Neutron-Diffraction Study of Magnetic Ordering in $UP_{0.75}S_{0.25}$†

G. H. LANDER AND MOSHE KUZNIETZ
Argonne National Laboratory, Argonne, Illinois, 60439

AND

D. E. COX
Brookhaven National Laboratory, Upton, New York, 11973

(Received 7 August 1969)

The magnetic ordering of $UP_{0.75}S_{0.25}$, which has the NaCl-type structure, has been determined by powder neutron-diffraction techniques. The initial ordering at about 100°K is ferromagnetic. At around 70°K, a ferrimagnetic structure appears in which ferromagnetic (001) sheets are directed along the c axis in the sequence $5+, 4-, 5+, 4-, \ldots$. This corresponds to a ferrimagnetic antiphase type of structure in which the period of modulation is $4.5c$ and which closely resembles the low-temperature structure of thulium. The ordered moment in this structure is about $1.4\mu_B$ per uranium atom, and the net spontaneous moment is $0.16\mu_B$, which is in agreement with magnetization measurements. Below about 20°K, a further transition occurs, resulting in the type-IA antiferromagnetic structure, in which the sheets are stacked in the sequence $2+, 2-, 2+, 2-, \ldots$ with an ordered moment of $1.7\pm0.05\mu_B$. The magnetic ordering in this material, which is a good conductor of electricity, provides strong evidence that long-range oscillatory interactions of Ruderman-Kittel-Kasuya-Yosida (RKKY) type between localized moments are important in actinide materials.

I. INTRODUCTION AND EXPERIMENTAL DETAILS

A RECENT powder neutron-diffraction study[1] of UP-US solid solutions ($UP_{1-x}S_x$, where $0<x<1$), which have the NaCl-type crystal structure, has shown that the type-I ordering found[2,3] in UP is markedly affected by the addition of sulfur. For $0.05<x<0.20$, the antiferromagnetic structure at 4.2°K was of a type not reported previously in the face-centered cubic lattice, and was designated type-IA.[4] In the type-IA structure, ferromagnetic (001) sheets are directed along the c axis in the sequence $++--$, rather than the simple alternating sequence $+-+-$, which forms the type-I structure found in UP and other uranium compounds. The type-IA arrangement does not exist on the basis of the molecular field calculations of ter Haar and Lines,[5] which take into account up to fourth nearest neighbors. A transition from a type-I to a type-IA structure at low temperatures has also been reported recently for UAs.[6]

The most interesting region in the UP-US system occurs around a sulfur concentration $x=0.25$, at which critical competition is found between the antiferromagnetic and ferromagnetic interactions. At about 100°K, $UP_{0.75}S_{0.25}$ orders ferromagnetically. As the temperature is lowered a metamagnetic structure is observed,[7] and, finally, at around 20°K type-IA antiferromagnetic ordering appears. This paper reports a neutron-diffraction examination of the intermediate ordering scheme and of the variation of the magnetic phases with temperature.

The sample preparation and characterization have already been described;[1,4] we used a sample from our previous investigations. The lattice parameter is 5.560 ±0.001 Å. The chemical analysis of this sample gives $x=0.235$. The neutron-diffraction experiments were performed at the Brookhaven High Flux Beam Reactor. Neutrons were reflected from the (311) planes of a germanium crystal to give a monochromatic beam of wavelength 1.025 Å. Use of the (311) reflection eliminates $\frac{1}{2}\lambda$ contamination, since the structure factor for the (622) reflection is zero. A collimation of 10 min of arc was utilized in-pile; and 20 min of arc in front of the detector. The sample was packed in a $\frac{3}{8}$-in.-diam aluminum holder in a helium atmosphere, and was mounted in a Cryogenic Associates variable-temperature Dewar. Temperatures below 30°K were measured with a calibrated germanium resistor; those above 30°K with a calibrated platinum resistor. The temperature was controlled to better than ±0.1°K. Data were obtained at a number of temperatures in the range of 4.2–120°K.

II. RESULTS

The initial neutron-diffraction pattern was taken at 120°K. At this temperature the sample was paramagnetic so that the coherent peaks are caused by the nuclear scattering only. The observed and calculated nuclear intensities are given in Table I. The agreement is good and the scattering length of the (P,S) site was determined as $(0.456\pm0.007)\times10^{-12}$ cm. This value

† Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. Kuznietz, G. H. Lander, and Y. Baskin, J. Appl. Phys. **40**, 1130 (1969).

