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Oxidation states of U and Ti in U–Ti–O ternary mixed oxides

Chie Miyake, Daisuke Sugiyama and Makoto Mizuno
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

Kazuo Taniguchi
Osaka Electro-Communication University, Neyagawa, Osaka 572 (Japan)

Abstract

$TiUO_5$ and Ti_2UO_6 were prepared and identified by powder X-ray diffraction analysis. The oxidation states of uranium and titanium in $TiUO_5$ were found to be basically hexavalent and tetravalent respectively by X-ray photoelectron spectroscopy, but owing to the non-stoichiometry of this compound, a trace of paramagnetic susceptibility was also observed. In Ti_2UO_6 both uranium and titanium are in the tetravalent state according to X-ray photoelectron spectra. However, the magnetic susceptibility for Ti_2UO_6 is temperature independent with a superimposed broad peak around 25 K. Considering the structure of Ti_2UO_6, this anomalous behaviour is discussed on the basis of crystal field theory and magnetic superexchange interaction between uranium ions.

1. Introduction

In nuclear engineering, titanium has been studied as a trace additive to increase the density and improve the high temperature stability of nuclear fuels [1, 2]. In addition, $TiO_2 \cdot nH_2O$ is a candidate as an inorganic adsorbent to extract uranium resources from seawater [3].

The preparation, crystal structure, etc. of $TiUO_5$ [4, 5] and Ti_2UO_6 [5, 6] have been reported previously. In this paper the mutual dependence of the oxidation states of uranium and titanium in these ternary oxides and their characteristic magnetic properties are studied by magnetic susceptibility measurements, X-ray photoelectron spectroscopy (XPS), etc.

2. Experimental details

2.1. Materials

2.1.1. $TiUO_5$

A concentrated sulphuric acid solution of TiO_2 and a nitric acid solution of uranium were mixed in the molar ratio U:Ti = 1:1. The coprecipitates produced by slowly adding aqueous ammonia with stirring were heated at 700 °C for 50 h in air. The green powder obtained was identified as $TiUO_5$ by powder X-ray diffraction analysis [5], but the low degree of crystallization seems to correspond to a previous report [4] that $TiUO_5$ is amorphous below 700 °C.

2.1.2. Ti_2UO_6

TiO_2 and UO_2 in the molar ratio 2:1 were mixed for 20 min and heated at 1450 °C for 3 h in a vacuum of about 10^{-3} Pa. The black sample obtained was identified as Ti_2UO_6 by powder X-ray diffraction analysis [6]. In contrast to $TiUO_5$, the sharp diffraction pattern indicated a high degree of crystallinity.

2.2. Measurements

Magnetic susceptibility measurements were performed from room temperature down to 4 K at 0.6 T with a Faraday-type torsion magnetometer. In order to confirm the absence of ferromagnetic impurities, the dependence of the magnetic susceptibility on the intensity of the magnetic field was measured at liquid nitrogen and room temperatures. XPS measurements were recorded on an ESCA-750 (Shimazu Co. Ltd.) using a magnesium target excited by 8 kV with an emission current of 30 mA under an atmosphere below 5×10^{-5} Pa. The diffraction patterns were recorded on a Rigaku Rad-γ A diffractometer using nickel-filtered Cu-Kα radiation.

3. Results and discussion

Figures 1(a) and 1(b) show the XP spectra of the valence band, U $4f_{5/2}$ and U $4f_{7/2}$ for $TiUO_5$ and Ti_2UO_6 together with those for UO_2 and UO_3 for comparison. In Fig. 2 the magnetic susceptibility–temperature curves for $TiUO_5$ and Ti_2UO_6 are shown.

