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BRIEF COMMUNICATION

Antiferromagnetic Ordering in CoU_2O_6 and NiU_2O_6

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Ternary uranium oxides CoU_2O_6 and NiU_2O_6 with hexagonal structure were prepared. From their magnetic susceptibility measurements, we have found that these compounds show antiferromagnetic transitions at 32.5 and 35.3 K, respectively. The oxidation states of uranium in the compounds are also discussed. © 1995 Academic Press, Inc.

INTRODUCTION

Magnetic properties of uranium-3*d* transition metal ternary oxides such as MUO_4 (M = Cr, Mn, Fe, Co) have been extensively studied and many interesting magnetic cooperative phenomena have been observed at low temperatures (1, 2). However, the magnetic properties of CoU_2O_6 and NiU_2O_6 have not yet been reported.

In this study, we prepared the compounds CoU_2O_6 and NiU_2O_6 and carried out their magnetic susceptibilty measurements from 4.2 K to room temperature to elucidate their magnetic properties.

EXPERIMENTAL

1. Sample Preparation

CoU_2O_6 was prepared by the following reactions:

$$3CoO + U_3O_8 \xrightarrow{in\ air} 3CoUO_4, \quad [1]$$

$$CoUO_4 + UO_2 \xrightarrow{in\ vacuo} CoU_2O_6. \quad [2]$$

The $CoUO_4$ was prepared by firing intimately ground mixtures of CoO and U_3O_8 in air at 1000°C for a day. The CoU_2O_6 was prepared by heating 1 : 1 mixtures of $CoUO_4$ and UO_2 in an evacuated quartz tube at 800°C for a day. To avoid the reaction of these mixtures with quartz, the mixtures were wrapped with molybdenum foil. After cooling to room temperature, the same grinding and heating procedures were repeated.

Since the compound $NiUO_4$ is not synthesized at ordinary pressure (3), we prepared NiU_2O_6 by the following reaction:

$$NiO + UO_2 + UO_3 \xrightarrow{in\ vacuo} NiU_2O_6. \quad [3]$$

The UO_3 was prepared by heating in air at 400°C the uranium precipitates formed by adding hydrogen peroxide to a nitric acid solution of $UO_2(NO_3)_2 \cdot 6H_2O$. The NiU_2O_6 was prepared by heating mixtures of NiO, UO_2, and UO_3, which was wrapped with molybdenum foil, in an evacuated quartz tube at 800°C for a day. After cooling to room temperature, the sample was crushed into a powder, pressed into pellets, and reacted under the same conditions.

2. Analysis

An X-ray diffraction study was performed with CuKα radiation on a Philips PW 1390 diffractometer. The lattice parameters of the samples were determined by a least-squares method applied to the diffraction lines.

The oxygen nonstoichiometry 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 with ferroin indicator. The results of the oxygen analysis indicate that in view of the error limits for this analysis, the samples prepared in this study are considered to be oxygen-stoichiometric.

3. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured with a Faraday-type torsion balance in the temperature range between 4.2 K and room temperature. The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at% Fe thermocouple and an Au–Co vs Cu thermocouple. To examine the field dependence, the magnetic suscepti-

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TABLE 1
Lattice Parameters of CoU_2O_6 and NiU_2O_6

Compounds	This study		Kemmler-Sack	
CoU_2O_6	a = 9.1124 Å c = 4.9987 Å	c/a = 0.549	a = 9.095 Å c = 4.990 Å	c/a = 0.549
NiU_2O_6	a = 9.0215 Å c = 5.0219 Å	c/a = 0.557	a = 9.015 Å c = 5.013 Å	c/a ≈ 0.556

bility was measured in each of the field strengths of 2800, 4700, 6900, 9000, and 10,600 G. Details of the experimental procedure have been described elsewhere (5).

RESULTS AND DISCUSSION

The X-ray diffraction analysis shows that both compounds presented here, CoU_2O_6 and NiU_2O_6, are crystallizing hexagonally in the Na_2SiF_6 structure (space group *P*321) (6), in which both cobalt (nickel) and uranium ions are in the distorted octahedral crystal field by six oxygen ions. Their lattice parameters are listed in Table 1. They are in good agreement with the results reported by Kemmler-Sack (7).

