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Structure, Magnetic and Electric Properties of Single-Component Molecular Alloy System, $[Ni_{1-x}Au_x(tmdt)_2]$ (x = 0 ~ 1.0)

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Introduction

The crystal of a neutral transition metal complex with extended-TTF ligand, $[Ni(tmdt)_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate), was reported in 2001, and was found that it had very high conductivity (σ_{rt} = *ca.* 400 S·cm^{-1}) and metallic behavior down to 0.6 K. Recently, $[Au(tmdt)_2]$ with comparatively large room temperature conductivity (σ_{rt} = *ca.* 50 S·cm^{-1}) was developed, which is isostructural to that of $[Ni(tmdt)_2]$. However, unlike the neutral nickel complex, the neutral gold complex has an odd number of total electrons, which makes the electromagnetic properties of the neutral gold complex very attractive. The susceptibilities study of $[Au(tmdt)_2]$ showed an unusual magnetic phase transition around 110 K.

Since the Fermi surfaces of $[Ni(tmdt)_2]$ are quite different from those of $[Au(tmdt)_2]$, the molecular alloy system will be expected to show a variety of physical properties with varying x-value without changing the crystal structure. Most recently, we have succeeded to prepare the first "alloy system" $[Ni_{1-x}Au_x(tmdt)_2]$ (x =0 ~ 1.0). In this report, the structure, magnetic and electric properties of $[Ni_{1-x}Au_x(tmdt)_2]$ are investigated.

Experimental

The synthesis of the extended-TTF ligand, tmdt, and the responding Ni(II) and Au(III) complex were preformed according to the literature methods. The metal source were $NiCl_2{\cdot}6H_2O$ and (n-Bu_4N)$[AuCl_4]$, respectively. The black plate-like single crystals of $[Ni_{0.75}Au_{0.25}(tmdt)_2]$ were prepared by the electrochemical oxidation from acetonitrile solution containing $(Me_4N)_2[Ni(tmdt)_2]$ and (n-Bu_4N)$[Au(tmdt)_2]$ with (n-Bu_4N)PF_6 as electrolyte in an H-shaped cell. And the micro-crystals of $[Ni_{1-x}Au_x(tmdt)_2]$ were obtained by the similar method except using tetrahydrofuran as solvent.

Results and discussion

The single crystal XRD analysis of $[Ni_{0.75}Au_{0.25}(tmdt)_2]$ indicate that this alloy system are also isostructural to that of $[Ni(tmdt)_2]$ and $[Au(tmdt)_2]$ (Figure 1). And the ratio of Ni to Au (0.75 to 0.25) was obtained from the occupation refinement. The lattice constants are a = 6.392 ± 0.001 Å, b = 7.430 ± 0.002 Å, c = 12.062 ± 0.002 Å, α= 90.45°±0.03°, β = 96.83 ± 0.03, γ = 103.41 ± 0.03, and V = 552.9 ± 0.2 Å^3 with space group P-1. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R value based on the1761 reflections [$I > 3.0\ \sigma(I)$] was 0.031.

Since the size of the micro-crystals of the other ratio of $[Ni_{1-x}Au_x(tmdt)_2]$ were very small, the synchrotron radiation powder X-ray diffraction experiment of those complexes was performed. From the XRD patterns (Figure 2), we could find the diffraction peaks are shifted systemically to the lower angle as the Au concentration (x) increasing, which indicate that Ni ions can be homogeneously substituted by Au ions in the $[Ni_{1-x}Au_x(tmdt)_2]$ molecules.

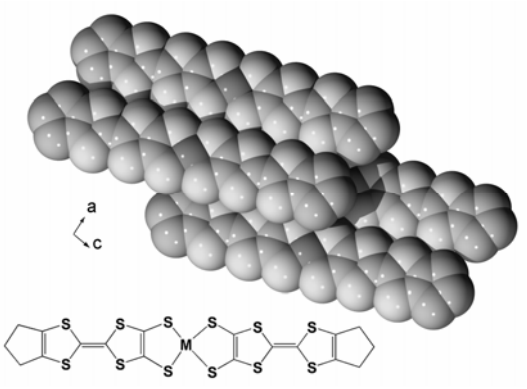

Figure 1. Crystal structure of $[Ni_{1-x}Au_x(tmdt)_2]$ viewing along the *b* axis

ESR spectra of polycrystalline samples of $[Ni_{1-x}Au_x(tmdt)_2]$ were measured in the temperature range of 3.4 ~ 300 K. The spin susceptibility and peak-to-peak line width revealed the magnetic phase transition occurred about 70 K for x = 0.8 and about 20 K for x = 0.6, respectively. The magnetic susceptibilities of $[Ni_{1-x}Au_x(tmdt)_2]$ when x < 0.6 showed a temperature-independent paramagnetic susceptibility about 2 ~ 4 × 10^{-4} emu mol^{-1}, except a very small amount of Curie-Weiss like impurity.

The resistivities were measured by the four-probe method from room temperature down to 5 K on compressed pellet samples of micro-crystals of $[Ni_{1-x}Au_x(tmdt)_2]$ (Figure 3). All of $[Ni_{1-x}Au_x(tmdt)_2]$ have a high conductivity in spite of the measurements of the compressed pellet samples. The conductivities at room temperature decrease from 40 to 6 S·cm^{-1} as x increasing from 0.2 to 0.8. All of the conductivities are only very slightly decreasing from the room temperature to 5 K. The room temperature conductivity of single crystal of $[Ni_{0.75}Au_{0.25}(tmdt)_2]$ is about 70 S·cm^{-1} and metallic behavior down to 0.4 K. Therefore, we think $[Ni_{1-x}Au_x(tmdt)_2]$ are really molecular alloys with a high conductivity and metallic state. The detail physical properties investigation of $[Ni_{0.75}Au_{0.25}(tmdt)_2]$ single crystal is in progress.

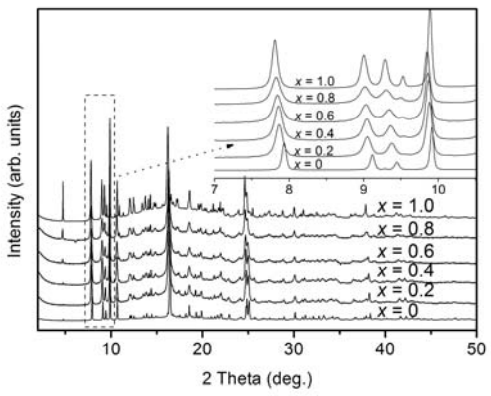

Figure 2. the synchrotron radiation XRD patterns of $[Ni_xAu_{1-x}(tmdt)_2]$

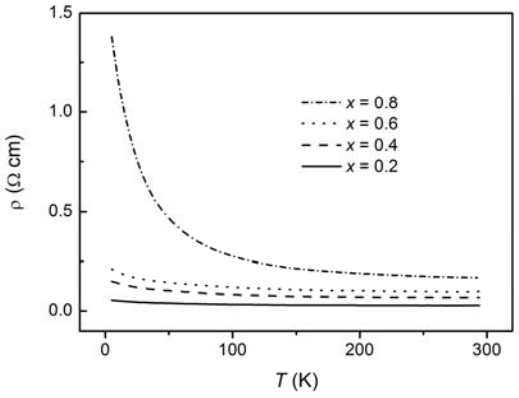

Figure 3. Temperature dependence of the resistivities of the compressed pellet sample of $[Ni_xAu_{1-x}(tmdt)_2]$

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