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MAGNETIC PROPERTIES OF COMPOUNDS OF URANIUM AND THORIUM WITH IRON, NICKEL, AND COBALT

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Measurements have been made of the magnetic susceptibility of the following compounds of actinides with 3d-metals; UFe_2, UCo_2, UNi_5, ThNi, $ThNi_5$, and $ThCo_5$. It was found that compounds isomorphous in their crystal structure have different magnetic properties; namely, that UFe_2 and $ThCo_5$ are ferromagnetics, whereas UCo_2 and $ThNi_5$ are temperature independent paramagnetics. The rigid band model is used to interpret the results obtained.

THE object of the present work is to study the magnetic properties of compounds of uranium and thorium with elements of the iron group. To this end we synthesized the compounds UFe_2, UCo_2, UNi_5, ThNi, $ThNi_5$, and $ThCo_5$ using uranium with 99.98% purity, thorium (99.9%), iron (99.98%) and cobalt and nickel (99.98%). Powders of the starting metals were mixed and then compressed under a pressure of 15×10^3 kg/cm^3. The compressed mixture was fused in an arc furnace in an argon atmosphere at a temperature of 1300–1400°C, after which a secondary treatment was carried out. Thus the compound $ThCo_5$ was annealed at a temperature of 700°C for three weeks; the remaining compounds were subjected to a temperature of 600°C for five hours. We carried out an x-ray structure analysis which showed that all the compounds obtained were single-phase compounds. The magnetic properties of the compounds synthesized were studied with a pendulum balance in the range 290–650°K and with a torsion balance in the range 80–300°K.

EXPERIMENTAL RESULTS

The compound UFe_2, which according to the data in [1] has a cubic structure of the C-15 type, is a ferromagnetic with $\Theta_f = 172°K$; the magnetic moment, determined from low-temperature measurements, was found to be 1.02 μ_B. We investigated this compound in the paramagnetic regime from 180 to 550°K only. Figure 1), the temperature dependence of the inverse specific susceptibility. A correction for the diamagnetism of the filled electron shells was included. For this we subtracted the value of $\chi_{Rn} - 2\chi_{Ar}$ (where $\chi_{Rn} = -23 \times 10^{-6}$ cm^3/g-atom and $\chi_{Ar} = -19 \times 10^{-6}$ cm^3/g-atom are the susceptibilities of the inert gases radon and argon) from the values obtained for the susceptibility of UFe_2.

As is clear from Figure 1, the Curie–Weiss law is not obeyed. If we put $\Theta_f = \Theta_p$, we can determine the temperature-independent part of the susceptibility from the dependence of χ on $1/(T - \Theta_p)$. This was found to be equal to $(4.0 \pm 1.0) \times 10^{-6}$ cm^3/g. Curve 2 in Fig. 1 was plotted taking the temperature-independent susceptibility into account. The paramagnetic Curie temperature $\Theta_p = 170 \pm 5°K$ and the effective magnetic moment $\mu_{eff} = 2 \pm 0.2\ \mu_B$.

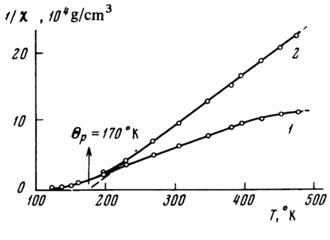

FIG. 1. Temperature dependence of the inverse specific susceptibility of UFe_2: in curve 1 a correction has been introduced for the diamagnetism of the filled electron shells; in curve 2 the temperature-independent susceptibility has been taken into account.

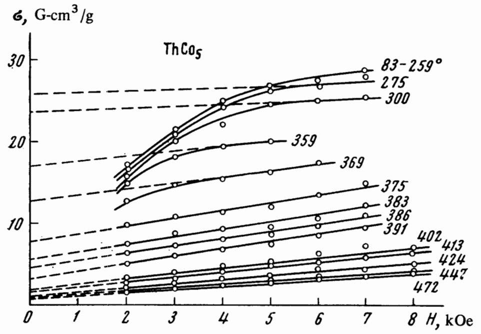

FIG. 2. Relative magnetization isotherms for $ThCo_5$.

The magnetic susceptibility of the compounds UCo_2, UNi_5 and $ThNi_5$ do not depend on temperature and are $(3 \pm 0.5) \times 10^{-6}$, $(1.4 \pm 0.2) \times 10^{-6}$ and $(0.7 \pm 0.2) \times 10^{-6}$ cm^3/g respectively. The crystal structure of the first two compounds is isomorphous to the structure of UFe_2, whereas the compound $ThNi_5$ has a hexagonal structure of the type C_6/nm.

