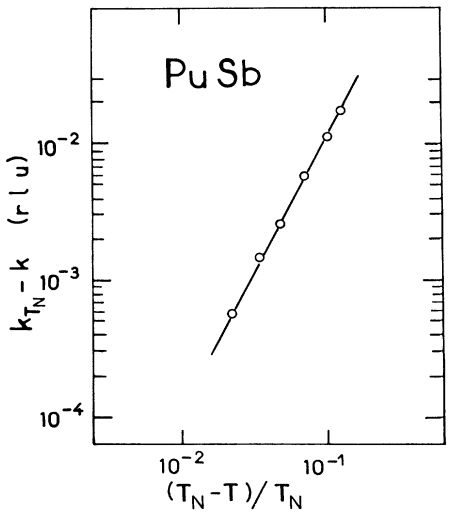

FIG. 3. Logarithmic plot of the variation of the wave vector function $k(T_N)-k$ vs reduced temperature in the incommensurate state.

$$I(3k)<10^{-3}I(k)\ .$$

The modulation is thus truly sinusoidal.[16]

The variation of k within the incommensurate phase has been discussed by McMillan.[17] Our results for the variation of k with temperature are in good qualitative agreement with Fig. 1 of Ref. 17. However, this theory predicts satellites developing near $T_{I\text{-}C}$, and our measurements show that they are very weak (amplitude of third harmonic is less than $\sim 3\%$ of primary). This observation means that the width of the domain walls in the incommensurate phase is rather large in PuSb, suggesting relatively strong interactions between the (001) planes.

B. Above T_N

The first point to note about the critical scattering above T_N is that it is weak. This is consistent with a small value of the ordered moment ($0.75\mu_B$).

The variation of the inverse correlation ranges $\kappa_\parallel$ and $\kappa_\perp$ are deduced from three-dimensional convolutions of the data using the known resolution ellipsoid and are plotted in Fig. 4 as a function of reduced temperature. Two points emerge from the figure. First, as with the other U and Ce compounds discussed in the Introduction, there is a constant ratio $R=\kappa_\parallel/\kappa_\perp$ as a function of temperature $t=(T-T_N)/T_N$. For PuSb, $R=1.8\pm0.2$. Second, the exponent in Fig. 4 is $\nu=0.58\pm0.05$, where $\kappa\propto t^\nu$. The measurements unfortunately extend over just a single decade in reduced temperature. This limitation is because on the one hand the scattering is very weak at large t and cannot be measured with any precision, and, on the other hand, at small t, κ becomes small and the resolution is too poor to measure κ accurately. This limitation may also be seen from Fig. 1(c), in which we plot directly the measured values of the full width at half maximum as a function of temperature. The large instrumental value of $\Delta q_\perp$ prevents the extraction of reliable κ values near T_N. κ values in PuSb extend from ~ 0.003 Å^{-1} to ~ 0.015 Å^{-1}, whereas in the same range of t in USb (Ref. 4) κ varies from 0.02 to 0.35 Å^{-1}.

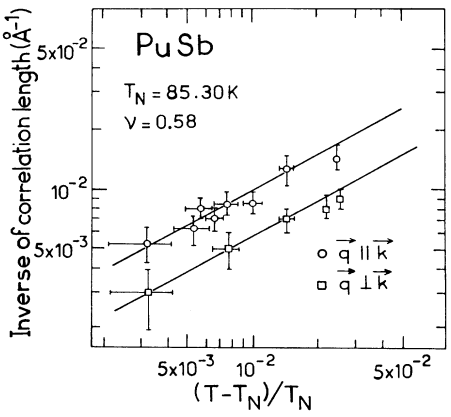

FIG. 4. Logarithmic plot of the variation of the inverse correlation length vs reduced temperature above T_N. Values for $\kappa_\perp$ and $\kappa_\parallel$ correspond to q scans made in the directions defined in Fig. 1.

TABLE I. Summary of critical parameters in Ce, U, and Pu monopnictides. R is the ratio of correlation lengths defined in Eq. (1). Numbers in parentheses refer to standard deviations of the least significant digit.

	β	ν	R	Ref.
CeSb	first-order transition		1.8(2)	21
CeBi	0.317(5)	0.63(6)	2.5(2)	22
UN	0.31(3)	0.84(5)	2.8(3)	6
UAs	first-order transition		3.8(5)	5
USb	0.32(2)	0.68(4)	5.0(5)	4[a]
PuSb	0.31(2)	0.58(5)	1.8(3)	
Classical mean field	0.5	0.5		
3D Heisenberg	0.345	~0.70		
3D Ising	0.3125	0.64		
2D Ising	0.125	1.0		

[a]New value of ν is from M. Hagen, W. Stirling, and G. H. Lander (unpublished).

