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MAGNETIC PROPERTIES OF URANIUM SELENIDES AND SULFIDES

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The magnetic properties of uranium selenides and sulfides with stoichiometric compositions 1 : 1, 3 : 4, 2 : 3, 3 : 5, and 1 : 2 are studied. The investigation is carried out between 77 and 1000°K at various magnetic field strengths. In the investigated temperature range the USe_2 and U_3S_5 compounds are found to be paramagnetic with $\Theta_p < 0$. The other compounds are ferromagnetic. The $\sigma(T)$ curve for USe exhibits a peak which shifts towards lower temperatures (from 156 to 135°K) with increasing H and which disappears at H = 7 kOe. The paramagnetic susceptibility of the USe_2 and U_3S_5 compounds obeys the Curie-Weiss law. In the other compounds this law is observed only in a restricted temperature range.

So far attention has mainly been accorded to the investigation of the magnetic properties of alloys and compounds of the transition d and 4f metals. As regards actinide alloys and compounds, in which as is well known the 5f shell begins to be filled, they have hardly been studied. The literature contains extremely little information about the magnetic properties of these substances, in particular of the uranium selenides and sulfides.[1,2]

However, the actinide compounds are of undoubted interest for the physics of magnetic phenomena, since by virtue of their electronic structure they occupy a position intermediate between the 3d and 4f elements. The actinides have no clearly expressed localization of the electrons of unfilled shells as is the case in the rare-earth metals. At the same time the 5f electrons are not so strongly collectivized as in the d metals. Such an electronic structure of the actinides leads one to expect that their alloys and compounds may realize various magnetic structures. This is indicated by the results of neutron diffraction studies[3,4] from which it follows that in certain uranium compounds there occurs an anti- or ferromagnetic interaction, depending on the stoichiometric ratio. By studying the magnetic properties of actinide compounds, one can obtain important information about the carriers of magnetic properties in these materials and clarify which interactions are responsible for the production of antiferromagnetic or ferromagnetic ordering.

Special interest attaches in this connection to uranium compounds, since the number of electrons in the uranium shell changes in different compounds.

In this paper we present the results of the investigation of magnetic properties of compounds of uranium with selenium and sulfur of various stoichiometric composition. The crystallographic structure of these compounds depends on the stoichiometric ratio. Thus for a 1 : 1 ratio the compounds formed have a cubic structure, for a 3 : 4 ratio—a structure of the Th_3P_4 type, for a 2 : 3 ratio—an orthorhombic structure, and for a 1 : 2 ratio—a tetragonal structure. Such a change in the crystallographic structure should also influence the magnetic properties of these compounds. The uranium selenidss and sulfides were synthesized from 99.9 percent pure uranium, selenium, and sulfur powders. The magnetic susceptibility of the initial components was measured before the synthesis.

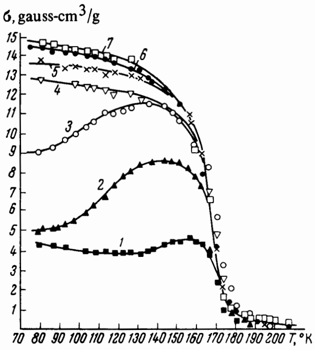

FIG. 1. Temperature dependence of the specific magnetization σ for the compound USe (the magnitude of the field is in oersted): curve 1 – 1000, 2 – 2000, 3 – 3000, 4 – 4000, 5 – 5000, 6 – 6000, and 7 – 7000.

The compounds were synthesized at 800°C in the course of 48 hours in corundum crucibles which were placed in quartz tubes evacuated down to 10^{-5} mm Hg. After this the obtained powder was carefully ground, mixed, and again placed in the furnace under the same

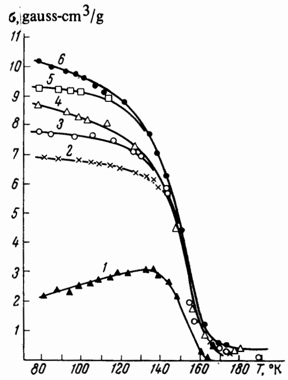

FIG. 2. Temperature dependence of the specific magnetization σ for the compound U_3Se_4 (in oersted): Curve 1 – 1000, 2 – 2000, 3 – 3000, 4 – 5000, 5 – 6000, and 6 – 7000.

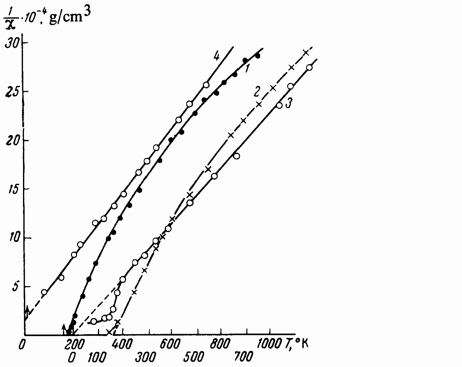

FIG. 3. Temperature dependence of the reciprocal specific susceptibility for the compounds: curve 1 – USe, 2 – U_3Se_4, 3 – U_2Se_3, 4 – USe_2 (1 and 4–upper temperature scale). The vertical arrows indicate the temperature of the maximum specific heat according to the data of [5,6].

conditions. In addition, compounds of the 1 : 1 and 3 : 4 composition were annealed for two hours at 2000°C. Debye-Scherrer photographs taken of the compounds prepared in this way showed that the synthesized compounds consisted of single phases.