The compound ThNi (rhombic structure) is paramagnetic in the temperature region investigated; the Curie–Weiss law, with $\Theta_p = 310 \pm 20°K$ and $\mu_{eff} = (0.9 \pm 0.1)\ \mu_B$, is obeyed in the temperature range 80–300°K.

We investigated the ferromagnetic compound $ThCo_5$, which has a structure isomorphous to $ThNi_5$, in the ferromagnetic regime only. Isotherms of the magnetization for this compound are shown in Fig. 2. One can see that in the region of large fields, σ varies linearly with H. This enabled us to determine the value of the

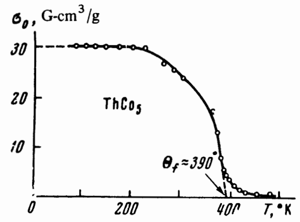

FIG. 3. Temperature dependence of the relative spontaneous magnetization σ_0 of ThCo$_5$.

spontaneous magnetization σ_0 (Fig. 3) at various temperatures and thereby to estimate σ_0 at absolute zero. It was found that this quantity is equal to (30 ± 0.1) Gauss-cm^3/g, $\Theta_f = 390 \pm 5°$K and μ_{eff}, calculated from the ferromagnetic regime, is equal to 2.84 μ_B.

A characteristic feature of the results we have obtained is the fact that compounds which are isomorphous in their crystal structure, such as UFe$_2$ and UCo$_2$, ThCo$_5$ and ThNi$_5$, possess different magnetic properties; namely, UFe$_2$ and ThCo$_5$ are ferromagnetics, whilst UCo$_2$ and ThNi$_5$ are temperature-independent paramagnetics.

DISCUSSION OF THE RESULTS

To explain the obtained results we make use of the rigid band model. The possibility of such an interpretation of the properties of alloys of uranium with d-metals was first pointed out by Bates and Leach.[2] They investigated the susceptibility of alloys of uranium with palladium as a function of temperature and concentration and found that the magnitude of the susceptibility of these alloys at first decreases with increase of the uranium content, passing through a minimum at 9% uranium, and then begins to increase again. It is characteristic that the susceptibility of the alloy with 9% uranium does not depend on temperature. Bates and Leach proposed that on dissolving uranium in palladium the band shape remains unchanged and only the Fermi level of the 4d-band changes; this band is completely filled at the above uranium concentration. The results of the investigations of Bates and Leach are evidence that the 5f- and 6d-electrons of the actinides are collectivized with the palladium 4d-electrons and are closer in nature to d-electrons than to 4f-electrons. This enables us to conclude that the band model is to be preferred to the model of localized magnetic moments for the interpretation of the results.

In order to be sure that the use of the rigid band model is correct for our compounds, we calculate the susceptibility of one of the compounds investigated by us, e.g., ThNi, and compare this with the experimental results. For this it is necessary to know the relative spacing of the 6d- and 3d-bands in the given compound. This can be done on the basis of the experimental results for the temperature-independent paramagnetic ThNi$_5$.

Using the data on the electronic heat capacity of thorium,[3] we can find the width of the 6d-band. Calculating the total density of states for the s- and d-electrons of thorium from known formulas[4] and, for the s-electrons, taking the thorium electron configuration to be $6d^3 7s^1$,[5] we find the density of states of the 6d-electrons $N(E_F)_d$. We determine the width of the 6d-band by assuming that it has the shape of an isosceles triangle and taking into account the thorium electron configuration given above. It is found to be 9.86 eV, which is in satisfactory agreement with the data from Lehmann's work.[6] Thus, the expression for the density of states of the 6d-band of thorium has the form

$$N(E)_d^{\text{Th}} = \begin{cases} 0{,}411E, & 0 \leqslant E \leqslant 4.93 \text{ eV} \\ 4{,}05 - 0{,}411E, & 4.93 \leqslant E \leqslant 9.86 \text{ eV} \end{cases}$$

To calculate the susceptibility of the compound ThNi, it is necessary to know also the magnitude of the coefficient Φ characterizing the electron-electron interaction of the 6d-electrons.[7] According to our data, the susceptibility of thorium does not depend on temperature and turns out to be $\chi^{\text{Th}} = 125.5 \times 10^{-6}$ cm^3/g-atom. Then, using the values $\chi_{\text{diam}} = -23 \times 10^{-6}$ cm^3/g-atom, $\chi_s + \chi_L = 9.4 \times 10^{-6}$ cm^3/g-atom, and $\chi^d_{\text{orb}} = 71.1 \times 10^{-6}$ cm^3/g-atom,[7] we find from the relation

$$\chi = \chi_s + \chi_L + \chi_d + \chi_{\text{orb}} + \chi_{\text{diam}}$$

that $\Phi = 0.16$ eV.

