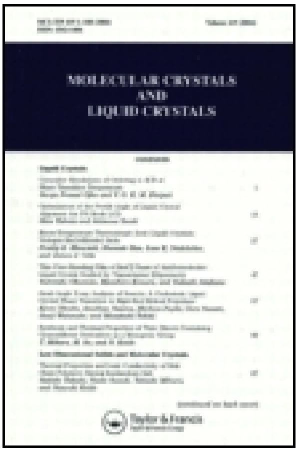

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Ferromagnetism of Organic Radical Crystals of Tempo Derivatives

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FERROMAGNETISM OF ORGANIC RADICAL CRYSTALS OF TEMPO DERIVATIVES

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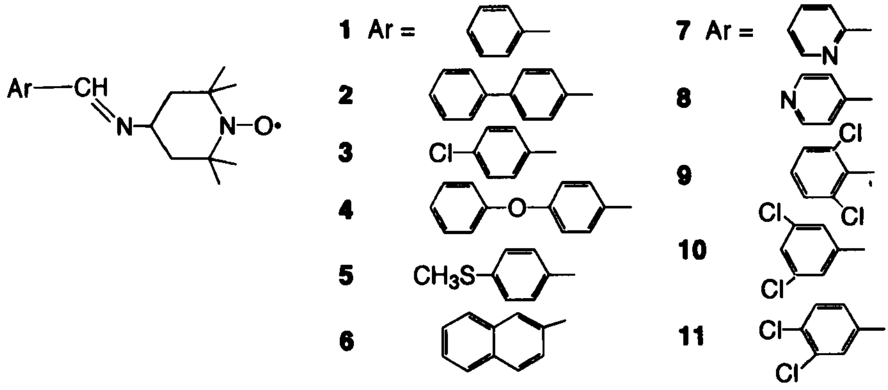
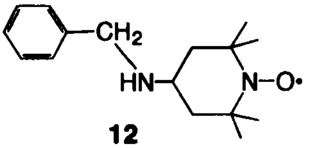
Abstract Several TEMPO-based radicals were found to be bulk ferromagnets with T_C of 0.2 - 0.4 K, as indicated by the measurements of ac magnetic susceptibilities and magnetization curves. On the basis of the X-ray crystal structure analysis, a possible mechanism of ferromagnetic interactions between neighboring N-O sites is proposed, in which the methyl or methylene groups play a role of ferromagnetic exchange couplers. New organic ferromagnets, 4-(*p*-methylthiobenzylideneamino)-TEMPO, 4-(benzylamino)-TEMPO, and 4-(hydroxyimino)-TEMPO as well as several metamagnets are reported.

INTRODUCTION

Ferromagnetism in organic materials is of current interest.[1] Several examples of purely organic ferromagnets with well-defined crystal structures appeared in the literature.[2-10] We have reported organic ferromagnets possessing a 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) group, **1** (T_C = 0.18 K),[5] **2** (T_C = 0.4 K),[6] **3** (T_C = 0.4 K),[9] and **4** (T_C = 0.2 K).[10] We discuss here a magneto-structure relationship and propose a possible mechanism of the intermolecular ferromagnetic couplings. In the course of our study on derivatives of **1** - **4**, we have very recently found a new organic ferromagnet **5** and **12** as well as organic metamagnets **6**,[10,11] **7** - **11**. Since other types of TEMPO derivatives are so far known to exhibit ferromagnetic interactions,[12-15] we re-examined the ferromagnetic interaction of **13**, and found its ferromagnetic transition. We report here the ferromagnetism of **5**, **12**, and **13** and the metamagnetism of **7** - **11**. Their X-ray crystal structures are described elsewhere.[16]





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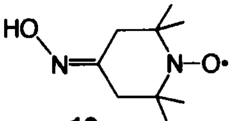

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MECHANISM OF FERROMAGNETIC INTERACTION

The ferromagnetic transition phenomena and crystal structures of organic radical crystals of **1** - **4** are published elsewhere.[5,6,9,10,16] Their crystal structures were discussed in connection with dimensionality of the arrangement of N-O spin centers. Since the spin is highly localized at the N-O site in the TEMPO group in comparison with delocalized π-spins in *p*-NPNN[2] and C_{60}•TDAE,[3] the arrangement of N-O sites must be most important to clarify the origin of ferromagnetic exchange interaction of a series of TEMPO radicals investigated here.

