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Magnetic Properties of Pentavalent Uranium Ternary Oxides with Fluorite Structure: $ScUO_4$, YUO_4, CaU_2O_6 and CdU_2O_6 *

C. MIYAKE†, T. ISOBE, Y. YONEDA and S. IMOTO

Department of Nuclear Engineering, Osaka University, Suita, Osaka 565, Japan

In uranium mixed oxides with a fluorite structure, such as $ScUO_4$, YUO_4, CaU_2O_6 and CdU_2O_6, both scandium and yttrium are stable trivalent ions, whereas calcium and cadmium are stable divalent ions. Therefore, the uranium ion is considered to be pentavalent. The simple electronic structure of the uranium ion, $[Rn]5f^1$, gives us a possibility of obtaining a deeper understanding of 5f electron behavior in these compounds. Magnetic measurements may be the most effective for this purpose. However, the magnetic susceptibility measurements of $ScUO_4$, YUO_4, CdU_2O_6 [1] and CaU_2O_6 [2] so far reported are very limited: only from room temperature to liquid nitrogen temperature. These measurements show a monotonic increase in the magnetic susceptibility with decreasing temperature. On the other hand, we have reported anomalous behavior of the magnetic susceptibility as well as electron spin resonance absorption of alkali monouranates with a perovskite structure, such as $LiUO_3$, $NaUO_3$, KUO_3 and $RbUO_3$ [3]. The crystal structure is cubic in both the fluorite and perovskite structures. However, the crystal field formed by oxygen atoms around a central U^{5+} has eight-fold cubic symmetry in the fluorite structure but six-fold cubic symmetry in the perovskite structure.

In the present study, the magnetic susceptibility and XPS spectra were measured on these uranium mixed oxides with a fluorite structure. The magnetic behavior of the 5f electrons of U^{5+} is discussed from magnetic superexchange interactions and in relation to XPS spectra of 5f electrons.

Experimental

Materials

$ScUO_4$

The sample of $ScUO_4$ was prepared by two methods: a mechanical mixing method and a coprecipitation method. In the former method, UO_2 was first reduced at about 1000 °C for 5 h in flowing H_2 gas. The required amounts of Sc_2O_3, UO_2 and UO_3 preheated at about 400 °C for 1.5 h in a vacuum, were ground and heated at 1000 °C for 5 days in flowing Ar gas. The obtained product shows a high crystallinity. In the latter method, Sc_2O_3 and U_3O_8 with a mole ratio of Sc:U = 1:1 were dissolved into 6 M nitric acid under heating and coprecipitated by slowly adding aqueous ammonia under stirring. The coprecipitates were dried in a vacuum and calcined at about 400 °C in air. We have modified the method already reported in ref. 4: the calcined coprecipitates were heated at 1400 °C for 5 h in flowing H_2 gas in order to reduce U_3O_8 to UO_2, because UO_2 has a fluorite structure which resembles the structure of the rare earth C-type of Sc_2O_3. After heating at 1400 °C for 120 h in flowing Ar gas, the solid solution of fluorite structure was obtained with a high degree of crystallinity.

YUO_4

Since a single phase of YUO_4 could not be obtained by the mechanical mixing method, the coprecipitation method was tried by three different ways. After being calcined, following the method described previously, the coprecipitates were: (a) heated at 1280 °C for 5 days in flowing O_2 gas; or (b) heated at 1280 °C for 5 days in flowing Ar gas; or (c) heated at 1400 °C for 17 h in flowing H_2 gas. The products obtained by methods (a) and (b) have a high crystallinity, while (c) gives a relatively lower crystallinity.

CaU_2O_6

The sample was prepared by a mechanical mixing method consisting of two procedures: formation of CaU_2O_7 and thermal decomposition of CaU_2O_7 in a vacuum leading to CaU_2O_6. Since phases other than the fluorite phase were always found in the final product by the mechanical mixing method, the following method was applied. The required amount of $Ca(CH_3COO)_2 \cdot H_2O$ and $UO_2(CH_3COO)_2 \cdot 2H_2O$ with a mole ratio of Ca:U = 1:2 were weighed and dissolved into 4.2 M acetic acid solution under heating at 80 °C. By evaporating the solvent, we obtained yellow crystalline precipitates which were dried in air, calcined at 350 ~ 400 °C and finally heated at 900 °C for 45 h in flowing O_2 gas. The final product of CaU_2O_6 was prepared by heating the obtained CaU_2O_7 at 1120 °C for 43 h under a vacuum below 10^{-3} Pa.

CdU_2O_6

The preparation of CdU_2O_6 consisted of two steps as follows.

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†Author to whom correspondence should be addressed.

