Tailoring structure and magnetic properties of $\text{Ni}_x\text{Co}_{1-x}(\text{N}(\text{CN})_2)_2$ molecular magnets

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Abstract

A series of transition metal $\text{Ni}_x\text{Co}_{1-x}(\text{N}(\text{CN})_2)_2$ dicyanamide molecular magnet, $0 \leq x \leq 1$, was chemically synthesized. Structure and magnetic properties were investigated by IR spectroscopy, neutron powder diffraction and temperature-dependent magnetization measurement. The neutron powder diffraction measurement established that all samples showed the rutile structure with $Pnnm$ space group. The detailed Rietveld refinement results revealed a systematic decrease of unit-cell volume with increasing Ni content. We also observed a concurrent increase of the Curie temperature with Ni content due to the increase of superexchange interaction.

Keywords: Molecular magnets; Transition metal dicyanamide; Neutron diffraction

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Introduction

Coordination chemistry based molecular magnets are a class of materials whose building blocks are molecular and differ from conventional magnets [1-12]. However, most of molecular based magnets have magnetic ordering at very low temperature due to the large separation among neighboring spin sites [1-7]. Therefore, one of ultimate challenges of molecular based magnets is achieving room temperature ferromagnetic ordering. Previously, room temperature ferromagnetic organometallic magnets, $V(TCNE)_x\gamma(CH_2Cl_2)$, $V[Cr(CN)_6]_{0.86}$ based on Prussian blue, and Ni_2TCNQ , Ni_2TCNE [13,14]. These discoveries open new doors for the potential applications utilizing these molecular-based magnets. However, the low-temperature process, solution-based simple chemistry, well-controlled room temperature molecular-based magnets are extremely rare due to the large separation among neighboring spin sites [1-7].

In the case of transition metal dicyanamide [dca, $N(CN)_2$] molecular magnets, magnetic ordering can vary substantially even in isostructural systems depending on the nature of the transition metal species. Experimental studies of the structural, electronic, and magnetic properties of transition metal dca [$M(dca)_2$, $M = Cu, Fe, Ni, Co$ and Mn] have been performed by various groups [15-23]. The possibility of tuning the magnetic ordering temperature by mixing transition metals in these systems has been established [24]. Here, we study in detail the Ni/Co system and show that its magnetic properties can be systematically tuned by controlling the Ni/Co ratio while maintaining a uniform single-phase crystal structure.

Experiments

Five different samples, $Ni_xCo_{1-x}(N(CN)_2)_2$ ($x = 0, 0.25, 0.5, 0.75, 1.0$), were synthesized using direct precipitation in aqueous solutions [15]. Specifically, for the synthesis $Co(NO_3)_2 \cdot 6H_2O$ (4.57 g) was dissolved in 100 ml H_2O . After the salt was completely dissolved, an aqueous solution of NaC_2N_3 , sodium dicyanamide, (2.8 g + 100 ml of H_2O) was added rapidly. The mixed solution was then heated to evaporate H_2O [25]. Upon evaporation, a pink solid, $[Co(C_2N_3)_2]$,

precipitated from solution. The solid solution (2.46 g) was collected by vacuum filtration and dried at room temperature in a vacuum overnight. $\text{Ni}(\text{C}_2\text{N}_3)_2$ was synthesized in a similar way from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaC_2N_3 . For the mixed compound $[\text{Ni}_x\text{Co}_{1-x}(\text{N}(\text{CN})_2)_2]$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed together in aqueous solution in the appropriate proportions before adding aqueous solution of NaC_2N_3 .

The crystal structures of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ samples were determined using neutron and X-ray powder diffraction at room temperature. Both measurements were carried out at the Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, at room temperature and ambient pressure. For the neutron measurements, the samples were filled in neutron-transparent vanadium cans and the counting time on the HIPPO neutron time-of-flight diffractometer [26, 27] was 60 minutes at a nominal proton current to the spallation target of 100 μA . The structure was refined using the Rietveld [28] method using the General Structure Analysis System (GSAS) software [29] with the EXPGUI interface [30]. The infrared (IR) absorption spectrum was collected at room temperature on a FTIR spectrometer (Thermo Nicolet Nexus 670) by scanning a range from 400 - 4000 cm^{-1} using an attenuated total reflectance state. The temperature-dependent magnetization of the samples was measured using a Quantum Design superconducting quantum interference device (SQUID).

