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Desorption-induced first-order phase transition in a cyano-bridged compound

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The guest-host interaction is one of the promising tools to control the material state. Here, we found that a cyano-bridged compound $\text{Na}_0.50\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$ shows a first-order structural phase transition below a critical pressure $P_c$ (150 Pa) at 300 K. Judging from suppression of the OH stretching mode in the infrared spectra, we ascribed the phase transition to desorption of the ligand waters. The phase transition accompanies a significant change of the visible absorption spectra, reflecting the strong hybridization between the Co $e_g$ state and the CN$\sigma$ states. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908049]

Recently, nanoporous compounds are attracting the interest of material scientists because the nanospaces of the host compound can be utilized as storage of the guest molecules, such as $\text{O}_2$, $\text{H}_2\text{O}$, NO, and so on.1 In an extreme case, the low-dimensional alignment of the nanospaces induces an interesting physical property of the guest molecules. For example, one-dimensional arrangement of $\text{O}_2$ within the framework of a copper coordination polymer, $[\text{Cu}_2(\text{pzdc})_2(\text{pyz})]_n$, causes a spin gap behavior.2 Another significant feature of the nanoporous material is the guest-host interaction, which may change the lattice structure3 as well as the electronic and magnetic properties of the host system. In this letter, we report the desorption-induced first-order phase transition of the host framework in a cyano-bridged transition metal compound.

The cyano-bridged compound, $\text{Na}_x\text{Co}[\text{Fe(CN)}_6]_{1-x}\text{H}_2\text{O}$, is a nanoporous material. The compound consists of a three-dimensional host framework, $\text{–NC–Fe–CN–Co–NC–}$, and the guest species, that is, alkaline metals and waters. A part of the waters locates at the $\text{Fe(CN)}_6$ vacancies and coordinates the $\text{Co}$ ion (ligand water). The residual waters (zeolite water) and the alkaline metals locate in the nanospaces of the host framework. A significant feature of the cyano-bridged compound is the controllability of the guest concentration by the chemical composition of the films are $\text{Na}_{0.50}\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$. The x-ray powder diffraction patterns are consistent with the face-centered cubic, the lattice constant is 1.030 24(1) nm at $x=0.88$ and 1.027 69(1) nm at $x=0.50$. The film color changes from transparent green to red with the decrease of $x$.

Figures 1 show the absorption spectra of these films in (a) infrared and (b) visible region. In the as-grown film ($x=0.88$), an intense absorption band is observed at 2080 cm$^{-1}$, which is ascribed to the stretching vibration of the CN moiety sandwiched by the low-spin Fe$^{III}$ and the high-spin Co$^{II}$.9 In the fullyoxidized film ($x=0.30$), an absorption band is observed at 2120 cm$^{-1}$, which is due to the CN moiety sandwiched by the low-spin Fe$^{III}$ and the low-spin Co$^{II}$.10 In the intermediate film ($x=0.50$), the absorption consists of two bands [see the least square-fitted broken curve of Fig.

Films of the Co–Fe compound were electrochemically synthesized on indium tin oxide (ITO) transparent electrodes (sheet resistance was 100 Ω) under potentiostatic condition at −0.5 V versus a standard Ag/AgCl electrode in an aqueous solution containing 0.5 mol/l $\text{K}_3[\text{Fe}^{II}(\text{CN})_6]$, 1.25 mmol/l $\text{Co}^{II}(\text{NO}_3)_2$, and 1 mol/l $\text{Na(NO}_3)$. The elemental analysis by the inductively coupled plasma method and a CNH organic elemental analyzer (Perkin–Elmer 2400 CHN Elemental Analyzer) yields $\text{Na}_{0.88}\text{Co}[\text{Fe(CN)}_6]_{0.70}3.8\text{H}_2\text{O} (x=0.88)$. The film thickness was about 500 nm, which was determined by the cross-sectional scanning electron microscope image. We further control $x$ by the oxidation process of the film at 0.5–0.7 V versus a standard Ag/AgCl electrode in 1 mol $\text{Na(NO}_3)$ aqueous solution. Here, we found that $x$ decreases in proportion to the total charge (electrons/Co site) flown in the oxidation process, while the $[\text{Fe(CN)}_6]$ concentration ($y=0.69–0.72$) and the water concentration ($z=0.38$) are nearly unchanged. The chemical composition of the films are $\text{Na}_{0.30}\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$ ($x=0.50$) and $\text{Na}_{0.38}\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$ ($x=0.30$). The x-ray powder diffraction patterns are consistent with the face-centered cubic, the lattice constant is 1.030 24(1) nm at $x=0.88$ and 1.027 69(1) nm at $x=0.50$. The film color changes from transparent green to red with the decrease of $x$.