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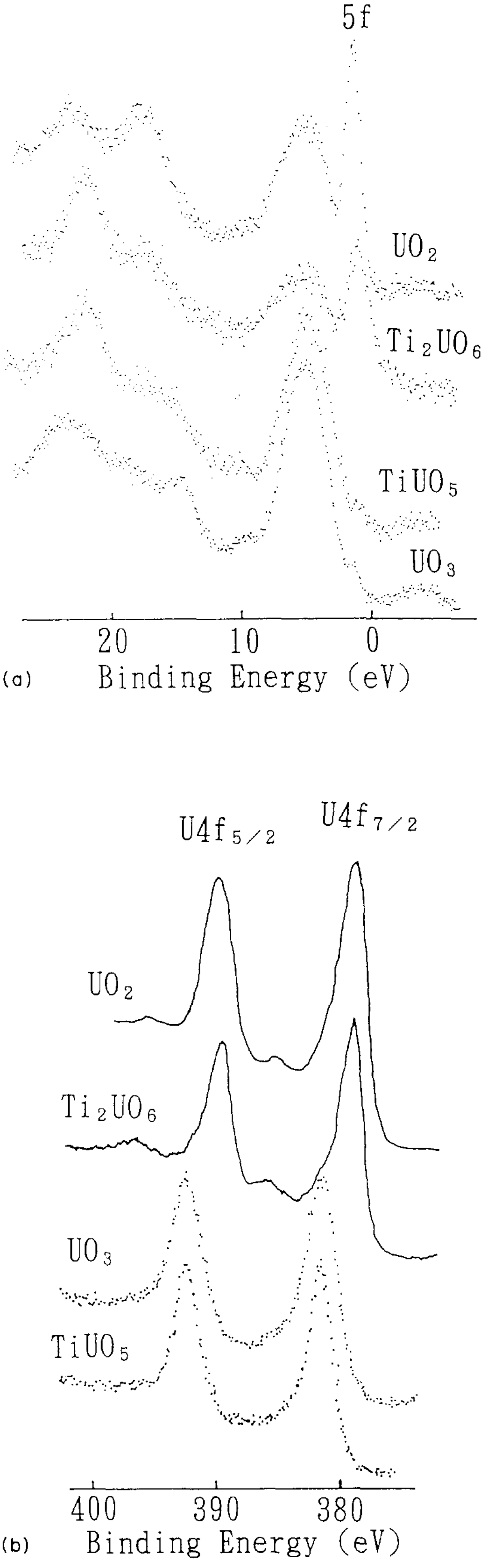


Fig. 1. (a) XP spectra of valence band for $TiUO_5$, Ti_2UO_6, UO_2 and UO_3. (b) XP spectra of U $4f_{5/2}$ and U $4f_{7/2}$ for $TiUO_5$, Ti_2UO_6, UO_2 and UO_3.

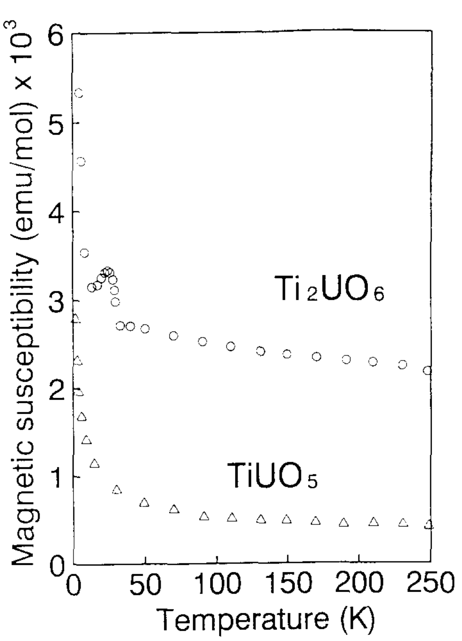


Fig. 2. Dependence of magnetic susceptibility on temperature for $TiUO_5$ and Ti_2UO_6.

3.1. $TiUO_5$

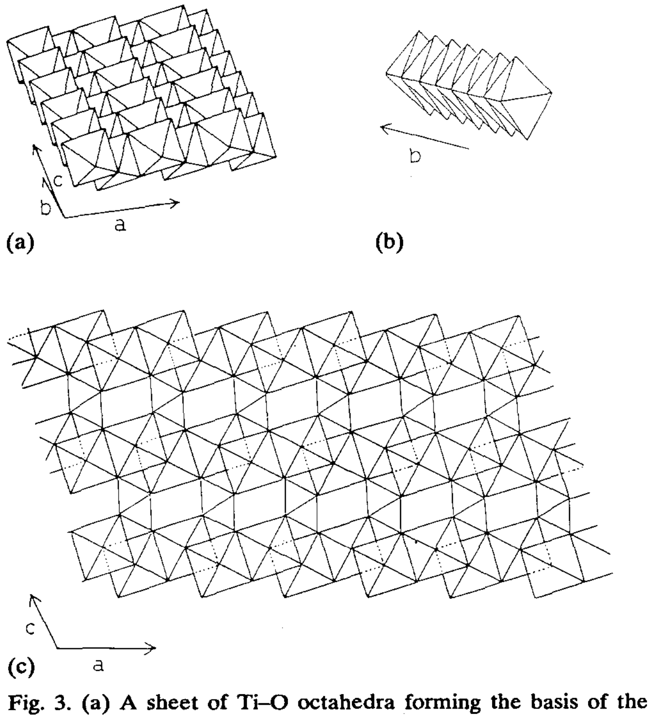
As can be seen in Fig. 1(a), the very sharp peak in the valence band spectrum characteristic of the 5f electron is absent, suggesting no 5f electron for U in $TiUO_5$. Moreover, the peaks of U $4f_{5/2}$ and U $4f_{7/2}$ for $TiUO_5$ in Fig. 1(b) can be clearly assigned to the hexavalent state by reference to the spectrum for UO_3. Titanium in $TiUO_5$ can be assigned to the tetravalent state from the XP spectrum. These oxidation states of U^{6+} and Ti^{4+} have no unpaired electrons, resulting in diamagnetism of $TiUO_5$. Figure 2 shows, however, that the dependence of the magnetic susceptibility on temperature for $TiUO_5$ obeys the Curie–Weiss law and the effective number of Bohr magnetons, μ_{eff}, is estimated to be 0.35.