[2] S. S. Sidhu, W. Vogelsang, and K. D. Anderson, J. Phys. Chem. Solids **27**, 1197 (1966).

[3] N. A. Curry, Proc. Phys. Soc. (London) **89**, 427 (1966).

[4] G. H. Lander, M. Kuznietz, and Y. Baskin, Solid State Commun. **6**, 877 (1968).

[5] D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. (London) **A254**, 521 (1962).

[6] J. Leciejewicz, A. Murasik, and R. Troc, Phys. Status Solidi **30**, 157 (1968).

[7] J. Crangle, M. Kuznietz, G. H. Lander, and Y. Baskin, J. Phys. **C2**, 925 (1969).

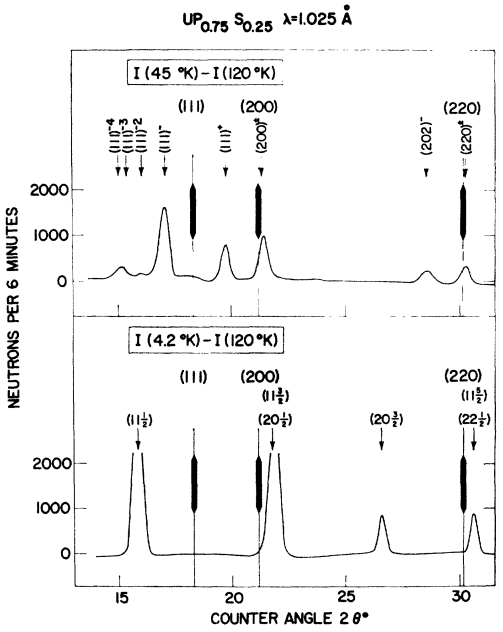

FIG. 1. Difference patterns for neutron diffraction at 45°K (antiphase structure) and 4.2°K (type-IA structure). The positions of the nuclear reflections are denoted by heavy vertical bars. The magnetic reflections in the 45°K pattern are denoted by their displacements from the fundamental nuclear peak.

corresponds very closely to that determined from the chemical analysis, using $b_P=0.51$, $b_S=0.28$ (in units of 10^{-12} cm).

The data taken at 45 and 4.2°K are shown in Fig. 1 in the form of difference patterns obtained after subtraction of the nuclear data taken at 120°K. The 4.2°K pattern (bottom) is characteristic of type-IA antiferromagnetic ordering.[4] The magnetic unit cell in this case is a_0, a_0, $2a_0$, in terms of the chemical unit cell, and the magnetic reflection conditions are $(h+k)$ even and l odd. The 45°K pattern (top) shows a completely different set of peaks which cannot be indexed on the basis of this double cell or of any other cell that is a simple multiple of the original one. However, the stronger reflections may be grouped into pairs of satellites that are characteristic of a sinusoidally modulated structure, and the displacements of the satellites from the fundamental nuclear reflections, such as (111), may be described in terms of a reciprocal-lattice vector $\tau=(0.222\pm0.001)c^*$. Hence, within the error limits, the periodicity of the modulation in real space is $4.5c$. In addition to the stronger satellite reflections, such as $(111)^-$ and $(111)^+$, there are a few weak reflections on the low-angle side of (111) which may be indexed as higher-order satellites displaced by 2τ, 3τ, etc. No first- or higher-order satellites associated with (000) were observed, and the direction of the spins must therefore be parallel to the c axis.

A simple sinusoidal model will not account for the observed higher-order harmonics, such as $(111)^{-3}$ and $(111)^{-4}$, which are clearly visible as a composite peak, and one must therefore consider other more complex arrangements. The magnetic configuration may be described by considering an extension of the type-I and type-IA structural pattern to a larger repeat unit. In the type-I structure the repeat unit is two layers of uranium moments in the sequence $+-$; in the type-IA the repeat is four layers arranged $++--$. For the new structure a repeat of nine layers is needed. The intensity of the satellite reflections is related to the arrangement of the layers as well as to the ordered magnetic moment. If the layers are assumed to have equal moments, it is not possible to arrange the nine layers to give a total net moment of zero. However, the neutron-diffraction patterns at 45°K reveal that any ferromagnetic component must be less than $0.2\mu_B$, so that configurations involving five positive and four negative layers are the only ones that need be considered. The problem is then reduced to the determination of which of the possible configurations (Table II) of the nine layers occurs. Cyclic permutations may be omitted, since they correspond physically to only a shift in the origin of the unit cell. Each of the paired

