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MAGNETIC ORDERING IN URANIUM MONOPHOSPHIDE

P. Burlet, S. Quezel and J. Rossat-Mignod

Centre d'Etudes Nucléaires, DRF/SPh - MDN,
85 X, 38041 Grenoble Cedex, France

R. Horyn

Institute for Low Temperature and Structure Research,
Polish Academy of Sciences, 59-950 Wrocław, Poland

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The magnetic ordering in uranium monophosphide (UP) has been studied by neutron diffraction from a single crystal in a magnetic field. UP orders at $T_N \cong 122 \pm 0.1$ K with the type-I antiferromagnetic structure (+-+-), the ordering taking place in a first-order transition. At $T_0 = 22.5$ K the ordered magnetic moment jumps from 1.7 μ_B to 1.9 μ_B. With a magnetic field H = 25 kOe applied along the $[1\bar{1}0]$ direction, it is found that UP has the collinear single-$\vec{k}$ type-I structure above T_0 and undergoes a first-order transition to the planar double-$\vec{k}$ type-I structure, accompanied by a "moment jump" due to the change in the moment direction from <001> to <110>.

1. INTRODUCTION

Uranium monophosphide (UP), having the NaCl-type crystallographic structure (a = 5.589 Å), was found by powder neutron diffraction[1,2] to order antiferromagnetically with the type-I structure (+-+-) below $T_N = 122 \pm 3$ K[1-7], with an ordered magnetic moment of $(1.72 \pm 0.05)\mu_B$ at T = 77 K[1]. Preliminary neutron measurements down to T = 4.2 K indicated[2] an increase in the ordered magnetic moment by more than 10 % at $T \sim 33$ K, within 7 K width in temperature, while further neutron measurements indicated[3] a sharper transition, at $T = 25 \pm 1$ K, with a jump of the ordered magnetic moment from 1.75 μ_B to 1.95 μ_B, and with apparently no change in magnetic structure. The low temperature transition was found to be even sharper and to occur at $T_0 = 22.5$ K in the measurements of specific heat[4], ^{31}P nuclear magnetic resonance (NMR) in the antiferromagnetic state[5], and magnetic susceptibility[6,7], all performed on UP powder. The ^{31}P NMR measurements indicated a jump of 11.4 % in the orde-ed moment, affecting the hyperfine field and thereby the ^{31}P NMR frequency : 46.82 MHz *versus* 42.01 MHz, below and above the transition, respectively. All measurements pointed out to a first-order transition at $T_0 = 22.5$ K, with the same type-I antiferromagnetic structure above and below T_0.

The transition in UP at T_0 was for long time unexplained in all simple theories. In fact several theoretical attempts were made[8,9] to explain its nature, and these have since been found to be in disagreement with other experiments.

A somewhat similar transition was found by neutron diffraction measurements on polycrystalline samples of $UP_{0.95}S_{0.05}$[10] and UAs[11], both isostructural with UP. The high temperature phase in these materials is also the type-I antiferromagnetic structure, and at T_0 ($\sim$ 30 K and $\sim$ 63 K, respectively) the ordered magnetic moment jumps by more than 10 %. However, the phase below T_0 is not the type-I as in pure UP, but rather the type-IA antiferromagnetic structure (++--), found initially in these materials.

At least in the case of pure UAs, neutron diffraction measurements on a single crystal[12,13] have solved the nature of the type-I-type-IA transition at T_0. Measurements on UAs single crystal, with uniaxial stress applied along a cubic axis[12], or with a magnetic field applied along a $[1\bar{1}0]$ direction[13], indicated the type-I phase to be collinear, i.e. described with a single wave vector $\vec{k}$ and with magnetic moments along the <001> directions, and on the contrary, the type-IA phase to be a double-$\vec{k}$ planar structure with magnetic moments along the <110> directions, in agreement with the magnetization measurements.

The possibility that in UP the transition at T_0 is of the same nature as in UAs is strongly supported by high field magnetization experiments on a single crystal of UP[14], which indicate that the $[110]$ direction is the easy direction and the direction of the moments in the ferrimagnetic phases induced at low temperature by rather high applied magnetic fields.

