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Magnetic studies on CoU_2O_6 and NiU_2O_6 by magnetic susceptibility, specific heat and neutron diffraction measurements

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A B S T R A C T

Magnetic properties of ternary uranium oxides CoU_2O_6 and NiU_2O_6 have been reported. X-ray and neutron diffraction measurements show that both compounds crystallize in the hexagonal Na_2SiF_6 structure (space group: $P321$), in which both cobalt (nickel) and uranium ions are in the distorted octahedral crystal field by six oxygen ions. Measurements of the magnetic susceptibility and specific heat reveal that CoU_2O_6 and NiU_2O_6 order antiferromagnetically at 32.5 and 35.3 K, respectively. Neutron diffraction measurements at 10 K show that the magnetic structure for CoU_2O_6 is a multi-sinusoidal structure with a propagation vector (0,0,1/6).

1. Introduction

The magnetic and optical properties of actinides are characterized by the behavior of 5*f* electrons. For the 5*f* compounds, the crystal field, spin-orbit coupling, and electron–electron repulsion interactions are of comparable magnitude, which makes the analysis of the experimental results complicated. In the case of actinide ions having the $[Rn]5f^1$ electronic configuration, such as a U^{5+} ion, the situation is considerably simplified because there is no electronic repulsion interaction. Therefore, the theoretical treatments of such ions are easier and we may obtain a deeper understanding of the behavior of 5*f* electrons in solids.

Among many uranium complex oxides, the materials containing a *d* block element attract our attention, because various magnetic properties due to the magnetic interaction between *d* and *f* electrons may be observed. For example, Ba_2CoUO_6 and Ba_2NiUO_6 with the double perovskite structure show ferromagnetic transitions at 9 and 25 K, respectively [1]. Previously, we reported the preparation of ternary uranates CoU_2O_6 and NiU_2O_6, and the results of magnetic susceptibility measurements [2]. Both CoU_2O_6 and NiU_2O_6 are isostructural and have a Na_2SiF_6 structure with space group $P321$ [3]. The valence configuration for CoU_2O_6 and NiU_2O_6 is $M^{2+}U_2^{5+}O_6^{2-}$ (M = Co, Ni) from the analysis of the magnetic susceptibility data [2]. Therefore, both uranium and transition elements should contribute to their magnetic properties. Magnetic susceptibility measurements showed that CoU_2O_6 and NiU_2O_6 ordered antiferromagnetically at 32.5 and 35.3 K, respectively.

In order to obtain further information about the magnetic properties of these compounds, we have performed magnetic susceptibility, specific heat, and neutron diffraction measurements in detail. Their results will be discussed here.

2. Experimental

2.1. Sample preparation

The CoU_2O_6 was prepared by heating 1:1 mixtures of $CoUO_4$ and UO_2 in an evacuated quartz tube at 1073 K for a day. The $CoUO_4$ was prepared by firing intimately grinding mixtures of CoO and U_3O_8 in air at 1273 K for a day. Since the compound $NiUO_4$ cannot be synthesized by heating in air, the NiU_2O_6 was prepared by heating mixtures of NiO, UO_2 and UO_3 in an evacuated quartz tube at 1073 K for a day.

2.2. Analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-Kα radiation equipped with a curved graphite monochromator. The data were collected by step scanning in the angle range of $10^\circ \leqslant 2\theta \leqslant 120^\circ$ at a 2θ step size of 0.02°.

The oxygen non-stoichiometry in the specimen was checked by the back-titration method [4]. A weighed sample was dissolved in excess cerium (IV) sulfate solution. Then, the excess cerium (IV) was titrated against a standard iron (II) ammonium sulfate solution. The results of the oxygen analysis indicate that the samples