If the s-band of the compound ThNi$_5$ is formed only from the s-electrons of Th and Ni, assuming that $\chi^{\text{Ni}}_{\text{orb}} = 71 \times 10^{-6}$ cm^3/g-atom,[8] we find that $\chi_d^{\text{ThNi}_5} = 30.1 \times 10^{-6}$ cm^3 g-mole. (In the calculation we used our experimental data for χ^{ThNi_5}.) Assuming that $\Phi = 0$, we obtain $N(E_F)_d^{\text{ThNi}_5} \leq 4.3$ eV^{-1} molecule^{-1}. The error arising from putting $\Phi = 0$, as we shall see below, does not affect the calculation of the susceptibility of the compound ThNi.

An expression for the density of states of Ni is given in the paper.[9] Carrying through the necessary calculations we find that the bottom of the 6d-band in the compound ThNi$_5$ is displaced relative to the bottom of the 3d-band by an amount $\epsilon_0 \geq 3.9$ eV. Therefore, taking the shape of the band into account, for complete occupation of the 3d-band there must be no fewer than 0.25 electrons per molecule in the 6d-band. It is important to note that this value is an overestimate, since in calculating $N(E_F)_d^{\text{ThNi}_5}$ we put $\Phi = 0$. Consequently in the compound ThNi, the 3d-band is completely filled and in the 6d-band there are 2.4 electrons per molecule.

Carrying through calculations for ThNi analogous to those for ThNi$_5$, we obtain the value for the susceptibility at $T = 0$, $\chi^{\text{ThNi}}_{\text{theor}} = 170.4 \times 10^{-6}$ cm^3/g-mole, which is in satisfactory agreement with our experimental results (300×10^{-6} cm^3/g-mole), obtained from extrapolation of the curve for $1/\chi(T)$. This enables us to draw conclusions about the correctness of interpreting the properties of compounds of actinides with 3d-metals from the standpoint of the rigid band model. The discrepancy in the resulting values is evidently caused by the fact that we chose a simplified shape for the 3d- and 6d-bands.

We shall consider from this standpoint the magnetic properties of the other compounds investigated, making the following assumptions. First, the relative spacing of the 5f-, 6d- and 3d-bands changes insignificantly from sample to sample. Secondly, if vacancies remain in the 3d-band of the compound, the magnetic properties of the compound will be similar to those of the ori-

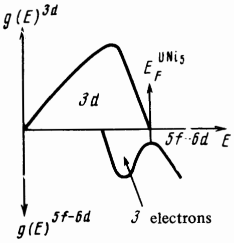

FIG. 4. Assumed relative positions of the 3d- and hybridized 5f-6d-bands.

ginal metal. We shall use also the uranium band structure proposed by Friedel[5] according to which in uranium there is a hybridized 5f-6d-band containing five electrons and a 7s-band with one electron. The shape of the 5f-6d-band is shown in Fig. 4. We assume, as in [2], that to fill the 3d-band, uranium can donate five 5f-6d-electrons and thorium three 6d-electrons (if this turns out to be insufficient to fill the 3d-band completely, one s-electron is added to these electrons). To explain the temperature-independent paramagnetism of UNi_5, it is necessary to assume that there are three electrons in the hybridized 5f-6d-band below the 3d-band (Fig. 4). We have assumed here that the valency of uranium is 6.

For the compound UFe_2, assuming that the electron configuration of iron is $3d^{7.77}4s^{2.23}$, we find the maximum number of electrons that can be accepted by the 3d-band and the part of the 5f-6d-band below the 3d-band (Fig. 4). This is found to be 7.46 electrons. Thus, in the 3d-band and below it there remain $n_0 = 1.46$ vacancies. This allows us to expect the occurrence of ferromagnetism in UFe_2, and this is observed experimentally.

In the compound UCo_2, according to the electron configuration $Co(3d^{8.3}4s^{1.7})$, the number of vacancies in the 3d-band of Co is 1.7, $n_{max} = 6.4$ and $n_0 = 0.4$. This is clearly not sufficient for the existence of ferromagnetic ordering in this compound, in agreement with the experimental results.

For the compound $ThCo_5$ the quantity n_{max} is found to be 8.5; Th can donate only four electrons ($n_0 = 4.5$). This can lead to the occurrence of ferromagnetism in ThCo, in agreement with the results of our measurement of the magnetic susceptibility.

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11