In all of the crystal structures of **1** - **4**, the N-O sites construct two-dimensional network and the oxygen atoms are located on zigzag planes.[16] The nearest neighbor O···O distances were found to be *ca.* 6 Å within a sheet (5.62 and 6.15 Å for **1**,[5] 5.96 and 6.09 Å for **2**,[6] 5.91 and 5.95 Å for **3**,[9] and 5.99 and 8.00 Å for **4**[16]). The distance between the sheets of **2** (14.2 Å) is longer than that of **1** (10.8 Å) owing to the bulkiness of the additional phenyl group in **2**. Considering the fact that the transition temperature of **2** is not lower than that of **1** and **3** in spite of the difference of the inter-sheet distances, the ferromagnetisms of **1** - **3** may be interpreted mainly as two-dimensional ordering of the radical spins.[9]

The above description for the O···O distances does not necessarily mean presence of direct interaction among the N-O sites, because there are methyl and methylene groups intervening between them. The most important feature is that the oxygen atoms of the N-O group always locate near methyl and/or methylene groups of adjacent molecules.

These intermolecular O···H distances were 2.5 - 2.8 Å, which are close to the sum of van der Waals radii (2.6 Å). We propose here a possible mechanism of ferromagnetic interactions between the nearest neighboring N-O sites; the intervening methyl and/or methylene groups play a role of ferromagnetic exchange couplers.

In the crystal of **1**, the N-O sites are arranged in a zigzag manner both along *b* and *c* axes. Figure 1 shows the arrangements of a part of TEMPO moiety based on the X-ray crystallographic analysis. All of the hydrogen atoms drawn in Figure 1 are attached to β-carbon atoms (carbon atoms of β-postions from the N-O group), and we call them β-hydrogen atoms. As Fig. 1a shows, the first and second nearest intermolecular O···H distances are 2.4_8 ($O \cdots H_{methylene}$) and 2.7_7 Å ($O \cdots H_{methyl}$) respectively along the *b* axis. Figure 1b illustrates that the nearest intermolecular $O \cdots H_{methyl}$ distance is 2.8_6 Å along the *c* axis. Although the positions of hydrogen atoms have relatively large experimental errors, it is safely asserted that β-hydrogen atoms are present between the oxygen atoms and β-carbon atoms.

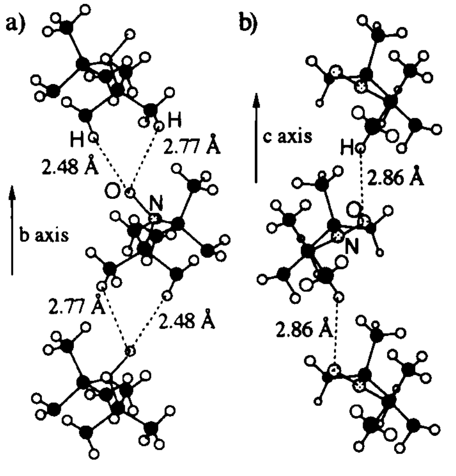


FIGURE 1 Arrangement of $CH_2(CH_3)_2CN(-O\bullet)C(CH_3)_2CH_2$ moieties in the crystal of **1**. a) Along the *b* axis. b) Along the *c* axis.

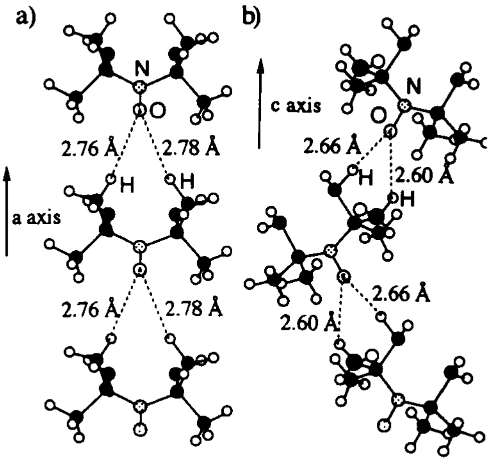
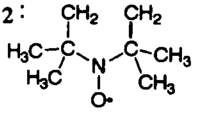
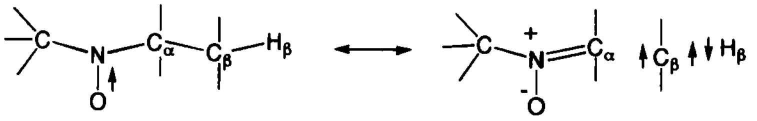


FIGURE 2 Arrangement of $CH_2(CH_3)_2CN(-O\bullet)C(CH_3)_2CH_2$ moieties in the crystal of **3**. a) Along the *a* axis. b) Along the *c* axis.

