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Pressure effects of a genuine organic crystalline ferromagnet dupeyredioxyl

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Abstract

We have revealed that the isothermal magnetization M of the genuine organic crystalline dupeyredioxyl (N,N'-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane; $T_c(0) = 1.48$ K) observed below 10 K converges on the $S = 1$ Brillouin function $B_1((H + \lambda M)/k_B T)$ with $\lambda = 2.4 \pm 0.2$ or $2zJ/k_B = 3.6 \pm 0.3$ K, where J and z are, respectively, the averaged exchange interactions and coordination numbers for the $S = 1$ spin system. This fact suggests that $S = 1$ is constructed within a molecule via a strong ferromagnetic coupling between two $S = 1/2$ spins on each of the two NO moieties. The modified notation of the Rushbrooke and Wood theory, $T_c = 2AzJS(S+1)/k_B$ ($A = 0.23 \pm 0.02$ for the three-dimensional Heisenberg systems), is found to quantitatively hold not only for this $S = 1$ spin system but also for other $S = 1/2$ ferromagnets β-phase p-NPNN ($2zJ/k_B = 3.6$ K) and 2,5-DFPNN ($2zJ/k_B = 2.8$ K). Pressure effects of this compound have been studied under the hydrostatic pressure (P) up to 15 kbar. $T_c(P)$ is revealed to show a negative pressure effect with the initial gradient $a = \mathrm{d}(T_c(P))/\mathrm{d}P = -0.047$ kbar^{-1}, nearly the same value for other organic ferromagnets as β-phase p-NPNN (-0.048 kbar^{-1}) and p-Cl-TEMPO radical (-0.03 kbar^{-1}), in contrast to the positive pressure effect for genuine antiferromagnets such as TANOL ($a = +0.15$ kbar^{-1}). Microscopically, different from the above two ferromagnets, the pressure-induced destruction of the orthogonality of molecular orbitals associated with the two NO moieties plays an effective role in reducing the intramolecular ferromagnetic interaction J_0. The possible weaker intermolecular interactions other than J_0 and J are also expected to be more susceptible to the stress of pressure to result in the reduction of their values perhaps even changing their sign, just as in the case of β-phase NPNN or p-Cl-TEMPO.

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Keywords: Organic ferromagnet; Pressure effect; Curie temperature; Biradical; Exchange interactions

1. Introduction

Strong antiferromagnetic interactions are generally possible in genuine organic compounds with negative value of 10^2 K, for instance, while the synthesis of the ferromagnets with high Curie temperature, T_c, is not easy. The realization of genuine organic bulk ferromagnets was reported in the early 1990s [1,2]. The crystalline dupeyredioxyl (N,N'-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane; $T_c(0) = 1.48$ K) has the highest Curie temperature among genuine organic ferromagnets with the saturation magnetic moments of the order 1 μ_B per molecule ever reported. Except for the fullerene compound TDAE-C60 with its $T_c = 16$ K and the saturation magnetic moment of 0.1 μ_B [3], the magnetism of these organic systems is derived from the unpaired electrons on the singly occupied molecular orbitals. Various strategies for introducing ferromagnetic interactions have been investigated, experimentally

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and theoretically, by manipulating the molecular stacking or molecular orbitals in the crystallized state.

In this work, we study the magnetic interactions of crystalline biradical dupeyredioxy molecule as a function of external pressure up to 15 kbar, as well as at ambient pressure, to examine the mechanism of its ferromagnetic interactions. The experimental results will be discussed in comparison with the pressure effects for other monoradical ferromagnets, such as β-phase *p*-NPNN [4–7] and *p*-Cl-TEMPO [8], whose magnetic interactions have been studied by controlling the overlap of the molecular orbitals continuously as a function of pressure.

Dupeyredioxy is a biradical with two NO moieties in a molecule and an unpaired electron is expected nearly localized on each NO radical [2,9]. The magnetic susceptibility of the crystalline compound is reported to have positive Curie–Weiss temperature of 10 K and shows an abrupt increase near around $T_c = 1.48$ K, followed by a characteristic plateau associated with the demagnetization effect of the ferromagnetic ordered state at the lower temperatures. At $T = 0.1$ K, 100% saturation of the magnetic moment of the expected value for two-spin $S = 1/2$ per molecule is confirmed up to the field of 14 T [2].

