MAGNETIC PROPERTIES OF US–ThS *ALLOYS*

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The magnetic properties of US–ThS alloys are studied throughout the full range of concentrations. The alloys containing up to 60 at.% ThS are ferromagnetic. In magnetic fields up to 7 kOe the magnetization is unsaturated. In the paramagnetic region the magnetic susceptibility obeys the Curie–Weiss law. The effective magnetic moment μ_{eff} per uranium atom increases with increase of the ThS content up to 3.6 μ_B for alloys with 90% ThS. In all the alloys the paramagnetic Curie temperature Θ_p is positive and ultimately vanishes with increase of the ThS content. X-ray structural analysis shows that all the alloys possess the NaCl structure and are solid solutions. The lattice constant a increases with the ThS content.

1. INVESTIGATIONS[1-3] of the magnetic properties exhibited by different compounds of uranium and group-V or group-VI elements have shown that both ferromagnetic and antiferromagnetic ordering can exist in these materials. For a more detailed study of the exchange interaction and an evaluation of the effects produced by the crystalline field it seemed reasonable to investigate the magnetic properties of uranium compounds when magnetically diluted; we are not aware that any such investigation of uranium alloys has previously been performed. We investigated US–ThS alloys, where it is of importance that when thorium atoms replace uranium atoms the electrical properties are observed to change.[4]

Our US–ThS alloys containing from 0 to 100 at.% ThS were synthesized from pure monosulfides of uranium and thorium that had been produced by the method described in [2]. The purities were 99.9% for uranium and thorium, 99.98% for sulfur. The monosulfide powders in suitable proportions were pressed into samples that were then subjected to high-temperature annealing in a 10^{-5}–10^{-6} Torr vacuum. During a 7–8-hr anneal the temperature was increased gradually from 1350° to 2100°C; the final temperature was maintained 40–50 min. All the samples except the pure US and alloys containing 90 or 95% US were melted to improve their homogenization. This step was extremely necessary because even small unhomogenized regions in a magnetically dilute solid solution can seriously affect the measurements. Our alloys were subjected to x-ray analysis, using CuK_α radiation and a Ni filter. It was thus established that all the samples were solid solutions having the NaCl structure, and that the lattice constant a increases with the ThS content (Fig. 5). The x-ray analysis also showed that samples containing 20, 40, and 70 at.% ThS had been oxidized during the synthesizing process; we did not investigate these samples.

2. The magnetic properties of the US–ThS alloys were studied at temperatures 77°–1000° K in fields from 1 to 7 kOe, using a pendulum balance. The alloys containing up to 60 at.% ThS were found to be ferromagnetic; the remaining samples were paramagnetic. In all the investigated alloys except those containing 90 or 95 at.% US the specific magnetization σ decreases monotonically as the temperature rises and approaches zero in the ferromagnetic transition region. In low magnetic fields the alloys containing 90 or 90 at.% US exhibit $\sigma(T)$ maxima that with increasing field strength are shifted toward lower temperatures and vanish at some value of the field strength (Fig. 1). It should be noted that with decreasing temperature the specific magnetization gradually approaches a constant value; it is observed to increase slightly with decreasing temperature only in a field of 575 Oe. It is interesting that the effect of thermomagnetic treatment is observed in the ferromagnetic region of all the alloys; the $\sigma(T)$ curves plotted for cooling from room to nitrogen temperature in a magnetic field differ considerably from analogous curves obtained for a sample that was cooled in zero field and was then heated (Fig. 1, curves 8 and 9). Characteristically, the $\sigma(T)$ maxima of the alloys with 90 or 95 at.% US are found to have disappeared following thermomagnetic treatment in the same field that was used for their earlier observation. The specific magnetization measured following thermomagnetic treatment is considerably higher than it was prior to such treatment. The magnetization isotherms of all the alloys are nonlinear; saturation magnetization is not achieved (Fig. 2). The shapes of the $\sigma(T)$ and $\sigma(H)$ curves indicate that the ferromagnetic alloys possess a

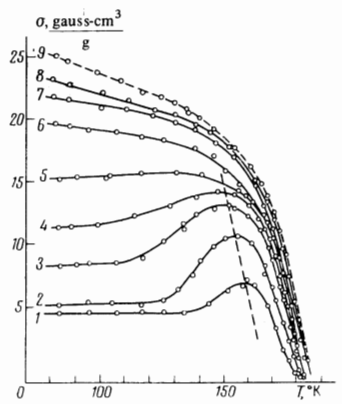

FIG. 1. σ versus T for a 90 at.% US – 10 at.% ThS sample in different magnetic fields (oersteds): 1 – 575, 2 – 1210, 3 – 2000, 4 – 2400, 5 – 3000, 6 – 4050, 7 – 6000, 8 and 9 – 700.

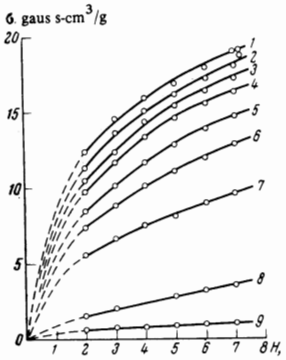

FIG. 2. Magnetization isotherms for an alloy containing 25 at.% ThS (in °K): 1 – 85, 2 – 109, 3 – 117, 4 – 129, 5 – 142, 6 – 152, 7 – 161, 8 – 169, 9 – 190. Magnetic field strengths are indicated in kilooersteds.

broad transition region near the magnetic transition temperature. This circumstance prevented accurate determination of the ferromagnetic Curie temperature, which must evidently be understood to represent an average temperature for these alloys.