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$$CdO + \frac{1}{3}U_3O_8 \xrightarrow{O_2\ \text{flow, 900 °C}} CdUO_4$$

$$CdUO_4 + UO_2 \xrightarrow{\text{Ar flow, 700 °C}} CdU_2O_6$$

The required amounts of CdO preheated at 400 °C in flowing Ar gas and U_3O_8 with a mole ratio of Cd:U = 1:2 were weighed, finely ground, mechanically well mixed, and finally heated at 700 °C for 20 h in air, at 800 °C for 100 h in air and at 900 °C for 40 h in air until crystalline powders with a high crystallinity were obtained. The color of the powders was orange. After heating the orange powders at 700 °C in flowing Ar gas, the final product was obtained with a relatively high crystallinity.

The identification of the sample was performed using powder X-ray diffraction patterns in comparison with the patterns reported previously.

Measurements

X-ray diffraction

Powder X-ray diffraction patterns were recorded with a Rigaku Rad-γA diffractometer using Ni-filtered Cu Kα radiations. The lattice constant of the sample was determined by the Cohen method applied to diffraction lines in the high angle range from 70° to 130° in 2θ (Table I).

Magnetic susceptibility

The magnetic susceptibility was measured from room temperature down to 1.7 K at 0.5 T with a Faraday-type torsion magnetometer. The diamagnetic contribution was corrected with Pascal's constants as follows.

Sc^{3+}: -6×10^{-6}, Y^{3+}: -12×10^{-6},

Ca^{2+}: -10.2×10^{-6}, Cd^{2+}: -22×10^{-6},

U^{5+}: -26×10^{-6}, O^{2-}: -12×10^{-6} (cgs).

XPS spectra

These were obtained on an ESCA-750 from Shimadzu Co. Ltd., with a Mg target excited by 8 kV with 30 mA emission current under a vacuum below 5×10^{-5} Pa.

Results and Discussion

The temperature dependence of the magnetic susceptibility per mole of uranium for each compound is shown in Fig. 1. For all of the compounds we have a maximum in the magnetic susceptibility–temperature curves. It is worth noting that all the compounds show nearly the same maximum of 6 ~ 7 K with a similar shape, while alkali metal monouranates with a perovskite structure (such as $LiUO_3$, $NaUO_3$, KUO_3 and $RbUO_3$) show a sharp maximum over a wide range of temperature from 16 ~ 32 K [3]; the magnitude of magnetic susceptibility per

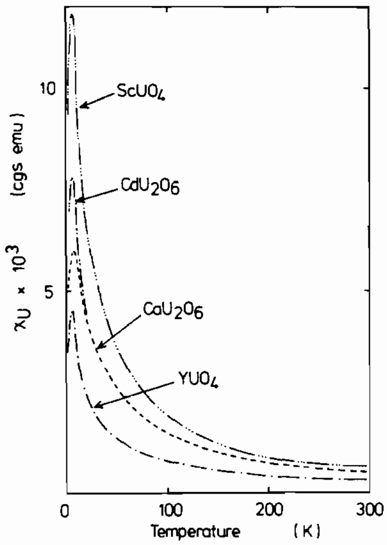

Fig. 1. Temperature dependence of magnetic susceptibilities.

TABLE I. Lattice Constants, Temperature-independent Paramagnetic Susceptibilities, Temperatures of χ_{max} and Effective Numbers of Bohr Magneton

Sample	Lattice constant (A)		$\chi_{t.i.p.}$ $(\times 10^{-3})$	$T(\chi_{max})$ (K)	μ_{eff} (B.M.)
	Observed	Literature			
$ScUO_4$[a]	5.235	5.235 [5]	0.45	6.5	1.2
$ScUO_4$[b]	5.238		0.54	7.0	1.2
YUO_4[c]	5.357	5.350 [5]	0.56	6.0	1.1
YUO_4[d]	5.358		0.50	6.5	0.9
YUO_4[e]	5.346		0.50	6.0	0.9
CaU_2O_6	5.383	5.379 [6]	0.30	6.5	1.3
CdU_2O_6	5.361	5.357 [7]	0.30	5.0	1.2

[a] Mechanical mixing. [b] Coprecipitation. [c] H_2 flow. [d] O_2 flow. [e] Ar flow.

uranium atom is in the order: $ScUO_4 > CdU_2O_6 > CaU_2O_6 > YUO_4$. In the present four systems, scandium, yttrium, calcium and cadmium ions are diamagnetic because of their closed-shell structures and the paramagnetic ion is limited only to pentavalent uranium, if we exclude the possibility that one-half of uranium ions are tetravalent and the remainder of uranium ions are hexavalent, resulting in the same average charge as pentavalent uranium. This has been supported by a measurement of the diffuse reflectance spectrum in the near infrared region [8]. In the perovskite structure, six oxygen atoms form the crystal field with an octahedral symmetry around the central uranium atoms, while in the fluorite structure eight oxygen atoms surround the central uranium forming the crystal field with an eight-fold cubic symmetry. In the former structure, a linear chain of –O–U–O–U– spreads three-dimensionally in the crystal, but in the latter threre is no linear chain such as –O–U–O–U–.

