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Magnetic Ordering in UGeY (Y = S, Se, Te) by Neutron Diffraction

By

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The magnetic structures and the magnitudes of the ordered magnetic moments for UGeS, UGeTe, UGeSe are determined by neutron diffraction using powder samples. The magnetic unit cell in UGeS is twice the chemical one along the c-axis; the sequence of ferromagnetic sheets is (+ + − −). In UGeTe and UGeSe the magnetic and chemical unit cells coincide. The sequence of ferromagnetic sheets is: in UGeTe (+ + − −) in UGeSe (+ − + −). In both the direction of the magnetic moment is along the c-axis. The magnitudes of magnetic moment on the uranium ion at 4 K amount to 1.26, 1.50, and $0.26\mu_B$ for UGeS, UGeTe, UGeSe, respectively. The Néel temperatures are determined to 88, 73, and 40 K, respectively.

An Pulverproben werden mittels Neutronenbeugung die magnetischen Strukturen und die Größen der geordneten magnetischen Momente für UGeS, UGeTe und UGeSe bestimmt. Die magnetische Einheitszelle in UGeS ist zweimal so groß wie die chemische in Richtung der c-Achse; die Folge der ferromagnetischen Schichten ist (+ + − −). In UGeTe und UGeSe fallen die magnetische und chemische Einheitszelle zusammen. Die Folge der ferromagnetischen Schichten ist für UGeTe (+ + − −) und in UGeSe (+ − + −). In allen ist die Richtung der magnetischen Momente parallel zur c-Achse. Die Größe des magnetischen Moments am Uranion beträgt bei 4 K 1,26; 1,50 und $0{,}26\mu_B$ für UGeS, UGeTe bzw. UGeSe. Die Néel-Temperaturen werden zu 88, 73 und 40 K bestimmt.

1. Introduction

The ternary uranium compounds UYX (where X = O, P, As, Sb, Bi, Si, Ge, Sn and Y = S, Se, Te) crystallize either in the PbFCl-type structure (space group P4/nmm) or in the UGeTe-type (space group I4/mmm). The basic unit of both structure-types is a UX_4Y_5 coordination polyhedron. Its point symmetry is C_{4v}, and the crystal field potential has a strong axial tendency [2, 5].

This fact and the presence of magnetic ordering suggests the appearance of collinear uniaxial magnetic structures in these compounds.

Possible antiferromagnetic collinear ordering schemes in PbFCl-type structure have been discussed previously [6, 7]. Among the PbFCl type compounds three types of antiferromagnetic arrangements and one ferromagnetic type were found [6, 8 to 10]. Possible kinds of stable magnetic ordering in UGeTe compounds have been also reported [11], but only ferromagnetic ordering has been hitherto found by neutron diffraction in UPTe and UAsTe [4].

Magnetic measurements performed on powder samples of UGeS (PbFCl type) and UGeTe, UGeSe (UGeTe type) revealed that all of them are antiferromagnets, with Néel points at 88, 73, and 40 K, respectively [5].

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The layer-like arrangement of U ions and the presence of four such layers in the chemical unit cell of UGeTe-type compounds implies that any consideration concerning the possible antiferromagnetic ordering both in UGeSe and UGeTe should start with a model in which the magnetic and chemical unit cells are of the same dimensions.

Since for UGeSe and UGeTe we did not find any evidence for a noncollinear moment alignment, our neutron diffraction data were inspected basing on three possible models of antiferromagnetic ordering which have been predicted for the UGeTe type [11] and are described briefly as a sequence of layers composed of U ions piled up in the direction of the *c* axis. The magnetic coupling within the layers is ferromagnetic, but the U ions belonging to neighbouring layers are coupled antiferromagnetically. The following coupling schemes are possible [11]: type AFI (+ — — +), type AFII (+ + — —), and type AFIII (+ — + —).

We report the results of a neutron diffraction study aiming at the determination of the magnetic structure and at refining of atomic parameters for UGeS, UGeSe, and UGeTe.

2. Experiment and Results

The chemical preparation of UGeTe and UGeSe samples has been described in detail elsewhere [1, 5]. They were obtained in polycrystalline form. X-ray diffraction patterns show that for UGeTe we obtained a single phase sample, but the UGeSe turned out to be contaminated with a small amount of elemental Ge. The lattice constants determined from the X-ray diffractograms and refined by a least-squares procedure are listed in Table 1.

