μSR of the Organic Radical Ferromagnet, 4-(*p*-Chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl

Ron Imachi, Takayuki Ishida, Takashi Nogami,* Seiko Ohira,† Kusuo Nishiyama,† and Kanetada Nagamine†
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182
†*Meson Science Laboratory, Faculty of Science, The University of Tokyo, Tsukuba, Ibaraki 305*

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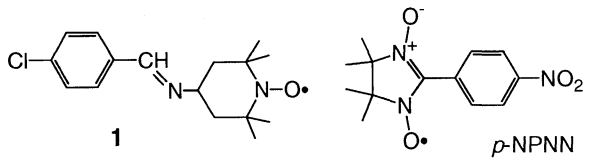
The presence of spontaneous magnetization in the crystal of the title radical below the Curie temperature (T_C) was confirmed by means of zero-field muon spin rotation and relaxation measurements. The T_C was determined to be 0.28 K. A critical magnetization exponent suggested the 3-dimensional ordering of the radical spins.

The research on organic ferromagnets with well-defined crystal structures has greatly progressed in recent years.[1-5] We have recently found organic ferro- and metamagnets having a TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) group, and discussed the correlation between the crystal structures and magnetism.[3-6] The organic radical crystal of *p*-chlorobenzylideneamino-TEMPO (**1**) was reported to exhibit a ferromagnetic transition at *ca.* 0.4 K in ac susceptibility (χ_{ac}) measurements,[7] and to possess a quasi-two-dimensional magnetic network supported by the crystallographic analysis,[7] solid-state ^{1}H NMR spectroscopy,[8] and molecular-orbital calculation[4,9] of **1** and its analogues. In this letter, we report a decisive evidence for spontaneous magnetization in the crystal of **1** below the Curie temperature (T_C). The magnetic dimensionality will be discussed.



The muon (μ^+) spin rotation and relaxation (μSR) technique using a spin-polarized μ^+ as a probe for an internal magnetic field is one of the most versatile tools for investigation of magnetic ordering. This technique was successfully used for the characterization of the ferromagnetic phase of β-*p*-NPNN.[10] However, there is no report on μSR studies of organic ferromagnets other than those of nitronyl nitroxide derivatives.[11]

The preparation of **1** was described elsewhere.[7] The μSR measurements of the crystal of **1** were carried out at a KEK-BOOM facility. The needle-like crystals of **1** were aligned and attached to a silver foil (30x30 mm^2), which was mounted on a top-loading ^{3}He-^{4}He dilution refrigerator (Oxford Instruments). The total amount of the sample was *ca.* 1 g. The environmental magnetic field was diminished to be < 0.01 Oe by a field-cancelling coil. Polarized μ^+ pulses were injected perpendicular to the *a* axis of the crystals. Each μ^+ decays with a mean lifetime of 2.2 μs, emitting a positron preferentially along the muon spin direction. The asymmetry is defined by $(N_F(t) - kN_B(t))/(N_F(t) + kN_B(t))$, where $N_F(t)$ and $N_B(t)$ are the time histograms of positron counts in the forward and backward detectors, respectively, and k is a factor which reflects the efficiency of the forward and backward detectors.

Figure 1 shows several typical asymmetries of zero-field μSR signals for **1**. Above T_C, the slowly relaxing signal without oscillation was obtained, which corresponds to a paramagnetic phase. Near T_C (275 and 260 mK), the signal consists of the superimposition of slowly and fast relaxing signals. Below T_C, the appearance of oscillation clearly indicates the presence of an appreciable internal magnetic field due to a spontaneous magnetization. With decreasing temperature the oscillation frequency increased, indicating that the spontaneous magnetization increased. However, the oscillation became ambiguous at lower temperatures (30 mK).

In the presence of an internal magnetic field, B_{int}, the muon spin undergoes Larmor precession with a frequency $\nu_\mu = (\gamma_\mu/2\pi)B_{int}$, where $\gamma_\mu/2\pi$ is the muon gyromagnetic ratio. The oscillation frequency can be reduced to the internal magnetic field by the relation that 1 MHz corresponds to an internal magnetic field of 75 G. The temperature dependence of the internal magnetic field is shown in Figure 2, the feature of which is similar to those of ferromagnets and cant-magnets containing a nitronyl nitroxide group,[10,11] although B_{int} in the crystal of **1** is somewhat larger than those in the latter materials.