In the present oxides U^{5+} and other cations, such as Sc^{3+}, Y^{3+}, Ca^{2+} and Cd^{2+}, are statistically distributed in a cation sublattice of the face-centered cubic structure and are bridged by two oxygen atoms with the angle M–O–M of 109.5°, as shown in Fig. 2a [9]. A magnetic superexchange interaction is expected to operate between U^{5+} via oxygen atoms. However, the linkage of U^{5+} does not spread over the crystal and is limited only to a cluster of a few U^{5+} due to the interception by other diamagnetic cations. The ratio of uranium to the other metal in $ScUO_4$ and YUO_4 is different from that in CaU_2O_6 and CdU_2O_6. No effect of the ratio on the temperature of the maximum could be observed. Furthermore, the density of the 5f electrons of U^{5+} towards the corner of the octahedron of six oxygen atoms is about three times as high as that in the direction of the corner of the cube of eight oxygen atoms. The distances of U–O are larger than those of alkali monouranates, as listed in Table II.

Therefore, in the present oxides, the superexchange interactions are insignificant with respect to the location of the maximum temperature (Table I). Each U^{5+} has at least one nearest neighbor of U^{5+} and all U^{5+} participate in a dimer, leaving no isolated U^{5+}. Actually, the shape around the maximum of the magnetic susceptibility–temperature curves is almost reproduced by scaling the curve to an isotropic Heisenberg interaction with $s = 1/2$. Furthermore, the independence of the maximum temperature on the U/M ratio, and the lack of increase in the paramagnetic susceptibility at temperatures below the maximum, are consistent with a dimer model.

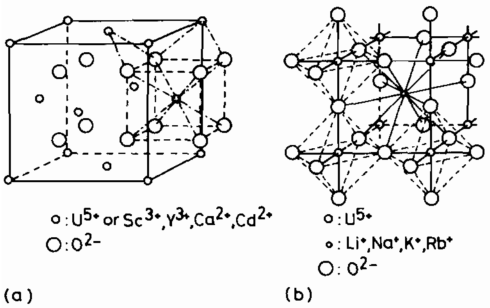

Fig. 2. (a) Cube of eight oxygen atoms in fluorite structure. (b) Octahedron of six oxygen atoms in perovskite structure.

TABLE II. U–O Bond Distances in the Crystals with Cubic and Octahedral Coordination around Uranium

Coordination	Sample	U–O Bond distance (Å)
Cube	$ScUO_4$	2.27
	YUO_4	2.32
	CaU_2O_6	2.33
	CdU_2O_6	2.32
Octahedron	$NaUO_3$	2.09
	KUO_3	2.15

The magnitude of magnetic susceptibility per uranium atom is in the order: $ScUO_4 > CdU_2O_6 > CaU_2O_6 > YUO_4$. Since the difference of temperature-independent paramagnetic susceptibilities is negligibly small and the susceptibility is independent of the lattice constant, as listed in Table I, the crystal field around U^{5+} is believed not to be responsible for the observed order.

It has been found that the electric conductivity of UO_2 increases by additions of Gd^{3+}, and that $(U,Gd)O_2$ solid solutions become semiconductors. If the present oxides behave similarly, the different cations such as Sc^{3+}, Y^{3+}, Ca^{2+} and Cd^{2+} may produce different energy gaps between the conduction band and the valence band, leading to different 5f electron densities. The smaller the 5f electron density, the smaller the magnetic susceptibility, because the Pauli paramagnetic susceptibility of conduction electrons is two orders of magnitude smaller than that of the paramagnetic susceptibility of 5f electrons. From XPS measurements of YUO_4, CaU_2O_6 and CdU_2O_6, the binding energies of 5f electrons are found to be in the order of $CdU_2O_6 > CaU_2O_6 > YUO_4$ with respect to those of the U–O bond and the $6p_{3/2}$ electron, as seen from Fig. 3. Therefore, the magnitude of magnetic susceptibility may depend on the 5f electron transfer to the conduction band.

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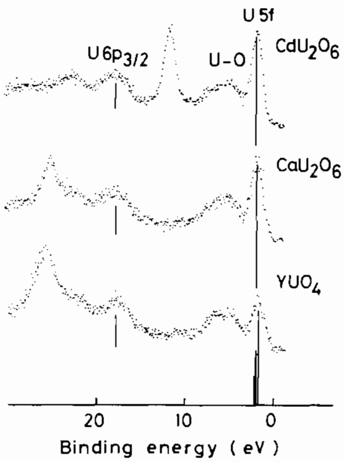

Fig. 3. XPS spectra of the valence band. The positions of the 5f band in CdU_2O_6 and CaU_2O_6 are the short and intermediate lines to the left of the YUO_4 line.

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