Neutron diffraction patterns at 4 and 300 K were obtained on the DN-500 neutron diffractometer at the EWA reactor in Świerk. The neutron wavelength was (1.324 ±

Table 1

Crystallographic data for UGeY compounds

Compound	type of structure	a (Å)	c (Å)	c/a	z_U	z_Y	R (%)
UGeS	PbFCl	3.820 ± 0.002	8.323 ± 0.010	2.179	0.2889 ± 0.0010	0.6368 ± 0.0042	3.43
UGeSe	UGeTe	3.932 ± 0.001	16.966 ± 0.006	4.315	0.1316 ± 0.0006	0.3114 ± 0.0006	6.58
UGeTe	UGeTe	4.110 ± 0.001	17.599 ± 0.009	4.282	0.1237 ± 0.0011	0.3139 ± 0.0019	6.30

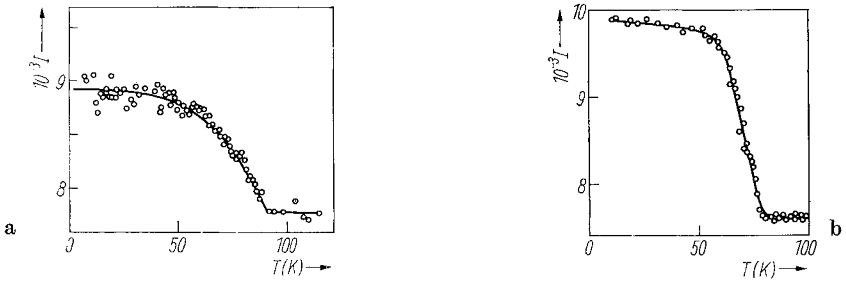

Fig. 1. Temperature dependence of the a) M $(10\frac{1}{2})$ peak height for UGeS and b) M(102) peak height for UGeTe

± 0.003) Å. Measurements of magnetic peak heights performed when the cryostat was slowly warming up gave the respective Néel temperatures (Fig. 1 a, b).

The crystal structure of UGeTe-type belongs to the space group I4/mmm [D_{4h}^{17}] with the following atomic positions:

$$0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} +$$
$$4\ \text{U in 4e}: 0, 0, z_U; 0, 0, \bar{z}_U ,$$
$$4\ \text{Te in 4e}: 0, 0, z_Y; 0, 0, \bar{z}_Y ,$$
$$4\ \text{Ge in 4c}: 0, \tfrac{1}{2}, 0; \tfrac{1}{2}, 0, 0 .$$

UGeS is of PbFCl-type (P4/nmm-D_{4h}^7):

$$2\ \text{U in 2c}: \tfrac{1}{4}, \tfrac{1}{4}, z_U; \tfrac{3}{4}, \tfrac{3}{4}, \bar{z}_U ,$$
$$2\ \text{S in 2c}: \tfrac{1}{4}, \tfrac{1}{4}, z_Y; \tfrac{3}{4}, \tfrac{3}{4}, \bar{z}_Y ,$$
$$2\ \text{Ge in 2a}: \tfrac{3}{4}, \tfrac{1}{4}, 0; \tfrac{1}{4}, \tfrac{3}{4}, 0 .$$

The atomic parameters were determined from neutron intensities measured at room temperature for UGaTe, and at 78 K for UGeSe and UGeS.

The values of z_U and z_Y with the corresponding R factors, were calculated and refined by the least-squares method (with all weights put equal to one (Table 1)) using a CYBER computer. The observed and calculated intensities are shown in Table 2.

The influence of the Debye-Waller temperature factor $2B$ on the parameters z_U, z_Y has been tested as an additional parameter in the calculations in the case of UGeTe. It was estimated to be 3.0 $Å^{-2}$ by use of a least-squares procedure with a simultaneous variation of z_U, z_Y in the range of fitting errors.

Table 2

Comparison of observed and calculated neutron intensities

hkl	UGeTe (300 K)		UGeSe (80 K)		*hkl*	UGeS (80 K)	
	I_{cal}	$I_{obs} \times K$	I_{cal}	$I_{obs} \times K$		I_{cal}	$I_{obs} \times K$
002	81.4	58.0	594.8	481.3	001	117.5	125.0
004	0.0	0.0	1.7	0.0	002	0.1	0.0
101	163.8	162.8	370.0	368.0	101	168.3	159.6
103	6.0	171.5	11.2	0.0	110	13 3	23.9
112	2252.0	2214.0	1595.0	1546.0	111	363.7	362.7
105	1469.0	1440.0	1339.0	1484.0	004	439.0	410.4
114	2206.0	2193.0	2542.0	2617.0	202	0.0	0.0
206	1029.0	1059.0	—	—	105	28.2	22.0
202	17.6	0.6	130.0	123.1	102 003	195.3	206.8
008	117.4	164.3	236.0	189.1	112 103	625.9	624.2
107	776.5	822.3	—	—	113 200	269.7	281.4
006 110	1142.0	1032.0	654.2	650.8	201 104	75.9	77.1
204 211	72.7	50.0	1.3 163.3	0.0 144.6	212 203	265.9	252.3
200 116	1830.0	1975.0	1728.0	1624.0	211 055 114	124.7	126.8
0010 109 118 213	603.1	680.7	707.7	651.4			