Figures 3 and 4 show the temperature dependence of the inverse specific susceptibility. The measurements showed that the paramagnetic susceptibility of all the alloys obeys the Curie–Weiss law in a broad temperature range. It should be noted, however, that in alloys containing a large US content (90 and 95 at.%) and in uranium monosulfide a deviation from this law appears at high temperatures in the form of a slight concavity toward the temperature axis. Deviations from the linear dependence of $1/\chi$ on T are also observed near the magnetic transition temperature, where the magnetic susceptibility increases steeply with decreasing temperature. This effect is most pronounced in the alloys containing 50 or 60 at.% ThS (Fig. 3). In this temperature region there also exists a dependence of χ on H which disappears at higher temperatures.

From the experimental data we determined the paramagnetic Curie point Θ_p and the effective magnetic moment μ_{eff} per uranium atom. We obtained Θ_p by extrapolating $\chi^{-1}(T)$ to the temperature axis; the effective magnetic moment was calculated from the familiar formula $\mu_{eff} = 2.84\sqrt{\chi(T - \Theta_p)}$, where χ is the atomic susceptibility of uranium. In calculating this susceptibility we took into account the diamagnetic contribution of each component and the paramagnetism of ThS. Our measurements showed that this compound is weakly paramagnetic; it exhibits only an insignificant decrease of susceptibility as its temperature is raised. These

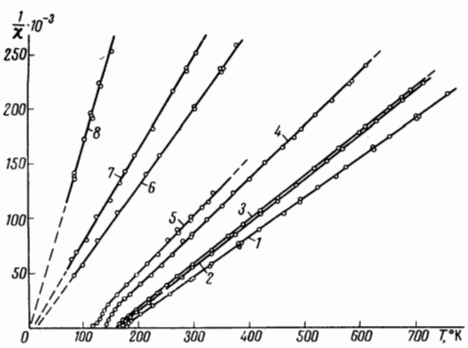

FIG. 3. $1/\chi$ versus T for US – ThS alloys containing different ThS contents (at.%): 1 – 15, 2 – 25, 3 – 30, 4 – 50, 5 – 60, 6 – 75, 7 – 80, 8 – 90.

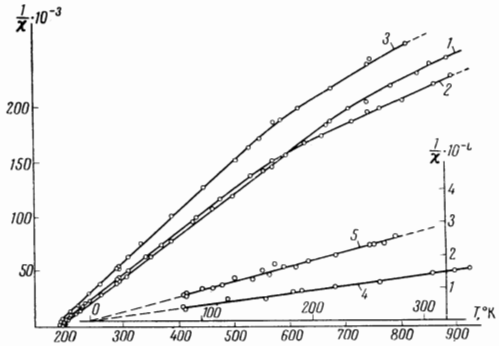

FIG. 4. $1/\chi$ versus T for US (curve 1) and for US – ThS alloys with different ThS contents (at.%): 2 – 5, 3 – 10, 4 – 95, 5 – 98.

results agree with the conclusions reached by Eastman et al.[5]

Figure 5 shows that the paramagnetic Curie point drops to zero as the ThS content is increased, but that its effective magnetic moment is increased to 3.6 μ_B. The same figure shows the dependence of the lattice constant a on the composition of the alloy. When the ThS content is small (up to 30 at.%) a remains fairly constant, but increases thereafter with the ThS content. Thus, when US–ThS solid solutions are formed we observe only a slight deviation from Vegard's linear law. We note that the values of Θ_p and μ_{eff} for the samples containing 0–90 at.% ThS were determined with quite high accuracy, as their susceptibilities are high in the paramagnetic region. The data obtained for the alloys containing 95 and 98 at.% ThS were averages of several measurements and are not fully reliable because of large experimental errors.

3. The observed magnetic properties of the US–ThS alloys showed that the effective magnetic moment obtained by extrapolating to infinite dilution is close to the theoretical value 3.58 μ_B that has been calculated in the case of LS coupling for the $5f^2$ electron configuration of the $^3H_4$ uranium ground state. We recall that for this same electron configuration with jj coupling and "frozen" orbital motion the magnetic moments are 3.84 μ_B and 2.83 μ_B, respectively. The monotonic decrease of Θ_p indicates that this constant of the investigated system results from exchange interactions between the uranium atoms, and that Θ_p approaches zero because of the small effect of the crystal field on neighboring uranium atoms arranged in the NaCl cubic structure. This agrees with Hutchinson and Candela,[6] who note that strong LS coupling is present in compounds of U^{4+} while the crystal field manifests only a weak effect. The strong influence of the orbital angular momentum

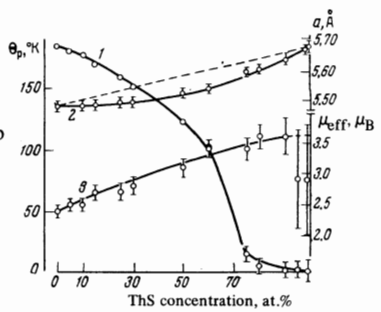

FIG. 5. Dependences of Θ_p (curve 1), μ_{eff} (curve 2), and the lattice constant α (curve 3) on ThS concentration.

is indicated by the fact that we observed the absence of ferromagnetic resonance absorption in the centimeter wavelength region for all the ferromagnetic alloys of the given system at 90°K.

As already mentioned, the paramagnetic susceptibility of the investigated alloys obeys the Curie–Weiss law in a broad temperature range. The deviation from this law at the magnetic transition point can be attributed to the complex character of this transition, where fluctuations of magnetic ordering occur within a broad temperature interval. The influence of thermomagnetic treatment on the magnetic properties of the alloys in the ferromagnetic region evidently results from disorder, which leads to antiparallel orientation of individual magnetic moments. However, a final determination of magnetic ordering in US–ThS alloys will require neutron diffraction studies; unfortunately, these are still to be performed.

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