TABLE I. Observed and calculated nuclear intensities for $UP_{0.75}S_{0.25}$ at 120°K. Scattering lengths[a] $b_U=0.85$, $b_P=0.51$, $b_S=0.28$ (in units of 10^{-12} cm). [Isotropic temperature factor $B=0.35$ Å^2; j is the multiplicity.]

hkl	$(\sin\theta)/\lambda$	j	I_{calc}	I_{obs}
111	0.156	8	141.4	143±4
200	0.180	6	878.8	873±7
220	0.254	12	868.4	892±15[b]
311	0.298	24	114.5	111±3
222	0.312	8	383.9	385±5
400	0.360	6	215.3	218±4

[a] Neutron Diffraction Commission, Acta Cryst. **A25**, 391 (1969).
[b] Contaminated with aluminum reflection from sample container.

TABLE II. Possible configurations for the nine layers of uranium atoms in the antiphase structure, and the corresponding calculated intensities expected for the low-angle harmonics of the (111) nuclear peak. Magnetic moment per uranium atom = $1.4\mu_B$.

Configurations	Intensities of harmonics			
	$(111)^-$	$(111)^{-2}$	$(111)^{-3}$	$(111)^{-4}$
+ + + + + − − − −	41.0	1.8	7.8	3.7
+ + + + − − − + −	24.1	9.5	7.8	23.1
+ + + + − + − − −				
+ + + + − − + − −	17.4	15.1	31.4	1.1
+ + + − − − + + −	13.1	31.3	7.8	12.9
+ + + − + + − − −				
+ + + − − + + − −	2.1	53.1	7.8	2.5
+ + + − − + − + −	7.3	17.1	7.8	42.6
+ + + − + − + − −				
+ + + − + − − + −	11.6	0.8	31.4	30.8
+ + − − + − + + −	4.9	6.4	55.0	8.7
+ + − + − − + + −				
+ + − − + + − + −	0.6	22.6	31.4	20.5
+ + − + − + − + −	1.4	2.7	7.8	72.0
Observed (at 45°K)	41±2	2.5±1	13±2	

configurations in the table is related to the other member of the pair by a cyclic permutation and a mirror inversion. Only one set of intensity values is given for each pair, since both members would give identical diffraction results. The structure factor for the kth harmonic is simply the kth Fourier coefficient of the square-wave that represents the respective configuration.

The calculated intensities of the first four magnetic reflections for the antiphase structure are listed for each of the possible configurations in Table II. These values have been calculated with the uranium $5f^3$ magnetic form factor, which, based on previous results for the UP-US system,[1-4] is a good approximation at low angles. The magnetic moment of the uranium atom was taken as $1.4\mu_B$; this value normalizes the observed intensity of the $(111)^-$ reflection to that predicted by the first model in Table II. The $(111)^{-3}$ and $(111)^{-4}$ reflections could not be resolved.

The intensities in Table II show that the first arrangement, 5+, 4−, may be chosen quite unambiguously, since all others are in complete disagreement, irrespective of the value chosen for the moment. The 5+, 4− model closely approximates an antiferromagnetic square wave or antiphase model, for which the even order harmonics would be totally absent. The accuracy of powder neutron-diffraction measurements is not sufficient, however, to preclude the possibility of some deviation from a perfect square wave. A complete list of observed and calculated intensities for this model is given in Table III. The remarkably close resemblance of this antiphase structure to the low-temperature

