Magnetic anisotropy of the uranium compounds UAsS and UAsSe

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The magnetization of UAsS and UAsSe compounds along various crystallographic directions is measured in stationary magnetic fields up to 12 kOe and in pulsed magnetic fields up to 200 kOe. The compounds are ferromagnetic at low temperatures and possess very high magnetic anisotropy. In the ferromagnetic region the magnetization in the difficult magnetization direction (basal plane of the crystal) is not saturated even in fields up to 200 kOe. The saturation is estimated to be of the order of 1000 kOe. In the paramagnetic region the susceptibility in the basal plane is smaller than that along the tetragonal crystal axis by an order of magnitude. The enormous magnetic anisotropy of UAsS and UAsSe is qualitatively explained within the framework of the crystal field theory.

We present here data on an unusually large magnetic anisotropy of the uranium compounds UAsS and UAsSe. These compounds have a crystal structure of the PbFCl type[1,2] (tetragonal syngony, space group P4/nmm). Magnetic measurements[2,3] have shown that at low temperatures these compounds are ferromagnetic, and that the easy-magnetization axis is parallel to the tetragonal axis (c axis) of the crystal. It was also established[2] that in the ferromagnetic state a field on the order of 10 kOe, directed perpendicular to the c axis, hardly deflects the magnetic moments of UAsS and UAsSe from the tetragonal axis.

We have undertaken measurements of the magnetic properties of single-crystal UAsS and UAsSe in constant and pulsed magnetic fields. Single crystals in the form of plates measuring $10 \times 5 \times 1$ mm, with the plane parallel to the basal plane, were grown by the transport-reaction method[4]. The samples for the measurements, in the form of small cubes 2 mm on the side, were glued together of several plates in such a manner that the c axes of the plates were parallel to each other (the accuracy of the orientation was 5—6°).

Measurements in strong pulsed magnetic fields have shown that at low temperatures the magnetizations of the compounds UAsS and UAsSe along the tetragonal axis become saturated in relatively weak fields and that with further increase of the field there is observed a small increase of the magnetization, due to the paraprocess (Fig. 1). The magnetization in the basal plane has an entirely different behavior. Up to 200 kOe, it depends linearly on the field and is many times smaller than along the c axis of the crystal (Fig. 1). This is evidence of a very large magnetic anisotropy of the compounds UAsS and UAsSe.

The conclusion that UAsS and UAsSe have very large magnetic anisotropy follows also from measurements in constant magnetic fields up to 12 kOe. Figure 2 shows (in polar coordinates) the experimental dependences of the magnetization of UAsS and UAsSe on the angle φ of rotation of the field about the z axis. The experimental points agree well with the theoretical $\sigma(\varphi)$ plots constructed under the assumption that the magnetic moment is not deflected in the field away from the c axis of the crystal, and that the magnetization in a field making an angle φ with the c axis is equal to the projection of the magnetization along the c axis on the field direction:

$$\sigma(\varphi) = \sigma_c \cos \varphi. \qquad (1)$$

Figure 3 shows the temperature dependences of the magnetization and of the paramagnetic susceptibility of the compounds UAsS and UAsSe along different crystallographic directions. We see that the large anisotropy of the magnetic properties of the compounds UAsS and UAsSe is observed not only in the ferromagnetic region,[1] but also in the paramagnetic region of temperatures, namely, the paramagnetic susceptibility of UAsS
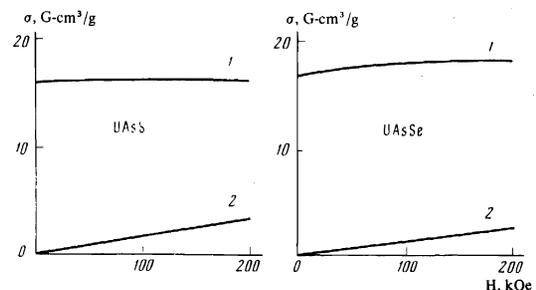
FIG. 1. Dependence of the magnetization of the compounds UAsS and UAsSe on the field at T = 78°K: 1—magnetization along the c axis, 2—magnetization in the basal plane.
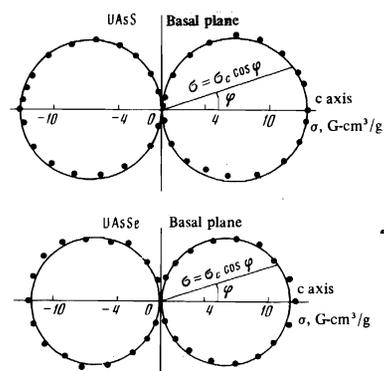
FIG. 2. Magnetization of UAsS and UAsSe vs. orientation of the field relative to the c axis; T = 105°, H = 12.2 kOe. Points—experimental data. Solid curve—theoretical plots constructed under the assumption that the magnetization in the field is not deflected away from the c axis.
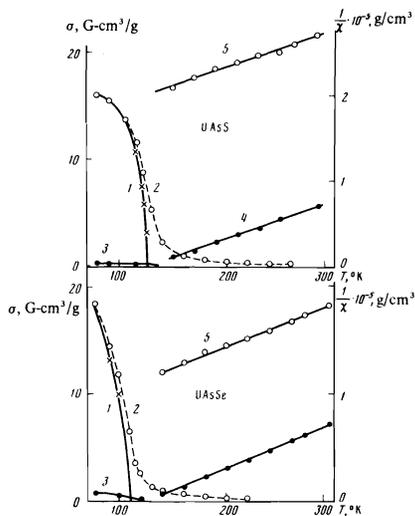
FIG. 3. Temperature dependences of the magnetization and of the reciprocal paramagnetic susceptibility of UAsS and UAsSe: 1—saturation magnetization along the c axis; 2—magnetization along the c axis in a field of 12 kOe; 3—magnetization in the basal plane in a field at 12 kOe; 4—reciprocal paramagnetic susceptibility along the c axis; 5—reciprocal paramagnetic susceptibility in the basal plane.