Results and Discussion

Figure 1 shows the IR spectra of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ for various Ni concentrations in the cyano stretch region. The inset shows the entire measured spectra. All spectra show typical characteristic of well-known dicyanamide-metal complexes [15, 31, 32], with strong stretches (ν_{CN}) around 2271 cm^{-1} and 2205 cm^{-1} . With increasing Ni content, the peak position shifts to higher wavenumbers, which implies a larger force constant between the C and N atoms and an increase of the electronic density on the corresponding chemical bond. Since IR spectra are influenced by crystal structure,

the similarity of the IR spectra reflects the structural similarities of the samples regardless of the presence of different transition metals (Ni or Co) in the system [33].

The crystal structures of the $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ were obtained from the neutron powder diffraction and the Rietveld refinement. Figure 2 shows a scheme of the refined crystal structure (Fig. 2(a) for full structure and Fig. 2(b) for enlarged view showing details of Co-N-C bonds) and diffraction pattern with the Rietveld fit corresponding to the structure (Fig. 2(c)) of $\text{Co}(\text{dca})_2$ solid solution. The neutron results reflect nuclear positions more accurately than X-ray data and were used systematically to obtain structural data. X-ray diffraction produced results (not shown here) that were completely consisted with the neutron results. From both analyses, we confirmed that all samples exhibited the same rutile structure with $Pnmm$ space group (space group No. 58) even though there were slight variations of bond lengths, lattice parameters, and unit cell volumes. Table I shows the refined lattice parameters, unit cell volume, and bond lengths between nitrogen (N1 or N2) and transition metal (Ni or Co) of the samples. All lattice parameters, unit cell volumes, and bond lengths between N1 and Ni (or Co) decrease monotonically as Ni concentration increases (see Fig. 3).

Figure 3(a) shows the Ni content dependent lattice parameters. In particular, the relative lattice parameter variation of the b and c -axes were larger (1.2% ~ 1.5%) than the a -axis change (< 0.3%). Since, the lattice parameters decreased linearly, the unit cell volume also decreased linearly as Ni content increased (Fig. 3(b)). These results are consistent with previously published results [24]. Considering the ionic radii of Co and Ni (for high-spin state of $\text{Co}^{2+} \sim 88.5$ pm, for low-spin state of $\text{Co}^{2+} \sim 79$ pm and for low-spin state of $\text{Ni}^{2+} \sim 83$ pm [34]), the contraction of the lattice with increased Ni content indicates that the Co^{2+} is pre-dominantly in the high-spin state. Furthermore, refinement of the atomic positions showed a decreasing distance between both nitrogen atoms and the transition metal atom (Co or Ni) with increasing Ni content in the samples (Fig. 3(c)). The bond lengths between N1 and Ni (or Co), the shorter of the nitrogen and

transition metal bonds, decreased $\sim 2.5\%$ between pure end members which were comparable to the unit cell volume changes ($\sim 3\%$). We observe a small discontinuity in the N2-Ni (or Co), the longer of the nitrogen and transition metal bonds, once the majority of transition metal is Ni. On the other hand, C-N bond length (1.1585(3) Å for C-N1 and 1.3064(3) Å for C-N2) and angles ($159.1(4)^\circ$ for Ni(Co)-N1-C, $174.7(5)^\circ$ for N1-C-N2 and $117.2(8)^\circ$ for C-N2-C) did not show noticeable changes with the increase of Ni contents. Those angles and bond length are consistent with previous published results [23]. This finding indicates that the dca molecules in the structure are rather rigid units. Therefore, the volume changes are mainly associated with the bond length variation between N1 and Ni (or Co).

