INTERMOLECULAR FERROMAGNETIC COUPLING IN ORGANIC RADICAL CRYSTALS

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ABSTRACT. This article describes a review of our recent experimental works on the magnetic properties of organic radical crystals with emphasis on the ferromagnetic intermolecular interactions. The samples dealt with are galvinoxyl, nitronyl nitroxides and lithium phthalocyanine(O_2 occluded). In particular, we have found a new phase(γ-phase) of p-nitrophenyl nitronyl nitroxide, which shows a larger ferromagnetic intermolecular interaction than the other phases. Furthermore, we have found a large g-factor shift in EPR absorption of these nitronyl nitroxides and lithium phthalocyanine at low temperature, which is discussed in terms of increased spin-correlation effect at low temperature.

1. INTRODUCTION

Electronic properties of organic solids have been extensively studied for several decades and it has been shown that organic solids are able to possess various interesting properties. The development of organic conductors and superconductors is a typical example. In contrast to such developments, the absence of a well-defined organic ferromagnet containing no transition metals is one of the most conspicuous problems at present, even though there have been a lot of extensive studies of magnetic properties of organic solids.

Most organic compounds take closed-shell structures. This leads immediately to the diamagnetic behavior. Even if one or more unpaired electrons are stably maintained in an organic molecule, they are coupled antiferromagnetically with those on the neighboring radicals in a solid state, though the strength of the coupling varies from one another. Such an antiferromagnetic (AFM) exchange is expected to originate in the overlap of the molecular orbitals occupied by the unpaired electrons, just as two hydrogen atoms form a chemical bond between them with antiparallel electron spin alignment. In order to establish organic ferromagnetism, this difficulty should be removed.

On the other hand, however, there have been known several organic
stable radicals, which show the ferromagnetic (FM) exchange in the sense that the temperature dependence of magnetic susceptibility gives rise to a positive Weiss constant(θ) in the Curie-Weiss equation;

\[ \chi_p = \frac{C}{(T - \theta)}. \]  

(1)

The compounds studied here, galvinoxyl, nitronyl nitroxides and lithium phthalocyanine, are examples of typical stable organic radicals, which consist of the elements in the first and second rows of the periodic table and exhibit the FM coupling. We thought that these radicals are of key importance for understanding the intermolecular FM interaction in organic crystals. From detailed studies of these radicals, we would learn or extract the conditions under which the FM intermolecular interaction takes place in organic crystals.

2. GALVINOXYL

Galvinoxyl (4-[[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadiene-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)phenoxy, see Fig. 1) is known to exhibit quite distinguished magnetic behavior from the work by Mukai[1]. The temperature dependence of the paramagnetic susceptibility follows the Curie-Weiss law above 85 K with a positive Weiss constant[1-3], thereby indicating the presence of FM interaction between the neighboring radicals. The crystal of this radical, however, undergoes a first-order phase transition at 85 K[4-5] and most of the paramagnetism disappears below 85 K[2]. The phase transition has prevented us from a detailed study of the FM interaction at low temperature comparable to the Weiss constant. Thus the details of the FM interaction of galvinoxyl have remained unclear.

In order to study the ferromagnetic coupling of galvinoxyl at low temperature, we have to suppress the phase transition. For this aim, we have initiated the study by examining the effect of an impurity on the phase transition. The closed-shell compound, hydrogalvinoxyl (see Fig. 1), was chosen as an impurity. Hydrogalvinoxyl has the molecular and crystal structures similar to those of galvinoxyl, and its crystal is known not to exhibit a phase transition. The mixed crystals were crystallized from a solution containing galvinoxyl and hydrogalvinoxyl in a proper mixing ratio in a 4:1 mixture of ethanol and diethyl ether. From the susceptibilities of the mixed crystals, we confirmed that the actual ratios in the mixed crystals are well corresponding with the mixing ratios.

2.1. Magnetic Susceptibility

The temperature dependence of paramagnetic susceptibilities \( \chi_p \) of the 4:1, 6:1, 9:1 and 19:1 mixed crystals was examined from 2 to 300 K. The result for the 6:1 mixed crystal is shown in Fig. 1, where the susceptibility of the neat galvinoxyl crystals is also shown in the