FIG. 4. Coordination polyhedron of the uranium ion U^{4+} in the compounds UAsS and UAsSe.

or UAsSe in the basal plane at temperatures 140—300° K is smaller by approximately one order of magnitude than along the c axis.

From measurements of the magnetization in strong magnetic fields we estimated the magnetic anisotropy of the compounds UAsS and UAsSe. Linear extrapolation of the magnetization in the basal plane (Fig. 1) yields a saturation field 800—1300 kOe for both compounds at 78°K. It follows therefore from the formula for the uniaxial-anisotropy constant

$$K = \tfrac{1}{2} H_s \sigma_c, \qquad (2)$$

that the anisotropy constants of UAsS and UAsSe at 78° K are equal to (6—10) × 10^6 erg/g, i.e., they are of the same order of magnitude as the anisotropy constants of rare-earth ferromagnets[2].

As follows from recent experimental and theoretical studies, the magnetic ordering of uranium compounds is satisfactorily described by the model of localized magnetic moments, and the exchange interaction is effected principally via the conduction electrons (see, for example,[5,6]). In the analysis of the anisotropic properties of uranium compounds it is necessary to take into account the influence of the crystal field on the state of the uranium ions. It is known that the f-electrons of the U^{4+} ions are less screened than the f-electrons in rare-earth ions, and therefore the ligand field in uranium compounds act more strongly than in rare-earth compounds.

In the compounds UAsS and UAsSe, the uranium ion is at the center of the UX_4Y_5 polyhedron (where X = As and Y = S or Se) (Fig. 4) with the point group C_{4v} and fourfold symmetry axis parallel to the c axis of the crystal. The crystal field of this polyhedron has an axial potential, and the presence of the ions X and I with high negative valence causes a strong splitting of the ground multiplet $^3H_4$ of the E^{4+} ion (preliminary calculations using experimental values of the paramagnetic susceptibility of UAsS and UAsSe polycrystals[2] show that the ion splitting of the multiplet is of the order of $\Delta \approx 10^3$—10^4 cm^{-1}[7]).
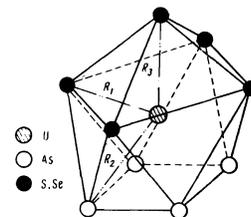
As a result of the strong crystal field, the ground state becomes the pseudodoublet Γ_{t3} and Γ_{t2}, described by the eigenfunctions $2^{-1/2}|+4\rangle \pm 2^{-1/2}|-4\rangle$. Located above it is the doublet Γ_{t5}, described by the function $a|\pm 3\rangle - b|\pm 1\rangle$ [7]. An approximate calculation of the anisotropy of the paramagnetic susceptibility of the compounds UAsS and UAsSe with allowance for only these energy levels shows that at low temperatures and at large values of the separation ($\Delta \sim 10^3$—10^4 cm^{-1}) between these levels, the susceptibility in the basal plane is smaller by an approximate factor 10—10^2 than along the c axis[7].

Thus, the experimental data on the anisotropy of the paramagnetic susceptibility of UAsS and UAsSe can be qualitatively explained when account is taken of the influence of the crystal field on the state of the U^{4+} ion.

The magnetic anisotropy of the uranium compounds UAsS and UAsSe in the magnetically ordered state can also be attributed to the influence of the crystal field on the U^{4+} ions; it is due to the fact that when the direction of the magnetic moment of the U^{4+} ion is changed, a change takes place in the orientation of the anisotropy charge cloud of the 5f electrons relative to the ligand field. Quantitative calculations of the magnetic anisotropy in this temperature region are more complicated since at temperatures below the Curie point it is necessary to take into account the influence exerted on the state of the U^{4+} ion not only by the crystal field but also by the exchange interaction.

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[1]The Curie points of the investigated compounds, determined by the method of thermodynamic coefficients and from measurements of the magnetization along the c axis, are 128°K for UAsS and 109°K for UAsSe.

[2]We note that the foregoing estimates are quite approximate and give only the correct order of magnitude. This is due both to the low accuracy of the extrapolation to the saturation field and to the influence exerted by imperfection of the samples on the results of measurements in the difficult directions.

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64