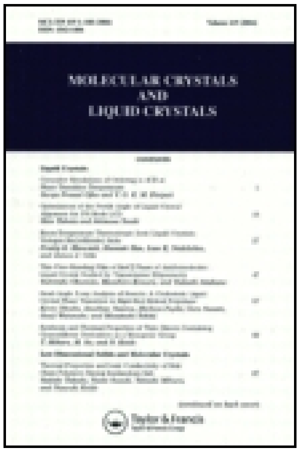

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Pressure Effect on Organic Radicals

Yuko Hosokoshi [a], Masafumi Tamura [b] & Minoru Kinoshita [c]

[a] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

[b] Department of Physics, Faculty of Science, Toho University, Miyama, Funabashi, Chiba, 274, Japan

[c] Science University of Tokyo in Yamaguchi, Onoda, Yamaguchi, 756, Japan

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PRESSURE EFFECT ON ORGANIC RADICALS

YUKO HOSOKOSHI,[1] MASAFUMI TAMURA,[2] AND MINORU KINOSHITA[3]

[1]Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
[2]Department of Physics, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274, Japan
[3]Science University of Tokyo in Yamaguchi, Onoda, Yamaguchi 756, Japan

Abstract The magnetic properties of galvinoxyl (4-[3,5-bis(1,1-dimethylethyl) -4-oxo-2,5-cyclohexadiene-1-ylidenemethyl]-2,6-bis(1,1-dimethyl-ethyl)-phenoxy) and F_5PNN (2-pentafluorophenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol -1-oxyl 3-oxide) under pressure are presented. We have found that the structural changes of both compounds can be suppressed by pressurization.

The phase transition to a diamagnetic state of galvinoxyl can be suppressed by applied pressure. It has been found that under 7 kbar, the transition is sufficiently suppressed and the ferromagnetic interactions are preserved down to low temperature. The temperature dependence of the paramagnetic susceptibility under 7 kbar obeys the ferromagnetic chain model with $2J/k_B = 25$ K.

The room-temperature crystal structure of F_5PNN involves a uniform chain, while the low-temperature magnetism can be interpreted by the alternating antiferromagnetic chain model with $2J/k_B = -5.6$ K and $\alpha = 0.4$. We found that under 5 kbar, the low-temperature magnetism obeys the uniform antiferromagnetic chain model with $2J/k_B = -5.6$ K, which is consistent with the room-temperature crystal structure.

INTRODUCTION

The study on molecular magnetic materials has attracted much attention in recent years. Search for a new phenomenon in molecular materials is a current interest.

We focus on the 'softness' of organic radicals. We have made a clamp cell for static magnetic measurements with high sensitivity. In this paper, we describe the pressure effect on magnetic properties of two organic radicals. We have found that some kinds of structural changes can be suppressed by pressurization.

STATIC MAGNETIC MEASUREMENTS UNDER PRESSURE

The static susceptibility and magnetization under pressure was measured using a Quantum Design MPMS SQUID magnetometer, with a high pressure clamp cell made of Cu-Ti alloy (YAMAHA, YCuTM). A cross-sectional view of the cell is given in Fig.1. The cell enables an internal pressure to be maintained up to *ca.* 7 kbar. As a pressure-transmitting medium, a fluorine oil (Montefluos, H-VAC140/13) was used. The actual pressure at low temperature was calibrated by the superconducting transition temperature of Pb according to the well-known relation,[1]

$$\frac{dT_C}{dp} = -0.0365 \text{ K kbar}^{-1} \tag{1}$$

The difference between the pressure at low temperature and the one applied at room temperature is below *ca.*0.3 kbar in the pressure region of 3–7 kbar.

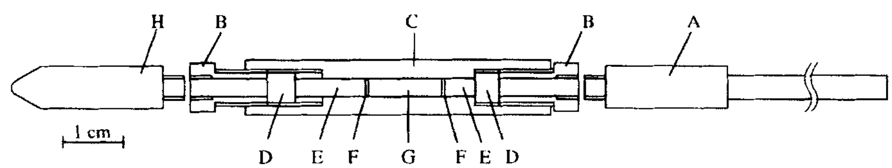
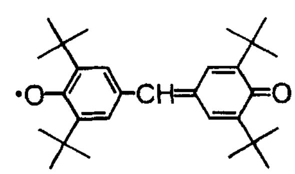


FIGURE 1 Cross-sectional view of the pressure clamp cell. A: Dummy cell (connected to a sample rod), B: Locking nut, C: Cylinder, D: Backing plate (ZrO_2, KYOCERA, Z703N), E: Piston (ZrO_2), F: Cu seal, G: Teflon bucket, H: Dummy cell.

