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Magnetic structures of U_2N_2M-type compounds

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Abstract. The magnetic structures and the magnitudes of the ordered magnetic moments for the hexagonal ternary U_2N_2M-type compounds (where M is P, As, S, Se) have been determined by neutron diffraction. In U_2N_2S and U_2N_2Se the observed magnetic unit cells have the same size as the chemical ones while in U_2N_2P and U_2N_2As the magnetic unit cell is doubled along the *c*-axis. At 4 K the magnetic moments on the uranium ion amount to 1·4, 1·7, 1·6 and 2·3 μ_B for U_2N_2S, U_2N_2P, U_2N_2As and U_2N_2Se, respectively. In all of them the direction of the magnetic moment is along the *c*-axis.

1. Introduction

Magnetic susceptibility measurements performed over a wide temperature range have shown that the ternary uranium compounds with the composition U_2N_2M (where M stands for P, As, S, Se) having a hexagonal crystal structure are all antiferromagnetic (Troć and Żołnierek 1973). The striking feature of the first two compounds, U_2N_2P and U_2N_2As, are their high Néel temperatures—363 and 403 K respectively. These two compounds exhibit the highest ordering temperatures among all ordered actinide compounds so far known. The lanthanide structural analogues of these ternary uranium compounds exhibit a variety of magnetic ordering schemes, so that it was also of interest to check by neutron diffraction whether in U_2N_2M the same situation is observed. The other objective was the determination of the magnitude of the magnetic moments in the antiferromagnetic state as well as the refinement of the crystal structure parameters.

2. Experimental

Polycrystalline samples were prepared by heating the uranium mononitride with stoichiometric quantities of the respective elements in evacuated quartz ampoules at 1000°C for 150 h. All ternary compounds obtained were checked on an x-ray diffractometer and by susceptibility measurements, and found to be single phase.

The neutron diffractometer DN 500 at the EWA reactor in Świerk was used to run neutron diffraction patterns at 4 K and 300 K. The adopted wavelength was 1·32 $\pm$ 0·01 Å. The neutron diffraction patterns for U_2N_2S and U_2N_2P made at 4 K and 300 K are displayed in figures 1 and 2 respectively. The measurements of the height of the magnetic peak M(100), performed as the cryostat slowly warmed up, gave the Néel temperatures of

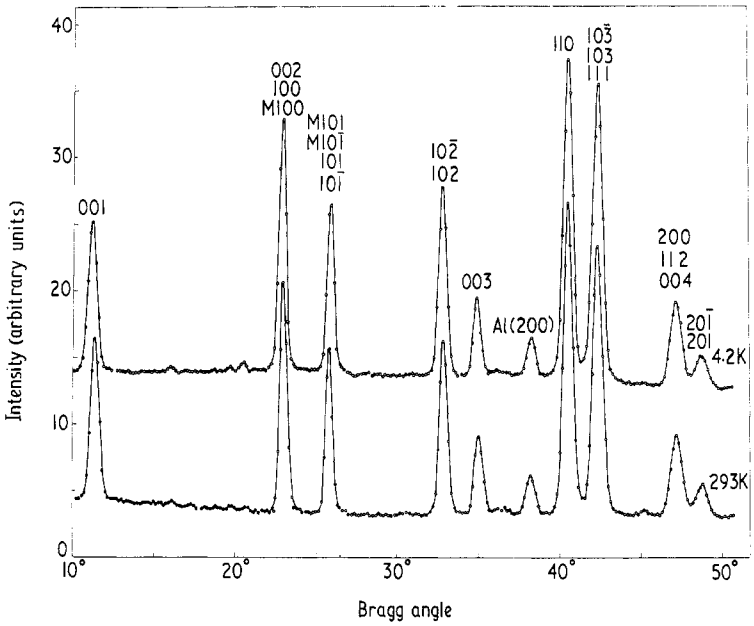

Figure 1. Neutron diffraction patterns at 4 K and 300 K for U_2N_2S.

