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A NEUTRON STUDY OF THE MAGNETIC ORDERING IN A $NpAs_2$ SINGLE CRYSTAL

J. ROSSAT-MIGNOD, P. BURLET, S. QUEZEL

Laboratoire de Diffraction Neutronique, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires, 85 X, 38041 Grenoble, France

A. BLAISE, J.M. FOURNIER

Section de Physique du Solide, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires, 85 X, 38041 Grenoble, France

D.A. DAMIEN

DEC-Pu, Centre d'Etudes Nucléaires, 92260 Fontenay aux Roses, France

and

A. WOJAKOWSKI *

DGR, Centre d'Etudes Nucléaires, 92260 Fontenay aux Roses, France

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A neutron diffraction study on a small $NpAs_2$ single crystal is reported. $NpAs_2$ orders at $T_N = 52$ K with a pure sine wave modulation propagating along a $\langle 100 \rangle$ direction of the tetragonal unit cell. The value of the wave vector is incommensurate with the lattice ($\boldsymbol{k} = \langle 0.141, 0, 0 \rangle$) and is temperature independent down to $T_{IC} = 18.5$ K where a first-order transition towards a commensurate ferromagnetic state occurs. At all temperatures the magnetic moments are aligned along the c-axis with a value of $(1.45 \pm 0.1)\mu_B$ at $T = 5$ K.

1. Introduction

Neptunium diarsenide $NpAs_2$ has a tetragonal structure of the Cu_2Sb type [1]. The unit cell, shown in fig. 1, contains two formula units ($a = 3.962$ Å, $c = 8.115$ Å) and the space group is P4/n m m (D^7_{4h}). Magnetic measurements [2] give evidence for an antiferromagnetic ordering below $T_N = 52$ K but $NpAs_2$ seems to be a ferromagnet below 18 K. These results are confirmed by Mössbauer spectroscopy [3] which indicate that above 18 K $NpAs_2$ is not a simple antiferromagnet.

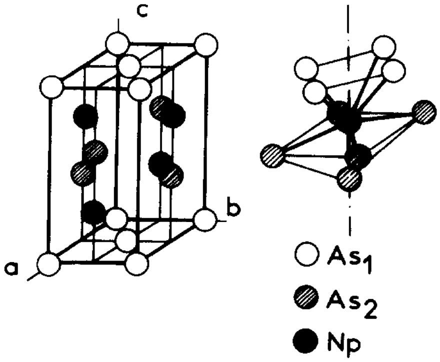

Fig. 1. Tetragonal unit cell of $NpAs_2$ and the neptunium site symmetry.

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* On leave from Institut for Low Temperature and Structure Research, P.O. Box 937, 50-950 Wroclaw 2, Poland.

Therefore neutron experiments are suitable to clarify the magnetic properties of this compound. The availability of small single crystals of $^{237}NpAs_2$ allows us to perform such an experiment and the main results are reported in this paper.

2. Experimental

Single crystals of $NpAs_2$ were prepared at the CEN Fontenay. They were grown by a chemical transport method in an evacuated quartz tube using iodine as a transport agent [4]. A single crystal of about 0.3 mm^3 was used for the neutron diffraction experiment. The crystal was oriented and encapsulated in an aluminium box to avoid any contamination and then put into a variable temperature cryostat with a (a, c) plane horizontal.

Neutron diffraction experiments have been carried out at the Siloe reactor at the CEN Grenoble on the two-axis spectrometer DN_3 equipped with a counter that allows measurements out of the horizontal plane. The neutron wave length was 2.4 Å provided by a graphite monochromator. Pyrolithic graphite filters were used to avoid $\lambda/2$ contamination.

3. Results

3.1. Nuclear scattering

Intensities of nuclear Bragg reflexions were measured at high temperature in the paramagnetic state. They are compared in table 1 with the square of the structure factor calculated taking into account that the unit cell contains two $NpAs_2$ molecules with the following atomic positions [1].

$$2\,\mathrm{Np} \quad \textit{in}\ (1)\ 0, \tfrac{1}{2}, z;\ \ (2)\ \tfrac{1}{2}, 0, \bar{z}\ \textit{with}\ z_{\mathrm{Np}} = 0.281,$$

$$2\,\mathrm{As}^{(2)} \quad \textit{in}\ (1)\ 0, \tfrac{1}{2}, z;\ \ (2)\ \tfrac{1}{2}, 0, \bar{z}\ \textit{with}\ z_{\mathrm{As}} = 0.639,$$

$$2\,\mathrm{As}^{(1)} \quad \textit{in}\ (3), 0, 0, 0;\ (4)\ \tfrac{1}{2}, \tfrac{1}{2}, 0.$$

The Fermi lengths $b_{\mathrm{As}} = 0.64$ and $b_{\mathrm{Np}} = 1.015$ [5] have been used.

