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Abstract

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ON THE MAGNETIC PROPERTIES OF U_2O_5

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As we have shown ([1]), the product of the interaction of uranium uranous-uranic oxide with acids in the absence of oxidizing agents is U_2O_5. It was suggested in this connection that U_2O_5 is a compound of pentavalent uranium. However, the possibility of another structure of this oxide was not excluded, namely that it is a compound of the type $UO_2 \cdot UO_3$, in which one uranium atom is in the 4-valent state and the other in the 6-valent state. We attempted to resolve this question by determining the magnetic moment of the uranium atoms in this compound.

The measurement of the magnetic susceptibility of U_2O_5 was carried out by the Gouy method ([2]). The apparatus was calibrated by measuring the specific magnetic susceptibility of water and benzene. The magnetic susceptibility was measured for two preparations of U_2O_5 obtained by treating uranium uranous-uranic oxide with dilute sulfuric acid. The method of preparing U_2O_5 will be described in greater detail in a separate paper. In addition, for comparison, the magnetic susceptibilities of uranium dioxide and also of uranium uranous-uranic oxide, from which the U_2O_5 samples were obtained, were measured. For the measurements, samples of substances weighing about 1–1.5 g were used. The values we obtained for the molar magnetic susceptibilities χ_M for all the indicated substances are given below in Table 1. In the temperature interval studied (between 6.5 and 60°), the magnetic susceptibilities of these compounds follow the Curie–Weiss law quite accurately (see Fig. 1).

Table 1

Sample	$\chi \cdot 10^6$ at 20° C	Δ°	μ_{exp}	Note
U_2O_5	1180	320 ± 15	1.77 ± 0.03	Experimental data
U_2O_5	1170	308 ± 15avg. $= 314 \pm 15$	1.70 ± 0.03avg. $= 1.74 \pm 0.03$	»
UO_2	2250	198 ± 10	3.01 ± 0.06	»

Fig. 1. Curves of the dependence of χ_M on temperature: I, II—for the U_2O_5 sample (samples 1 and 2), III—for U_3O_8

Figure 1: Fig. 1. Curves of the dependence of χ_M on temperature: I, II—for the U_2O_5 sample (samples 1 and 2), III—for U_3O_8

Sample	$\chi \cdot 10^6$ at 20° C	Δ°	μ_{exp}	Note
UO_2	–	–	2.92	Data of Wedekind and Horst ([4])
U_3O_8	1380	163 ± 15	1.59 ± 0.04	Experimental data
U_3O_8	–	170	1.39	Data of Haraldsen and Bakken ([5])

Table 1 gives the values of the Weiss constants (Δ°), as well as the magnetic moments (μ_{exp}) calculated from the susceptibility data, expressed in Bohr magnetons. In calculating the paramagnetic component, a correction was introduced for the diamagnetic susceptibility inherent in each compound, on the basis of the data given in Selwood' s monograph. For U_3O_8, moreover, the polarization paramagnetism of the UO_3 group ([3]) was taken into account. The composition of each given sample of U_2O_5, UO_2, and U_3O_8 was checked before and after the magnetic measurements. According to chemical analysis, the composition of these samples remained unchanged from the time of preparation to the end of the measurements and corresponded to their formulas.

Discussion of the results. The average value of the magnetic moment of U_2O_5, equal to 1.74, was obtained from the experimental data under the assumption that U_2O_5 is a compound of pentavalent uranium. It practically exactly coincides with the theoretical value of the magnetic moment, 1.73, due only to the spin of one unpaired electron. Evidently, in the crystal field of U_2O_5 there is complete suppression of the orbital component. If it is assumed that U_2O_5 is a compound of the $UO_2 \cdot UO_3$ type, the experimental data lead to a value of μ_s equal to 2.30. This value differs substantially from the theoretical value 2.83 for two unpaired electrons. Thus, our data convincingly show that U_2O_5 is a compound of pentavalent uranium.

The magnetic moment of UO_2, calculated from our measurement data, as is seen from Table 1, agrees well with the values available in the literature ([4]) and exceeds the value 2.83 by only 6%.

Fig. 1. Curves of the dependence of χ_M on temperature: *I*, *II*—for the U_2O_5

sample (samples 1 and 2), *III*—for U_3O_8

As regards U_3O_8, the following must be noted. Haraldsen and Bakken ([5]), on the basis of the agreement of the experimentally obtained magnetic moment $\mu = 1.39$ with the theoretical μ_s, equal, in their opinion, to 1.42 for one unpaired electron, came to the conclusion that U_3O_8 has the structure $UO_3 \cdot U_2O_5$. As is known, μ_s is proportional not to the number of unpaired electrons (n), but to the quantity $\sqrt{n(n+2)}$. This circumstance often leads to incorrect conclusions if it is erroneously assumed that μ_s for one unpaired electron is half as large as for two. Evidently, it was precisely this error that Haraldsen and Bakken made. Consequently, they should have compared the two quantities 1.39 and 1.73, and, of course, as a result of this they would not have arrived at the conclusion indicated above. Meanwhile, the value 1.42 and the conclusions of Haraldsen and Bakken are cited, for example, by Katz and Rabinowitch ([6]).

The value of μ_s obtained by us for U_3O_8, equal to 1.59, differs from the value 1.73 by only 9%. Therefore, in the present case the conclusion concerning the presence of pentavalent uranium atoms in the structure of U_3O_8 appears better substantiated. The comparatively large value of the Weiss constants for U_2O_5, UO_2, and U_3O_8 possibly indicates a strong exchange interaction between uranium ions in these oxides.

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