2. Experimental

The dupeyredioxyl compound was prepared in accordance with the previous report [9]. The crystal structure is monoclinic with space group $C2/c$ ($a = 8.371$ Å, $b = 14.482$ Å, $c = 10.329$ Å, and $\beta = 105.35°$) [2]. In the present experiments, the magnetic measurements above $T = 2$ K were mostly performed with the commercial SQUID magnetometer and in the lower temperatures we used an a.c. bridge ($H_{\mathrm{a.c.}} = 0.02$ Oe peak-to-peak, $f = 15.9$ Hz). The pressure was attained with two pressure cells of different type depending on the pressure range. Mostly, the conventional miniature Cu–Be clamp cell was used and designed to produce hydrostatic pressure up to 10 kbar and a diamond-anvil-cell (DAC) was employed for the high-pressure region in combination with the coil system of the a.c. bridge for the magnetic measurement [10]. The value of the pressure was determined by the pressure dependence of the superconducting metal of Pb [11] set in the pressure cells or by the measurement of the shift of R1-line of ruby fluorescence [12] at room temperature when we used DAC. The heat capacity was measured by the use of the Cu–Be pressure clump cell adiabatically set in the cryostat [13]. The ratio of the heat capacity of the sample to that of the pressure cell was so small that we only used this method for the determination of the transition temperature under pressure.

3. Results and discussion

3.1. Exchange interactions at ambient pressure

From the molecular symmetry of dupeyredioxyl, two $S = 1/2$ spins on each of the two NO moieties within a molecule are expected to interact ferromagnetically by the orthogonality of their molecular orbitals [2,9]. In reality, a strong exchange intramolecular interaction J_0 is estimated from ESR measurement ($2J/k_B = 170$ K) [14]. In the crystallized state, each NO moiety has three NO neighbors, one on the opposite site of the same stereoscopic molecule and two on the other molecules. So, we may approximate the magnetic $S = 1/2$ spin system of crystallized state as in Fig. 1(a), where the intramolecular interaction is indicated by J_0. At higher temperatures ($T > 150$ K), the value of $\chi T = 0.774$ emu K mol^{-1} (χ, magnetic susceptibility) is reported to be greater than 0.750 emu K mol^{-1} for two non-interacting $S = 1/2$ spins, and in between $\chi T = 1.0$ emu K mol^{-1} for the $S = 1$ system [9]. At lower temperatures, χT gradually increases and rapidly approaches to its maximum of 3.19 emu K mol^{-1} at $T_c = 1.48$ K. At temperatures below 10 K, for example, it is reasonable for us to approximate that the strong J_0 couple make two $S = 1/2$ spins to construct effectively the $S = 1$ spin state within each molecule and then the $S = 1/2$ system (Fig. 1(a)) will be equivalent to the $S = 1$ spin system (Fig. 1(b)), where the dominant interaction is indicated with J_1. In this lattice with coordination number $z_1 = 4$, the magnetic ordering theoretically rules out for the two-dimensional Heisenberg spin system [15], which is realistic especially for the genuine organic system with minute anisotropy. Regarding the experimental fact that the ordering is realized at $T_c = 1.48$ K in this compound, we must take the interlayer interactions J_i ($i \geqq 2$ and z_i the corresponding coordination number) into consideration, though they are omitted in Fig. 1.

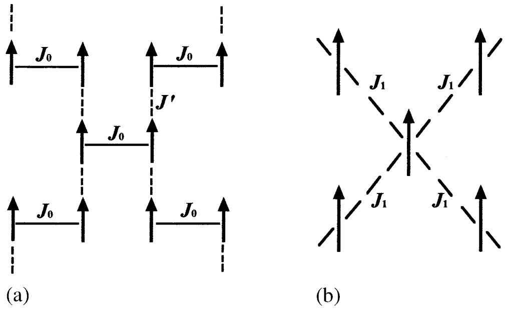

Fig. 1. A schematic model of the magnetic interactions of the crystalline dupeyredioxyl: (a) the $S = 1/2$ spin system. J_0 is the intramolecular exchange interaction between two NO moieties. The nearest neighbor intermolecular interaction J' is approximated to be the same. (b) The reduced $S = 1$ spin system. J indicates the effective interaction between adjacent $S = 1$ spins.