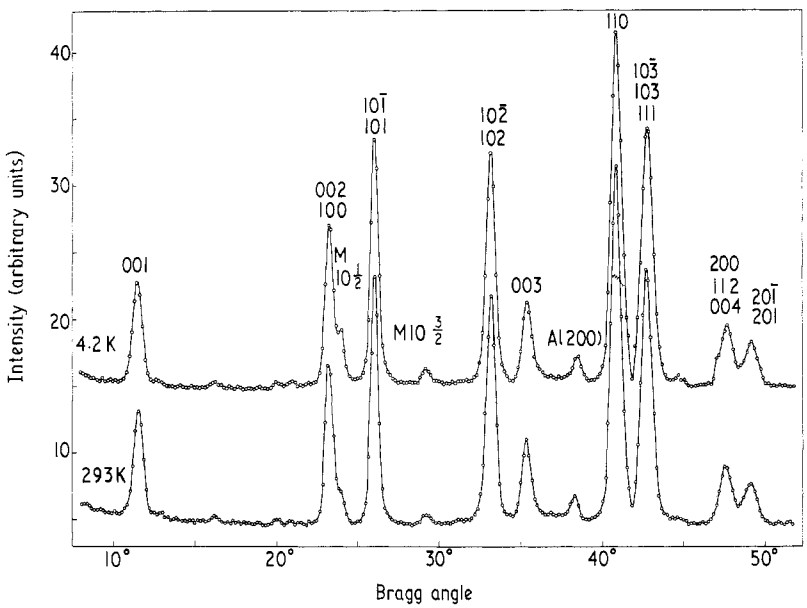

Figure 2. Neutron diffraction patterns at 4 K and 300 K for U_2N_2P.

U_2N_2S and U_2N_2Se. In the case of U_2N_2P and U_2N_2As, whose reported Néel points were above room temperature, the samples were transferred from the cryostat into the vacuum furnace. The M($10\frac{1}{2}$) peak height was then measured while the samples were heated up to 500 K (figures 3 and 4).

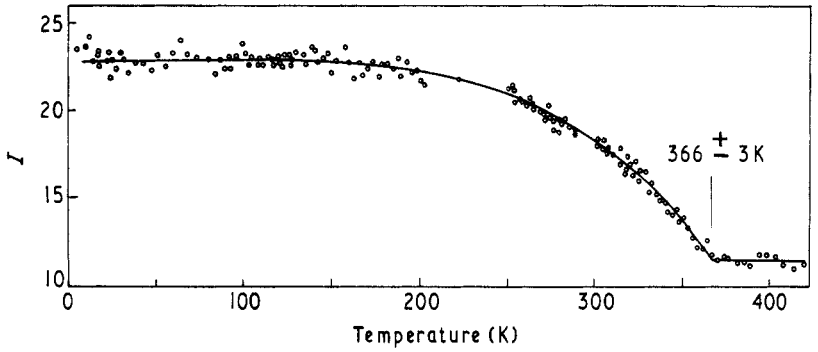

Figure 3. Temperature dependence of the M($10\frac{1}{2}$) peak height for U_2N_2P.

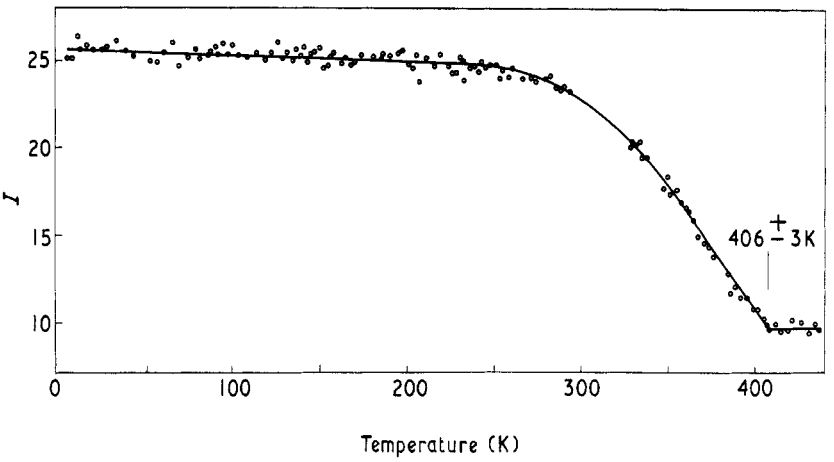

Figure 4. Temperature dependence of the M($10\frac{1}{2}$) peak height for U_2N_2As.

