Talk 8, 12:00–

Discovery of the First Organic Ferromagnet: Professor Takahashi's Contribution to a Breakthrough in Material Research

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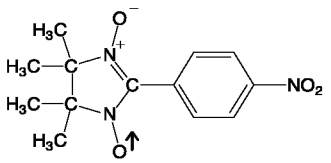
It was 16 years ago that we observed the first sign of ferromagnetic ordering in an organic crystal, the γ-phase sample of p-NPNN. In Professor Ishikawa's Lab. (in the basement of the old ISSP building at Roppongi), a drastic increase of ac susceptibility and a sharp peak of specific heat (C) were detected at 0.6 K. Over several decades, we had been looking for such a purely organic ferromagnet. These measurements were motivated by the comparison of the paramagnetic susceptibilities $\chi(T)$ of γ-p-NPNN, which were measured by Prof. Turek and Prof. Kinoshita, with Prof. Takahashi's exact calculation of $[\chi(T)]$ for a one-dimensional (1D) Heisenberg ferromagnet by the Bethe Ansatz method. His calculation well explained the observed behavior quite. However, the experimental $\chi(T)$ showed a small excess below 6 K, indicating that ferromagnetic interchain couplings were operating. This suggested the possibility of a bulk ferromagnetic transition below 1 K [1].

Discussions with Prof. Takahashi urged Prof. Kinoshita's group to get into the experiments below 1 K with Prof. Ishikawa, Dr. Nakazawa and Dr. Shirakawa. They quickly led the detection of ferromagnetic signals. I prepared and X-ray-characterized the other three polymorphs of p-NPNN, the α-, β- and δ-phases.



para-NPNN
(β-Phase: T_C = 0.60 K, γ-Phase: T_N = 0.65 K)

Among them, the β-phase has been soon found to undergo bulk ferromagnetic transition at $T_{\rm C} = 0.6$ K [2]. What puzzled us at that time was the less reproducible behavior of the γ-phase. Now, we know that the γ-phase is metastable below room temperature and the ferromagnetic signal observed for the γ samples are from the more stable β-phase formed in the crystal during the low-temperature treatment [3]. The C peak of the γ-phase is due to the antiferromagnetic ordering at $T_{\rm N} = 0.65$ K [3].

To understand what was going on, we had to prepare many samples and carry out many X-ray, thermal and magnetic analyses. Finally we concluded that the β-phase is an organic ferromagnet but the γ-phase is an antiferromagnet [3]. The instability of the γ-phase and the closely located $T_{\rm C}$ and $T_{\rm N}$ caused the puzzle.

Once it turned out to be clear, Prof. Takahashi has analyzed the low-temperature magnetic and thermal behavior of the γ-phase, taking account of the interchain couplings between the 1D ferromagnets in terms of his mean-field theory. He found that there are

stronger ferromagnetic coupling and weaker antiferromagnetic coupling between the chains; the latter brings about the antiferromagnetically ordered ground state [3]. The theoretical physicist (Prof. Takahashi), the experimental physics group (Prof. Ishikawa's) and the physical chemistry group (Prof. Kinoshita's), collaborate thus efficiently in ISSP at Roppongi for the discovery and establishment of the first organic ferromagnet β-*p*-NPNN in 1991. Prof. Takahashi always provides precise and useful discussions on the low-dimensional quantum spin systems, which helps us to extract essential points from the complicated structures of the organic magnetic materials. I think it should have been impossible to interpret the low-temperature physical behavior of the organic magnets, without the theoretical understanding of low-dimensional ferromagnets. The door being opened, many organic materials have been found to exhibit ferromagnetism at low temperature so far [4].

It has been turned out that organic magnetic molecules can provide almost ideal quantum low-dimensional spin systems. Therefore, not only ferromagnetic materials but also antiferromagnetically interacting organic spin systems attracts attention. For instance, an organic radical ion salt DEOCC-TCNQF$_4$ is the most ideal example of the 1D S = 1/2 Heisenberg antiferromagnet [5], which provides an experimental support for the theory by Eggert, Affleck and Takahashi. Another important category is the organic Mott insulators. Some of them have layered triangular structures with frustrated quantum spins, and recently provided a gapless spin-liquid [6] and a pressure-induced superconductor adjacent to a two-dimensional spin-gapped state [7]. Let us return to the organic ferromagnet. Why we focused on *p*-NPNN? The π-electron system of this molecule belongs to the odd alternant type, i.e., a bipartite finite lattice with different site numbers. This molecular connectivity is identical to a finite Lieb ferrimagnetic spin system (S = 1/2). Spin polarization plays a significant role in such a molecule, as pointed out by Awaga and Kinoshita [8]. This enables the intermolecular kinetic coupling between the unpaired electron and the valence electron on neighboring molecule, leading to extension of the Lieb ferrimagnetic system. If a 3D network is achieved in this way, we would obtain a bulk ferromagnet. This roadmap, which is based evidently on the physics of quantum spin systems, has given the first organic ferromagnet.

[1] M. Takahashi *et al.*: *Phys. Rev. Lett.* **67** (1991) 746. [2] M. Tamura *et al.*: *Chem. Phys. Lett.* **186** (1991) 401; M. Kinoshita: *Jpn. J. Appl. Phys.* **33** (1994) 5718. [3] Y. Nakazawa *et al.*: *Phys. Rev. B* **46** (1992) 8906; M. Tamura *et al.*: *J. Phys. Soc. Jpn.* **72** (2003) 1735; N. Shirakawa and M. Tamura: *Polyhedron* **24** (2005) 2405. [4] S. J. Blundell and F. L. Pratt: *J. Phys.*: *Condens. Matter* **16** (2004) R771. [5] S. Takagi *et al.*: *Mol. Cryst. Liq. Cryst.* **334** (1999) 247. [6] Y. Shimizu *et al.*: *Phys. Rev. Lett.* **91** (2003) 107001. [7] M. Tamura *et al.*: *J. Phys. Soc. Jpn.* **75** (2006) 093701; Y. Ishii *et al.*: *J. Phys. Soc. Jpn.* **76** (2007) 033704. [8] K. Awaga *et al.*: *Chem. Phys. Lett.* **141** (1987) 540.