IV. DISCUSSION

The most important result of the present investigation is the determination of the anisotropy ratio in the critical correlations, $R = 1.8 \pm 0.2$. This value is exactly the same as found in CeSb,[7] but considerably smaller than the 5.0 ± 0.5 found in USb. Kioussis and Cooper[8] have considered the variations of R across the Ce, U, and Pu monopnictides. They find that the strong anisotropy arises from the resonant hybridization of the moderately delocalized $5f$ electrons with band electrons. The hybridization-mediated interaction yields strong intraplanar coupling and a much weaker coupling between planes transverse to the moment direction, as observed experimentally. In the case of Ce compounds the theoretical agreement with experiment is excellent (see Fig. 5 of Ref. 8). For these compounds the $4f$ electrons are almost completely localized and the theory is thus a truly perturbational one. In addition, from an experimental point of view, the crystal-field splitting between the Γ_7 doublet and Γ_8 ground state in the paramagnetic state is known from inelastic neutron scattering, so that it is not a variable parameter in the theory. For actinide systems, however, the crystal-field parameters are not unambiguously established. The early experiments[13] on PuSb, particularly that of the magnetic form factor,[14] established that the $5f$ electrons were almost localized and that the coupling was of the intermediate type, i.e., L-S coupling with the inclusion of a large spin-orbit parameter. Kioussis and Cooper[8] find that for intermediate coupling (IC) and L-S coupling, R in PuSb is less than one. Long periodic structures (specifically $k = \frac{1}{3}$ and $\frac{1}{5}$) are stable in the IC case, but are polarized transverse to the propagation direction. Both the value of R and the polarization of the state at T_N are therefore in disagreement with experiment. Some of these discrepancies with experiment could be removed by introducing a j-j coupling scheme, but this in its turn, is in strong disagreement with experimental findings for PuSb.[13,14]

More recently, Hu *et al.*[18] and Cooper *et al.*[19] have shown that whereas the initial theory included only the effects of hybridization with the first dominant resonant scattering channel, essentially coupling states of $m_l = 0$, it is possible to extend these calculations to include higher terms of the interaction in $m_l = 0 \leftrightarrow m_l = 1$ and $m_l = 1 \leftrightarrow m_l = 1$. When this is done for PuSb the results for the IC case reverse from a transverse to a longitudinal polarization and the value of R becomes greater than one, in fact $R = 2.2$. Much better agreement is also obtained with the inelastic scattering results[15] with the inclusion of these higher terms. Whereas the agreement with the critical scattering results is satisfying, we must await tests of the theory to other systems. We may, for example, raise the question of whether the reasonable agreement for the U systems obtained in the first order $m_l = 0 \leftrightarrow m_l = 0$ theory will be altered with the extension to higher terms. A further test of the theory will be the extension to Np systems, single crystals of which are now becoming available.[20]

The critical exponents β and ν, and the R values of a number of cerium and actinide monopnictides with the rocksalt structure are given in Table I. Given the uncertainties, the parameters are consistent with a three-dimensional (3D) Ising model. A similar conclusion was drawn from a combined magnetization and neutron study[23] of the uranium ferromagnets US and UTe. Kioussis and Cooper[8] have, in fact, used their parameters to calculate ν for the cerium systems and obtain 0.56 ± 0.05, which is in reasonable agreement with the experiments. Because many of these systems are close to instabilities, e.g., close to a Lifshitz point,[5] it is probably unreasonable to expect uniform behavior in the critical exponents and each case may have to be examined on its own; see, for example, the discussion by Kaski and

TABLE II. Summary of inverse correlation lengths κ at a reduced temperature $t = 10^{-2}$ for those compounds with second-order phase transitions in Table I. References are as in Table I. Note that because of uncertainties in T_N for UN the magnitudes of κ should be regarded as approximate, see Ref. 6.

	CeBi	UN	USb	PuSb
T_N (K)	25.4	(54.5)	212.2	85.3
$\kappa_\perp$ (10^{-3} Å^{-1})	14	~3	16	6
$\kappa_\parallel$ (10^{-3} Å^{-1})	36	~7	80	10

Selke[24] of how ν can vary.

We may also usefully compare the magnitude of the inverse correlations at a given value of reduced temperature, and this we show in Table II. We recall here that the real space correlations are proportional to the reciprocal of the numbers in Table II. One may see immediately from this table that the real space correlations in UN and PuSb are long range (thus giving relatively sharp critical scattering) and those in USb are very short range (thus giving broad critical scattering in reciprocal space). The USb case is, in fact, exceptional in that the correlations are so short range. The one difference between USb and the other systems is that the former orders at T_N with a triple-**k** structure, whereas all the others are single **k**.[13,16] As yet the question of how the spatial correlations develop at T_N in a triple-**k** antiferromagnet have not been studied theoretically, but one can intuitively imagine that the competing interactions in a triple-**k** arrangement will result in short-range critical fluctuations. Since NpSb also probably has the triple-**k** structure[16] at T_N, it will be interesting to continue our studies on that system.

For comparison with Table II the theoretical value for κ at $t=0.01$ for a 3D Heisenberg system is $\sim 5\times 10^{-3}$ Å^{-1}. Kioussis and Cooper[8] calculate (see Fig. 3 of Ref. 8) values of 34 and 72×10^{-3} Å^{-1} for a case appropriate to CeBi (lattice parameter $=6.5$ Å) so that apparently in this theory the microscopic interactions give rise to fairly short-range interactions in real space. We note that Kioussis and Cooper also find the value of R independent of temperature, as observed experimentally with the precision available to date.

V. CONCLUSIONS

In this paper we describe neutron (elastic) scattering experiments to examine the critical (near T_N) region of the actinide monopnictide PuSb. Magnetic correlations are found that suggest a tendency for planar ordering, i.e., (001) planes with all their moments aligned ferromagnetically. This result shows strong similarity to those found for some cerium and uranium systems and confirms that for this Pu compound the $5f$ electrons are still hybridizing with the band electrons. The agreement with the theory of Kioussis and Cooper is good.[8] We draw attention to the difference between the absolute magnitude of the κ values in PuSb and USb, and suggest that the large values (see Table II) found for USb are a consequence of the triple-**k** structure which develops in USb.

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