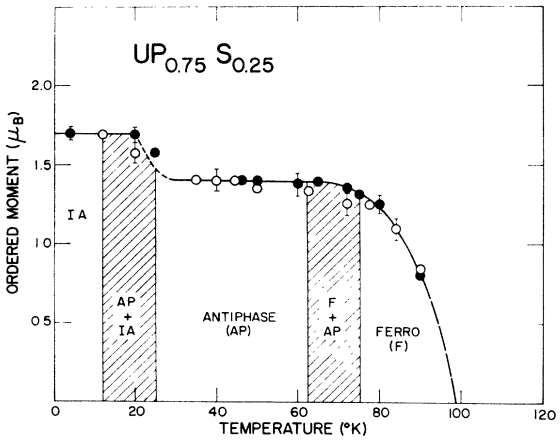

FIG. 2. Ordered moment per uranium atom in $UP_{0.75}S_{0.25}$ as a function of temperature. IA represents the type-IA antiferromagnetic structure, AP the antiphase configuration, and F ferromagnetism. The structures coexist over the temperature ranges indicated by the shading. Values taken during cooling are represented by open circles (○), and those taken on heating by filled circles (●).

structure of thulium[8] is of interest. Thulium is hexagonal close-packed, with a low-temperature magnetic structure that consists of a layered arrangement 4+, 3− that propagates along the c axis, and has the spin parallel to c. The diffraction theory for calculating the intensities of the satellite reflections is fully presented in Ref. 8.

All the configurations in Table II give a small contribution to the nuclear reflections, corresponding to the net ferromagnetic moment of 1.4/9 (or $0.16)\mu_B$ per uranium atom. For the nuclear reflections this moment results in a predicted increase of 0.6% due to magnetic scattering. Such a small contribution cannot be de-

TABLE III. Observed and calculated intensities for the antiphase structure of $UP_{0.75}S_{0.25}$ at 45°K. Only the zero- and first-order harmonics are included in the table. Higher-order harmonics are too weak to be seen except on the low-angle side of the (111) nuclear peak, for these see Table II. (q^2 is the magnetic interaction vector, f is the magnetic form factor.)

hkl	$(\sin\theta)/\lambda$	j	q^2	f	I_{calc}	I_{obs}
$(111)^-$	0.145	8	0.767	0.90	40.8	41±2
(111)	0.156	8	0.667	0.885	0.9	<1
$(111)^+$	0.168	8	0.573	0.865	20.6	20±2
(200)	0.180	6	0.667	0.85	0.5	<1
$(200)^\pm$	0.181	8	0.988	0.85	29.8	27±5
$(202)^-$	0.241	8	0.559	0.75	7.5	9±2
(220)	0.254	12	0.667	0.72	0.4	<1
$(220)^\pm$	0.255	8	0.994	0.72	10.9	12±3
$(202)^+$	0.269	8	0.448	0.67	3.8	2±1
$(113)^-$	0.280	8	0.259	0.62	1.8	1±1
$(311)^-$	0.293	16	0.943	0.60	11.1	14±2
(311)	0.298	24	0.667	0.585	0.3	<1
$(222)^-$	0.300	8	0.717	0.58	3.7	5±3
$(311)^+$	0.305	16	0.870	0.58	8.9	8±3
(222)	0.312	8	0.667	0.54	0.1	<1
$(113)^+$	0.316	8	0.162	0.54	0.7	<2
$(222)^+$	0.323	8	0.618	0.50	2.0	2±1

TABLE IV. Observed and calculated intensities for the type-IA antiferromagnetic structure of $UP_{0.75}S_{0.25}$ at 4.2°K. Magnetic moment per uranium atom = $1.7\mu_B$. The magnetic reflections have been indexed on the chemical unit cell.

hkl	$(\sin\theta)/\lambda$	j	q^2	f	I_{calc}	I_{obs}
$(11\frac{1}{2})$	0.135	8	8/9	0.91	95.2	94±4
$(11\frac{3}{2})$	0.185	8	8/17	0.84	22.7	68.0	70±10
$(20\frac{1}{2})$		8	16/17		45.3		
$(20\frac{3}{2})$	0.225	8	16/25	0.77	17.8	17±2
$(22\frac{1}{2})$	0.258	8	32/33	0.71	9.2	14.2	16±5
$(11\frac{5}{2})$		8	8/33		5.0		
$(20\frac{5}{2})$	0.288	8	16/41	0.60	4.2	32.8	35±2
$(31\frac{1}{2})$		16	40/41		20.5		
$(22\frac{1}{2})$		8	32/41		8.1		
$(31\frac{3}{2})$	0.315	16	40/49	0.54	11.7	10±3

[8] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962).

tected by the present experiments, (see Table III) but a small residual magnetization of $\sim 0.14\mu_B$ is obtained by extrapolation of magnetization measurements to zero field.[7]

Table IV gives the observed and calculated magnetic intensities for the type-IA antiferromagnetic structure at 4.2°K. The magnetic moment is determined as $1.7 \pm 0.05\mu_B$ per uranium atom.