GALVINOXYL



Galvinoxyl is known to possess the largest positive Weiss constant among organic radicals, but to undergo a phase transition to a diamagnetic state at 85 K.[2] This transition is a first-order one with a large entropy change.[3] This transition has prevented the detailed study of the ferromagnetic interactions of this material at low temperature, although the suppression of the transition by an impurity effect was reported in the mixed crystals with the precursory closed shell compound, hydrogalvinoxyl[4] and in the freeze-dried materials obtained from a highly dilute benzene solution.[5]

Here, presented is the suppression of the transition in pure galvinoxyl under pressure. This is the first observation of the ferromagnetic interactions in pure galvinoxyl at low temperature. The low-temperature magnetic properties are examined and the pressure effect on the transition is discussed.

Pressure Effect on Magnetic Properties of Galvinoxyl

Galvinoxyl was prepared and purified by the method described in the literature[6] and crystallized from a solution of acetonitrile. The magnetic properties at ambient pressure was measured using the crystals packed in a bucket made of thin aluminum so as to avoid the stress as far as possible, because the magnetic properties of galvinoxyl is very sensitive to pressure. The phase transition to a diamagnetic state was observed at 82 K in the cooling process and at 84 K in the warming process. The observed data above the transition temperature (T_D) can be reproduced by the Curie-Weiss law with the Curie constant, $C = 0.364$ emu K mol^{-1} and the Weiss constant, $\Theta = 11$ K. The radical content can be estimated from the value of C to be 97%. These results are consistent with the reported ones.[2,4]

The temperature dependence of paramagnetic susceptibility, χ_p, under 7 kbar is compared with that at ambient pressure in Fig. 2, where $\chi_p T$ is plotted as a function of T. It is clear that under 7 kbar, the transition is sufficiently suppressed and the ferromagnetic interactions are preserved down to low temperature. The magnetization curves below 10 K are shown in Fig. 3, together with the theoretical ones calculated on the basis of the expression,

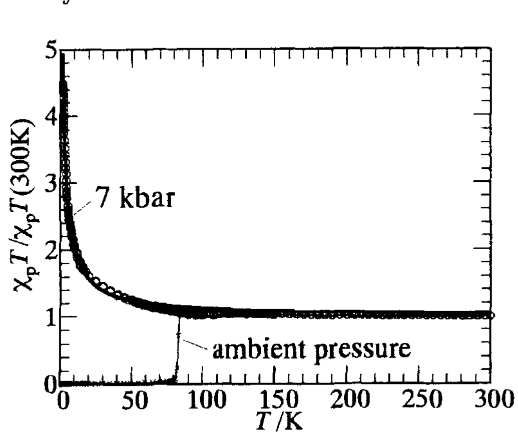


FIGURE 2 Temperature dependence of $\chi_p T$ of galvinoxyl under 7 kbar compared with that at ambient pressure. Solid curve for the data under 7 kbar is the fit by the ferromagnetic chain model with $2J/k_B = 25$ K.

$$M(H/T) = (N_A/2S)g\mu_B S B_s(x) \quad (2)$$

where $B_s(x)$ is the Brillouin function and $x = gS\mu_B H/k_B T$. The saturation rates become faster and faster as temperature decreases, and the one at 1.8 K is corresponding to the calculated one for $S = 5$. This means that more and more molecules are coupled ferromagnetically with lowering temperature and ferromagnetic interactions extend more than ten molecules at 1.8 K.

The temperature dependence of $\chi_p T$ under 7 kbar was analysed on the basis of the room-temperature crystal structure.[7] The observed data above 3 K can be well reproduced by the ferromagnetic chain model[8] with $2J/k_B = 25$ K. This value is consistent with the Weiss constant of $\Theta = 11$ K and more reliable.

The temperature dependence of χ_p^{-1} below 7 K is shown in Fig. 4. The linear temperature dependence is lost at low temperature, which is reflecting the low-dimensionality of this material. The extrapolation of the χ_p^{-1} to the low temperature region suggests the possibility of the ferromagnetic ordered state below 0.5 K, if it occurs. In spite of the large exchange coupling, the one-dimensionality seems to prevent a magnetic ordering.

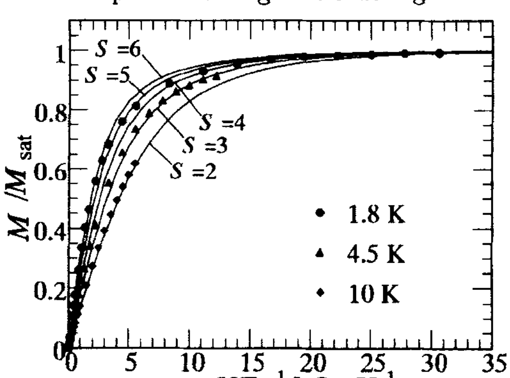


FIGURE 3 Magnetization curves of galvinoxyl under 7 kbar. Solid curves represent the calculation based on the Brillouin function.