Figure 1 shows the temperature dependence of the magnetic susceptibilities of CoU_2O_6 and NiU_2O_6. This figure indicates that both the compounds show the antiferromagnetic-type transitions at low temperatures. Their Néel temperatures (T_N) are 32.5 and 35.3 K, respectively. The T_N

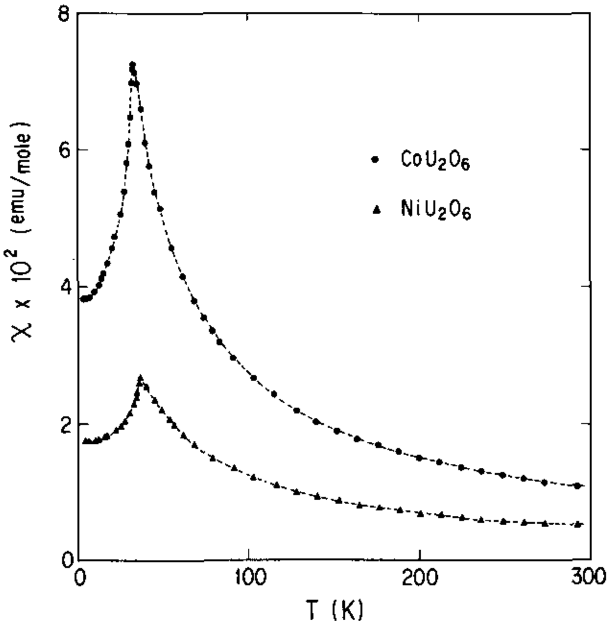

FIG. 1. Magnetic susceptibility vs temperature curves for CoU_2O_6 and NiU_2O_6.

TABLE 2
Magnetic Data for CoU_2O_6 and NiU_2O_6

Compounds	T_N(K)	$\mu_{eff}(\mu_B)$	θ(K)	χ_0(emu/mole)
CoU_2O_6	32.5	5.27	−27.8	—
NiU_2O_6	35.3	3.11	−6.9	1.1×10^{-3}

of CoU_2O_6 is higher than those of the starting materials $CoUO_4$ (T_N = 12 K) (8) and UO_2 (T_N = 30.8 K) (9). The results of the susceptibility measurements for CoU_2O_6 and NiU_2O_6 at different magnetic fields indicate that the susceptibility does not depend on the applied magnetic field. Below T_N, the susceptibility for both compounds drops very rapidly with decreasing temperature. At very low temperatures (<8 K), the susceptibility remains constant.

Table 2 lists the magnetic parameters for these two compounds. For CoU_2O_6, the Curie–Weiss law holds in the temperature region between 120 K and room temperature. Its effective magnetic moment is calculated to be 5.27 μ_B. In the case where the ionic model $Co^{2+}U_2^{5+}O_6^{2-}$ is valid for this compound, one Co^{2+} ion and two U^{5+} ions contribute to the effective magnetic moment of 5.27 μ_B. If we assume that the effective magnetic moment of Co^{2+} ion in the CoU_2O_6 is comparable to the moment for $CoUO_4$ (8), the moment for the U^{5+} ion is calculated to be 1.18 μ_B. This value is quite reasonable for the moment of a U^{5+} ion in an octahedral crystal field (10). If the ionic model $Co^{2+}U^{4+}U^{6+}O_6^{2-}$ were valid, such a compound should show a large temperature-independent paramagnetism, due to the magnetic property of a U^{4+} ion in an octahedral crystal field (11). The results of the magnetic susceptibility measurements deny this ionic model. From these considerations, we infer the ionic model $Co^{2+}U_2^{5+}O_6^{2-}$.

The magnetic susceptibility of NiU_2O_6 does not follow the Curie–Weiss law. From the extrapolation of the reciprocal temperature, $1/T$ to 0, the temperature-independent susceptibility (χ_0) is obtained to be 1100×10^{-6} emu/mole. The experimental magnetic susceptibility (χ_{exp}) is found to follow a modified Curie–Weiss law; $\chi_{exp} = 1.21/(T + 6.9) + 1.1 \times 10^{-3}$. When the effective magnetic moment for NiU_2O_6 is determined from the temperature-dependent part of the susceptibility, it is calculated to be $\mu_{eff} = 2.828\sqrt{1.21} = 3.11\ \mu_B$. This value is larger than the moment calculated for Ni^{2+} ($\mu_{eff} = 2\sqrt{S(S+1)} = 2.83\ \mu_B$), from which the moment of U^{5+} ion is calculated to be 0.92 μ_B. This value is an appropriate moment for the U^{5+} ion in an octahedral crystal field (10), which suggests the ionic model $Ni^{2+}U_2^{5+}O_6^{2-}$ for NiU_2O_6.

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