$CH_2(CH_3)_2CN(-O\bullet)C(CH_3)_2CH_2$:

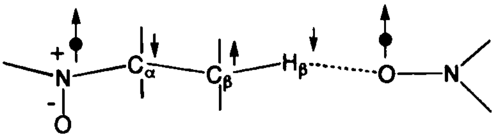


The ENDOR and NMR studies on TEMPO and related compounds revealed that the signs of the ^1H and ^{13}C hyperfine splitting constants (hfsc's) alternated throughout the hydrocarbon framework and that negative spin was induced on the β-hydrogen atoms.[17] The β-hydrogen hfsc is generally larger than the α-hydrogen hfsc.[18] These facts can be interpreted in terms of hyperconjugation as drawn below.[18,19]



The alternate spin distribution to the methyl and methylene groups was also confirmed by UHF/MNDO-PM3 calculation[20] based on the geometry of **1**. The spin densities on the α-carbon, β-carbon, and β-hydrogen atoms through the nearest pathway along the *b* axis were calculated to be -0.0173, 0.0013, and -0.0006 respectively. Those along the *c* axis were -0.0173, 0.0060, and -0.0004 respectively. The spin densities induced on β-hydrogen atoms were negative.

The Heitler-London theory of chemical bond tells us that the negative spin density on the β-hydrogen atoms can induce positive spin density on an adjacent N-O site when the 1s(H) orbital overlaps with the π^*(N-O) orbital. The structure analysis showed that their orbitals were not geometrically orthogonal. Therefore, a spin propagation scheme is illustrated as follows.



The crystal structure of **2** is very similar to that of **3** except for the inter-sheet distance.[9] Since the intra-sheet arrangements of N-O sites of **2** and **3** are almost the same, we discuss here the case of **3** on behalf of them. Figure 2 shows the arrangements of a part of TEMPO moiety in the crystal of **3**. The methyl groups intervene between the N-O sites. The methyl hydrogens were located near the N-O site in adjacent molecule with the nearest intermolecular O···H distances of 2.7_6 and 2.7_8 Å along the *a* axis (Fig. 2a) and with those of 2.6_0 and 2.6_6 Å along the *c* axis (Fig. 2b).

The spin distribution to the methyl groups was confirmed by UHF/MNDO-PM3 calculation.[20] The calculation based on the geometry of **3** revealed that the spin densities on the α-C, β-C and β-H atoms through the nearest pathway along the *a* axis are calculated to be -0.020, 0.024, and -0.002 respectively, and those along the *c* axis to be -0.022, 0.054, and -0.001 respectively. The crystallographic analysis showed that the structure of TEMPO moieties in a series of the derivatives investigated here were quite similar,[16] and consequently the calculated spin distribution has the general tendency that the signs of polarized spin densities alternate throughout the hydrocarbon framework. Thus, the above spin polarization scheme seems to hold for the crystal of **3** (and also **2**) as described in eq. (1), and the intermolecular O···H orbital overlaps can cause ferromagnetic coupling both along the *a* and *c* axes (eq. (2)).

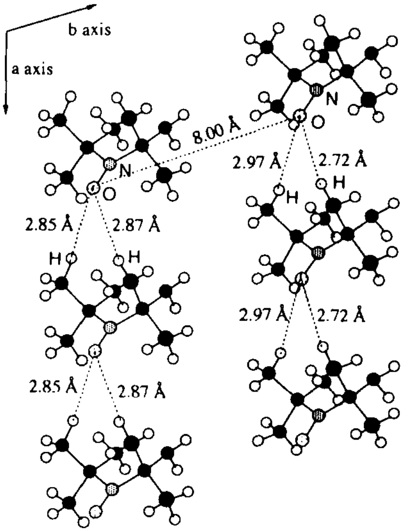


FIGURE 3 Two-dimensional network of $CH_2(CH_3)_2CN(-O\bullet)C(CH_3)_2CH_2$ moieties in the crystal of **4**.

The crystal structure of **4** is somewhat unique;[16] the N-O network was almost flat. The sheet structure is shown in Fig. 3. The intermolecular O···O distances were 5.99 and 8.00 Å along the *a* and *b* axes respectively. The nearest O···H distances were found to be 2.7_2 - 2.9_7 Å along the *a* axis and ferromagnetic interaction between the nearest neighboring molecules along the *a* axis is understood by the mechanism described in eqs. (1) and (2).