3. Refinement of atomic parameters

All four U_2N_2M compounds investigated are isostructural. Their crystal structure is of the Ce_2O_2S-type (Zachariasen 1949). The space group is $P\bar{3}ml$—D_{3d}^3 No 164, with the following atom positions:

2 U in $\pm(\frac{1}{3}\,\frac{2}{3}\,u)$,

2 N in $\pm(\frac{1}{3}\,\frac{2}{3}\,z)$.

1 M in (0 0 0).

The positional parameters u and z were determined from the neutron intensities collected

Table 1. Crystallographic and magnetic data for U_2N_2M compounds.

Compound	Lattice constants (Å)	Crystal structure parameters 4 K	300 K	Magnetic moment 4 K	300 K	Néel temperatures (K)
U_2N_2S	$a = 3{\cdot}818 \pm 0{\cdot}002$ $c = 6{\cdot}610 \pm 0{\cdot}002$	$u = 0{\cdot}2798 \pm 0{\cdot}0023$ $z = 0{\cdot}6264 \pm 0{\cdot}0029$ $R = 0{\cdot}0622$	$u = 0{\cdot}2798 \pm 0{\cdot}0013$ $z = 0{\cdot}6274 \pm 0{\cdot}0022$ $R = 0{\cdot}0538$	1·3† 1·5		233 ± 3
U_2N_2Se	$a = 3{\cdot}863 \pm 0{\cdot}001$ $c = 6{\cdot}867 \pm 0{\cdot}002$	$u = 0{\cdot}3054 \pm 0{\cdot}0049$ $z = 0{\cdot}6306 \pm 0{\cdot}0054$ $R = 0{\cdot}0855$	$u = 0{\cdot}2965 \pm 0{\cdot}0015$ $z = 0{\cdot}6244 \pm 0{\cdot}0017$ $R = 0{\cdot}0258$	2·2 2·3		245 ± 3
U_2N_2P	$a = 3{\cdot}805 \pm 0{\cdot}001$ $c = 6{\cdot}596 \pm 0{\cdot}003$	$u = 0{\cdot}2770 \pm 0{\cdot}0015$ $z = 0{\cdot}6290 \pm 0{\cdot}0018$ $R = 0{\cdot}0608$	$u = 0{\cdot}2747 \pm 0{\cdot}0015$ $z = 0{\cdot}6280 \pm 0{\cdot}0015$ $R = 0{\cdot}0480$	$1{\cdot}71 \pm 0{\cdot}08$‡ $1{\cdot}58 \pm 0{\cdot}07$	$1{\cdot}40 \pm 0{\cdot}08$ $1{\cdot}33 \pm 0{\cdot}07$	366 ± 3
U_2N_2As	$a = 3{\cdot}830 \pm 0{\cdot}001$ $c = 6{\cdot}739 \pm 0{\cdot}002$	$u = 0{\cdot}2789 \pm 0{\cdot}0012$ $z = 0{\cdot}6190 \pm 0{\cdot}0015$ $R = 0{\cdot}0390$	$u = 0{\cdot}2802 \pm 0{\cdot}0033$ $z = 0{\cdot}6203 \pm 0{\cdot}0030$ $R = 0{\cdot}0722$	$1{\cdot}62 \pm 0{\cdot}07$ $1{\cdot}53 \pm 0{\cdot}08$	$1{\cdot}33 \pm 0{\cdot}05$ $1{\cdot}35 \pm 0{\cdot}08$	406 ± 3

† The first value is derived from the intensity of the M(100) reflection and the second from M(101) + M(10$\bar{1}$) reflections

