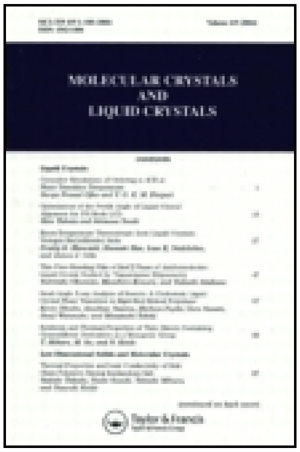

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Magnetic Properties of 1,5-Dimethyl-6-Oxoverdazyl Radical Crystals. Observation of a Spin-Peierls Transition in 3-(4- CYANOPHENYL)-1,5-DIMETHYL-6-OXOVERDAZYL RADICAL, p-CyDOV

Kazuo Mukai [a] , Naoki Wada [a] , Javad B. Jamali [b] , Norio Achiwa [b] , Yasuo Narumi [c] , Koichi Kindo [c] , Tatsuo Kobayashi [c] & Kiichi Amaya [d]

[a] Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama, 790-77

[b] Department of Physics, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, 812

[c] Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka, 560

[d] Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560, Japan

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MAGNETIC PROPERTIES OF 1,5-DIMETHYL-6-OXOVERDAZYL RADICAL CRYSTALS. OBSERVATION OF A SPIN-PEIERLS TRANSITION IN 3-(4- CYANOPHENYL)-1,5-DIMETHYL-6-OXOVERDAZYL RADICAL, p-CyDOV

KAZUO MUKAI,[a] NAOKI WADA,[a] JAVAD B. JAMALI,[b] NORIO ACHIWA,[b] YASUO NARUMI,[c] KOICHI KINDO,[c] TATSUO KOBAYASHI,[c] and KIICHI AMAYA[d]
[a]Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790-77, [b]Department of Physics, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812, [c]Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560, [d]Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract Magnetic susceptibilities of 5 kinds of 3-(4-R-phenyl)-1,5-dimethyl-6-oxoverdazyl radicals (PDOV (R=H), p-MDOV (R=CH_3O), p-MeDOV (R=CH_3), p-CyDOV (R=CN), and p-NDOV (R=NO_2)) have been measured in the temperature range of 4.2-300 K. The susceptibilities of PDOV, p-MDOV, and p-MeDOV can be explained by an antiferromagnetic Heisenberg alternating chain model. The susceptibility of p-CyDOV shows a broad maximum at 54 K, and decreases abruptly at 15 K, suggesting a spin-Peierls transition. High-field magnetization data (H = 0 to 35 T) which provide a clear evidence for a spin-Peierls transition were reported. The magnetic susceptibilities of diluted crystal, $(p\text{-CyDOV})_{1-x}(p\text{-CyDOV-H})_x$ (x = 0 ~ 0.10), were measured to study the effects of nonmagnetic impurities, p-CyDOV-H (amine precursor of p-CyDOV), on the spin-Peierls transition. The transition temperature reduced rapidly upon p-CyDOV-H substitution and the spin-Peierls state disappeared around x = 0.07.

INTRODUCTION

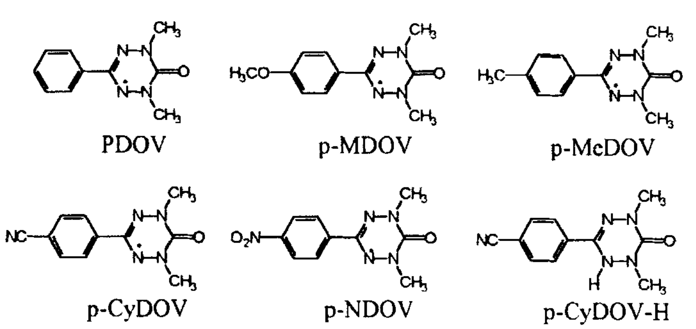
Spin-Peierls (SP) transition is well known as one of the most interesting magnetic behavior observed for organic compound. The SP transition occurs when a system of uniform antiferromagnetic (AFM) Heisenberg linear chains undergoes a transformation to a system of dimerized or alternating AFM linear chains.[1-3] The most striking feature in SP transition is that the susceptibilities exponentially drop to small constant values below the transition temperature (T_{sp}). Such a magnetic behavior was observed for several ionic radical salts, such as TTF-CuBDT[1,2] and MEM- $(TCNQ)_2$,[3] and recently for an inorganic compound $CuGeO_3$.[4] However, the examples of SP transition compound reported are very limited; it is only six as far as we know.