The first observation is that extinction effects are not negligible in spite of the small volume of the crystal. The observed intensities of reflexions corresponding to large structure factor are too small to be compatible with the other intensities. If we do not take into account the two largest intensities in a normalisation procedure, a satisfactory agreement is obtained for all the other measured intensities as can be seen in table 1. Then the scaling factor deduced from only the weaker nuclear Bragg peaks will be used to normalize the magnetic intensities. These large extinction effects indicate that the crystal is indeed of a very good quality.

Table 1
Comparison between observed and calculated intensities of nuclear Bragg peaks in the paramagnetic state $T > 52$ K. The scaling factor $K = 4.5 \times 10^{-3}$ has been calculated excluding the strong reflexions $\langle 1\,0\,3 \rangle$ and $\langle 0\,0\,3 \rangle$ which are assumed to be affected by extinction effects

hkl	I_{obs}	F^2_{calc}	I_{obs} norm (barn/cell)
$\bar{1}01$	239 ± 20	1.022	1.08
$\bar{1}02$	36 ± 10	0.238	0.163
$\bar{1}03$	860 ± 60	5.43	3.94*
001	0	0.004	0
002	132 ± 10	0.63	0.60
003	1770 ± 100	12.31	8.06*
004	452 ± 50	2.32	2.06

3.2. Low temperature ferromagnetic phase

A ferromagnetic contribution is easily detected in the measurement of the nuclear Bragg peaks at low temperatures. This contribution, as shown in fig. 2, remains approximately constant up to $T_{\mathrm{IC}} = (18.5 \pm 0.2)$ K where it vanishes abruptly. Some hysteresis effects have been observed at this transition, which is a first-order transition.

The magnetic contributions superimposed to the nuclear reflexions are reported in table 2. As there is no contribution to (001) reflexions, the magnetic moment of neptunium ions must be parallel to the tetragonal *c*-axis.

Then using the form factor for a Np^{4+} ion measured in a polarized neutron experiment [5] a correct agreement between observed and calculated intensities is obtained for a moment value of

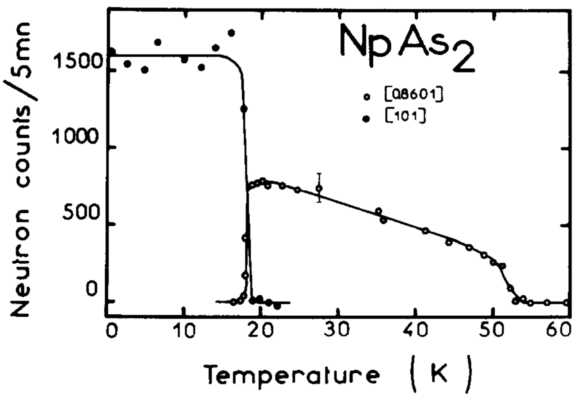

Fig. 2. Temperature dependence of a magnetic Bragg peak in the ferromagnetic ([101]) and the incommensurate ([0.86, 0, 1]) states.

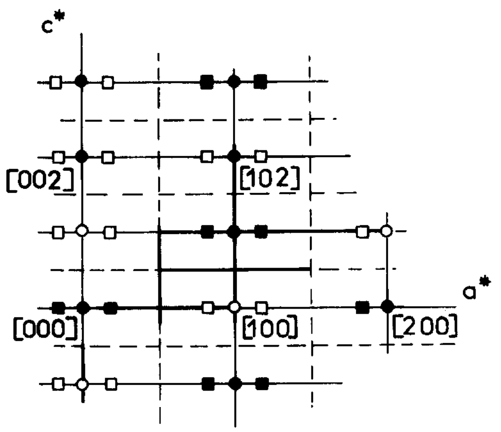

Fig. 3. Reciprocal lattice (a^*, c^*) plane. Circles represent the Brillouin zone centers and squares the magnetic superlattices peaks. Open squares and circles correspond to positions at which no intensity was observed.