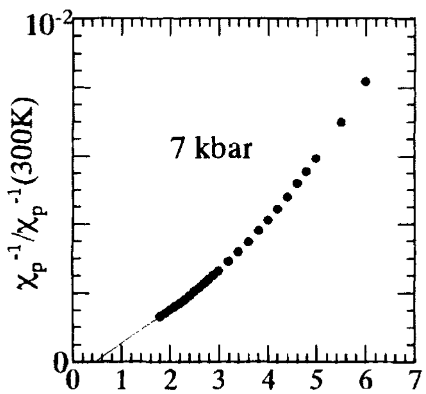


FIGURE 4 Temperature dependence of χ_p^{-1} of galvinoxyl under 7 kbar.

About the Mechanism of the Pressure Effect on Galvinoxyl

The magnetic properties of galvinoxyl are affected by pressure and thermal histories. The temperature dependences of $\chi_p T$ under 2 kbar for the same specimen suffered from rapid and slow coolings are compared in Fig. 5. Cooling rate affects the magnetic behaviour. The cooling rate in the rapid cooling was 10 min. from 300 to 4.2 K and the one in the slow cooling was 300 → 150 K, *ca.*9 h; 150 → 100 K, *ca.*2.5 h; 100 → 50 K, *ca.*4 h. In both cases, the discontinuous decrease in $\chi_p T$ around 95 K($= T_D$) is observed but paramagnetic portion still remaines below T_D. Even in the slow cooling process, $\chi_p T$ takes a finite value. In order to check the cooling rate is enough slow to reach an equilibrium state, we have checked the χ_p value for the sample kept at 90 K during 5 days, which changes within 0.5 %.

The effect of the cooling rate was also examined for the sample at ambient pressure. At ambient pressure, paramagnetic reminder is observed only by a very rapid cooling within 5 min. from 300 to 4.2 K. The moderate cooling with the cooling rate of 20 min. from 300 to 4.2 K cannot maintain any paramagnetic portion and $\chi_p T$ value goes down to 0. Even the small stress when the crystals are dipped in oil works as pressure. For the crystals dipped in oil, the paramagnetic portion remaines by the moderate cooling.*

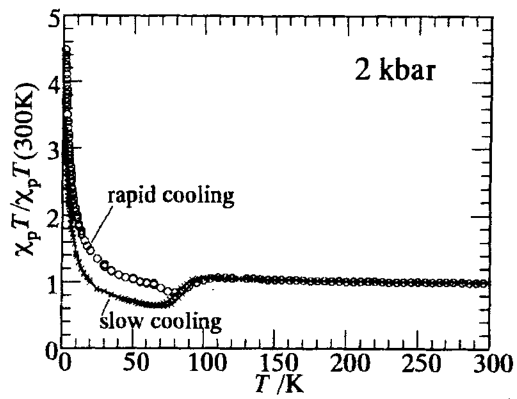


FIGURE 5 Temperature dependences of $\chi_p T$ of galvinoxyl under 2 kbar for the same specimen suffered from rapid and slow coolings.

Figure 6 shows the plots of $\chi_p T$ *versus* T around T_D in slow cooling and warming processes under several pressures. With applied pressure, T_D becomes higher and the amount of the paramagnetic reminder increases. All the paramagnetic reminder under each pressure shows the same magnetization process, the H/T dependence of M/M_{sat}. The rapid-cooled sample at ambient pressure also shows the same H/T dependence of M/M_{sat}. It is worth mentioning that the incomplete transition never occur in a first-order phase transition, in other words, the incomplete transition is corresponding to the observation of a non-equilibrium state. From these, the paramagnetic reminder is considered to be the quenched high-temperature phase, which is in a metastable (non-equilibrium) state. This can be occured in the

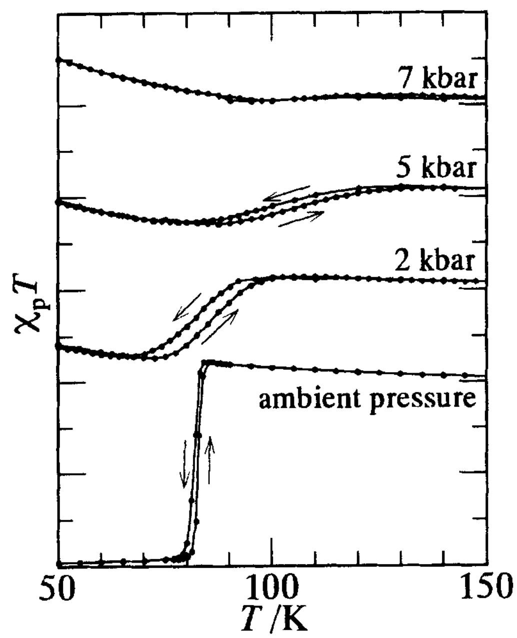
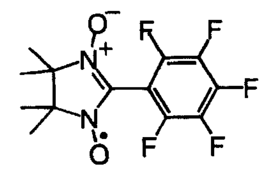


FIGURE 6 Temperature dependences of $\chi_p T$ around the transition temperature in the cooling and warming processes under several pressures.