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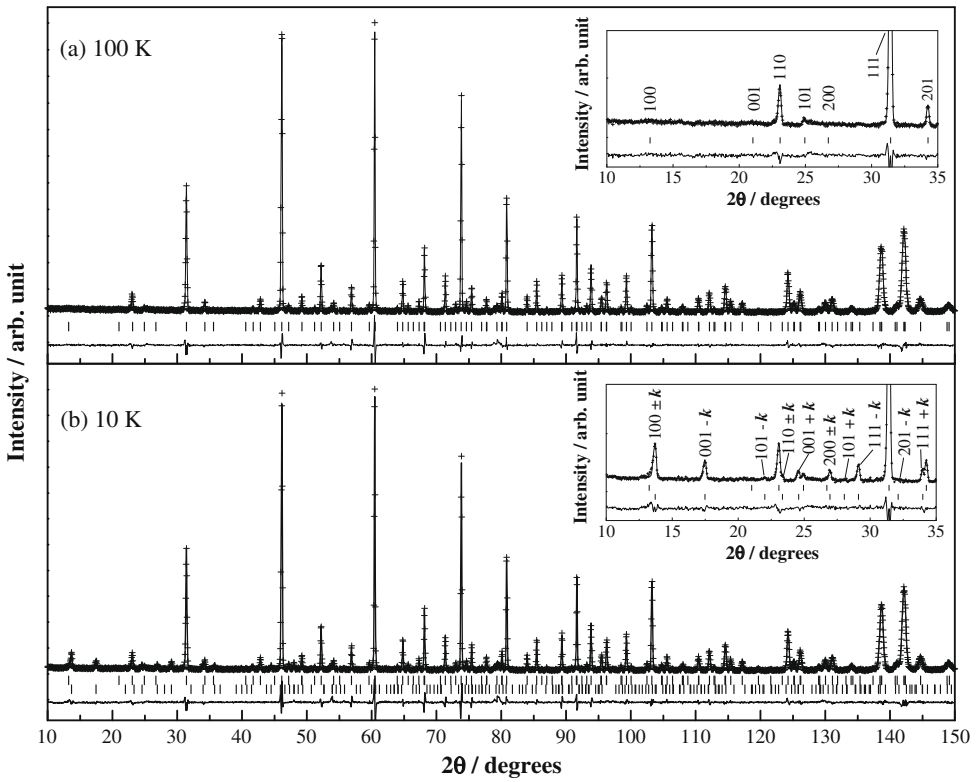

Fig. 1. Powder neutron diffraction profiles for CoU_2O_6 at (a) 100 K and (b) 10 K. The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. In (b), the nuclear reflection positions are shown as upper vertical marks and magnetic ones are shown as lower ones. The lower trace is a plot of the difference between calculated and observed intensities. The inset of each figure shows the diffraction profiles at low angles and indexing.

prepared in this study are oxygen-stoichiometric, in view of the error limits of this analysis.

2.3. Magnetic susceptibility measurement

The temperature dependence of the magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design, MPMS) under both zero-field-cooled conditions (ZFC) and field-cooled conditions (FC). The former was measured on heating the sample up to 400 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 400 to 1.8 K under 0.1 T. The field dependence of magnetization was measured at 2 and 100 K over the applied magnetic field range of $-5.5\ \mathrm{T} \leqslant H \leqslant 5.5\ \mathrm{T}$.

2.4. Specific heat measurement

The specific heats were measured using a relaxation technique applied by a specific heat measuring system (Quantum Design, PPMS) in the temperature range of $1.8 \leqslant T \leqslant 300$ K. The sample in the form of a thin plate was mounted on a sample holder (thin alumina plate) with Apiezon for better thermal contact.

2.5. Neutron diffraction measurement

Powder neutron diffraction measurements were performed for CoU_2O_6 at 10–100 K and room temperature, and for NiU_2O_6 at room temperature, using a high-resolution powder diffractometer (HRPD) at the JRR-3 M reactor (Japan Atomic Energy Agency), with a Ge (331) monochromator ($\lambda = 1.8230$ Å). Measurements were performed in the range of $10^\circ \leqslant 2\theta \leqslant 150^\circ$.

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction analysis shows that both compounds crystallize hexagonally in the Na_2SiF_6 structure (space group $P321$). This result is in good agreement with the results reported previ-

Table 1
Structural parameters for CoU_2O_6 and NiU_2O_6.

