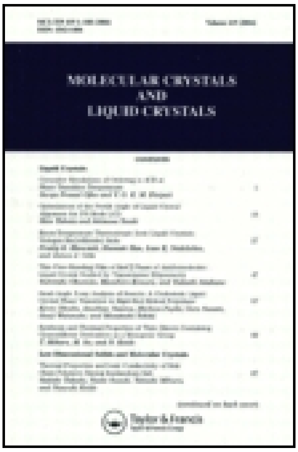

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Pressure Effect on the Curie Temperature and Inter- Molecular Interactions in Organic Ferromagnet β -Phase p-Npnn

Kensuke Konishi [a] , Kazuyoshi Takeda [b] , Masafumi Tamura [c] & Minoru Kinoshita [c]

[a] Department of Physics, Faculty of Science, Ehime University, Matsuyama, 790-77, Japan

[b] Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka, 812, Japan

[c] Institute for Solid State Physics, Tokyo University, Roppongi, Minato-ku, Tokyo, 106, Japan

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PRESSURE EFFECT ON THE CURIE TEMPERATURE AND INTER-MOLECULAR INTERACTIONS IN ORGANIC FERROMAGNET β-PHASE p-NPNN

KENSUKE KONISHI, KAZUYOSHI TAKEDA*, MASAFUMI TAMURA† and MINORU KINOSHITA†
Department of Physics, Faculty of Science, Ehime University, Matsuyama 790-77, Japan; * Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan; † Institute for Solid State Physics, Tokyo University, Roppongi, Minato-ku, Tokyo 106, Japan

Abstract The magnetic properties of the β-phase p-NPNN have been investigated by the simultaneous observation of heat capacity and ac-susceptibility under hydrostatic pressures in magnetic fields. A drastic reduction of the Curie temperature from 0.61 K at an ambient pressure to 0.35 K at 7.2 kbar has been observed. The magnetic heat capacity under 7.2 kbar shows a characteristic shoulder of a two-dimensional Heisenberg ferromagnet with spin S=1/2, just above the heat capacity peak. By the application of weak external fields up to 1 kOe, the peak disappears and the shoulder grows its height and shifts to higher temperatures, as in the case of one-dimensional Heisenberg ferromagnets in external fields.

INTRODUCTION

The first genuine organic ferromagnet was discovered in β-phase p-NPNN (para-nitrophenyl nitronyl nitroxide) and has been well characterized by the various measurements.[1] The bulk ferromagnetic ordering in p-NPNN is confirmed at the Curie temperature T_c=0.6K. The origin of ferromagnetic inter-molecular interaction has been investigating theoretically and experimentally,[2,3,4] but the details of ferromagnetic interactions are not clear. To get further information of the inter-molecular interactions, we investigate magnetic properties of p-NPNN by the simultaneous measurement of heat capacity and ac-susceptibility under hydrostatic pressures, P=0～7.7 kbar, in external magnetic fields.

EXPERIMENTAL

The crystals of β-p-NPNN ($C_{13}H_{16}N_3O_4$, molecular weight:278.29) belongs to the space group of F2dd, and has lattice parameters a=12.374Å, b=19.350Å, c=10.960Å.[1,4]

Figure 1 shows the apparatus for simultaneous measurement of heat capacity and ac-susceptibility under pressures in magnetic fields. The powdered specimen (0.3887g) is packed and pressurized at room temperature in the clamp cell made of CuBe alloy with Apieson-J oil as a pressure-transmitting medium, and set to the cryostat. The pressure P at low temperature is calibrated against the pressure dependence of the superconducting transition temperature T_{sc} of a metal (Sn) by $T_{sc}(P)=T_{sc}(P_0)+aP+bP^2$ ($T_{sc}(P_0)$=3.732K, $a=-4.95\times10^{-5}$ K/atm, $b=3.9\times10^{-10}$ K/atm^2).[5] Thermometers are carbon resisters; Speer 500 Ohm and/or Allen-Bradley 100 Ohm, calibrated by Ge resister of Lake Shore Inc. above 0.3K and by the magnetic susceptibility of $CrK(SO_4)_2 \cdot 12H_2O$ at lower temperatures.