In order to get information for these interactions, we show the results of the isothermal magnetization observed below 10 K, $T < 6T_c$, as in Fig. 2. Now, we consider the local field at a spin site when an external field H is applied at a temperature T. In addition to the external field H, each spin suffers the exchange field H_{ex} from the surrounding spins with the averaged magnitude $\langle S \rangle$,

$$H_{ex} = \frac{(2z_1J_1 + 2z_2J_2 + \cdots)\langle S \rangle}{g\mu_B} = \frac{2zJ\langle S \rangle}{g\mu_B} = \lambda M \qquad (1)$$

where

$$M = Ng\mu_B\langle S \rangle \text{ and } \lambda = \frac{2zJ}{N(g\mu_B)^2} \qquad (2)$$

Although it is difficult to determine each value of J_i, we can determine their total contribution to H_{ex} by the analysis of the isothermal magnetization. It is noted that all data points converge near on the $S = 1$ Brillouin function when we set $\lambda = 2.4 \pm 0.2$ or $2zJ/k_B = 3.6 \pm 0.3$ K (Fig. 3). In the present analysis, the correction for the demagnetization field $-nM'$ is negligible as in the case of the same experiment for β-phase p-NPNN (n, demagnetization factor; M', magnetization converted for unit volume) [7]. This experimental fact indicates that the $S = 1$ spin state is realized except for the temperature region where the critical fluctuation becomes significant near T_c. The present data for $T = 2$ K, just above $T_c = 1.48$ K, look to deviate a little for this reason.

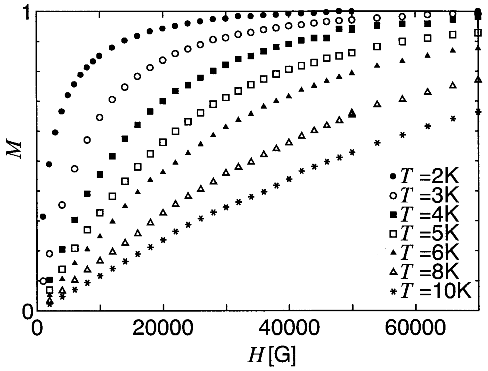

Fig. 2. Isothermal magnetization of the crystalline dupeyredioxyl at

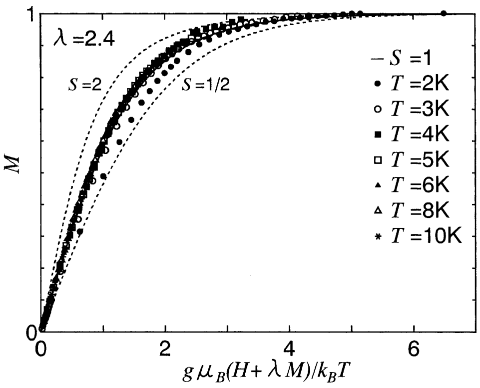

Fig. 3. Isothermal magnetization of the crystalline dupeyredioxyl plotted for $g\mu_B(H+\lambda M)/k_BT$. The solid curve indicates the $S = 1$ Brillouin function for $\lambda = 2.4$ or $2zJS(S+1)/k_BT = 3.6$ K. The dotted curves are the corresponding Brillouin functions for $S = 1/2$ and $S = 1$.

The value $2zJ/k_B = 3.6$ K obtained here should be compared with the other genuine organic ferromagnets such as β-phase p-NPNN ($2zJ/k_B = 3.6$ K, $T_c = 0.61$ K) [7] and 2,5-DFPNN ($2zJ/k_B = 2.8$ K, $T_c = 0.48$ K) [16]. It looks strange that T_c of these three compounds differs largely (by three times), but they have nearly the same order of magnitude of $2zJ$. However, when we consider the effective spin values in these compounds (β-phase p-NPNN ($S = 1/2$) and 2,5-DFPNN ($S = 1/2$)), we recognize that the values of T_c and $2zJ/k_B$ of these three ferromagnets are quantitatively connected by the modified notation of the Rushbrooke and Wood theory as

$$T_c = \frac{2AzJS(S+1)}{k_B} \qquad (3)$$

where A ranges 0.23 ± 0.02 for the Heisenberg ferromagnets with $z = 6$ (s.c.), $z = 8$ (b.c.c.), and $z = 12$ (f.c.c.) (when $A = 1/3$, T_c is equal to the Curie–Weiss temperature) [17].

The highest value of T_c of the present compound of the genuine organic ferromagnets may be partially originated from its effectively larger spin value $S = 1$ within a molecule. In other words, the intermolecular ferromagnetic interactions in genuine organic ferromagnets may be the same order of magnitude at present.