On the other hand, the interaction along the *b* axis is hardly explained so far, because there is no van der Waals contact of adjacent TEMPO moieties along the *b* axis. The above mechanism can be applied to the cases that the oxygen atoms of N-O sites are located near β-hydrogen atoms in adjacent molecules; the N-O sites are *ca.* 6 Å apart from each other. The weak interaction due to the long O···O distance (8.00 Å) seems to be responsible for the lower T_C of **4** than those of **1** - **3**,[6,9] and **5** (see below).

Preliminary results of the crystallographical study on **5**[21] revealed that the N-O sites were arranged in a zigzag plane just like those of **1**. The nearest O···O distances are 6.21 and 5.67 Å, which are close to 6 Å, along the *b* and *c* axes respectively. The nearest O···$H_{methylene}$ distance is 2.5_3 Å and O···H_{methyl} distance is 2.9_4 Å along the *b* and *c* axes respectively. The intra-sheet ferromagnetic interaction of **5** can be apparently interpreted in terms of the mechanism through intervening methyl and methylene groups.

Despite of the positive Weiss constant of the crystal of **6**, the magnetic measurements of **6** exhibited a Néel transition at about 0.12 K (T_N) and a typical metamagnetic behavior below T_N.[10,11]

The crystal structure analysis of **6** revealed that the molecules have an almost columnar structure with the nearest intermolecular O···O distance of 5.70 Å (Fig. 4). The intra-columnar ferromagnetic interaction can be interpreted by the above mechanism because the oxygen atoms were located close to the β-hydrogen atoms in neighboring molecules within a column (O···H distances are 2.7_2 and 2.7_9 Å).

The metamagnetism of **6** is explained as antiferromagnetic interaction, though not clarified yet, among the ferromagnetic columns.

The spin polarization mechanism is frequently applied so far to π-electron conjugated systems and the adequacy has been examined theoretically and experimentally.[22] However, the present mechanism of the ferromagnetic interaction in a series of TEMPO derivatives is based on the spin polarization in σ-electron systems of saturated hydrocarbon frameworks. The interactions through σ-electron systems seem to be very weak, compared with those through π-electron systems. For valuation of them, more accumulation of experimental instances and theoretical calculations are necessary.

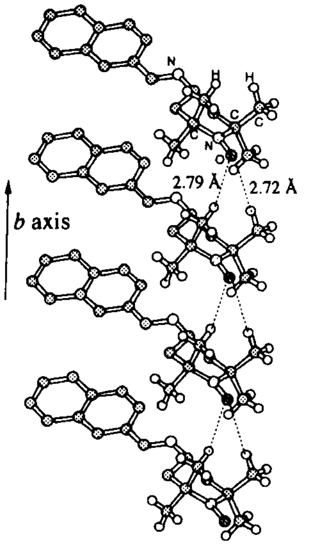


FIGURE 4 Molecular arrangement of **6** along the *b* axis.

The original reason of the introduction of methyl groups to a piperidin-1-oxyl radical is to protect the N-O radical site from chemical reaction by the steric hindrance. We proposed here that the methyl groups were also useful to ferromagnetic exchange couplers in TEMPO-based magnetic materials. The high probability of affording materials with positive Weiss temperatures[10] seems to be mostly explained in terms of this mechanism. Furthermore, this mechanism may also be applicable to the explanation of the ferromagnetic interactions of tetramethyltetraazaadamantane-*N*,*N*'-dioxyl[4] and TEMPOL suberate.[15]

NEW ORGANIC FERROMAGNETS

Radical **5** was prepared by the condensation between 4-amino-TEMPO and *p*-methylthiobenzaldehyde in refluxing ethanol. The product was recrystallized from ethanol to give the polycrystalline sample of **5**, mp 94 -95 °C. The static magnetic susceptibility, χ_{dc}, was measured on a Quantum Design MPMS-7 SQUID magnetometer down to 1.8 K at 0.5 T. The diamagnetic contribution was estimated from Pascal's constants. The χ_{dc} measurement of **5** revealed the presence of ferromagnetic interaction. The magnetic moment of **5** monotonously increased with decreasing temperature and reached 2.09 μ_B at 1.8 K. The plots of the reciprocal susceptibility against temperature gave positive Weiss temperature of +0.52 K.