The non-stoichiometry of $TiUO_5$ was examined next. Elemental analysis for U and Ti indicated the chemical formula $TiUO_{4.83}$, suggesting that oxygen defects exist in the crystal and the oxidation states of the metal ions are reduced for electrical neutrality. U^{5+}, U^{4+} and Ti^{3+} are possible as the paramagnetic species responsible for the observed paramagnetic susceptibility. Considering the oxidation–reduction potentials of Ti and U and the stability of U^{5+} in oxides, U^{5+} is thought to be the most probable [7]. The observed value of $\mu_{\mathrm{eff}} = 0.35$ is estimated to correspond to the existence of about 2% U^{5+}, because μ_{eff} for the free U^{5+} ion is 2.535. Consequently, the trace of paramagnetic behaviour, in spite of the preparation in air, is explained by the non-stoichiometry of this compound.

3.2. Ti_2UO_6

In the valence band spectrum shown in Fig. 1(a) the sharp 5f electron peak is clearly observed for Ti_2UO_6. In the spectrum in Fig. 1(b) Ti_2UO_6 displays peaks corresponding to tetravalent uranium and satellite peaks are also observed 7 eV towards the higher binding energy side of the respective U 4f peaks. These indicate uranium to be tetravalent with two 5f electrons. In addition, it was confirmed from the IR absorption spectrum that uranium is not in the hexavalent state because of the absence of absorption around 800 cm^{-1} due to the stretching vibration characteristic of the uranyl unit. The titanium ions are in the diamagnetic tetravalent state. Therefore U^{4+} is responsible for the magnetic properties of Ti_2UO_6. As seen from Fig. 2, the dependence of the magnetic susceptibility on temperature does not obey the Curie–Weiss law, but shows an anomalous behaviour where the χ–T curve has a broad maximum at approximately 25 K and a relatively large value of the temperature-independent paramagnetic susceptibility of 2×10^{-3} e.m.u. mol^{-1}.

The crystal structure of Ti_2UO_6 is analogous to that of Ti_2ThO_6 [8]. The Ti atom is octahedrally coordinated by six O atoms with some distortion. The octahedra are built up into infinite zigzag sheets as shown in Fig. 3(a). The formation of Ti–O octahedra and the combination of octahedra joined by common edges are characteristic features of titanates [9]. The U atoms bind the Ti–O octahedron sheets together and are located in octahedral interlayer positions, but the U–O octahedron is long, slender and far from regular. The U–O octahedra are joined in a series along the *b* axis by common edges and inserted between the Ti–O octahedron sheets as shown in Figs. 3(b) and 3(c).



(a) (b)

(c)

Fig. 3. (a) A sheet of Ti–O octahedra forming the basis of the structure of Ti_2UO_6. (b) A chain of U–O octahedra. (c) Crystal structure of Ti_2UO_6.