We report here the results of a neutron diffraction investigation of a single crystal of UP in a magnetic field, carried out to solve the nature of the "moment jump" transition at

T_0. These results were first presented at the 12èmes Journées des Actinides in Orsay[15].

2. EXPERIMENTAL

2.1. Sample preparation

The elements U and P of 99.9 % purity were used as starting materials for the preparation of polycrystalline UP. The UP_2 compound was first synthesized by a low-temperature (800-850°C) process of diffusion of the elements. UP_2 was then decomposed to UP under dynamic vacuum at elevated temperatures (up to 1700°C), obtained by a high frequency furnace in tungsten crucibles. The polycrystalline UP was dissolved in metallic gallium at the 1150-1100°C interval, and UP single crystals, up to 3 mm in size, were grown from the gallium solvent held either in quartz encapsulated (0.4 atm argon) graphite or, even better, in completely welded tungsten crucible (the latter permitting higher temperatures). Further details on the preparation are described elsewhere[16].

2.2. Neutron diffraction measurements

Neutron diffraction measurements were carried out at the Siloe reactor of the Centre d'Etudes Nucléaires de Grenoble using the DN3 double-axis diffractometer, equiped with a moving-up counter arm. This diffractometer allows the measurement of diffraction in three directions and the observation, in the same experiments, of magnetic reflections belonging to the three equivalent wave vectors [00k], [0k0], and [k00].

The UP single crystal was mounted in a cryomagnet assembly with a temperature variation from 300 K down to 1.5 K and with a magnetic field variable up to 100 kOe, so that the vertical field was along the $[1\bar{1}0]$ direction of the crystal. This geometry was chosen because it allowed the differentiation between single-$\vec{k}$, double-$\vec{k}$, and triple-$\vec{k}$ structures.

2.3. Differentiation between multi-$\vec{k}$ structures

The type-I antiferromagnetic phase is characterized by wave vectors $\vec{k}_1 = [100]$, $\vec{k}_2 = [010]$ and $\vec{k}_3 = [001]$ and a longitudinal polarization of the moments ($\vec{m}_{\vec{k}} // \vec{k}$). This phase was found to be of a single-$\vec{k}$ structure, i.e. to consist of the stacking of ferromagnetic (001) planes, perpendicular to k, coupled antiferromagnetically. Therefore three K-domains exist for the single-$\vec{k}$ type-I structure. The double-$\vec{k}$ ordering involved two $\vec{k}$ wave vectors and corresponds to a layered multiaxial ordering formed by identical (001) planes in which the magnetic moments are along the four <110> directions. Also here three K-domains exist, corresponding to the three possible pairs of $\vec{k}$-vectors ($\vec{k}_1,\vec{k}_2$ or $\vec{k}_2,\vec{k}_3$ or $\vec{k}_3,\vec{k}_1$) (see refs. 12,13). The triple-$\vec{k}$ structure involves a complete set $\vec{k}_1,\vec{k}_2,\vec{k}_3$ of $\vec{k}$-vectors, and thus only one K-domain exists which consists in of a cubic multiaxial structure with magnetic moments along the four <111> directions (Fig. 1).

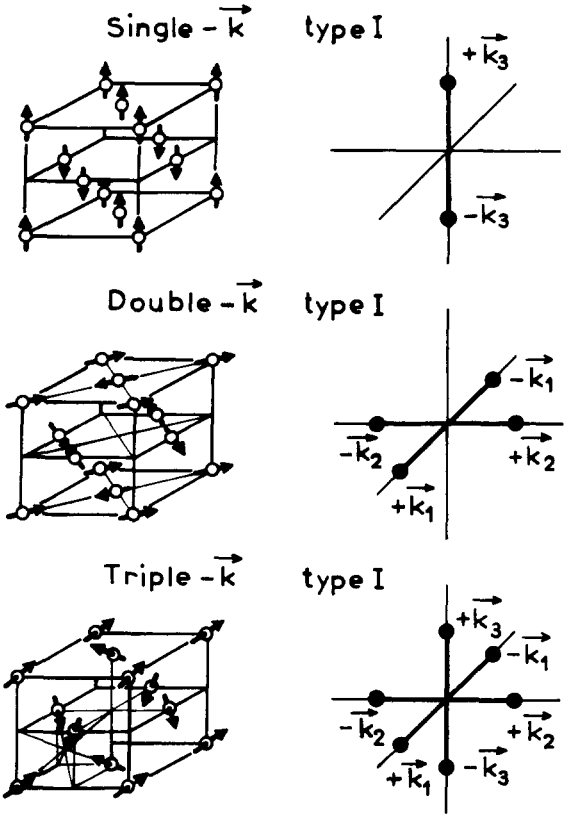

Fig. 1. Multi-$\vec{k}$ structures of type-I ($\vec{k}$ = <001>, $\vec{m}_{\vec{k}} // \vec{k}$) and the associated diffraction peaks located in the reciprocal space.