The magnetic properties were studied with a pendulum balance in the temperature range from 77 to 1000°K for various values of the magnetic field (1–7 kOe).

Figures 1 and 2 show the temperature dependence of the specific magnetization σ for the compounds USe and U_3Se_4 for various values of the magnetic field intensity. It is seen that in the range of low fields the σ(T) dependence in these compounds has a maximum which is particularly clearly exhibited in the compound USe. With increasing field intensity the maximum of the curves of the temperature dependence of the magnetization becomes more and more washed out and shifts gradually towards lower temperatures.

Thus in USe for 1 kOe this maximum lies in the 160°K range, for 2 kOe at 145°K, and for 3 kOe at about 135°K. In the region of higher fields the magnetization maximum disappears, and σ almost reaches saturation. In U_3Se_4 the maximum on the σ(T) curve is observed at 1 kOe (T_m = 136°K). As regards U_2Se_3, no maxima are observed in its σ(T) dependence, and with decreasing temperature σ continues to increase appreciably. It is characteristic that in U_2Se_3 the magnetization at 80°K is smaller by two orders than that of the USe and U_3Se_4 compounds.

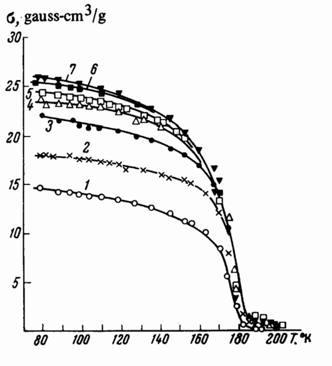

FIG. 4. Temperature dependence of the specific magnetization σ for the compound US (the field intensity is in oersted): curve 1 – 1000, 2 – 2000, 3 – 3000, 4 – 4000, 5 – 5000, 6 – 6000, and 7 – 7000.

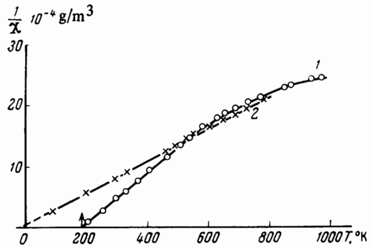

FIG. 5. Temperature dependence of the reciprocal specific susceptibility for the compounds: 1 – US, 2 – U_3S_5. The vertical arrow indicates the temperature of the maximum specific heat according to the data of [5,6].

The compound USe_2 is in the entire investigated temperature range a paramagnet whose susceptibility χ follows the Curie-Weiss law with a negative value of the paramagnetic Curie temperature. (Θ_p = –48°K) (see Fig. 3). The same figure shows the dependence of 1/χ on T for the remaining uranium selenides. It is seen that whereas USe_2 follows the Curie-Weiss law throughout the entire range of temperatures, U_2Se_3 follows it between 200 and 1000°K, U_3Se_4 between 180 and 400°K, and USe between 180 and 300°K. In the last two of these some curvature directed towards the temperature axis appears at higher temperatures.

Figure 4 shows the temperature dependence of the specific magnetization σ for uranium monosulfide, US. It is seen that this dependence differs considerably from that of USe. In the case of US the T dependence of σ is for all the investigated values of the fields the same as in the usual ferromagnets: with increasing temperature the magnetization decreases monotonically. The ferromagnetic Curie point of this compound is 180°K. A sample of the composition $US_{1.33}$ had an analogous σ(T) dependence. As regards U_3S_5, as well as USe_2 it is in the entire temperature range that was investigated a paramagnet with Θ = –16°K. The magnetic susceptibility of this compound follows the Curie-Weiss law in a broad range of temperatures (77–700°K) (Fig. 5). Analyzing the magnetization isotherms, it is seen that they have a clearly nonlinear form; at the same time, in compounds of the composition 1 : 1 and 3 : 4 the specific magnetization for H > 2 kOe changes very little with increasing magnetic field intensity almost reaching saturation. In U_2Se_3 the magnetization isotherms have no saturation. It is also characteristic that above a certain temperature which is the Curie temperature Θ_f the isotherms become linear, and the magnetic susceptibility for T > Θ_f follows the Curie-Weiss law.