‡ The first value is derived from the intensity of the M(10$\frac{1}{2}$) and M(10$\bar{\frac{1}{2}}$) reflections and the second from M(10$\frac{3}{2}$) and M(10$\bar{\frac{3}{2}}$) reflections

at 4 K and 300 K and subsequently refined on a CYBER 70 computer by the least-squares method. The values of u and z at 4 K and 300 K, with the corresponding R factors, are compiled in table 1. The reliability factor R is defined as $R = \Sigma(I_{obs} - I_{calc})/\Sigma I_{calc}$ where I_{calc} is the integrated intensity, including the Lorenz factor $(\sin\theta \cdot \sin 2\theta)^{-1}$ and the multiplicity factor j. No temperature factor was allowed for. The following neutron scattering amplitudes (in 10^{-12} cm) were taken for the computations (*Neutron Diffraction Commission* 1972):

$$b_U = 0{\cdot}85 \qquad b_N = 0{\cdot}94 \qquad b_P = 0{\cdot}51$$
$$b_S = 0{\cdot}28 \qquad b_{As} = 0{\cdot}64 \qquad b_{Se} = 0{\cdot}78.$$

The lattice constants were determined from the powder x-ray diffractometer pattern and refined by the least-squares method. They are also included in table 1. The lattice constants and structure parameters for U_2N_2M compounds have been previously given by Benz and Zachariasen (1969) from x-ray investigations. Their values are in fairly good agreement with our data.

4. Magnetic structures

Liquid helium neutron diffraction patterns for U_2N_2S and U_2N_2Se indicate that in these compounds the dimensions of the chemical and magnetic unit cell are the same. From the comparison of the 4 K and room temperature M(001)-peak intensities one can conclude that $\langle q^2\rangle_{(001)} = 0$, so that the magnetic moment alignment at 4 K is along the c-axis. No additional reflections of magnetic origin were observed, indicating that the occurrence of a non-collinear moment arrangement should be excluded. The proposed magnetic structure of U_2N_2Se and U_2N_2S presented in an orthohexagonal unit cell, is shown in figure 5*a*. The propagation vector for such a magnetic structure is $k[000]$.

Subtraction of the room-temperature (100 + 002)-peak intensity from the one measured at 4 K gave the contribution of magnetic scattering from which the magnitude of the magnetic moment at 4 K was determined. The same has been done for the (101) peak. This procedure has been adopted because the scaling factors determined from the 4 K and 300 K diffraction patterns turned out to differ within the experimental errors. For example in the case of U_2N_2S they are at 4 K and 300 K: 0·0150 ± 0·0004 and 0·0156 ± 0·0004, respectively. Also the atomic parameters as determined at 4 K and 300 K practically do not differ (table 1).

The uranium form factor for the $5f^2$ configuration has been used for derivation of μ values from observed intensities. The $5f^2$ form factor of uranium is known with considerable accuracy from single-crystal data (Wedgwood 1972). For $\sin\theta/\lambda$ above which magnetic peaks appear the difference between $5f^2$ and $5f^3$ form factors are still small (Wedgwood 1972), so that the errors which might follow from misconceiving the state of the U atom are contained in statistical errors involved in intensity measurements.

The magnitudes of magnetic moments determined from both reflections M(100) and M(101) are inserted in table 1.

Two magnetic superstructure reflections were found on the 4 K and 300 K neutron diagrams of U_2N_2P and U_2N_2As. One of them, which could be indexed as M($10\frac{1}{2}$), is partially overlapping with the (002) and (100) nuclear peaks, whereas the other one M($10\frac{3}{2}$) is well separated. The indices indicate that the magnetic unit cell is obtained by doubling the chemical one in the c-direction, that is, the propagation vector of the struc-

ture is $k = [00\frac{1}{2}]$. The absence of any reflections of $M(00\frac{1}{2}l)$-type is a clear indication that the magnetic moment of the U ions are directed along the c-axis. The magnetic unit cell corresponding to the proposed type of the antiferromagnetic ordering is shown in figure 5*b*.