Atom	Site	x	y	z	B/Å
CoU_2O_6 at room temperature					
Space group $P321$; $z = 3$					
$a = 9.1041(2)$ Å, $c = 4.9932(1)$ Å					
$R_{wp} = 8.92\%$, $R_I = 2.54\%$, $R_F = 1.74\%$, $R_e = 5.34\%$					
Co(1)	1*a*	0	0	0	0.5(2)
Co(2)	2*d*	1/3	2/3	0.530(4)	0.5(2)
U(1)	3*e*	0.6414(4)	0	0	0.48(3)
U(2)	3*f*	0.3080(5)	0	1/2	0.48(3)
O(1)	6*g*	0.0939(9)	0.8706(8)	0.7708(9)	0.73(3)
O(2)	6*g*	0.4566(9)	0.5674(9)	0.7344(9)	0.73(3)
O(3)	6*g*	0.2194(8)	0.7741(7)	0.2719(8)	0.73(3)
NiU_2O_6 at room temperature					
Space group $P321$; $z = 3$					
$a = 9.0157(3)$ Å, $c = 5.0180(1)$ Å					
$R_{wp} = 9.02\%$, $R_I = 2.29\%$, $R_F = 1.76\%$, $R_e = 5.35\%$					
Ni(1)	1*a*	0	0	0	0.82(6)
Ni(2)	2*d*	1/3	2/3	0.504(1)	0.82(6)
U(1)	3*e*	0.6397(4)	0	0	0.35(4)
U(2)	3*f*	0.3063(5)	0	1/2	0.35(4)
O(1)	6*g*	0.0934(9)	0.8701(9)	0.7721(9)	0.67(3)
O(2)	6*g*	0.4561(9)	0.5706(9)	0.7317(8)	0.67(3)
O(3)	6*g*	0.2177(9)	0.7716(7)	0.2701(9)	0.67(3)

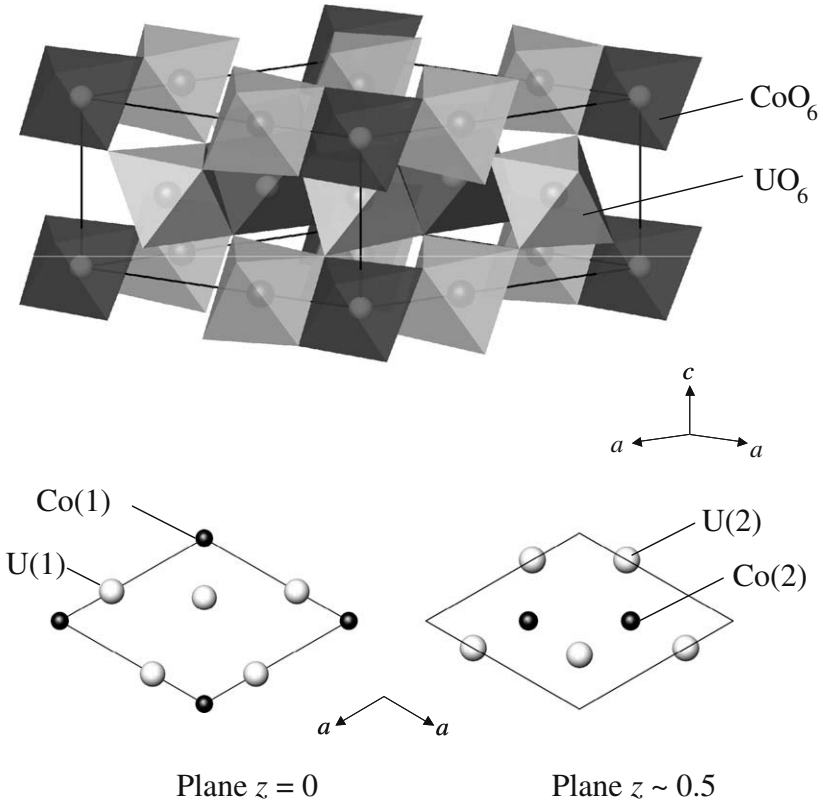

Fig. 2. The crystal structure of CoU_2O_6.

ously [2,3]. The precise crystal structures are determined by the Rietveld analysis for the powder neutron diffraction data. The neutron diffraction profiles for CoU_2O_6 measured at 10 and 100 K are shown in Fig. 1. The refined structural parameters for CoU_2O_6 and NiU_2O_6 are listed in Table 1. Fig. 2 depicts the crystal structure for CoU_2O_6. In this structure, Co and U ions are in the distorted octahedral field by six oxygen ions. The analysis for the low-temperature data indicates that the crystal structures at low-temperatures are the same as that at room temperature except for a slight contraction of the unit cell. In addition to the chemical analysis, the Rietveld analysis for the neutron diffraction profiles also indicates that the samples are oxygen-stoichiometric.