In the present work, we studied the magnetic property of five kinds of 3-(4-R-phenyl)-1,5-dimethyl-6-oxoverdazyl radicals, i.e. PDOV, p-MDOV, p-MeDOV, p-CyDOV, and p-NDOV (see Fig. 1).[5] Strong AFM intermolecular exchange interactions were observed for these verdazyl radicals. Especially, the magnetic susceptibility of p-CyDOV radical crystal exhibited the characteristic properties of the spin-Peierls transition. To our knowledge, this is the first example of SP transition compound found for a genuine organic non-ionic radical crystal. The magnetic susceptibilities of diluted p-CyDOV crystal, $(\text{p-CyDOV})_{1-x}(\text{p-CyDOV-H})_x$ ($x=0 \sim 0.10$), were measured to study the effects of nonmagnetic impurities, p-CyDOV-H (amine precursor of p-CyDOV), on the SP transition.

EXPERIMENTAL

PDOV, p-MDOV, p-MeDOV, p-CyDOV, and p-NDOV radicals and p-CyDOV-H were prepared according to the method of Neugebauer et al.[6,7] The powder samples of diluted p-CyDOV crystal, $(\text{p-CyDOV})_{1-x}(\text{p-CyDOV-H})_x$ ($x = 0.01$, 0.03, 0.05, 0.07, and 0.10), were obtained by the following procedures: the p-CyDOV and p-CyDOV-H were dissolved into CH_2Cl_2 in the round-bottomed flask in the ratio of 1-x to x at 20°C. The CH_2Cl_2 solvent was slowly evaporated using rotary evaporator. This flask was connected to a vacuum line (5×10^{-3} Torr) for two hours to remove the CH_2Cl_2 solvent completely.

The paramagnetic susceptibility was measured in the temperature range of 4.2-300 K by a SQUID magnetometer. The susceptibilities of verdazyl radicals have been corrected for the diamagnetic contribution of χ_{dia} calculated by Pascal's method. Magnetization (M) was obtained at 4.2 K as a function of magnetic field (H) in pulsed magnetic fields up to 35 T with a pulse duration of about 0.4 msec at the Research Center for Materials Science at Extreme Conditions, Osaka University.[8]


PDOV p-MDOV p-McDOV

p-CyDOV p-NDOV p-CyDOV-H

FIGURE 1 Molecular structures of PDOV, p-MDOV, p-MeDOV, p-CyDOV, p-NDOV, and p-CyDOV-H.

RESULTS AND DISCUSSION

Magnetic Susceptibilities of PDOV, p-MDOV, p-MeDOV, and p-NDOV

The magnetic susceptibility, χ_M, obtained for p-MDOV is shown in Fig. 2 as a function of the temperature. The susceptibility of p-MDOV shows a broad maximum at 33 ± 1 K. The small increase in the susceptibility observed at low temperature will be attributable to isolated monoradicals. Impurity radical concentration calculated from the small increase in susceptibility is only 0.5% for p-MDOV. Similar behavior was observed for the magnetic susceptibility of PDOV radical.

The measured susceptibilities of PDOV and p-MDOV were compared with theoretical predictions based on Heisenberg exchange-coupled alternating linear chains.[9,10] The corresponding spin Hamiltonian is given by

$$H = -2J_1\sum_{i=1}^{N/2} S_{2i}S_{2i+1} - 2J_2\sum_{i=1}^{N/2} S_{2i-1}S_{2i} \qquad (1)$$

where J_1 and J_2 are the nearest-neighbor exchange integrals. Negative values of J_1 and J_2 corresponding to AFM coupling are appropriate to the free radicals considered here. α ($= J_2 / J_1$) is a parameter which conveniently indicates the degree of alternation and $\alpha = 1$ corresponds to the uniform limit, that is, a nonalternating antiferromagnetic chain. $\alpha = 0$ corresponds to an isolated dimer (spin-pair) system and in this case the susceptibility should be interpreted by the singlet-triplet equilibrium model.

In Fig. 2, the corrected susceptibility-temperature data (open circles) for p-MDOV are given along with the theoretical curves for $\alpha = 0.4$ and 0.6.[10] The "best fit", the $\alpha = 0.5$ curve (not shown in Fig. 2), corresponds to $2J_1/k = -55$ K and $2J_2/k = -27$ K. Similarly, the magnetic susceptibilities of PDOV were analyzed. The values of $2J_1$, $2J_2$ and α obtained are summarized in Table I.