3.2. The variation of $T_c(P)$ and exchange interactions under pressure

Fig. 4 shows the results of magnetic susceptibility measurements under pressure up to 9.7 kbar by the use

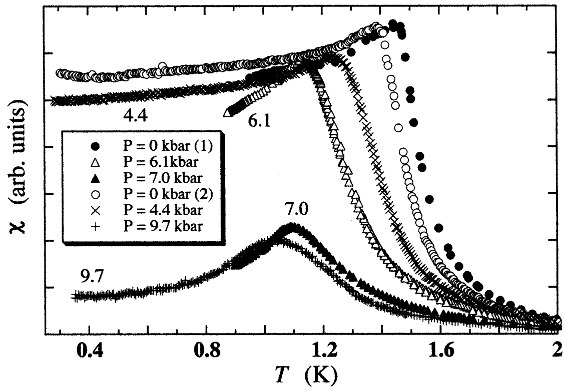

Fig. 4. Pressure dependence of the magnetic susceptibility of the crystalline dupeyredioxyl up to 9.7 kbar by the use of the Cu–Be clamp cell. The turn of the measurement is 0 kbar (1) → 6.1 kbar → 7.0 kbar → 0 kbar (2) → 4.4 kbar → 9.7 kbar.

of the Cu–Be clamp cell. At ambient pressure, the behavior of χ reproduces well the previous report including the appearance of the cusp at $T_c(0) = 1.48$ K and the low-temperature plateau. As P increases, the cusp and plateau shift to the lower temperatures, and turn into a small and broad hump, in the pressure region 6.1–7.0 kbar, with its maximum at 1.05 K for $P = 9.7$ kbar. This seems to be a precursor of the disappearance of ferromagnetic moment or of a transition to an antiferromagnetic state as observed in the pressurization of the ferromagnetic β-phase p-NPNN and p-Cl-TEMPO in the range 6–7 kbar [5–8]. As seen in Fig. 5, for the higher pressure ($P = 15$ kbar), the magnetic signal, if any, looks to be temperature-independent, although the data points are scattering because of the experimental condition with DAC. Around this pressure range, the genuine organic crystals are expected to shrink about 6–10% in volume [5,6,18]. Considering other experimental evidence that ferromagnetic moment is also lost in 2,5-DFPNN under $P = 15$ kbar [18], we may say that the molecular orbitals are merged in some non-magnetic or band structure in this pressure range. The results of heat capacity under pressure $P = 0$ and 6.1 kbar are given in Fig. 6 to confirm the shift of $T_c(P)$, where the heat capacity peak appears at the temperatures corresponding to $T_c(P)$ determined by the susceptibility. The overall results of $T_c(P)$ of dupeyrediоxy are given in Fig. 7 together with the results for three other organic ferromagnets. Except for 2,5-DFPNN, Curie temperature shows the negative pressure effect of the same order of magnitude: $a = \mathrm{d}(T_c(P))/\mathrm{d}P = -0.047$ kbar^{-1} (β-p-NPNN (-0.048) and p-Cl-TEMPO (-0.03)). This makes a good contrast to the positive pressure effects of genuine organic antiferromagnets including TANOL ($a = +0.15$) [5–7,19]. To our knowledge, no genuine organic antiferromagnets show the negative pressure effects. These facts imply that the realization of enhancement of the Curie temperature seems to be so rarely possible in reality.

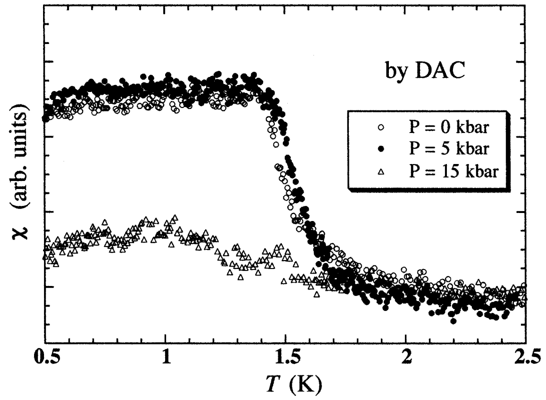

Fig. 5. Magnetic susceptibility of the crystalline dupeyredioxyl observed by the use of DAC.

As for the microscopic mechanism of the reduction of $T_c(P)$ of the present compound, first we think of a pressure-induced destruction of the orthogonality of the singly occupied orbitals associated with the two NO moieties within a molecule. The relative rotation of NO axes may effectively change to result in the reduction of the ferromagnetic coupling J_0 itself. It is theoretically pointed out that the relative rotation on a simple two-radical model gives effect to change the magnetic interaction including its sign [20]. Next, we must consider the variation of the intermolecular interactions under pressures, although it is expected to be complicated. Taking the possible exchange paths on the crystal structure into consideration, the interlayer interaction J_i ($i \geqq 2$; $0 < J_i < J_1 < J_0$) are much weak and therefore susceptible to the mechanical stress by pressure (shrinkage, share, and/or rotation), just as is expected in β-phase NPNN and p-Cl-TEMPO around the pressure region 6–7 kbar. In the former ferromagnet, the pressure-induced rotation of radical groups by about