Finally, Figure 4 shows the composition-dependent Curie temperature of the solid solution. The observed Curie temperature of the pure end members, Co(dca)_2 and Ni(dca)_2 was 9.0 and 21.0 K, respectively. These values agreed well with the previously reported values by Lappas *et al.* [24]. As Ni content increased, the Curie temperature also increased and fell between that of the parent compounds. However, the Ni content-dependent Curie temperature variation shown in Fig. 4 is not linear. Unlike the unit cell volume variation but consistent with the observed discontinuity in the N2-Ni (or Co) bond lengths, we observed for the Ni content-dependent Curie temperature variation two distinct regions. Before $x = 0.5$, i.e. with the majority of the transition metal sites occupied by Co atoms, the Curie temperature increased rapidly. However, the Curie temperature increased slower for $x > 0.5$, i.e. with the majority of transition metal sites occupied by Ni atoms. It is known that the transition metal ions are the source of magnetic moments and the magnetic interaction between the magnetic centers (transition metal ions) are mediated by organic species in means of superexchange interaction [18, 19]. The Rietveld refinements show that the distance between the nitrogen atom (N1 and N2) and the transition metal ions (Ni, Co) decreases with increasing Ni content. Furthermore, the variation of bond length between N2-Ni (or Co) mimics the variation of Curie temperatures. Previously, it was known that the magnetic ground state of transition metal based dca originates from the balance between antiferromagnetic and

ferromagnetic superexchange interaction through the N1-C-N2 unit, since the direct interaction between adjacent transition metals is small due to the large separation [24, 35]. Therefore, the volume contraction and the decrease of bond lengths (both N1-Ni(Co) and N2-Ni(Co)) is accompanied by an increase in electron density of the dicyanamide, which suggests increased superexchange interaction between the adjacent transition metal ions with increasing Ni content. The inset in Fig. 4 shows temperature dependent normalized magnetization of the various samples. The magnetization is normalized with respect to the magnetization measured at 2 K.

Summary

A simple chemical synthesis allowed for the design of a molecular magnet system with tunable ferromagnetic ordering temperature within an isostructural system. In the case of the Co/Ni based dicyanamide system, the samples maintained the distorted rutile structure at room temperature due to the different bond lengths between N(1,2) and Ni (Co). However, the unit-cell volume, lattice parameters, and N1-Ni (or Co) bond length decreased linearly with increasing Ni content. On the other hand, the magnetic ordering temperature increased from 9 K (for Co(dca)₂) to 21 K (for Ni(dca)₂) with increasing Ni content. Furthermore, N2-Ni (or Co) bond length and Curie temperature varied non-linearly with a discontinuity observed at the same composition for both of these independent measurements. The primary origin of the Curie temperature tunability in an isostructural system is related to the variation of superexchange interaction length due to the different size of the transition metal.

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Table I. Rietveld refinement results of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ solid solution obtained from neutron powder diffraction measurement for various Ni concentration. The numbers inside the parenthesis indicate the calculated errors.

Ni_x	a (Å)	b (Å)	c (Å)	Volume (Å ³)	N1-(Ni, Co) (Å)	N2-(Ni, Co) (Å)
0	6.0226(2)	7.0906(2)	7.4048(4)	316.211(2)	2.1157(1)	2.1570(2)
0.25	6.0220(3)	7.0632(3)	7.3812(4)	313.956(3)	2.1054(1)	2.1543(2)
0.5	6.0155(2)	7.0358(2)	7.3480(4)	310.993(2)	2.0921(9)	2.1523(9)
0.75	6.0135(3)	7.0288(3)	7.3287(5)	309.764(3)	2.0835(1)	2.1420(2)
1.0	6.0071(3)	7.0058(3)	7.2997(4)	307.204(3)	2.0689(1)	2.1409(2)

Figures

Fig. 1. (Color online) Infrared (IR) spectra of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ for various Ni contents. The inset shows full IR spectra.

Fig. 2. (Color online) Refined structure of $\text{Co}(\text{dca})_2$ (a) in full view and (b) expanded view. (c) Room temperature neutron powder diffraction pattern and Rietveld refinement result of $\text{Co}(\text{dca})_2$ (for $x = 0$) solid solution.

Fig. 3. (Color online) Ni content-dependent refined (a) lattice parameters, (b) unit cell volume and (c) nitrogen and Ni bond length of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$. The solid lines are linear fitted results and the error bar is smaller than the size of symbol.

Fig. 4. Curie temperature (T_C) of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ compounds as function of the Ni content. The solid lines are linear fitted results. The inset shows the normalized dc magnetization as a function of temperature, M/M_{2K} of $\text{Ni}_x\text{Co}_{1-x}(\text{dca})_2$ ($x = 0, 0.25, 0.50, 0.70$ and 1.0) measured on cooling in an applied field ($H = 100$ Oe).

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 3

Figure 4