The ac magnetic susceptibility, χ_{ac}, was measured at the ac magnetic field of about 35 mOe (125 Hz) down to about 50 mK by a ^{3}He-^{4}He dilution refrigerator. The result of **5** is plotted as a function of temperature in Figure 5a, which shows that a sharp divergence starts at about 0.3 K and reaches a maximum at 0.22 K. We here define the transition temperature, T_C, where χ_{ac} starts to diverge.

In order to elucidate the nature of the magnetic phase transition of **5** at 0.3 K, we measured *M-H* curves below and above this temperature. The experimental details on the magnetization curves were described elsewhere.[5,23] As Figure 5b shows, a typical hysteresis curve with a coercive force of about 130 Oe was obtained below T_C (53 mK). On the other hand, a linear paramagnetic feature was observed above T_C (560 mK).

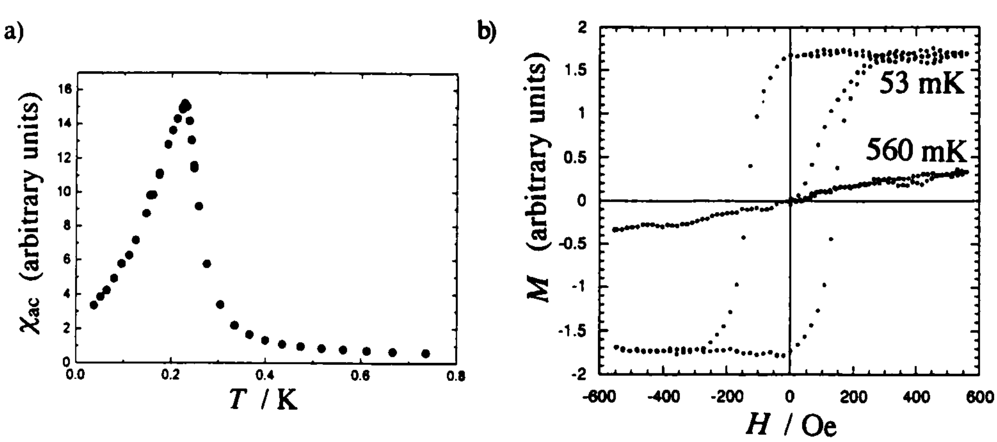


FIGURE 5 a) Temperature dependence of the ac susceptibility of **5** below 0.8 K, showing the ferromagnetic transition at about 0.3 K. b) The *M-H* curves of **5** measured at 53 mK (below T_C) and at 560 mK (above T_C)

Radical **12** was prepared by reductive amination[24] of 4-oxo-2,2,6,6-tetramethyl-piperidin-1-oxyl with benzylamine hydrochloride and NaBH$_3$CN in methanol. Recrystallization from ethanol gave orange crystals of **12**, mp 54 - 55 °C. The χ_{dc} measurement of **12** above 1.8 K gave a positive Weiss temperature of +0.55 K. The χ_{ac} measurement of **12** showed a sharp divergence of χ_{ac} at about 0.3 K and a peak at 0.18 K. As Fig. 6 shows, the isothermal

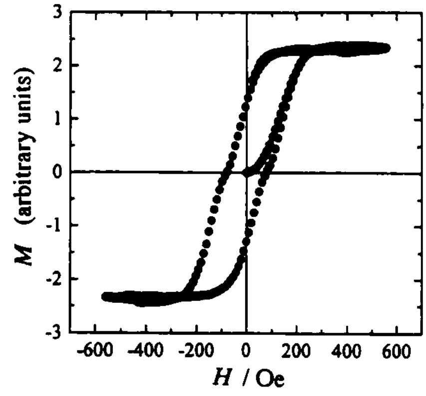


FIGURE 6. The *M-H* curve of **12** measured at about 30 mK (below T_C).

magnetization curve indicated that **12** was a ferromagnet with a T_C of 0.3 K.

Radical **13** has been reported to exhibit intermolecular ferromagnetic interaction indicated by the positive Weiss constant of +0.45 K.[12] However, no more magnetic study has not been reported. We reinvestigated the magnetic properties of **13**.

We reproduced a positive Weiss constant (0.48 K) of **13** in the χ_{dc} measurements. The temperature dependence of χ_{ac} is plotted as a function of temperature in Figure 7a, which shows that a sharp divergence starts at about 0.25 K which is defined as T_C here, and χ_{ac} is almost saturated below 0.2 K. The *M-H* curves below and above this temperature were measured. As Figure 7b shows, a typical hysteresis curve with a coercive force of about 120 Oe was obtained below T_C (53 mK) and a linear paramagnetic feature above T_C (560 mK). Thus, **13** was clarified to be a bulk ferromagnet with a T_C of 0.25 K.