$(1.45 \pm 0.1)\mu_B$ at $T = 5$ K. This value is in agreement with the value obtained by [5] ($\mu_{Np} = 1.46\mu_B$) and by the Mössbauer experiments [3] ($\mu_{Np} = 1.5\mu_B$).

3.3. High temperature phase

Above $T = 18.5$ K an ordered state, if it exists, must be characterized by a wave vector $\boldsymbol{k}$ and then the magnetic scattering would give rise to superlattice peaks located in the reciprocal space at $\boldsymbol{h} = \boldsymbol{H} \pm \boldsymbol{k}$, where $\boldsymbol{H}$ is a reciprocal lattice vector. To determine the value of the wave vector $\boldsymbol{k}$ scans along the symmetry directions of the Brillouin zone have been performed as indicated in fig. 3. As can be seen in fig. 4, superlattice reflexions have been detected, by scanning the [h01] direction, at the positions [0.858, 0, 1] and [1.141, 0, 1]. These peaks correspond to magnetic satellites belonging to the Brillouin zone [101] and are associated to a wave vector $\boldsymbol{k} = [0.141, 0, 0]$. Magnetic reflexions corresponding to the equivalent wave vector $\boldsymbol{k} = [0, 0.141, 0]$ are also present. When the temperature

Table 2
Comparison between observed and calculated magnetic intensities at $T = 5$ K. In the table n.o. means not observed

hkl	I_{obs} (barn/cell)	I_{calc} (barn/cell)
101	0.37 ± 0.05	0.30
102	0.04 ± 0.02	0.034
103	0.08 ± 0.03	0.084
001	n.o.	0
002	n.o.	0
003	n.o.	0
004	n.o.	0
201	n.o.	0.011

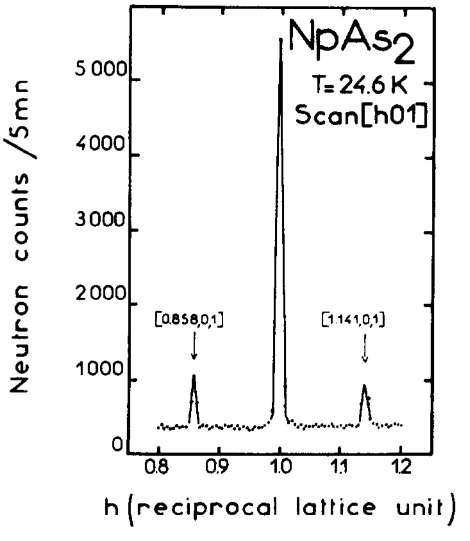

Fig. 4. Scan along [h01] reciprocal lattice direction performed on a $NpAs_2$ single crystal at $T = 24.6$ K showing the two superlattice magnetic peaks inside the [101] Brillouin zone.

increases the value of the wave vector remains constant and the magnetic peak intensities decrease continuously to vanish at $T_N = 52$ K which is unambiguously identified as the ordering temperature (fig. 2).

The magnetic structure associated with such a wave vector can be either a helical one or a sine-wave modulation. The helical model is ruled out by the non-observation of a magnetic intensity for the scattering vectors [0.14, 0, 1], [0.14, 0, 2] and [0.14, 0, 3] because, whatever the choice of the phase between the two Bravais lattices, it is not possible to cancel simultaneously these three intensities for a helical structure. So, the magnetic ordering in NpAs$_2$ at high temperature corresponds to a modulation of the moment. An accurate search for higher harmonics $2\boldsymbol{k}$ and $3\boldsymbol{k}$ leads to the conclusion that, if they exist, their amplitude is lower than 2% of the value of the fundamental harmonic. Therefore the magnetic structure of NpAs$_2$ can be considered as a pure sine-wave modulation. The fact that the reflexions with scattering vectors nearly parallel to the c-axis are not observed indicates that the magnetic moment direction lies along the c-axis. Then the only remaining parameter to determine is the coupling between the two Bravais lattices Np$^{(1)}$ and Np$^{(2)}$, As the two satellites [0.86, 0,0] and [1.14, 0,0] are not observed, the phase shift between them must be $\phi = \pi k_x$ (fig. 5). In table 3 the calculated and the observed intensities at $T = 24.6$ K of the magnetic superlattice peaks are compared for the K_x-domain defined by $\boldsymbol{k}_x = [k\ 0\ 0]$. Taking into account for the domain population a good agreement is obtained for an amplitude value $A_k = (1.58 \pm 0.1)\mu_B$ of the modulation of the neptunium magnetic moments.