We can differentiate between the multi-$\vec{k}$ structures in neutron diffraction experiments only with single crystals and by applying a magnetic field, for example, parallel to the $[1\bar{1}0]$ direction. In a collinear (single-$\vec{k}$) structure the domain characterized by the wave vector $\vec{k}_3 = [001]$ is favoured, since the magnetic moments are strictly perpendicular to the magnetic field and a monodomain state is achieved. In neutron diffraction this state should result in a single pair of superlattice magnetic Bragg reflections around each Brillouin zone center. In a planar (double-$\vec{k}$) structure the domain reorientation is driven by the component of the magnetic field perpendicular to the plane containing the moments. The favoured domains are those for which this field component is the largest. In the present crystal alignment the domain K_{XY} defined by the pair of wave vectors $\vec{k}_1 = [100]$ and $\vec{k}_2 = [010]$ is less favoured with respect to the domains K_{XZ} and K_{YZ} defined by the pair $\vec{k}_1 = [100]$ and $\vec{k}_3 = [001]$ and the pair $\vec{k}_2 = [010]$ and $\vec{k}_3 = [001]$, respectively. For a complete domain reorientation only these latter domains must be observed with equal intensities for the $\vec{k}_1$ and $\vec{k}_3$ peaks in the first pair of these two, and with equal intensities for the $\vec{k}_2$ and $\vec{k}_3$ peaks in the second pair. Therefore the intensities of the magnetic peaks corresponding to the three wave vectors $\vec{k}_1$, $\vec{k}_2$ and $\vec{k}_3$ are related by the reduced intensities $I/f^2\sin^2\alpha$

(f - form factor; α - angle between moments and scattering vector) :

$$I/f^2\sin^2\alpha[\vec{k}_3] = I/f^2\sin^2\alpha[\vec{k}_1] + I/f^2\sin^2\alpha[\vec{k}_2]$$

In the triple-$\vec{k}$ structure only one domain exists and the magnetic diffraction pattern must consist of three pairs of peaks around each Brillouin zone center with equal intensities, independent of the field direction.

In order to obtain a domain reorientation as large as possible, the crystal was cooled from the paramagnetic state in the magnetic field.

3. RESULTS

In zero applied magnetic field the magnetic intensities corresponding to the three equivalent wave vectors are equal at any temperature below T_N. In cooling the crystal in a field of 25 kOe from the paramagnetic to the antiferromagnetic state, the magnetic peaks corresponding to $\vec{k}_3 = [001]$ appear abruptly at $T = 122 \pm 0.1$ K (Fig. 2), while no satellites are observed corresponding to the $\vec{k}_1 = [100]$ and $\vec{k}_2 = [010]$ wave vectors. As reciprocal-space

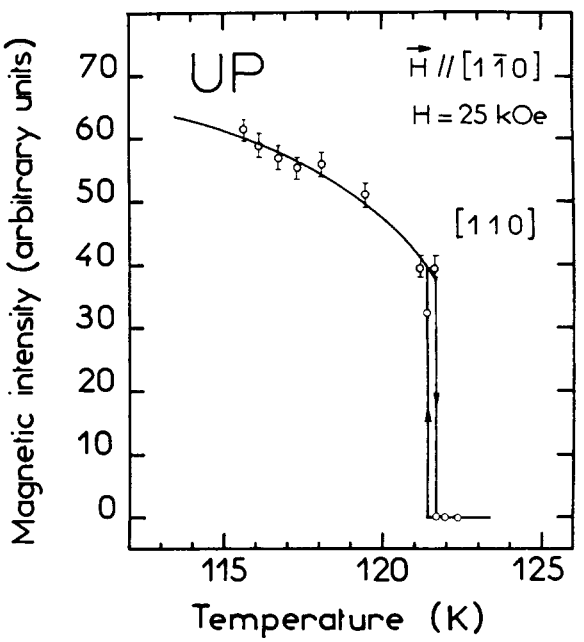

Fig. 2. Intensity of the magnetic [110] peak in UP single crystal in a magnetic field H = 25 kOe, applied along the [1$\bar{1}$0] direction; the field was used to produce a single-domain state.