The deuterated derivative **13**-d_1-OD has been synthesized. However, the magnetic experiments exhibited no appreciable difference from those of **13**. The investigation of isotope effect of perdeuterio **13**-d_{17} is now in progress.

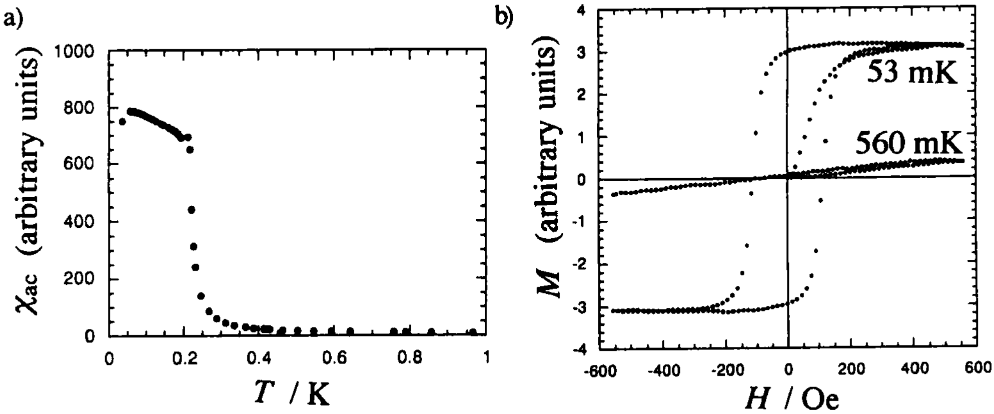


FIGURE 7 a) Temperature dependence of the ac susceptibility of **13** below 1 K, showing the ferromagnetic transition at about 0.25 K. b) The *M-H* curves of **13** measured at 53 mK (below T_C) and at 560 mK (above T_C)

NEW ORGANIC METAMAGNETS

In the course of studies on various analogs of **1** - **5**, we found organic metamagnets **6** - **11**. They were prepared by the condensation of 4-amino-TEMPO and the corresponding aromatic aldehydes; **7**: mp 94 - 96 °C (lit.[25] 96.5 - 97.5 °C), **8**: mp 117 - 118 °C (lit.[25] 113 - 114 °C), **9**: mp 109 - 110 °C, **10**: mp 148 - 149 °C, and **11**: mp 106 - 108 °C.

Figure 8 shows the *M*-*H* curves of **7** and **8**. The metamagnetic critical fields were found to be very small (10 - 100 Oe) for **7** - **11**. The Néel temperatures of **6** - **11** were determined by the temperature dependence of the ac susceptibilities; **6** (T_N = 0.21 K),[10,11] **7** (T_N = 0.26 K), **8** (T_N = 0.12 K), **9** (T_N = 0.20 K), **10** (T_N = 0.12 K), and **11** (T_N = 0.10 K).

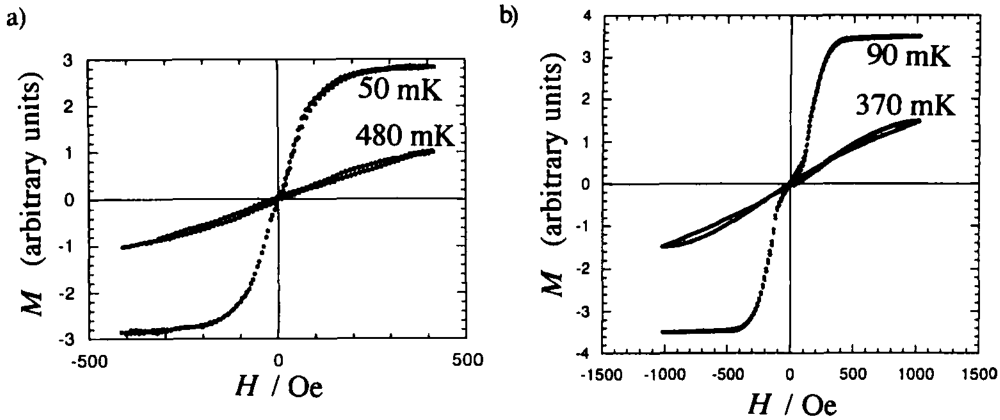


FIGURE 8 The *M*-*H* curves measured below and above T_N for **7** (a) and **8** (b).

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