*The 'anomalous' behaviour reported by Mukai,[2] where the sample dependent paramagnetic remainder with a positive Weiss constant is left below T_D, is probably due to the rapid cooling effect for stressed samples, the authors think.

case that the activation energy of the transition is larger than the thermal energy. The activation energy affects the relaxation time to reach the equilibrium state. In galvinoxyl, the activation energy is considered to be very sensitive to pressurization. Pressurization heighten the activation energy of the transition in galvinoxyl. The upward tendency of T_D is corresponding to the higher activation energy; the system needs larger thermal energy to overcome it. The increase of the amount of the paramagnetic reminder as increasing pressure is corresponding to the longer relaxation time to reach the equilibrium state. When the activation energy is too high, the relaxation time becomes too long to reach the thermal equilibrium state within an experimental time scale. This is the case under 7 kbar.

F_5PNN



We have already reported the crystal structure at room temperature and magnetic properties at ambient pressure.[9] In spite of the uniform chain structure at room temperature, the magnetism at low temperature is better described by the alternating antiferromagnetic chain model[10] with $2J/k_B = -5.6$ K and $\alpha = 0.4$ than by the uniform chain model. The difference is considered to come from the symmetry breaking of the crystal structure at low temperature, which is suggested from the single-crystal EPR measurements.

The Hamiltonian we use may be written as

$$\mathcal{H} = -2J\sum_{i}(\boldsymbol{S}_{2i-1}\cdot\boldsymbol{S}_{2i} + \alpha\boldsymbol{S}_{2i}\cdot\boldsymbol{S}_{2i+1}) \quad (3)$$

where J is the exchange integral between a spin and its right neighbour and αJ is the exchange integral between a spin and its left neighbour. When $\alpha = 1$, the system describes a uniform chain.

Pressure Effect on Magnetic Properties of F_5PNN

F_5PNN was prepared by the reported path[11,12] and crystallized from concentrated hexane solutions.

The temperature dependence of χ_p under 5 kbar is compared with that at ambient pressure in Fig. 7. There are two remarkable differences between them. The maximum value around 3.4 K under 5 kbar is smaller than the one at ambient pressure. Under 5 kbar, the extrapolation of χ_p behaviour to the low-temperature region expects that the χ_p value at $T = 0$ takes a finite value. This behaviour suggests the gapless excitation spectrum. This is in strong contrast to the existence of the energy gap at ambient pressure confirmed by the recent experiments.[13]

The observed data under 5 kbar were analysed on the basis of the above Hamiltonian[10] and satisfactory fit was obtained for the parameter set of $2J/k_B = -5.6$ K and $\alpha = 1$. It can be thought that under 5 kbar, the room-temperature crystal structure with a uniform chain is preserved down to low temperature.

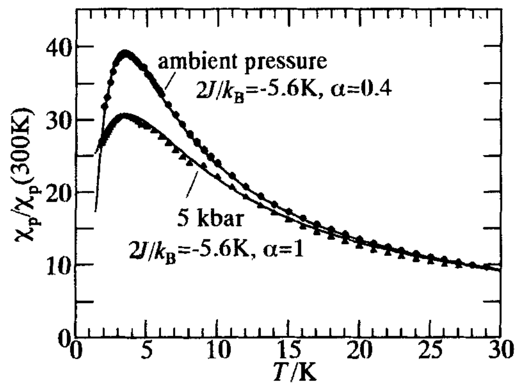


FIGURE 7 Temperature dependence of χ_p of F_5PNN under 5 kbar compared with that at ambient pressure. Solid curves represent the fitting results on the basis of the antiferromagnetic alternating chain model.[10] When $\alpha = 1$, the system is a uniform chain.

SUMMARY

The magnetic properties of galvinoxyl and F_5PNN under pressure have been examined.

In galvinoxyl, the suppression of the phase transition to a diamagnetic state was observed under 7 kbar. The examination of the pressure dependence of the magnetic properties revealed that the pressurization enhances the activation energy of the transition. By applying pressure, the study of the ferromagnetic interactions at low temperature becomes possible. The analysis of the susceptibility data under 7 kbar, yielded the exchange coupling of $2J/k_B = 25$ K. In spite of the large exchange coupling, ferromagnetic order below 0.5 K is expected, if it occurs.

In F_5PNN, it has been found that the magnetic properties under 5 kbar can be interpreted on the basis of the room-temperature crystal structure with a uniform chain, while the magnetism at ambient pressure suggests the structural change at low temperature.

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