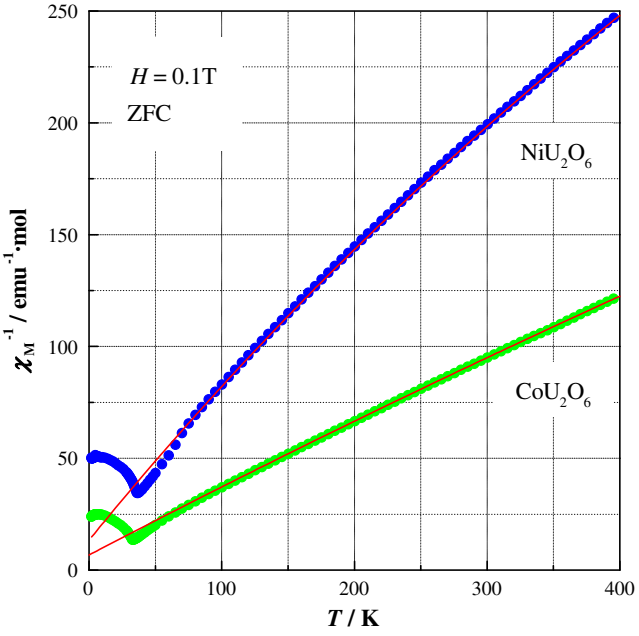

Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility for MU_2O_6 (M = Co, Ni). The solid lines are the Curie-Weiss fitting.

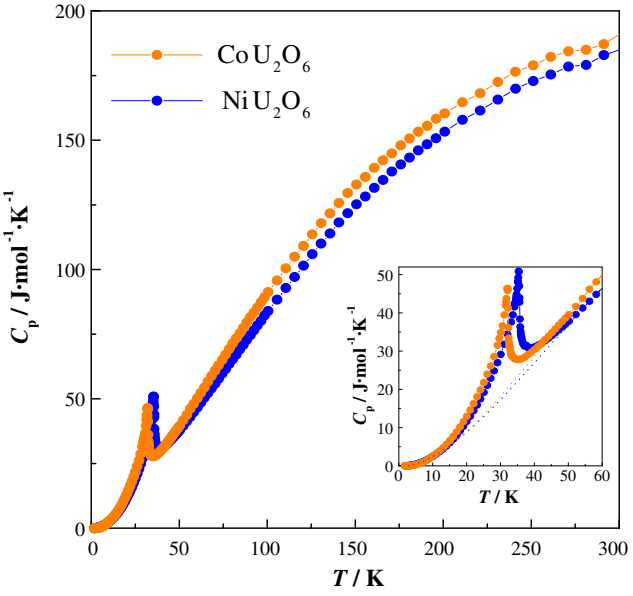

Fig. 4. Temperature dependence of the specific heat C_p for MU_2O_6 (M = Co, Ni). The inset shows the detailed temperature dependence below 60 K. The dotted lines are the calculated lattice specific heat (see text).

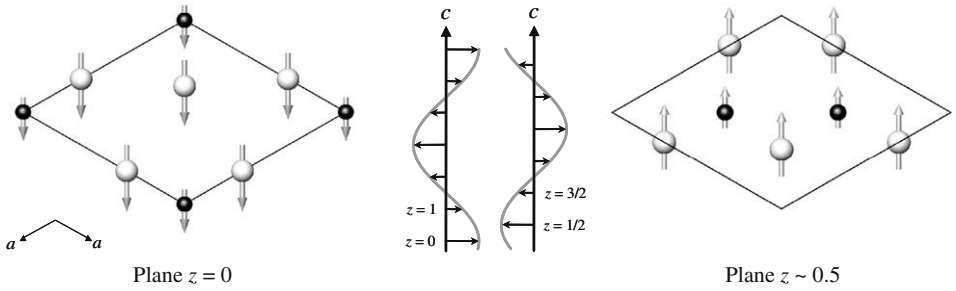

Fig. 5. The magnetic structure for CoU_2O_6.