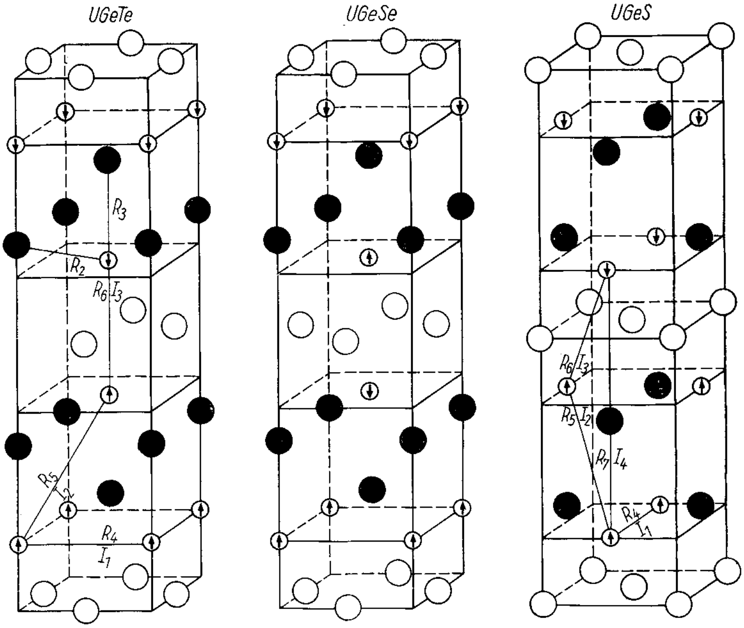

Fig. 2. Magnetic structures of UGeTe, UGeSe, UGeS and principal magnetic interactions between U ions. Small circles represent U atoms; black circles: Te, Se, S; empty circles: Ge

The crystallographic and magnetic unit-cells of UGeTe and UGeSe are shown in Fig. 2. The prinicipal interatomic distances are listed in Table 3 and 4.

3. Magnetic Structure

3.1 UGeSe and UGeTe

The neutron diffraction patterns of UGeSe taken at 4 and 78 K are very interesting. No separate magnetic reflections were observed. Only small contributions to the nuclear peaks (101), (103) were detected. At 40 K the susceptibility versus temperature curve displays a peak characteristic for a transition to the antiferromagnetic state (see Fig. 3 and 4 in [5]). In the UGeTe case, a distinct peak of magnetic origin was observed at 4 K. It disappeared at $T = 70$ K, which agrees well with the Néel temperature at 73 K determined from susceptibility measurements. This peak was readily indexed as M (102) assuming that the magnetic and chemical unit-cells have the same dimensions. The three possible models: AF-I (+ − − +), AF-II (+ + − −),

Table 3

Principal interatomic distances in UOS and UGeY compounds

atom	neighbour	C.N.	dis. Fig. 5	distance (Å)			
				UOS	UGeS	UGeSe	UGeTe
U	O, Ge	4	R_1	2.34	3.071	2.975	2.975
U	S, Se, Te	4	R_2	2.93	2.771	2.944	3.107
U	S, Se, Te	1	R_3	2.93	2.896	3.051	3.347

Table 4
Comparison of the magnetic and crystallographic properties of UOS and UGeY compounds