In order to obtain T_C and a critical magnetization exponent

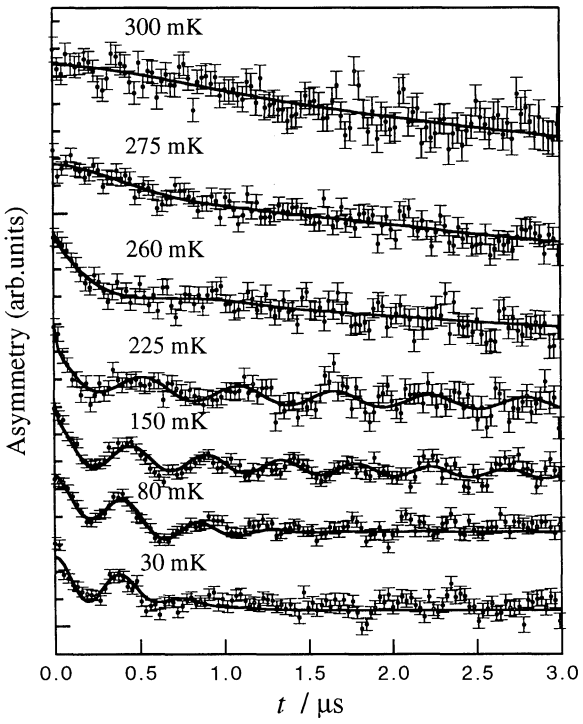


Figure 1. Temperature dependence of μSR asymmetry observed in aligned single crystals of **1** in zero field.

(β), the data were fit to the solid curve of $M(T) \propto [1 - (T/T_C)^{\alpha}]^{\beta}$ with $T_C = 277 \pm 3$ mK, $\alpha = 3.2$ ($\pm$ 1.3), and $\beta = 0.46$ ($\pm$ 0.15). Near T_C, a better fit to $M(T) \propto (T_C - T)^{\beta}$ afforded $T_C = 277 \pm 3$ mK and $\beta = 0.38 \pm 0.08$. Whereas the theoretical 2-dimensional Ising model gave $\beta = 0.125$, the 3-dimensional Ising and Heisenberg models gave $\beta = 0.325$ and 0.364, respectively.[12] Therefore, the experimental results are consistent with bulk ferromagnetism due to 3-dimensional ordering within the experimental errors.

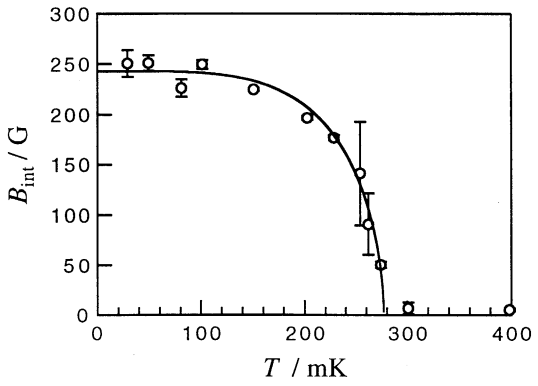


Figure 2. Temperature dependence of the internal magnetic field in the crystals of **1**. For the solid line, see the text.

A transverse field of 10 Oe was applied along the *a* axis of the crystal of **1**, *i.e.* perpendicular to the direction of the initial muon polarization, in lowering the temperature from 400 to 200 mK, and it was then removed. The presence of the remnant magnetization was confirmed by μSR measurements; B_{int} was *ca.* 200 G at 200 mK. The remnant magnetization decreased on heating the sample, and completely disappeared at 280 mK. A similar analysis of the oscillation frequency gave almost the same results as above. The amplitude of the remnant magnetization was found to be as large as that of spontaneous magnetization in the zero-field measurements. As the hysteresis curve of **1**[7] showed, the specimen may possess a very soft character which gives rise to a reversible magnetization process within 10 Oe.

The X-ray crystallographic analysis revealed that the radical crystal of **1** possessed a two-dimensional ferromagnetic network with intra-sheet O···O distances of 5.91 and 5.95 Å according to the proposed β-hydrogen mechanism.[4-6] The present results indicate that the inter-sheet interactions should also be ferromagnetic. Because of the long inter-sheet distance (the shortest O···O distance was 10.86 Å),[7] mechanism for inter-sheet interactions is not clear at present. Drillon *et al.* suggested that layered ferromagnets with large inter-sheet spacings might have dipolar interactions among the sheets.[13]

The T_C was determined to be 0.28 K from Figure 2, which is lower than that determined by the upsurge in the χ_{ac} measurements (0.4 K).[7,14] One of possible explanations of this difference in T_C is as follows. The divergence of the χ_{ac} may be attributed to the two-dimensional magnetic ordering within a sheet of the N-O arrangement.[7] On the other hand, N-O spins are three-dimensionally ordered below T_C which is defined by the appearance of B_{int} in the zero-field μSR measurements.

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14 The peak of the χ_{ac} was 0.32 K,[7] which was found to be close to the T_C defined by the μSR measurements.