MAGNETIC PROPERTIES OF USb_2—$ThSb_2$ *SOLID SOLUTIONS*

V. I. CHECHERNIKOV, R. N. KUZ'MAN, L. G. CHACHKHIANI, V. A. GOLOVNIN, S. M. IRKAEV, V. K. SLOVYANSKIKH, and T. M. SHAVISHVILI

Moscow State University

Submitted February 18, 1969

Zh. Eksp. Teor. Fiz. 57, 125–129 (July, 1969)

Solid solutions of the USb_2-$ThSb_2$ system have been synthesized for the first time and their magnetic properties are investigated at various temperatures (80—700°K). It is found that solutions containing less than 0.5 $ThSb_2$ are antiferromagnetic; the Neel temperature decreases with increasing $ThSb_2$ content. The effective number of Bohr magnetons μ_{eff}, the paramagnetic Curie temperature Θ_p, and the lattice parameters have been determined for all compositions. A suggestion regarding the ground energy state of the U ion is made.

THE magnetic properties of many antiferromagnetic uranium compounds of the type UX_2, where X = P, As, Sb, and Bi, have been recently investigated in the magnetically concentrated state[1-3]. However, to obtain the most complete information concerning the character of the exchange interaction, it is of interest to investigate these compounds by replacing the uranium ions in them with thorium ions. Such a replacement is equivalent to magnetic dilution, since thorium has no 5f electrons and is a weakly-magnetic metal. We chose for the investigation the compound USb_2, which in accordance with[1] is antiferromagnetic with a Neel temperature equal to 260°K; we also investigated USb_2-$ThSb_2$ solid solutions.

It was necessary to investigate, first, the very formation of the USb_2-$ThSb_2$ solid solutions, using an x-ray method, and, second, to obtain information on the ground state of the uranium ions in the solid solutions from the temperature dependence of the magnetic susceptibility and to establish the dependence of the critical temperature T_N on the concentration of the weakly magnetic Th ion.

The compounds USb_2 and $ThSb_2$ have a structure of the Cu_2Sb type ($T_d^{4\prime 2}$ = C38), and a space group D_{4h}^7—P^4/n, m, m; Z = 2. The atoms U and Th occupy in the lattice the double position occupied in Cu_2Sb by the antimony, and for this reason the compounds USb_2 and $ThSb_2$ are anti-isomorphic to Cu_2Sb.

Since the metal atoms form a closest cubic packing following slight displacement, and the atoms Sb I are located in tetrahedral voids every other layer while the Sb II atoms occupy all the octahedral voids, the magnetic structure of the antiferromagnetic compound USb_2 is such that the magnetic moments of U have antiparallel directions in the basal planes and in the faces, and have a common direction along the C axis[2]. When the Th is diluted, the collinear magnetic structure of USb_2 should disintegrate. A preliminary synthesis of samples of dilute solutions of the system $U_{1-X}Th_XSb_2$ was carried out by a previously described procedure[4]. The samples obtained by this procedure were subsequently pressed and annealed in a vacuum of 10^{-6} mm Hg at a temperature of 1000°C for 100 hours.

Since the samples were highly pyrophoric, the entire operation on them was performed in an atmosphere of argon. The purities of the initial materials were U—99.9%, Th—99.9%, and Sb—99.9%. Powders of the prepared samples were subjected to an x-ray structure analysis (Cu K_α irradiation with Ni filter), which showed the presence of solid solutions in the entire concentration range from USb_2 to $ThSb_2$. The lattice parameters of the USb_2-$ThSb_2$ solid solution, depending on the composition of the alloy, varied linearly from a = 4.27 Å, c = 8.74 Å (USb_2) to a = 4.34 Å, c = 9.15 Å ($ThSb_2$), i.e., they satisfied the Vegard additivity law (Fig. 1).

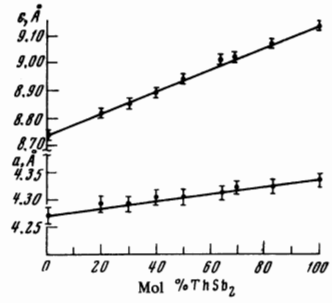

FIG. 1. Variation of the lattice parameters of USb_2-$ThSb_2$ solid solutions.

The magnetic susceptibility was measured with a pendulum balance in the temperature interval from 80 to 650°K in magnetic fields from 1.5 to 10 kOe. It was established that the susceptibility χ of all the obtained samples does not depend on the applied external magnetic field, and in the case of the $ThSb_2$ compound it is also independent of the temperature and equals -90×10^{-6}. The USb_2 compound and the solid solutions $U_{0.8}Th_{0.2}Sb_2$, $U_{0.7}Th_{0.3}Sb_2$, and $U_{0.6}Th_{0.4}Sb_2$ are antiferromagnetic. The temperature dependence of the susceptibility has maxima that shift towards lower temperatures with increasing dilution and become gradually smeared out, so that the maximum of the $U_{0.6}Th_{0.4}Sb_2$ sample is very weakly pronounced (Fig. 2). Samples with large thorium contents are paramagnetic in the entire investigated temperature range. From the obtained experimental data on the specific susceptibility we calculated the susceptibility per uranium ion in the solid solution. At the same time, a correction was introduced for the diamagnetic susceptibility of the $ThSb_2$ solvent, and also for the diamagnetism of USb_2[5].