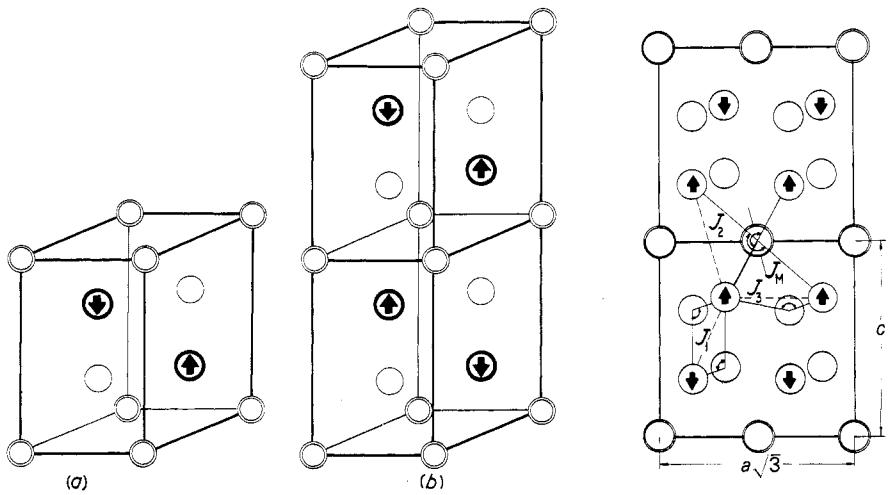

Figure 5. The magnetic structure of (*a*) U_2N_2S and U_2N_2Se and (*b*) U_2N_2P and U_2N_2As. Single circles represent N atoms, double circles, M atoms

Figure 6. Principal magnetic interactions between U ions in U_2N_2M compounds (compare table 2).

The magnitudes of the magnetic moments at 4 K and 300 K were calculated from the intensities of the above-mentioned superstructure magnetic reflections. These intensities were put on an absolute scale, using the scaling factors obtained in the course of the least-squares refinements of the atomic positional parameters at relevant temperatures. As before, the $5f^2$ form factor and determined atomic uranium parameters u were used in the computations. The results are collected in table 1: the magnitudes of μ as obtained from $M(10\frac{1}{2})$ and $M(10\frac{3}{2})$ are listed separately.

5. Discussion

5.1. Exchange interactions

The problem of stability of various possible magnetic moment configurations in the hexagonal Ce_2O_2S-type structure has been considered in detail by Ballestracci *et al* (1968) using Bertaut's matrix method.

In both ordering schemes as found in U_2N_2M compounds two Bravais lattices based on U_I at $(\frac{1}{3}\ \frac{2}{3}\ u)$ and U_{II} at $(\frac{2}{3}\ \frac{1}{3}\ \bar{u})$ can be distinguished. Each uranium ion is surrounded by eight U neighbours belonging to the other sublattices with different U–U spacings. The corresponding exchange integrals have been denoted by J_1 and J_2 (direct interactions) and J_M (superexchange)—see figure 6. In addition, there are 6 uranium ions situated in the same plane at the distance equal to the lattice constant a, all belonging to the parent

sublattice. The corresponding exchange integral has been labelled by J_3 (direct interactions). The possible direct and superexchange interactions, together with the respective angles, are shown in figure 6 and collected in table 2.

Table 2. Principal exchange integrals in the U_2N_2M-type magnetic unit cell

Average U–U distance (Å)	Type of exchange	Average angle	Exchange integral	Coupling mode [000]	Coupling mode [$00\frac{1}{2}$]
3·7	direct				
	superexchange U–N–U	106°	J_1	AF	AF
3·8	direct				
	superexchange U–N–U	82°	J_3	F	F
	superexchange U–M–U	82°			
4·4	direct				
	superexchange U–M–U	98°	J_2	F	AF
5·6	superexchange U–M–U	170°	J_M	F	AF