DISCUSSION OF RESULTS

The results of the investigation of the magnetic properties of uranium selenides and sulfides show that these properties depend to a large extent on the stoichiometric composition of the compound; both ferromagnetic and antiferromagnetic ordering apparently occurs in the investigated compounds. This is most clearly seen in analyzing the data obtained for compounds of the composition 1 : 2 and 3 : 5 in which $\Theta_p < 0$. This is also confirmed by the results of the work of Westrum and

Gronvold[5,6] in which they studied the temperature dependence of the specific heat of certain uranium selenides and sulfides. As these investigations showed, in USe_2 a maximum of the specific heat is observed at 13°K, the entropy increase at the maximum being according to the calculations of the authors 0.16 cal/g-mole °K. The authors relate this specific heat maximum with an antiferromagnetic transformation. As regards the compound U_3S_5, it too should at low temperatures be a ferromagnet ($\Theta_p = -16$°K).

It can be assumed that the antiferromagnetic structure of the USe_2 and U_3S_5 compounds is close to the structures of UAs_2 and UP_2 which according to neutron diffraction investigations[3,4] have a layered magnetic structure. The magnetic moments are oriented parallel to the c axis of the crystal and have a ferromagnetic ordering in each layer and antiferromagnetic ordering with respect to each other. With increasing uranium content in the compounds under investigation the ferromagnetic interaction becomes stronger and stronger than the antiferromagnetic interaction. Thus in U_2Se_3 there appears a small spontaneous magnetization which remains up to 180°K. For 80°K $\sigma_s = 0.15$ gauss-cm³/g. The presence of antiferromagnetism in U_2Se_3 is indicated by the negative value $\Theta_p = -10$°K.

The compounds USe and US are on the other hand ferromagnetic with a Curie temperature of 180°K which was determined from the vanishing of the spontaneous magnetization ($\sigma_s \approx 0$). However, from the nature of the $\sigma(T)$ dependence one can assume that USe still retains a weak antiferromagnetic interaction. This apparently explains the fact that the maximum of the specific heat in USe is clearly exhibited at 160°K, i.e., at the same temperature at which a maximum is observed in the $\sigma(T)$ dependence at 1 kOe. We recall that the presence of antiferromagnetism in UP which has a structure similar to that of USe has been proved by means of neutron diffraction investigations.[7] As already noted, in the compound US the specific magnetization σ decreases monotonically with increasing temperature for all values of the field, having as in USe the sharpest decrease in the region of 180°K. However, it is characteristic that the specific heat maximum in US also occurs at 180°K. It should at the same time be noted that the entropy increase in US is also somewhat larger and the specific heat peak is sharper than in USe, and in fact we have 1.17 cal/g-mole °K for the monosulfide and 1.00 cal/g-mole °K for the monoselenide. We recall that in USe_2 the increase in the entropy is almost by an order of magnitude smaller.

Compound	$\chi \cdot 10^6$ cm³/ at 293°K	Θ_f, °K	Θ_p, °K	P_p, μ_B	Temperature (°K) of maximum of Cp	Temperature (°K) of maximum of $\sigma(T)$ curves for 1 kOe
USe	14,0	180	182	1,8	160	156
U_3Se_4	15,3	160	164	2,45	—	135
U_2Se_3	12,5	180	10	3,2	—	—
USe_2	9,1	—	—48	3,2	13	—
US	22,7	180	190	2,25	180	—
U_3S_5	12,5	—	—16	3,10	—	—

All this attests to an appreciable difference in the nature of the magnetic transformation in uranium selenides and sulfides. Apparently three types of magnetic transitions occur in these uranium compounds: a "mixed" transition (in which antiferromagnetic and ferromagnetic structures are destroyed), an antiferromagnetic, and a ferromagnetic transition. However, the final answer as to the presence of antiferromagnetism in these compounds can be provided by neutron diffraction investigations, and by the nature of the change in the anisotropy constant with temperature.

At temperatures above the magnetic transitions the magnetic susceptibility of uranium selenides and sulfides has a different temperature variation; in some compounds this change occurs in accordance with a complicated law. Thus in USe $1/\chi$ changes linearly with temperature in the temperature range from ~180 to 300°K, in U_3Se_4—from 180 to 400°K, and in US—from 190 to 600°K. Curvature appears above these temperatures. The effective magnetic moments P_p (see the Table) calculated from the linear portions of the $1/\chi$ dependence on T do not agree with the value of the magnetic moment for the various electron configurations of uranium. These moments also differ appreciably from the magnetic moments determined from the ferromagnetic region at 80°K. Thus for USe $P_f = 0.7$ μ_B and for US $P_f = 1.1$ μ_B which is considerably less than P_p for these compounds.

Such a behavior of the investigated compounds in the paramagnetic region cannot be explained by the presence of van Vleck polarization paramagnetism and the susceptibility of the conduction electrons only. Apparently in these compounds an important role is played by the orbital magnetic moment and by the magnitude of the multiplet level splitting which can be comparable with the mean thermal energy; this leads to a temperature dependence of the magnetic moment at high temperatures.

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