Low Dimensional Organic-Inorganic Hybrid Nanomaterial synthesized in solvothermal condition

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We present new organic-inorganic hybrid nanomaterial denoted as *Zebra sheet* synthesized by solvothermal technique. The Zebra sheet is synthesized from ethylene glycol, iron chloride and potassium acetate under moderate solvothermal conditions with chemical composition of $Fe_7(C_2H_4O_2)_9O_x$ and expected to be antiferromagnetic material with low dimensional character, but exhibits 3D ordering at T_N~19K proved by bulk measurements. Although it is known that ethylene glycol and iron oxide are alternatively stacking in the nanosheet, the details of crystal structure of this compound have not been clarified so far as well as the magnetic ordering, due to very complicated structure in a large unit cell. In this work, we would like to show not only suggested crystal structure and but also magnetic and thermal properties in the Zebra sheet.

The organic-inorganic hybrid nanomaterials have attracted great interest because they exhibit novel properties, which are combinations of the properties of organic molecules and the inorganic nanostructures. It is significant that the morphology, such as, crystal size and aspect ratio, of the hybrid materials are often controlled by physico-chemical properties of the organic molecules. The zebra sheet seems to be one of quite unique hybrid nanomaterials since low dimensional electronic system is plausibly realized, that is, the 1D iron oxide and the organic molecular chain units are stacked alternatively in the nanosheet with the period of ~ 1 nm, as indicated in the STM image [1].

Low-dimensional materials realized often in organic metallic complexes and molecular crystals have been intensively investigated. Due to large spin and charge fluctuations with low dimensional characteristics, the electron system exhibits novel physical phenomena, such as, superconductivity, metal-insulator transition and multistage magnetic ordering. Actually, although the crystallographic structure is not determined precisely yet, the zebra sheet shows a typical 1D characteristic behaviour in magnetism: the temperature dependence of magnetic susceptibility, $\chi(T)$, shows round maximum at T = 120 K and can be fitted by the Fisher model [2] with an exchange constant of J = 17 K as shown in Figure 1.

In this compound, the chemical composition was determined to be $Fe_7(C_2H_4O_2)_9O_x$ with x ~ 23 by several chemical analyses. Currently, the crystallographic structural information was quite limited, since the x-ray and neutron diffraction patterns show single intense peak at $d \approx 8$ Å corresponding roughly the stacking period of the iron oxide and organic molecule chains with several weak peaks indicated. In Mössbauer spectroscopy, it was shown obviously that the Fe-ion indicate trivalent state with S = 5/2 surrounded tetrahedrally by oxygen ions above the magnetic transition. This observation is consistent also with the fact that magnetic entropy estimated from specific heat measurement for the zebra sheet accords with that of the spin state S = 5/2. The antiferromagnetic transition was indicated at 19 K, while small spontaneous magnetization emerges below the magnetic transition. Expectedly, magnetic field dependences in magnetic and thermal quantities are indicated at low temperatures due to the fluctuations.

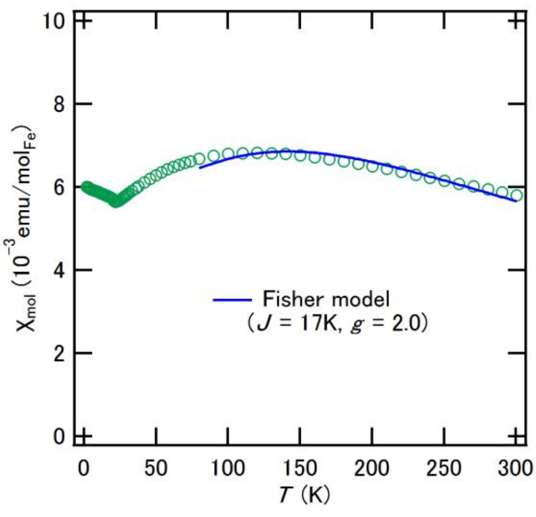

Figure 1. Magnetic susceptibility for the Zebra-sheet as a function of temperature. Solid line represents a calculated curve (see text).

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[1] O. Gerber *et al*. Nanoscale, **9**, 305 (2017).
[2] M. E. Fisher, Am. J. Phys. **32**, 343 (1964).