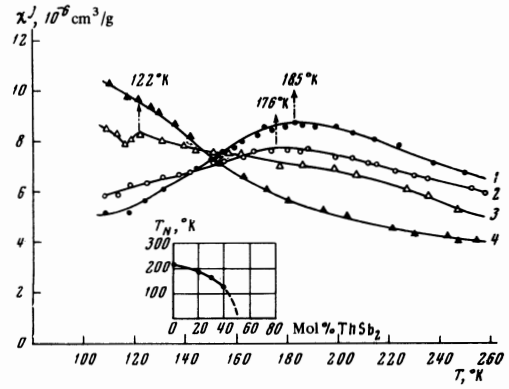

FIG. 2. Specific susceptibility χ^g vs. temperature in USb_2-$ThSb_2$ system. The arrows denote the Neel temperatures: Curves: 1 – $U_{0.8}Th_{0.2}Sb_2$; 2 – $U_{0.7}Th_{0.3}Sb_2$; 3 – $U_{0.6}Th_{0.4}Sb_2$; 4 – $U_{0.5}Th_{0.5}Sb_2$. The variation of the Neel temperature T_N with the composition is shown in the insert.

	$\chi^{mol}_{T=T_N}\cdot 10^6$	Θ_T, °K	T_N, °K	μ_{eff} (μ_B)	$\chi^{mol}_{U^{4+}}\cdot 10^6$ $T = 296°$ K	$T_N - \Theta_p$, °K	$C^{mol}\cdot\chi^{-1}_{T=T_N}$ °K
USb_2*	5200	22	206	3.04	3520	—	—
$U_{0.8}Th_{0.2}Sb_2$	5250	18±2	186±3	2.79±0.02	3420	168	185
$U_{0.7}Th_{0.3}Sb_2$	5260	18±3	176±5	2.83±0.03	3596	158	190
$U_{0.6}Th_{0.4}Sb_2$	6580	12±3	122±5	2.80±0.03	3350	104	148
$U_{0.5}Th_{0.5}Sb_2$	—	12±3	—	2.82±0.03	3520	—	—
$U_{0.35}Th_{0.65}Sb_2$	—	8±4	—	2.81±0.04	3420	—	—
$U_{0.3}Th_{0.7}Sb_2$	—	6±4	—	2.81±0.04	5400	—	—
$U_{0.15}Th_{0.85}Sb_2$	—	5±5	—	3.2±0.3	5266	—	—
$ThSb_2$	—	—	—	—	−90 **	—	—

*From the data of [1].
**Does not depend on the temperature.

The temperature dependence of the reciprocal specific susceptibility $1/\chi$, with allowance for the corrections for the diamagnetism, is shown in Fig. 3. We see that in the temperature region from 200 to 600°K, the compounds USb_2 and the solutions $U_{0.8}Th_{0.2}Sb_2$, $U_{0.7}Th_{0.3}Sb_2$, and $U_{0.6}Th_{0.4}Sb_2$ satisfy the Curie-Weiss law. This has made it possible to determine the paramagnetic Curie temperature Θ_p and to calculate the effective number of Bohr magnetons per U ion in the solid solution. For the composition $U_{0.5}Th_{0.5}Sb_2$, the Curie-Weiss law is satisfied in a narrower temperature interval, from 350 to 650°K. In the temperature region 80—350°K, a noticeable deviation from this law is observed. The deviation is particularly pronounced in $U_{0.35}Th_{0.65}Sb_2$ and $U_{0.3}T_{0.7}Sb_2$ in the temperature region from 420 to 650°K. By plotting the dependence of $1/\chi$ on $1/(T - \Theta_p)$ and extrapolating it to the temperature axis, we determined the temperature-independent susceptibility, which for these compounds turned out to be $+0.3 \times 10^{-6}$ cm^{3}g^{-1}. Curve 8 of Fig. 3 has been plotted with allowance for the temperature-independent part of the susceptibility. We see that in the temperature region 80—150°K the reciprocal susceptibility does not follow a linear law. At higher temperatures, however, the Curie-Weiss law is satisfied. The values of Θ_p and μ_{eff} for all the investigated compositions are listed in the table and are shown in Fig. 4.

