Report of MERIT Oversea Dispatch

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Host institute: light and material laboratory(Univ. of Rennes, France)

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Research theme: Elucidation of dynamics of phase transition in Cyanido-bridged CoW assembly

Research background

Phase transitions in solids are useful as switching materials, and in particular, molecular magnetic materials with many functionalities have been reported due to their high molecular designability and are expected to become new functional materials. Among these, cyano-bridged bimetal assemblies have potential as functional switching materials, not only for their functionality, but also because they induce phase transitions by spin crossover and charge transfer. In particular, cyanido-bridged Co-W assemblies with Co and W have two interesting physical properties: a temperature-induced charge-transfer phase transition with hysteresis and a photo-induced magnetization at low temperature, which is derived from a charge-transfer-induced spin transition between Co^{II}-W^{V} (high temperature) phase and Co^{III}-W^{IV} (low temperature) phase. For the application of these compounds with such interesting properties, it is important that the hysteresis of the thermal phase transition exists at room temperature. Therefore, I have synthesised a two-dimensional cyanido-bridged CoW asembly, $Cs^{+}_{0.1}(H_5O_2^{+})_{0.9}[Co(4\text{-bromopyridine})_{2.3}\{W(CN)_8\}]$ (**CsCoW**), which is bistable at room temperature. Subsequent studies have shown that this complex can be used for photoinduced magnetization at low temperatures (3 K), as well as for the magnetization of the CoW assembly at high temperature. Subsequent studies have shown that this compound is capable of photo-reversible phase transitions at low temperatures (3 K) by using light of two different wavelengths in the photo-induced magnetization

Research purpose

The mechanism of the phase transition of cyanido-bridged CoW assembly has been identified as charge-transfer-induced spin transition (CTIST), but its dynamics has not been clarified. In this study, we aim to elucidate the dynamics of the CTIST phase transition by using cyanido-bridged CoW assembly that exhibits a temperature phase transition and a reversible optical phase transition synthesized by ourselves, and to elucidate the factors responsible for the temperature hysteresis and the factors important for increasing the phase transition temperature and Curie temperature in future research.

Research method

The host institute which is the laboratory in Univ. of Rennes 1 has elucidated the dynamics of many optical phase transitions using pump-probe spectroscopy. In this study, we aim to elucidate the mechanism of the charge-transfer phase transition, the factors responsible for the temperature hysteresis and the dynamics of this complex by using the femtosecond-scale pump-probe spectroscopy technique of the collaborating institute. The light used in the optical phase transition was used as the pump light and white light was selected as the probe light. Measurements were carried out on a short time scale and a long time scale. Intermediate time ranges were also performed if necessary.

Research results and discussion

The results of the short-time-domain measurements of the compound showed attenuation of a specific part of the wavelength and an increase in another wavelength region. In both wavelength regions, the absorbance changed in a wavy pattern with oscillations. Furthermore, the increased wavelengths suggest a new charge state in the shorter wavelength region, temporarily different from that before and after the phase transition. In addition, measurements in the long time region showed no significant change in the attenuated wavelengths, suggesting that the phase transition reaction was completed in the short time region, but the wavelength region that showed an increase in wavelength also showed an increase in the long time region. These results indicate that, in addition to a temporary new charge state, the phase transition occurs in multiple stages. Further discussions with Prof. Eric Collet and additional experiments will be carried out to collectively publish the results of this study.

Life in the area

The author stayed in Rennes, a city about an hour and a half west of Paris by tgv (like Shinkansen), which is rich in nature and culture. Nearby are tourist attractions such as Mont Saint-Michel and Saint-Malo, which were very nice. In addition, June is the longest day of the year in Rennes, with sunset exceeding 10 pm. Therefore, from around five or six o'clock, people who have finished work relax in parks or on terraces in the city, and the humidity and temperature are not too high, and there are many sunny days, so I was able to lead a comfortable and relaxed life. As for research life, I went to the laboratory in the morning to conduct experiments and had lunch with everyone in the laboratory. Once or twice a week, we also went to the laboratory's favorite bar to drink a beer. In the afternoons, I continued experiments and analyses, and usually returned home from the laboratory at around 5 pm. The main difference between France and Japan in terms of daily life is that there are few shops open on Sundays. Therefore, if you don't buy food for Sunday on Saturday, you will be in trouble. However, many shops were open on Sundays in tourist areas, so I had no particular problems when travelling. A major difference in research is the ease of discussion. I felt that discussions often proceeded on an equal footing because English and French do not have the deep-seated honorifics of Japanese.

Our favorite bar

Acknowledgments.

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