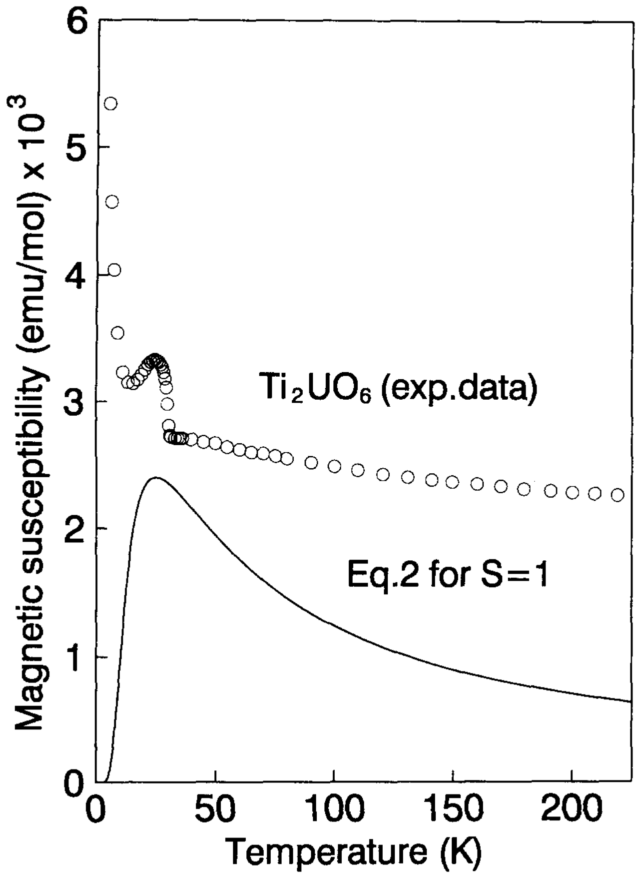
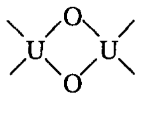


Fig. 4. Temperature dependence of magnetic susceptibility calculated in one-dimensional Ising model for $S=1$ and comparison with experimental values.

Considering the characteristic feature of the crystal structure of Ti_2UO_6 and the relation between the U^{4+} ions combined with double-bridged O atoms to form a chain,



the broad maximum around 25 K observed in Fig. 2 seems to be caused by magnetic superexchange interaction between tetravalent uranium ions. The spin–spin interaction is expressed as follows in the Ising model with limiting nearest-spin coupling:

$$H=-2J\sum S_iS_{i+1} \qquad (1)$$

where J is the exchange integral between nearest neighbours and S is the z component of the spin operator. Suzuki *et al.* [10] gave the axial magnetic susceptibility of a one-dimensional chain in the Ising model for $S=1$

as

$$\chi=\frac{2(g\mu)^2N}{kT}\frac{1}{4a^2(a+2)}\left(1+\frac{4a^3+5a^2-a+1}{a[(a+a^{-1}-1)^2+8]^{1/2}}\right) \tag{2}$$

where $a=\exp(-2J/kT)$ and μ denotes the Bohr magneton. For the U^{4+} ion with two 5f electrons and $S=1$ the calculated values are shown in the lower part of Fig. 4 for a Landé g factor of 0.8 and a suitable $J=-6.81$ cm^{-1} to fit the maximum temperature to 25 K. The maximum of the experimental χ–T curve is thought to be caused by a magnetic superexchange interaction between U^{4+} ions combined with double-bridged O atoms.

On the contrary, the relatively large value of the temperature-independent paramagnetic susceptibility is considered to arise from the U^{4+} ion with the $5f^2$ configuration which is located in the crystal field with octahedral symmetry [11]. The large increase in χ at the lowest T seems to be due to a trace of paramagnetic impurities such as isolated U^{4+}, Ti^{3+}, etc., because the contribution of paramagnetic species in the lowest temperature range is very noticeable.

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References

1 H. Landspersky and M. Voboril, *J. Inorg. Nucl. Chem.*, *29* (1967) 250.
2 J.B. Ainscough, F. Rigby and S.C. Osborn, *J. Nucl. Mater.*, *52* (1974) 191.
3 T. Hori, M. Yamawaki and M. Kanno, *J. Nucl. Sci. Technol.*, *24*(5) (1987) 377.
4 R.H. Marshall and H.R. Hoekstra, *J. Inorg. Nucl. Chem.*, *27* (1965) 1947.
5 J.C. Bobo, *Rev. Chim. Miner.*, *1* (1964) 1.
6 J.E. Patchett and E.W. Nuffield, *Can. Miner.*, *6* (1960) 483.
7 C. Miyake, T. Isobe and S. Imoto, *J. Nucl. Mater.*, *152* (1988) 64.
8 R. Ruh and A.D. Wadsley, *Acta Crystallogr.*, *21* (1966) 274.
9 S. Andersson and A.D. Wadsley, *Acta Crystallogr.*, *15* (1962) 194.
10 M. Suzuki, B. Tsujiyama and S. Katsura, *J. Math. Phys.*, *4* (1963) 124.
11 C.A. Hutchison Jr. and G.A. Candela, *J. Chim. Phys.*, *27* (1957) 707.