compounds		UOS	UGeS	UGeSe	UGeTe
type of structure		PbFCl	PbFCl	UGeTe	UGeTe
type of ordering		AF-II	AF-II	AF-III	AF-II
		(+ + − −)	(+ + − −)	(+ − + −)	(+ + − −)
T_N (K)		50	88	40	73
θ		−51	+77	−20	+27
μ_{eff} (μ_B)		2.78	2.60	3.03	2.84
z_U		0.200	0.2889	0.1316	0.1237
distance U–U	ex. integr.				
(Å)	I				
R_4	I_1	3.843, $I_1 > 0$	3.820, $I_1 > 0$	3.932, $I_1 > 0$	4.110, $I_1 > 0$
R_5	I_2	4.850, $I_2 > 0$	4.392, $I_2 > 0$	4.886, $I_2 < 0$	5.311, $I_2 > 0$
R_6	I_3	3.815, $I_3 < 0$	5.514, $I_3 < 0$	4.466, $I_3 < 0$	4.354, $I_3 < 0$
R_7	I_4	6.694, $I_4 < 0$	8.323, $I_4 < 0$	—	—
value of ex. integral (10^{-16} erg)					
		$I_1 + I_2 = 0.0213$	$I_1 + I_2 = 4.0437$	$I_1 = 0.3617$	$I_1 = 0.3617$
		$I_3 + I_4/2 = -2.165$	$I_3 + I_4/2 = -0.2694$	$-0.542 < I_2 < -0.069$	$I_2 = 0.8465$
				$I_2 + I_3/8 = -0.542$	$I_3 = -3.779$
μ_{AF}		1.9	1.28	0.245	1.5
$H_{ex} \times 10^5$ Gs		5.59	6.24	0.477	6.06
E_{ex} (cm^{-1})		49.73	37.36	0.546	42.51

AF-III (+ − + −) were therefore considered, to select the one which gives good agreement with the experimental results. First of all, if one assumes that the magnetic moments are aligned along the fourfold axis, which is a very reasonable assumption, then all M (001) type magnetic reflections should remain unobserved because $\langle q^2 M\ (001)\rangle$ is zero in that case.

The values of the magnetic intensities multiplied by μ^2 (μ magnitude of magnetic moment on the uranium ion), for all collinear antiferromagnetic models are listed in Table 5. The magnetic form factor for the $5f^2$ configuration [14], the Lorentz factor, and the multiplicity factor are accounted for. The observed magnetic intensities for UGeSe and UGeTe multiplied by respective factors are listed in Table 4. The scaling factors K were determined from neutron diffraction patterns obtained above T_N.

The type of the magnetic ordering in UGeTe can be determined, since a well separated magnetic peak with indices M [102] has been observed, and is found to be AF-II. The magnitude of the magnetic moment on the uranium ion at 4 K amounts to $(1.50 \pm 0.05)\ \mu_B$. The only possible model for UGeSe is AF-III. The magnitude of the magnetic moment on the U ion was determined to be $(0.26 \pm 0.10)\ \mu_B$ and $(0.23 \pm \pm 0.10)\ \mu_B$ from the intensities of the (101) and (103) magnetic reflections, respectively.

Table 5

Comparison of observed and calculated neutron magnetic intensities at 4 K

M (hkl)	$(I_M)_{cal}$ type AF-I (+ − − +)	$(I_M)_{cal}$ type AF-II (+ + − −)	$(I_M)_{cal}$ type AF-III (+ − + −)	$(I_M)_{obs} \times K$	
				UGeTe	UGeSe
M (100)	$66.82 \times \mu^2$	0.0	0.0	not obs.	not obs.
M (102)	$0.61 \times \mu^2$	$97.33 \times \mu^2$	0.0	220.46	not obs.
M (101)	0.0	0.0	$64.40 \times \mu^2$	not obs.	42.50
M (103)	0.0	0.0	$22.14 \times \mu^2$	not obs.	11.56

3.2 UGeS

Magnetic superstructure peaks characteristic for antiferromagnetic ordering were observed in the neutron diffraction pattern taken at 4 K. These additional peaks were indexed on the basis of a c-doubled unit-cell. The magnetic ordering can be uniquely determined from the intensity of the M $(10\frac{1}{2})$ and M $(10\frac{2}{3})$ reflections. The sequence of ferromagnetic sheets is (+ + − −). The corresponding μ values at 4 K for this type of magnetic ordering are as follows:

$$\text{from } M\ (10\tfrac{1}{2}) \qquad \mu = (1.26 \pm 0.05)\ \mu_B\,,$$

$$\text{from } M\ (10\tfrac{3}{2}) \qquad \mu = (1.30 \pm 0.05)\ \mu_B\,.$$

The Néel point determined from the temperature dependence of the M $(10\frac{1}{2})$ peak height is (90 ± 2) K (Fig. 1a).

4. Discussion

Our neutron diffraction results show that in UGeS the same type of antiferromagnetic ordering occurs as in UOSe and UOS (+ + − −).