So below $T_N = 52$ K, NpAs$_2$ orders with a transverse sine-wave modulation propagating along a [100] direction.

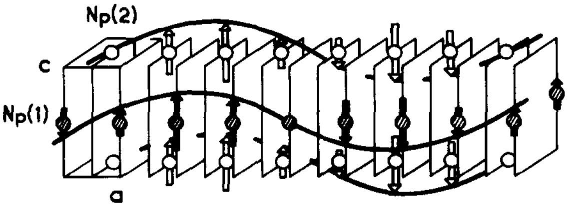

Fig. 5. Sine-wave modulation observed above $T_{IC} = 18.5$ K in NpAs$_2$.

Table 3

Observed and calculated intensities of the magnetic superlattice reflexions in the modulated phase at $T = 24.6$ K. These reflexions correspond to the K_x-domain defined by $\boldsymbol{k} = [k\ 0\ 0]$. The volume of this domain is 75% whereas the volume of the K_y domain ($\boldsymbol{k} = [0\ k\ 0]$ is only 25% of the crystal volume

hkl	I_{obs} (barn/cell)	I_{calc} (barn/cell)
0.14 0 1	n.o.	0.0004
0.14 0 2	n.o.	0.002
0.14 0 3	n.o.	0.0003
0.86 0 0	n.o.	0 (extinction)
1.14 0 0	n.o.	0 (extinction)
0.86 0 1	0.11 ± 0.02	0.092
1.14 0 1	0.09 ± 0.02	0.095
0.86 0 2	n.o.	0.007
1.14 0 2	n.o.	0.009
1.86 0 0	0.07 ± 0.02	0.088
1.86 0 1	n.o.	0.003
1.14 0 3	0.02 ± 0.01	0.023

The value of the wave vector $k_x = 0.141$ in $2\pi/a$ unit is indeed incommensurate with the crystal lattice. This value remains temperature independent down to $T_{IC} = (18.5 \pm 0.5)$ K where a first-order transition occurs into a ferromagnetic state. At any temperature below T_N the magnetic moment direction is parallel to the tetragonal c-axis of the structure. At low temperatures the neptunium magnetic moment has a value of $(1.5 \pm 0.1)\mu_B$.

In NpAs$_2$ Mössbauer [3] and polarized neutron [5] experiments lead to the conclusion that neptunium ions are in a Np^{4+} configuration. Thus the $^4I_{9/2}$ ground state multiplet is split by the crystal field into five Kramers doublets. The observed magnetic ordering indicates that the ground state doublet has an Ising-like anisotropy along the c-axis and a large moment reduction ($1.5\mu_B$ instead of $3.2\mu_B$). This strong Ising anisotropy together with competitive exchange interactions give rise to a sine-wave modulation at T_N. But, usually, with decreasing temperature either the wave vector value varies to lock into a commensurate value when the system is close to a Lifschitz point or higher order harmonics develop to lead to a square wave modulation. However, such a behaviour is not observed in $NpAs_2$ in which the ground state is presumably a Kramers doublet; indeed down to $T_N/3$ the modulation remains a pure sine-wave without any change of the wave vector value. This result is very unusual. Moreover the driving mechanism for the incommensurate–ferromagnetic transition is also very mysterious. This non-trivial magnetic behaviour of $NpAs_2$ originates, more likely as in cerium and uranium monopnictides [6,7], from a strong hybridization between f-electrons close to the Fermi level and p-electrons of the valence band.

This neutron experiment on $NpAs_2$, which is the first magnetic structure investigation performed on a single crystal of a neptunium compound, is very interesting because it reveals that neptunium, like cerium and uranium, can exhibit exotic magnetic properties which are not well understood. Therefore it is interesting to continue such single crystal studies on other neptunium compounds, in particular on neptunium monopnictides which also have complex magnetic properties [8].

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