III. TEMPERATURE-DEPENDENCE STUDIES

The temperature dependence of the magnetic phases was studied in some detail. The ordered moments were calculated at a number of temperatures from integrated intensities obtained from scans of the $(111)^-$ and (111) reflections. Previous experience with the cryostat has established that thermal equilibrium of a powder sample in a helium atmosphere is attained within a few minutes, whereas the scans lasted 2 to 3 h. Figure 2 shows the ordered moment as a function of temperature. The transition temperatures are in agreement with the magnetic phase diagram previously reported.[1] Coexistence of two phases over a range of roughly 10°K was noticed around both the 20 and 70°K transitions, and a hysteresis effect of some 5°K was also observed in each case. The coexistence of magnetic phases has been observed in a number of compounds in the UP-US system, and observations at room temperature of broadening in x-ray diffraction and ^{31}P NMR lines[9] show that small local variations of the sulfur concentration occur in the sample. These variations may account for the stable two-phase regions, although not for the observed hysteresis. Over the temperature range in which the modulated structure is stable, no evidence has been found for any variation of the periodicity.

The ordered moments plotted in Fig. 2 in the two-phase regions represent average values of μ, where

$$\mu^2 = [I(111)/I_0(111)] + [I(111)^-/I_0(111)^-], \text{ for } 70°\text{K}$$

or

$$\mu^2 = [I(111)^-/I_0(111)^-] + [I(11\tfrac{1}{2})/I_0(11\tfrac{1}{2})], \text{ for } 20°\text{K}.$$

The I_0 terms are the calculated intensities for unit moments for the magnetic reflections indicated, and the I terms are the observed values placed on an absolute basis by normalization with respect to the nuclear intensities. Within the error limits, the transition from the ferromagnetic to the antiphase structure is a smooth one. However, the ordered moment appears to increase about 20% at the transition to the type-IA arrangement. A similar increase has also been observed in UP,[10] although in this case no change occurs in the simple type-I magnetic structure.

IV. DISCUSSION

The magnetic ordering in the Uv and Uvi compounds, where v and vi are elements of group VA and VIA, respectively, is antiferromagnetic with the type-I structure for the Uv compounds (as in UP), and ferromagnetic for the Uvi compounds (as in US). The compounds all have the NaCl-type crystal structure and are good conductors ($\rho \sim 300\ \mu\Omega$ cm). In the UP-US system the uranium-to-uranium distance is 3.9 Å, which is considerably greater than the minimum interatomic distance of 2.75 Å in metallic uranium. The precise roles of the various types of interaction—direct, superexchange, long-range RKKY, etc.—in the determination of the magnetic ordering are not known at present. A recent model proposed[11] for the magnetic properties of the Uv and Uvi compounds was based on magnetic interactions between the uranium ions via the conduction electrons in an RKKY mechanism. The model accounts for the type-I antiferromagnetic structure in the Uv compounds, although this structure could equally well be explained by molecular field theory. The antiphase structure found for $UP_{0.75}S_{0.25}$ represents the most direct evidence to date that a long-range oscillatory interaction is effective in determining the magnetic ordering in actinide materials. The existence below 20°K of the type-IA structure is further support for RKKY-type interaction, since the type-IA structure is not predicted by the molecular field treatment. The type-IA structure can be considered as an ideal antiphase arrangement with a periodicity of $2c$. The change in periodicity from $4.5c$ to $2c$ is accompanied by an appreciable increase in the ordered moment. Both effects may be connected with changes in the electronic properties of the material.

ACKNOWLEDGMENTS

This study was possible only because of the cooperation of Dr. Y. Baskin, who provided the sample of $UP_{0.75}S_{0.25}$.

[9] M. Kuznietz, F. P. Campos, and Y. Baskin, J. Appl. Phys. **40**, 3621 (1969).

[10] L. Heaton, M. H. Mueller, K. D. Anderson, and D. D. Zauberis, J. Phys. Chem. Solids **30**, 453 (1969).

[11] J. Grunzweig-Genossar, M. Kuznietz, and F. Friedman, Phys. Rev. **173**, 562 (1968).