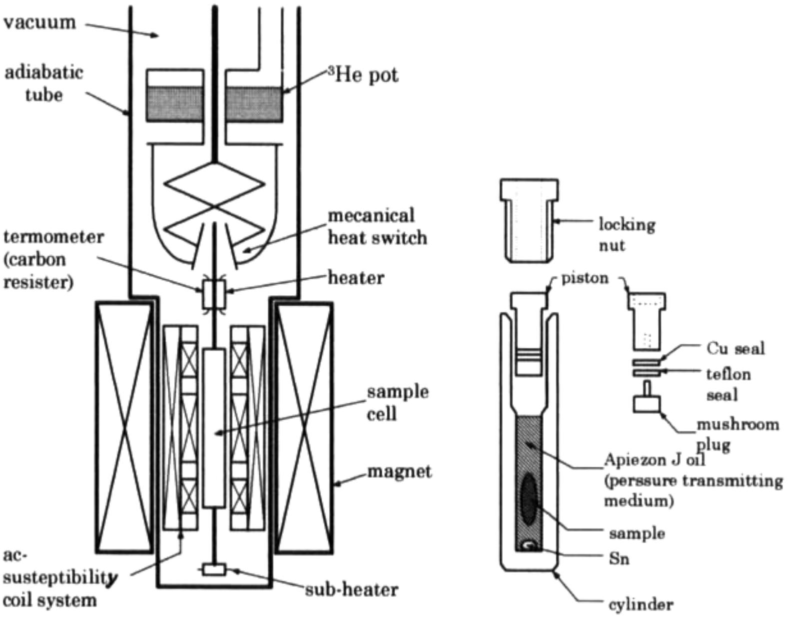

FIGURE 1 Schematic diagram of the apparatus for simultaneous measurement of heat capacity and ac-susceptibility, and clamp cell (made of CuBe).

After the determination of pressure, the sample together with clamp cell is cooled down to about 0.6K by connecting it to ^{3}He pot. Further cooling is performed down to about 0.2K by adiabatic demagnetization with the use of magnetic entropy of sample itself. Then the simultaneous measurement of heat capacity and ac-susceptibility is started. Heat capacity is measured by conventional adiabatic heat pulse method, and ac-susceptibility is measured by Hartshorn bridge method at the frequency f=204Hz. The value of heat capacity of pressure-transmitting medium (Apiezon-J oil) is referred to the previously reported value.[6] The contribution of specimen itself is quite larger than that of clamp cell, addenda and Apieson-J oil below 1K.

RESULTS

The measurements are carried out at P=0.001(P_0; atmospheric pressure), 2.5, 5.4, 7.2, 7.7 kbar.

Figure 2 shows the heat capacity at pressure P=0, 2.5 and 7.2 kbar. At atmospheric pressure (P= P_0), heat capacity shows a sharp peak accompanied with ferromagnetic long range order at the Curie temperature T_c=0.61±0.02 K. The ac-susceptibility signal abruptly upsurges near 0.6K as shown in Figure 3. The large susceptibility signal for P_0 below T_c is suppressed by the external fields. These results agree with the previous studies.[1]

Under the higher pressures, The sharp peak of heat capacity shifts to low temperature side, and the magnitude of peak is suppressed with increasing pressure. Ac-susceptibility shows similar temperature dependence, and the susceptibility signal below $T_c(P)$ shows a suppressed cusp-like behavior with increasing pressure, as seen for P=7.2 and 7.7 kbar. The cusp appears apparently above the corresponding heat capacity peak. These behaviors of the ac-susceptibility and the heat capacity are quite reproducible for pressurization cycles of $P_0 \Leftrightarrow P$.

A drastic reduction of the Curie temperature $T_c(P)$ of β phase p-NPNN is found under the hydrostatic pressure; from $T_c(P_0)$=0.61K to $T_c(P$=7.2 kbar)=0.35K, for instance. The reduction of the Curie temperature depends linearly on pressure as

$$T_c(P)=T_c(P_0)(1+aP) \qquad (1)$$

with negative value of a=-0.050±0.010 kba r^{-1}. On the contrary, the Néel temperature of some antiferromagnetic free radicals and compounds previously reported[7,8] increases linearly on pressure as in Figure 4. This phenomenon of reduction of the Curie temperature is very novel in localized spin systems, and suggests that inter-molecular magnetic interactions become effectively small by applied pressure. On the other hand, it is reported that the Weiss temperature observed in susceptibility becomes large with increasing pressure.[9] Generally, the Weiss temperature is proportional to exchange interaction. The present results for T_c under pressures is inconsistent with the behavior of the Weiss temperature.