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Films of the Co–Fe compound were electrochemically synthesized on indium tin oxide (ITO) transparent electrodes (sheet resistance was 100 Ω) under potentiostatic condition at −0.5 V versus a standard Ag/AgCl electrode in an aqueous solution containing 0.5 mol/l $\text{K}_3[\text{Fe}^{II}(\text{CN})_6]$, 1.25 mmol/l $\text{Co}^{II}(\text{NO}_3)_2$, and 1 mol/l $\text{Na(NO}_3)$. The elemental analysis by the inductively coupled plasma method and a CNH organic elemental analyzer (Perkin–Elmer 2400 CHN Elemental Analyzer) yields $\text{Na}_{0.88}\text{Co}[\text{Fe(CN)}_6]_{0.70}3.8\text{H}_2\text{O} (x=0.88)$. The film thickness was about 500 nm, which was determined by the cross-sectional scanning electron microscope image. We further control $x$ by the oxidation process of the film at 0.5–0.7 V versus a standard Ag/AgCl electrode in 1 mol $\text{Na(NO}_3)$ aqueous solution. Here, we found that $x$ decreases in proportion to the total charge (electrons/Co site) flown in the oxidation process, while the $[\text{Fe(CN)}_6]$ concentration ($y=0.69–0.72$) and the water concentration ($z=0.38$) are nearly unchanged. The chemical composition of the films are $\text{Na}_{0.30}\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$ ($x=0.50$) and $\text{Na}_{0.38}\text{Co}[\text{Fe(CN)}_6]_{0.72}3.8\text{H}_2\text{O}$ ($x=0.30$). The x-ray powder diffraction patterns are consistent with the face-centered cubic, the lattice constant is 1.030 24(1) nm at $x=0.88$ and 1.027 69(1) nm at $x=0.50$. The film color changes from transparent green to red with the decrease of $x$.
The modification also changes the visible absorption spectra. At \( x = 0.50 \), however, the 2.0 eV band disappears and a much stronger band appears at 2.4 eV. Ohkoshi et al. reported a similar 2.0 eV band in \( \text{Fe}^{II}\text{Mn}_{0.59}\\text{Co}_{0.41}\text{CN}_{6}\text{H}_{2}\text{O} \), which is ascribed to the chargetransfer excitation from the Fe\(^{II}\) site to the high-spin Co\(^{II}\). The valence modification also changes the visible absorption spectra. At \( x = 0.43 \) and \( x = 0.50 \), the spectra consists of the intense 3.2 eV band and the weak 2.4 eV band. At \( x = 0.50 \), the strong 2.4 eV band at \( x = 0.50 \) is ascribed to the charge-transfer excitation from the Fe\(^{II}\) site to the Co\(^{III}\) site. The 3.2 eV band is insensitive to pressure in the pressure-increasing run. The respective spectrum on the spectral change, we measured the spectra at each pressure beyond 100 Pa, which is discribed by the brown straight lines.

To quantitatively investigate the depressurization effect on the phase transition and the spectral change. First of all, appearance of the Co\(^{II}\) band can be ascribed to the asymmetric ligand field around the Co\(^{II}\) site. In the Fe–Co cyanide, the \( d-d \) transition of the four-coordinate tetrahedral Co\(^{III}\) site. On the other hand, the stronger 2.4 eV band at \( x = 0.50 \) is ascribed to the charge-transfer excitation from the Fe\(^{II}\) site to the Co\(^{III}\) site. The 3.2 eV band is insensitive to pressure.

