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The Magnetic Phase Diagram of the $UAs_{2-x}Se_x$ Solid Solution

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Introduction The magnetic behaviour of solid solutions, in which one of the end members is antiferromagnetic whereas the other ferromagnetic was the subject of several neutron-diffraction investigations (1 to 5).

In particular, studies of uranium compounds with rock-salt-type structure have shown that the transition from antiferromagnetic UAs and UP to ferromagnetic USe and US proceeds through transient phases which are stable over fairly broad composition and temperature ranges.

This paper is the first one in which we are going to report the results of measurements performed on solid solutions of uranium compounds with PbFCl-type structure.

The $UAs_{2-x}Se_x$ samples The following compositions in the $UAs_{2-x}Se_x$ system were synthesized and investigated by neutron diffraction: $UAs_{1.50}Se_{0.50}$, $UAs_{1.40}Se_{0.60}$, $UAs_{1.35}Se_{0.65}$, and $UAs_{1.25}Se_{0.75}$. All were prepared by mixing the required amounts of UAs_2 and UAsSe and sintering the mixtures at 900 °C for 10 d in high vacuum. The lattice parameters were determined from the X-ray photographs which showed the materials to be single phases.

Experimental Neutron-diffraction powder patterns were obtained on the KSN-2 spectrometer installed at the reactor EWA. For each sample data were recorded at least twice - at room and liquid helium temperatures. Moreover, the measurements included also the temperature dependence of the heights of magnetic peaks as the cryostat was warmed up slowly. The temperature of the sample was controlled by a gold-chromel thermocouple.

Results The data obtained at room temperature were used for the refinement of crystal structure parameters. In the UXY structure (space group P4/nmm), the atoms are located as follows:

2 U in 2c: 1/4, 1/4, u; 3/4, 3/4, u;

2 X in 2c: 1/4, 1/4, z; 3/4, 3/4, $\bar{z}$;

2 Y in 2a: 3/4, 1/4, 0; 1/4, 3/4, 0.

In the first trial model it was assumed that As and Se atoms are distributed at random between 2a and 2c positions, however, the reliability factor R turned out to be very large. The next check was made by an assumption that 2 As atoms occupy 2a positions whereas the rest of As is located together with Se at 2c.

For the latter case it became possible to minimize the R factor to a reasonably low value, using a trial and error procedure programmed for a GIER computer. (An alternative distribution 2 As in 2c and 2(1 - x)As + 2xSe in 2a, had to be ruled out for the same reason as the first model considered.) A comparison of observed and calculated neutron intensities gave the R factors listed in Table 1. Neutron scattering lengths for U, As, and Se were taken after (6).

Neutron-diffraction patterns obtained at 4.2 °K show that the sample with composition x = 0.5 is a single antiferromagnetic phase with the magnetic unit cell doubled in the [001] direction. This type of magnetic order can be described as a framework of ferromagnetic sheets stacked in the [001] direction with the sequence ++-- ... The sheets with opposite uranium moment alignment are the nearest ones. This type of magnetic ordering has been previously observed in UP_2, UAs_2, UOs, and UOSe (7 to 11).

Table 1

The magnetic data for the $UAs_{2-x}Se_x$ system

composition x	lattice constant (Å) a	lattice constant (Å) c	u	z	R	magnetic order	T_N (°K)	T_C (°K)	μ (BM)	reference
0.00	3.954	8.116	0.283	0.641		AF	283		1.61±0.11	(8)
0.50	3.972	8.284	0.277	0.636	0.06	AF	160±5		1.35±0.08	
0.60	3.975	8.325	0.273	0.623	0.06	AF+F*)	170±5			
0.65	3.974	8.396	0.278	0.623	0.09	F+AF*)		107±5		
0.75	3.979	8.390	0.276	0.629	0.07	F		95±3	1.13±0.10	
1.00	3.989	8.398	0.271	0.631	0.06	F		113±3	1.5 ±0.1	(12)

*) Distinct traces.

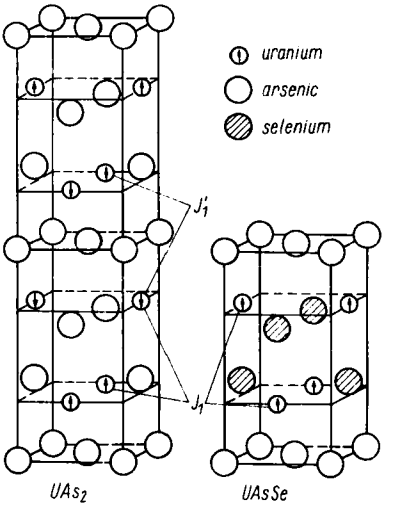

Fig. 1. The magnetic structure of UAs_2 and UAsSe

The increase of selenium content is accompanied by a gradual decrease in intensity of magnetic superstructure peaks characteristic of the antiferromagnetic structure. Simultaneously an increase in the intensity of the (101) nuclear peak is observed. The composition $UAs_{1.25}Se_{0.75}$ is already a single ferromagnetic phase. Our observations indicate that in a fairly broad composition range the antiferromagnetic and ferromagnetic phases are present simultaneously. This fact is probably connected with not the best homogeneity of samples.

Discussion In the magnetic structures consisting of ferromagnetic sheets stacked in one direction as observed in UAs_2 and other related compounds, the sequence of sheets either ++-- or +-+- depends mainly on the signs of two exchange integrals J_1 and J_1' (see Fig. 1). Assuming that other interactions are negligible, we have for UAs_2: $J_1 < 0$ and $J_1' > 0$, whereas in ferromagnetic UAsSe both J_1 and J_1' should be positive. For the compositions between UAs_2 and UAsSe one may expect a competition between negative exchange interaction J_1 (due to the presence of As) and a positive exchange interaction J_1' (due to the presence of Se). As the number of selenium atoms is increasing the positive interaction becomes dominant leading to an overall ferromagnetic coupling.

The exchange integral J_1 in UAsSe seems to be weaker than in UAs_2 since the composition $UAs_{1.50}Se_{0.50}$ is still antiferromagnetic. This suggestion is also supported by a fairly large difference in the corresponding magnetic transition temperatures (Table 1). On the other hand, J_1' is expected in all compositions to be fairly constant - such an assumption is based on the fact that the environment and geometry of the two ferromagnetically aligned sheets do not differ much, even for the end members UAs_2 and UAsSe (12).

In the course of the present neutron-diffraction study we observed collinear moment alignment in the whole system. The absence of any transient magnetic phases is a result of the high anisotropy due to a strong uniaxial crystal field.

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