For the [000] and [$00\frac{1}{2}$] modes observed in the $U_2N_2S(Se)$ and $U_2N_2P(As)$ magnetic structures, respectively, the following stability conditions hold:

(1) mode [000] with:

$\lambda_+ = 6J_2 + 3(J_1 + J_3 + J_M)$—ferromagnetic ordering,

$\lambda_- = 6J_2 - 3(J_1 + J_3 + J_M)$—antiferromagnetic ordering;

(2) mode [$00\frac{1}{2}$] with:

$$\left.\begin{aligned}\lambda_+ &= 6J_3 + 3(J_2 - J_1 + J_M)\\ \lambda_- &= 6J_3 - 3(J_2 - J_1 + J_M)\end{aligned}\right\}$$ —both antiferromagnetic ordering.

From the requirement that λ has its maximum value one can derive the signs of the particular exchange interactions. For the case of the mode [000] ordering schemes the situation is unambiguous because only antiferromagnetic ordering has been found experimentally.

The antiferromagmetic ordering schemes corresponding to the [$00\frac{1}{2}$] mode can be visualized in the frame of a magnetic unit cell as ferromagnetic sheets piled up in the c-direction with the following sequences:

either $+ - - + (\lambda_+)$

or $+ + - - (\lambda_-)$.

In the first model the shortest distance is between the U–U ions belonging to neighbouring sheets with antiferromagnetic coupling (see table 2), whereas in the second one the nearest U ions are coupled ferromagnetically. To each model correspond different $F(10\frac{1}{2})$ and $F(10\frac{3}{2})$, so that both models yield different values of the magnetic moment at the site of the U ion. The magnitudes of μ in U_2N_2P and U_2N_2As listed in table 1 were in fact derived from the observed neutron intensities assuming the $+ - - +$ sequence. We have also made calculations for the $+ + - -$ model. The 4 K intensities for U_2N_2P give $\mu = 1{\cdot}93 \pm 0{\cdot}08\ \mu_B$ from the $M(10\frac{1}{2})$ reflection and $\mu = 1{\cdot}38 \pm 0{\cdot}08\ \mu_B$ from the $M(10\frac{3}{2})$, whereas for the case of U_2N_2As the derived values are $1{\cdot}97 \pm 0{\cdot}08\ \mu_B$ and

1·23 ± 0·08 μ_B, respectively. In both compounds the discrepancy between $\mu_{M(10\frac{1}{2})}$ and $\mu_{M(10\frac{3}{2})}$ for the + + − − model is far outside the experimental error. This inclines us to draw the conclusion that the + − − + structure is more stable.

It seems proper to mention here that the isostructural rare earth compounds $RE_2O_2S(Se)$, (RE = Tb, Dy, Ho, Yb) also exhibit antiferromagnetic properties, but their magnetic structures as determined by neutron diffraction (Ballestracci *et al* 1968, Abbas *et al* 1973, 1974) are for most of them different from those found in U_2N_2M compounds.

5.2. Crystal-field interactions

To account for observed magnitudes of the ordered magnetic moments, one should first consider the crystal-field effect on the U^{4+} ion with $5f^2$ configuration which is usually assumed for uranium in its intermetallic compounds. In the U_2N_2M structure the crystal-field symmetry around the U^{4+} ion is a trigonal C_{3v}. For such a symmetry the crystal-field ground state might be either one of the singlets or doublets. The first possibility usually leads to a zero ordered magnetic moment in the absence of any magnetic exchange interactions. In the opposite case, a small induced magnetic moment may be brought about by these interactions. In such a situation the expected transition temperature (Néel points) should be low, but the observed fairly large values of both the magnetic moment and the Néel temperature contradict a singlet to be the ground state. Therefore, probably one of the doublets is the ground state.

In the actinide compounds the three important interactions (Coulomb repulsion, spin–orbit coupling and crystal field) are of comparable magnitude. Therefore, only simultaneous diagonalization of all these interactions may yield the eigenvectors and eigenvalues to the experimental data. Such calculations are now planned.

Acknowledgments

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