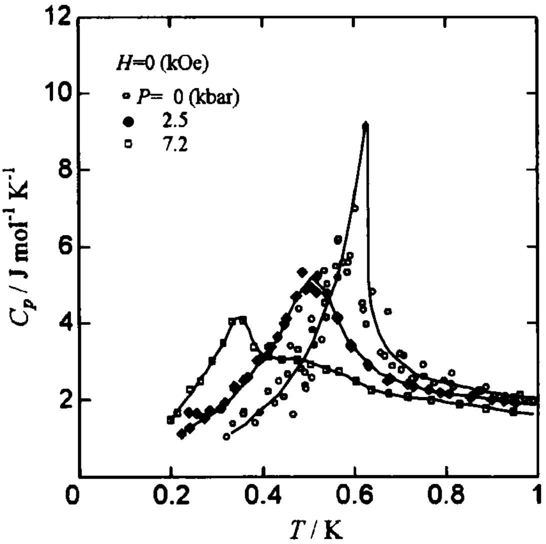

Figure 2 Heat capacity of *p*-NPNN under pressure. (○) $P=P_0=0.001$ kbar. (◆) $P=2.5$ kbar. (□) $P=7.2$ kbar. The solid curves are to guide the eye.

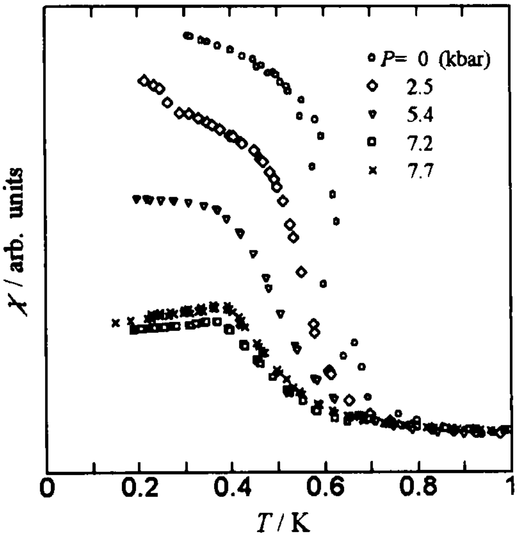

Figure 3 Ac-susceptibility of *p*-NPNN under the pressures.

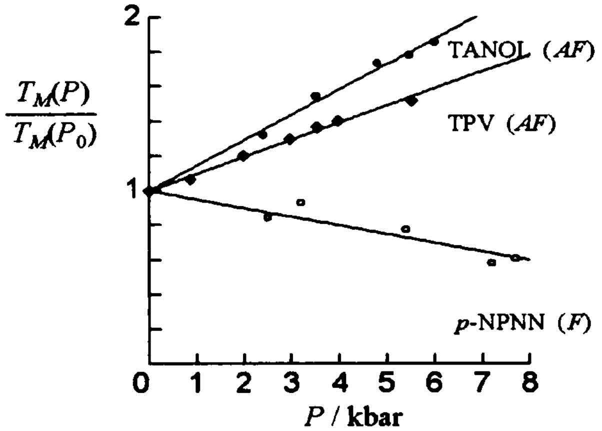

Figure 4 Pressure dependence of magnetic phase transition temperature for organic radicals; *p*-NPNN (ferromagnetic radical) and TANOL, TPV (antiferromagnetic organic free radicals)

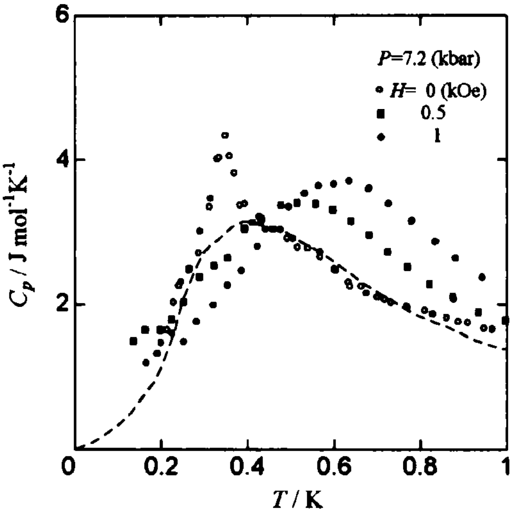

Figure 5 Heat capacity of *p*-NPNN in magnetic fields (H=0, 500, 1000 Oe) at P=7.2 kbar. Broken curve shows the heat capacity of S=1/2 two-dimensional ferromagnet (J k_B=0.8K).

The heat capacity under high pressures, P>7kbar, demonstrates that a rounding shoulder appears above T_c as in Figure 5, which is reproduced by the value expected theoretically for the two-dimensional ferromagnet with S=1/2 (broken curve in Figure

5).[10] The total magnetic entropy does not changes under pressures. In other words, the spin value in *p*-NPNN is kept constant under pressures.