It follows from the experimental data that as the

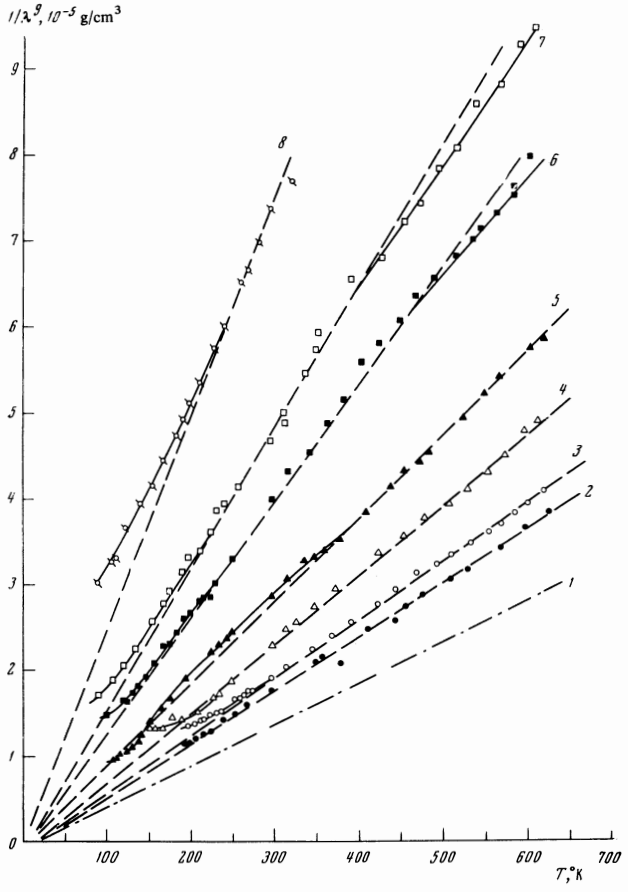

FIG. 3. Reciprocal susceptibility $1/\chi^g$ vs. the temperature in the USb_2ThSb_2 system. 1 – USb_2 [1], 2 – $U_{0.8}Th_{0.2}Sb_2$, 3 – $U_{0.7}Th_{0.3}Sb_2$, 4 – $U_{0.6}Th_{0.4}Sb_2$, 5 – $U_{0.5}Th_{0.5}Sb_2$, 6 – $U_{0.35}Th_{0.65}Sb_2$, 7 – $U_{0.3}Th_{0.7}Sb_2$. 8 – $U_{0.15}Th_{0.85}Sb_2$..

uranium ions become replaced by the thorium ions, the antiferromagnetic transformation shifts nonlinearly towards lower temperatures, depending on the concentration (Fig. 2). Such a shift was predicted by Blume[6] for a system with magnetic ions in a state with a ground singlet level Γ_1 and located somewhat higher than the triplet levels Γ_5. For other antiferromagnetic systems, namely MnO-MgO and CaO-MgO, a linear shift of Θ_N as a function of the concentration is observed, which is typical of ions with a magnetic ground energy level[7].

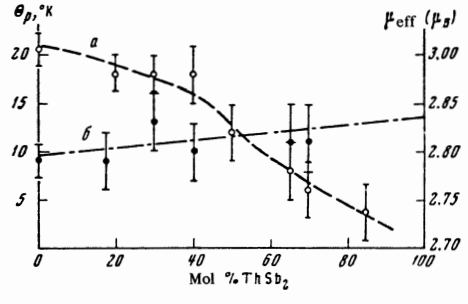

FIG. 4. Paramagnetic curie temperature Θ_p (a) and effective number of Bohr magnetons μ_{eff} vs. the composition in mol. % of ThSb for the system USb_2-$ThSb_2$.

As established for many compounds[8], in the case of a nonmagnetic ground level in the absence of exchange interactions, the susceptibility may be independent of the temperature in a certain temperature interval (the Van Vleck paramagnetism). The observed deviations from the Curie-Weiss law in the temperature region 80–150°K are possibly due to the appearance of a temperature-independent susceptibility. However, it is not excluded that these deviations are connected with the formation of "clusters" in the USb_2-$ThSb_2$ solid solutions. The affected number of Bohr magnetons per uranium ion in the solid solution increases with increasing substitution, and approaches the value calculated for the "quenched" orbital momentum for the ground state $^3H_4$ (2.83 μ_B). As to the deviation from the Curie-Weiss law in the high-temperature region, this is apparently connected with the paramagnetism of the conduction electrons. It should be noted that a final solution to the problem of the ground energy state of the uranium ion in these compounds calls for further magnetic measurements at lower temperatures.

Additional information on the magnetic properties of solid solutions can be obtained from temperature investigations of the Mossbauer spectra, which are presently under way.

[1] W. Trzebiatowski, A. Sepichowska, and A. Zugmunt, Bull. Acad. Polon., Sci. Ser. Sci. Chem. **12**, 687 (1964).

[2] J. Leciejewicz, R. Troc, A. Muzarik, and A. Zugmunt, Phys. Stat. Sol. **22**, 517 (1967).

[3] J. Przystawa, Phys. Stat. Sol. **24**, 313 (1967).

[4] V. I. Chechernikov, A. V. Pechennikov, M. E. Barykin, V. K. Slovyanskikh, E. I. Yarembash, and G. V. Éllert, Zh. Eksp. Teor. Fiz. **52**, 854 (1967) [Sov. Phys.-JETP **25**, 560 (1967)].

[5] P. W. Selwood, Magnetochemistry, Wiley, 1956.

[6] M. Blume, Phys. Rev. **141**, 517 (1966).

[7] J. M. Baker, Proc. Phys. Soc., London **77**, 1038 (1961).

[8] T. Tsuchida and G. Wallace, J. Chem. Phys. **43**, 2885 (1965).

Translated by J. G. Adashko
16