The depressurization process further induces the 2 eV band, as seen in the differential spectrum (broken curve). These spectral changes are reversible in repeated pressure-cycles (see the bottom spectra of Fig. 2). The desorption process of the water molecules takes a few minutes, while the adsorption process takes a few hours. We investigated the depressurization effect on the electronic state of the Fe and Co ions by means of X-ray absorption near edge structure (XANES) around the K-edge region at 300 K and found that only the Co spectrum shows a detectable change. Therefore, we ascribed the desorption-induced 2 eV band to the intratomic \( d-d \) transition of the Co\(^{II}\) site and call the band as “Co\(^{II}\) band.”

To quantitatively investigate the depressurization effect on the spectral change, we measured the spectra at each pressure in the pressure-increasing run. The respective spectrum was measured after waiting for 5–10 min. We plotted in Fig. 3 the pressuredependence of the spectral weights for (a) the Co\(^{II}\) band \( (I_{Co}) \), (b) the OH stretching band \( (I_{OH}) \), and (c) the two CN stretching bands \( (I_{CN}) \). The magnitude of \( I_{Co} \) remains nearly constant (\( \approx 0.75 \)) below 10 Pa and then steeply decreases to \( \approx 0.3 \). The reduction of \( I_{Co} \) is completed at a critical pressure \( P_c \) (150 Pa), showing a kink structure. Similar kink structures are observed in the \( P-I_{OH} \) curve [Fig. 3(b)] and the two \( P-I_{CN} \) curves [Fig. 3(c)] as indicated by the broken straight lines.

We further investigated the depressurization effect on the structure. In this measurement, the film was carefully removed from the ITO glass with a microspatula and then the ground fine powders were filled into the 0.1 mm\( \phi \) glass capillary. The capillary was depressurized at 2 Pa for 30 min and then kept at the respective pressure for 30–60 min to reach an equilibrium state. Then, the capillary was sealed up in a Debye–Schererr camera at the BL02B2 beamline of SPring-8. The lattice constant \( a \) was refined by the Rietveld method, and was plotted in Fig. 3(d). With an increase of pressure beyond 100 Pa, \( a \) discontinuously increases from 1.006 nm to 1.022 nm. We emphasize that the small-\( a \) phase (volume fraction is 0.37) and the large-\( a \) phase (0.63) coexist at 100 Pa. Thus, the desorption-induced phase transition is of the first-order, accompanying a significant structural change.

We think that the ligand waters play an essential role on the phase transition and the spectral change. First of all, appearance of the Co\(^{II}\) band can be ascribed to the asymmetric ligand field around the Co\(^{II}\) site. In the Fe–Co cyanide, the \( e_g \) orbital strongly hybridized with the \( \sigma \) state of the ligands, that is, CN and \( \text{H}_2\text{O} \). Then, if the ligand waters are removed, the \( d-d \) transition of Co\(^{II}\) becomes dipole-allowed via the strong \( d-\sigma \) hybridization. Secondly, the ligand waters bear a part of the host framework. Then, desorption of the ligand waters causes reduction of the cell parameter. We, however, need a cooperative mechanism to explain the first-order nature of the phase transition. A most plausible mechanism may be the spin state transition of the Co\(^{III}\) site from the high-spin state \( (S = 3/2) \) to the low-spin state \( (S = 1/2) \). We measured the temperature dependence of the magnetic susceptibility of the sample sealed in the glass capillary and estimated the effective moment \( \mu_{\text{eff}} \). The magnitude of \( \mu_{\text{eff}} \) decreases from 3.67 \( \mu_\text{B}/\text{Co} \) at ambient pressure to 2.93 \( \mu_\text{B}/\text{Co} \) at 3 Pa. This observation supports the idea of the spin state transition.

In conclusion, we observed vacuum-induced phase transitions...
transition \( P_c = 150 \text{ Pa} \) at 300 K in \( \text{Na}_{0.50}\text{Co[Fe(CN)]}_6\text{O}_{0.72} \cdot 3.8\text{H}_2\text{O} \). The phase transition is of the first-order and accompanies a significant spectral change in the visible region. Such a property can be utilized as the simple pressure marker. A systematic investigation with changing Na concentration \( x \), which is in progress, is significant to finely control the critical pressures.

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