scans along symmetry directions do not give evidence to any magnetic reflection above this transition, we conclude that UP orders at $T_N = 122$ K with a collinear single-$\vec{k}$ type-I structure, and the transition is strongly first-order (see Fig. 2). This ordering persists at lower temperatures down to $T_0 \cong 22.5$ K, where a drastic change of the neutron diffraction pattern is observed (Fig. 3). The intensity of the peaks corresponding to $\vec{k}_3$ decreases, while peaks corresponding to $\vec{k}_2$ and $\vec{k}_1$ appear (Fig. 3). This behaviour cannot be accounted for by domain reorientation

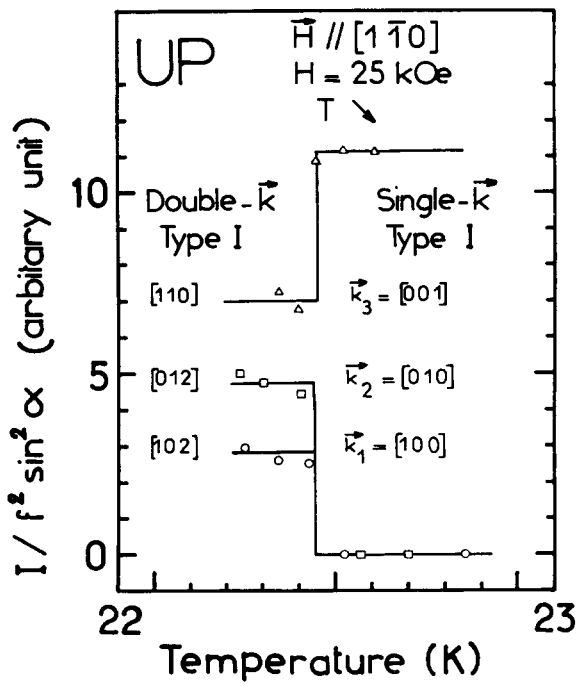

Fig. 3. The magnetic structure factor in UP single crystal in a magnetic field H = 25 kOe applied along the [1$\bar{1}$0] direction as a function of temperature (around T_0) for the [110], [012] and [102] reflections, showing the single-$\vec{k}$-double-$\vec{k}$ transition.

in the single-$\vec{k}$ structure, and must be accounted for by a change from a single-$\vec{k}$ to a multi-$\vec{k}$ structure. The triple-$\vec{k}$ structure is readily eliminated as it should have given rise to equal intensities for all three $\vec{k}$ wave vectors. We are left with the double-$\vec{k}$ structure below T_0, as the only possible structure. As expected from equation (1) we observe (Fig. 3)

$$I/f^2\sin^2\alpha[110] = I/f^2\sin^2\alpha[012] + I/f^2\sin^2\alpha[102]$$

thus verifying the assumption that below T_0 the ordering in UP transforms into the double-$\vec{k}$ type-I structure (Fig. 4). The intensities of the [102] peak ($\vec{k}_1$) and the [012] peak ($\vec{k}_2$) are not the same due to different volumes of

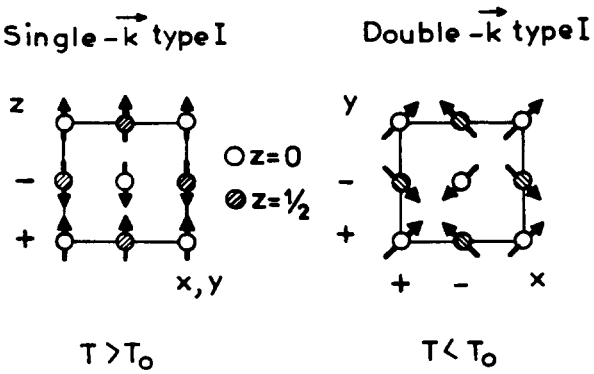

Fig. 4. Magnetic structure of UP below the single-$\vec{k}$-double-$\vec{k}$ transition at $T = T_0$. The moment direction changes from <001> to <110>.