It is noted that the sharp peak of heat capacity at $T_c(P)$ disappears in the external magnetic fields, and a broad maximum appears at rather higher temperature than $T_c(P)$. In the case for atmospheric pressure, the temperature of C_{max} increases and the value of C_{max} becomes small with increasing field. This behavior at $P=P_0$ agrees with the previous works.[1] In low-pressure region, for example P=2.5kbar, the behavior of heat capacity in the field is similar to the case at P_0. In the high pressure region, however, the value of C_{max} grows up and the temperature of C_{max} also shifts to the higher temperatures with increasing field. This behavior is similar to the heat capacity of one-dimensional Heisenberg ferromagnet for isotropic quantum spin $S=1/2$.[11]

DISCUSSION

The pressure dependence of the Curie temperature, defined from the heat capacity peak, is roughly summarized as eq. (1). The reduction of the Curie temperature $T_c(P)$ observed in the present experiment is the first example for genuine organic ferromagnets. In our previous work on antiferromagnetic organic radicals, the Néel temperature under hydrostatic pressures, $T_N(P)$, increases linearly on pressure as eq.(1) where the coefficient a is positive; a=0.14 kbar^{-1} and 0.1 kbar^{-1} for TANOL and TPV, respectively.[7,8] We have attempted to explain the pressure effect of the Néel temperature for these radicals based on the half-filled Hubbard model,

$$H = -t\sum_{ij\sigma} c_{i\sigma}^{+} c_{j\sigma} + U\sum n_{i\uparrow} n_{i\downarrow}, \tag{2}$$

where t is transfer integral and U is the on-site Coulomb potential. At the limit of $U/t \to \infty$, the Hamiltonian is practically expressed by the Heisenberg model as

$$H = -2\sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \tag{3}$$

where the constant term is omitted. In the case of single band, the interaction J corresponds to $-t^2/U$ and has negative value. Since the Néel temperature is generally proportional to the exchange interaction, the equation (1) may be rewritten

$$J(P)/J(P_0)=1+aP. \tag{4}$$

Here, it is assumed that the on-site Coulomb potential U is independent on pressure and the pressure effect is only due to the transfer integral t. Then, the relation,

$$t(P) = t(P_0)\sqrt{1+aP}\,, \qquad (5)$$

is found. This relation shows that the Néel temperature is increased with increasing the transfer integral by pressure.

In the case of radical crystals, however, J is a complicated function of the molecular orbitals, as generally expressed by

$$J = J^K + J^P, \qquad (6)$$

where J^K corresponds to kinetic exchange of the form $-t^2/U$ and J^P is the potential exchange. For the orthogonal molecular orbitals, J^P is positive and the ferromagnetism of p-NPNN is discussed from this point of view.[4] On the other hand, the mechanism of ferromagnetic inter-molecular interactions are studied to be possible by the electronic transfer between the SOMO and NHOMO and/or NLUMO.[12] The ferromagnetism of p-NPNN may be accomplished on the balance between J^K and J^P.

Our present result of the enhanced $T_c(P)$ of p-NPNN indicates the impossibility of its ferromagnetism induced by the dipole-dipole couplings.[13]

The theoretically calculation of molecular orbitals, energy and inter-molecular interaction are carried out for organic free radicals. The dependence on inter-molecular distance and on the angular of rotation of molecules is discussed in H_2NO radical.[14] In the present results ($P < 8$ kbar), the ratio of the exchange interactions, $J(P)/J(P_0)$, is about 0.6 at P=7 kbar. The ratio of change in the inter-molecular distance and the rotational angle among the molecules in the present pressurized system is expected about $\Delta r/r < 1$ % and $\Delta\theta/\theta < 1$ % at most, respectively. The change of J expected from the change of r or θ is too small to explain the experimental value from this theory only. We may have to consider some other mechanism for ferromagnetism of organic radicals, which is sensitive to small deformation of atomic configuration.

CONCLUSION

The magnetic properties of β phase p-NPNN are investigated by the simultaneous observation of heat capacity and ac-susceptibility under hydrostatic pressures in external magnetic fields. The reduction of the Curie temperature under pressures is first found in this genuine organic ferromagnet. The mechanism of ferromagnetic interaction is discussed on the pressure effect. The pressure dependence of the Curie temperature is explained by assuming that the net ferromagnetic coupling is given by competition among ferro- and antiferro-magnetic interactions. The two-dimensional behavior (*ac*-plane) appearing under high pressure suggests that the ferromagnetism in β-phase *p*-NPNN is due to the cooperation of intra- and inter-layer exchange interactions, in which the latter is more sensitively reduced with pressure. The experiment at higher pressures, especially around at P=20 kbar where $T_c(P)$ is expected to be zero, is interesting and being undertaken.

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