The magnetic unit cell is doubled in the direction of the fourfold axis c. On the other hand, the magnetic and chemical unit cells of UGeSe and UGeTe are of the same dimensions. The sequence of ferromagnetic sheets in UGeSe is (+ − + −), whereas in UGeTe it is (+ + − −).

The magnetic ordering in UXY-type compounds is different, because the values of atomic parameters and the interactions for the U^{4+} ions are different in this case.

In the case of UGeS the lattice constant c, and the parameter z_U are larger than the corresponding parameters in UOS (Table 1). These changes lead to different values of the distances between magnetic U–U ions (Fig. 2).

The corresponding exchange integrals have been denoted by I_1, I_2, I_3, I_4. For the case of the magnetic ordering scheme $(+ + - -)$ observed in UGeS the molecular field relations are as follows:

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(-8I_3 - 4I_4)\,,$$

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(8I_1 + 8I_2)\,,$$

where T_N (Néel point), θ (Curie-Weiss constant) and μ_{eff} are known from experiment, $g = 0.8$, $J(J + 1) = \mu_{\text{eff}}/g^2\mu_B^2$ (Table 4) (k_B Boltzmann constant).

Since R_4 [UOS] $= R_4$ [UGeS], the corresponding exchange integrals are assumed to be equal, so that if R_5 [UOS] $> R_5$ [UGeS] we have I_2 [UOS] $< I_2$ [UGeSe], and if R_6, R_7 [UOS] $< R_6$, R_7 [UGeS] we get $(I_3 + I_4/2)$ [UOS] $> (I_3 + I_4/2)$ [UGeS].

It becomes evident that an increase in the parameters z_U and c in the PbFCl type structure leads to an increase of the ferromagnetic interactions $(I_1 + I_2)$ and to a decrease of the antiferromagnetic interactions $(I_3 + I_4/2)$.

Using the calculated values of exchange integrals and the experimental magnetic moment of uranium at 5 K in the antiferromagnetic state, μ_{AF}, we obtained values of H_{ex} and E_{ex}:

$$H_{ex} = \frac{2\mu_{AF}}{g^2\mu_B}(4I_1 + 4I_2 - 4I_3 - 2I_4)\,,$$

$$E_{ex} = -\mu_{AF}\,H_{ex}\,. \qquad \text{(Table 4)}$$

The large difference between the values of the magnetic moments at 5 K in UOS and UGeS suggests the conclusion that the crystal-field and the molecular-field level schemes for the uranium ions in UOS and UGeS are different. The existence of two different ordering schemes in UGeSe and UGeTe can be similarly explained in a simple way on the basis of the molecular field theory. For the UGeTe case $(+ + - -)$

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(+8I_1)\,,$$

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(-16I_2 - 2I_3)\,.$$

In the case of UGeSe $(+ - + -)$ the molecular field relations are as follows:

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(8I_1 + 16I_2)\,,$$

$$k_B(T_N - \theta) = \frac{2J(J + 1)}{3}(-2I_3)\,.$$

The exchange integrals I_1, I_2, I_3 are dependent on the U–U distances, denoted as R_4, R_5, R_5 in Fig. 3. The distances listed in Table 4 are determined by three factors: the lattice constants a and c, and the atomic parameter z_U of uranium. Considering the U–U distance denoted as R_5, one can notice that while passing from UGeSe to UGeTe it changes much more than the distances R_4 and R_6 (see Table 4). The change in the sign of I_2, which is negative in UGeSe and positive in UGeTe, may be thus attributed to the weakening of antiferromagnetic interaction occurring as R_5 increases until ferromagnetic coupling is attained (as observed in UGeTe). On the other hand, the signs of I_1 and I_3 do not change, since the change of R_4 and R_6 is rather small.

The observed different values of the magnetic moment on the U ion in the ordered state cannot be explained quantitatively at present.

The magnetic behaviour of all the three compounds is undoubtedly determined by a combined effect of the crystal electric field (CEF) and the molecular field due to exchange interactions. The symmetry of CEF in the [UY_4X_5] coordination polyhedron is tetragonal (C_{4v}). If one assumes that the U ion is in the (+4) state, the corresponding ground state is $^3H_4$. The latter is split into two doublets (T_5, Γ_5) and five singlets. In the ordered state, the molecular field leads to further splitting of the doublets, so that there are in total 9 Stark levels. Without detailed knowledge of the field parameters it is impossible to find the eigenvectors and eigenvalues for an U ion in a field of such low symmetry. Consequently we are unable to propose a splitting scheme which gives a magnetic moment close to the experimentally observed one.

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