the two domains K_{xz} and K_{yz} as a result of a small misorientation ($\sim 0.5°$) of the $[1\bar{1}0]$ axis with respect to the magnetic field. The ordered magnetic moment of the uranium is found to jump at T_0 from 1.70 μ_B to 1.90 μ_B ($\pm$ 0.05 μ_B), in good agreement with the powder values. Therefore the moment jump in UP is due to the change in the moment direction from <001> to <110>.

4. DISCUSSION

In UP, as in all uranium monopnictides, the ordering wave vectors are aligned along the cubic axes, as a result of strongly anisotropic exchange interactions minimizing the energy for such interactions[17].

As long as only second-order terms are considered in the hamiltonian, single-$\vec{k}$ and multi-$\vec{k}$ structures are completely degenerate in energy ; fourth or higher-order terms can, however, stabilize a multi-$\vec{k}$ structure. Such terms can originate from the exchange interaction and/or from the single-ion anisotropy. Below T_N, with only fourth-order terms, the triple-$\vec{k}$ structure is possible, while sixth-order terms are required for the double-$\vec{k}$ ordering in a cubic symmetry. In the uranium monopnictides such terms exist and manifest themselves even at high temperature (around T_N), as it is evident from the triple-$\vec{k}$ structure developing at T_N in USb[18], and from the first-order character of the ordering transition in UP (Fig. 2) and UAs[12,13,19]. However, in the last two compounds the double-$\vec{k}$ structure does not develop below T_N, but actually at a much lower temperature T_0. This behaviour cannot be accounted for by only a competition between a single-ion anisotropy and anisotropic interactions of bilinear type as can be done in the case of USb. Therefore in UP, as well as in UAs, the low temperature single-$\vec{k}$-double-$\vec{k}$ transition can be explained only by the existence of high-order anisotropic exchange interactions, at least of quadrupolar type, the origin of which is likely due to the mixing between the 5f and band electrons.

Actually, this transition does not exist in UN, which retains the collinear single-$\vec{k}$ structure down to the lowest temperature. While UP and UAs order at about the same temperature, T_0 increased from UP (22.5 K) to UAs (63 K). In the heavier uranium monopnictides, as in USb and likely also in UBi, the single-$\vec{k}$ structure does not exist anymore, and actually they develop below T_N a triple-$\vec{k}$ structure. As the transition temperature T_0 increases on going from light to heavier monopnictides it is therefore tempting to suggest that the high-order anisotropic exchange interactions are connected with the p-f mixing interaction rather than with the d-f mixing interaction. In heavy monopnictides the latter interaction is weaker due to the increased uranium-uranium distances, while the former becomes stronger as the p-character of the conduction electrons increases. This conclusion is strongly supported by the much higher ordering temperatures for the heavy monopnictides.

Theoretical effort was done by Thayamballi and Cooper[20] and by Cooper *et al.*[21] who performed quantitative calculations for the case where the hybridization-mediated two-ion interaction is dominant. This calculation of the interaction, arising from the mixing of 5f electrons with band electrons, is an extension of the Coqblin-Schrieffer model[22], where several f-electrons are taken into account. These calculations can account for non-collinear phases (double-$\vec{k}$ or triple-$\vec{k}$ structures) with transitions to collinear structures as the temperature increases. However, when the crystal field becomes sufficiently large, the transition no longer exists.

Whatever their origin, anisotropic exchange interactions lead to peculiar magnetization process and phase transitions under a magnetic field, as emerged in studying the magnetic phase diagram of UAs (H vs T)[13], of $USb_{1-x}Te_x$ (T vs X)[23], and of the compounds CeSb and CeBi[24]. Unfortunately, in the case of UP the critical magnetic fields determined by the magnetization measurements[14] are so high that neutron diffraction measurements cannot be actually undertaken.

A good description of the magnetic behaviour of the uranium monopnictides has been obtained from neutron diffraction measurements on single crystal. The extension of these measurements to neptunium and plutonium monopnictides, for which samples are now available, is underway.

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