

Structural analysis of CsZn[Fe(CN)6]

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The coefficient of thermal expansion is usually positive, reflecting the inherent anharmonicity of bond vibration. In several compounds with a network structure, e.g., ZrW₂O₈ and Zn_xCd_{1-x}(CN)₂, however, the coefficient is negative (negative thermal expansion). Recently, Matsuda et al. reported an unusual thermal response in a series of transition metal cyanides, A_xM[Fe(CN)₆]_yzH₂O (A and M are alkaline metal and metal, respectively); the coefficient of thermal expansion changes the sign from positive to negative with increasing *a*.

The transition metal cyanide, A_xM[Fe(CN)₆]_yzH₂O, belongs to a face-centered cubic lattice, except for the compounds that contain Jahn-Teller-active Mn³⁺ and Cu²⁺ ions. The compounds form a three-dimensional rock-salt-type network with metal ions (M²⁺ or M³⁺) and Fe(CN)₆ octahedra; alkaline metal ions and water molecules are accommodated in the nanopores of the network. Significantly, the three-dimensional network contains the Fe(CN)₆ octahedra as rigid bodies, and hence, has an intrinsic rotational degree of freedom of the octahedra.

In order to investigate the instability of the Prussian blue lattice, we determined the temperature variation of anisotropic atomic displacement parameter of Cs_{0.97}Zn[Fe(CN)₆]_{0.99}0.5H₂O by means of the neutron powder diffraction. The measurements were performed using the Kinken powder diffractometer for high efficiency and high resolution measurements (HERMES). Atomic positions, occupancy *g* and anisotropic atomic displacement parameter, U₁₁ and U₂₂, were obtained by the Rietveld method (RIETAN-FP program) with space group of F43m. In

Fig. 1, we plotted the transversal components of Cs_{0.97}Zn[Fe(CN)₆]_{0.99}0.5H₂O against temperature.

One may notice that the transversal atomic displacement of N is larger than that of C, which suggests that the transversal displacement of the light elements can be ascribed to the thermally-excited rotational motion (or rotational disorder) of the [Fe(CN)₆] unit. With such a rotational motion of the [Fe(CN)₆] unit, the M-N bond distance effectively elongates. If we fixed *a*, the effective elongation from 10 K to 300 K is estimated to be 0.0076 Å from the difference in U₂₂. Then, the negative thermal expansion is driven to compensate the bond length elongation due to the rotational motion. The rotational motion should be enhanced in the large-*a* region with sufficient open space for atomic displacement, but be suppressed in the small-*a* region by steric confinement. Thus, the Prussian blue lattice has the intrinsic rotational instability of the [Fe(CN)₆] unit

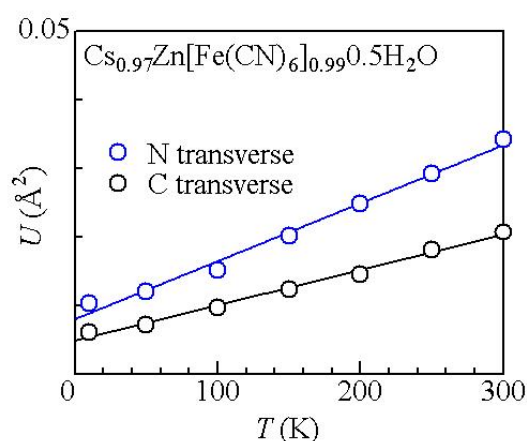


Fig. 1. transversal components of Cs_{0.97}Zn[Fe(CN)₆]_{0.99}0.5H₂O against temperature.