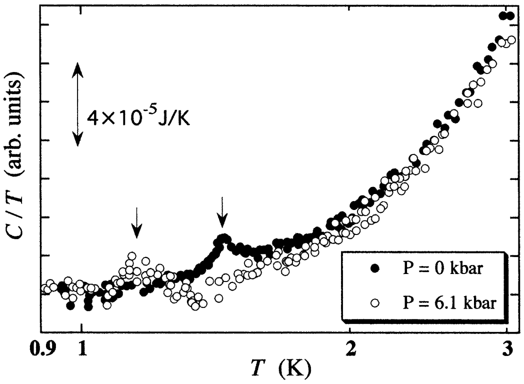

Fig. 6. Low-temperature heat capacity of the crystalline dupeyredioxyl divided by temperature under pressure at $P = 0$ and 6.1 kbar.

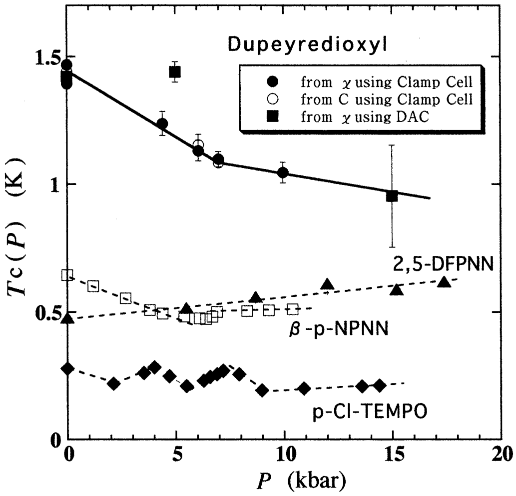

Fig. 7. Pressure dependence of the Curie temperature of the crystalline dupeyredioxyl and other typical organic ferromagnets (β-phase p-NPNN [5,6], p-Cl-TEMPO [8], and 2,5-DFPNN [18]).

5° gives an effect to change the sign of the exchange interaction [7]. At the present stage of experiment, however, we cannot describe the scenario of the negative pressure effect of this system in more detail. In reality, the situation will be more complex to explain.

4. Conclusion

Of the genuine organic ferromagnets, with the magnetic moment greater than μ_B per molecule, the crystallized biradical molecule dupeyredioxyl has the highest Curie temperature ($T_c = 1.48$ K). By the analysis of the isothermal magnetization at various temperatures ($T_c < T < 6T_c$) at ambient pressure, the magnetization is revealed to obey Brillouin function for $S = 1$ or $B_1((H + \lambda M)/k_B T)$ with $\lambda = 2.4 \pm 0.2$ or $2zJ/k_B = 3.6 \pm 0.3$ K. This further evidenced that at low temperatures, each unpaired electron ($S = 1/2$) on two NO moieties within a molecule couples to reduce $S = 1$ via intramolecular ferromagnetic interaction J_0, and $S = 1$ spins interact each other with the averaged interaction $2zJ$. The theoretical relation $T_c = A2zJS(S+1)/k_B$ is revealed to be hold not only for the present Heisenberg system but also for other typical $S = 1/2$ ferromagnets β-phase p-NPNN ($2zJ/k_B = 3.6$ K) and 2,5-DFPNN ($2zJ/k_B = 2.8$ K). In other words, the high value of T_c of this compound is partially originated in the biradical character of the molecule.

A negative pressure effect of $T_c(P)$ is detected by the measurements of the magnetic susceptibility and the heat capacity under pressure up to 15 kbar, as observed for β-phase p-NPNN and p-Cl-TEMPO under pressure of more than 6–7 kbar, where the latter two ferromagnets turn into antiferromagnets at higher pressures. These negative pressure effects make a good contrast to the positive effects generally observed in genuine organic antiferromagnets. As for the microscopic reason of the reduction of $T_c(P)$ for the present compound, different from the above two ferromagnets, the pressure-induced destruction of the orthogonality of the molecular orbitals associated with the two NO moieties in a molecule is suggested to reduce the intramolecular ferromagnetic interaction J_0. Secondly, the possible weaker exchange interactions J_i ($i \geqq 2$) rather than J_0 and J_1 are pointed out to be more susceptible to the stress of pressure to result in the reduction of its value including its sign, just as in the case of β-phase p-NPNN or p-Cl-TEMPO.

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