3.2. Magnetic properties

Fig. 3 shows the temperature dependence of the reciprocal magnetic susceptibilities for CoU_2O_6 and NiU_2O_6. The antiferromagnetic transitions are observed at 32.5 and 35.3 K, respectively, which corresponds to the previous results [2]. The solid lines in Fig. 3 show the Curie-Weiss fittings for the magnetic susceptibilities in the temperature region between 150 and 400 K. The effective magnetic moment (μ_{eff}), Weiss constant (θ) and temperature-independent paramagnetic susceptibility (χ_{TIP}) are calculated to be 5.07 (2) μ_B, −22 (1) K, and 5.6(4) $\times 10^{-4}$ emu/mol for CoU_2O_6, and 3.27 (1) μ_B, −20 (1) K, and 8.2(1) $\times 10^{-4}$ emu/mol for NiU_2O_6, respectively. If we assume that the effective magnetic moment of Co^{2+} ion in the CoU_2O_6 is comparable to the moment for $Co^{2+}U^{6+}O_4$ (μ_{eff} = 4.99 μ_B) [5], the moment for U^{5+} is calculated to be 0.63 μ_B. This value is reasonable for the moment of a U^{5+} ion in an octahedral crystal field [6]. By using this value, the moment for Ni^{2+} in the NiU_2O_6 is calculated to be 3.15 μ_B. This value is also reasonable for the Ni^{2+} ion ($3d^8$). Therefore, we infer the ionic model $M^{2+}U_2^{5+}O_6^{2-}$ (M = Co, Ni). The negative Weiss constant corresponds to the existence of antiferromagnetic transition at low-temperatures. No divergence between the ZFC and FC susceptibilities was observed, and the field dependence of the magnetization has no hysteresis loop. Therefore, there is no ferromagnetic moment in the CoU_2O_6 and NiU_2O_6.

Fig. 4 shows the variation of the specific heat (C_p) as a function of temperature in the temperature range between 1.8 and 300 K. One clear λ-type specific heat anomaly was observed for each compound, which indicates that both the magnetic moments of Co (Ni) and U order at the same temperature. This anomaly corresponds to the antiferromagnetic transition found in the magnetic susceptibility. In order to estimate the magnetic entropy change due to the magnetic ordering, we have to subtract the lattice specific heat contribution from the total specific heat. It was estimated by using a polynomial function of the temperature $f(T) = aT^3+bT^5+cT^7$ [7], in which the constants were determined by fitting this function to the observed specific heat data between 15 and 40 K (see the inset figure of Fig. 4). The magnetic specific heat (C_{mag}) was obtained by $C_{mag}(T) = C_p(T) - f(T)$. The magnetic entropy changes due to the antiferromagnetic ordering for CoU_2O_6 and NiU_2O_6 are about 7.0 and 7.5 emu/mol K, respectively. In general, the magnetic entropy change is expressed by the $S_{mag} = R \ln W$ (R = molar gas constant, W: number of states for the magnetic ion). The experimental value corresponds to the case for $W = 2$ for each magnetic ion (M and Ln ions). The results for the magnetic entropy change indicate that the degeneracy of the ground states for the M^{2+} ion and U^{5+} ion in MU_2O_6 should be both twofold.

3.3. Magnetic structure

In order to determine the magnetic structure for CoU_2O_6, neutron diffraction measurements were performed at 100 and 10 K, and its diffraction profiles are shown in Fig. 1(a) and (b), respectively. In the profile measured at 10 K, some magnetic Bragg peaks are present, and they can be indexed with a propagation vector (0,0,1/6) (see the inset figure of Fig. 1(b)). Fig. 5 shows the magnetic structure for CoU_2O_6. It is a multi-sinusoidal structure with a propagation vector (0,0,1/6), in which the magnetic moments of the Co ions are parallel to a (1 1 0) direction and the magnetic moments of the U ions have a component of 0.46 μ_B along the (1 1 0) direction and a component of 0.25 μ_B along the (0 0 1) direction.

4. Summary

Measurements of the magnetic susceptibility and specific heat revealed that CoU_2O_6 and NiU_2O_6 order antiferromagnetically at 32.5 and 35.3 K, respectively. The magnetic structure for CoU_2O_6 was presented.

Acknowledgements

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