The magnetic susceptibility, χ_M, obtained for p-MeDOV radical also shows a broad maximum at $T_{max} = 19 \pm 1$ K. However, in the case of p-MeDOV radical, the theoretical curve calculated from the 1D AFM Heisenberg model ($\alpha = 1$) gives an excellent fit to the observed one. The exchange integral ($2J/k$) was estimated to be -30 K, using the relation $kT_{max}/J = 1.282$.[9] On the other hand, the susceptibility of p-NDOV follows the Curie-Weiss law with a Curie constant of 0.350 K emu/mol and a Weiss constant of -2.0 ± 0.2 K in the temperature region above 4.2 K. 6-Oxo- and 6-thioxo-verdazyl radicals have comparatively small molecular weight and a delocalized π-electron system, and thus the strong intermolecular exchange interaction ($2J$) between neighboring radical molecules has been expected.[11,12] In fact, the AFM exchange interactions ($2|J_1|/k = 83$, 55 and 30 K) observed in solids PDOV, p-MDOV and p-MeDOV, respectively, are extraordinarily large, as listed in Table I.

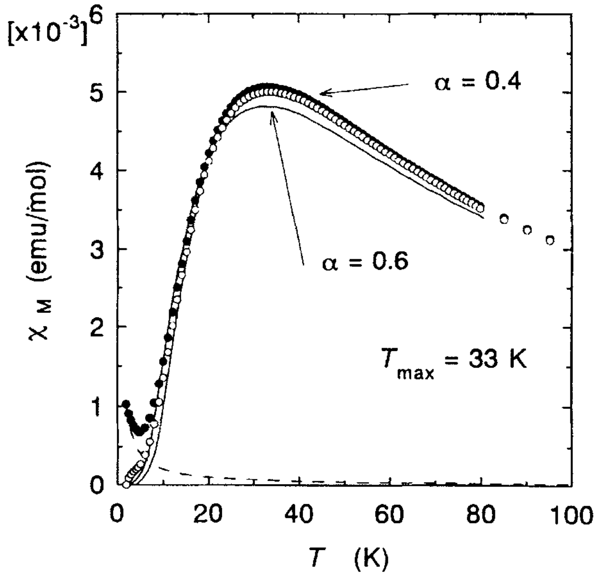


FIGURE 2 Paramagnetic molar susceptibility (χ_M, ●) of p-MDOV radical. The open circle (O) curve gives the difference between experimental and impurity curves. The solid line curves are theoretical fits corresponding to the indicated values of α = 0.4 and 0.6.

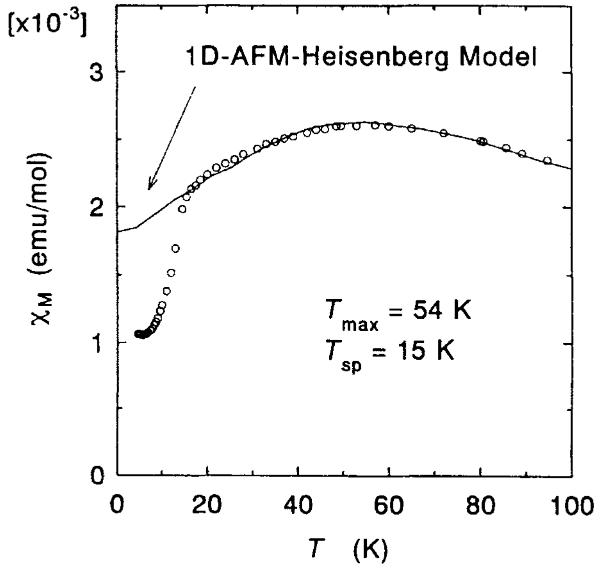


FIGURE 3 Paramagnetic molar susceptibility (χ_M) of p-CyDOV radical (4.2-100 K). The solid line curve is the theoretical susceptibility calculated with the 1D AFM Heisenberg model.

Observation of a spin-Peierls transition in p-CyDOV

The molar susceptibility, χ_M, of p-CyDOV is shown in Fig. 3 as a function of the temperature. The susceptibility of p-CyDOV also shows a broad maximum at 54 ± 2 K. However, at 15 K, the susceptibility decreases suddenly and shows a minimum at 5.6 K. Such a magnetic behavior cannot be explained by an 1D AFM Heisenberg alternating chain model. Our calculations for several large α values fail to reproduce the sharpness of the decrease in χ_M at 15 K.[5,10] The temperature dependence of magnetic susceptibility in p-CyDOV radical crystal may be explained by a SP transition.[1-4]

The spin-Peierls transition occurs when a system of uniform AFM Heisenberg linear chains undergoes a transformation to a system of dimerized or alternating AFM linear chains.[1-3] This dimerization is mainly caused by the spin-phonon coupling between the 1D spin system and the three-dimensional (3D) phonon system. Below the transition temperature (T_{sp}), the ground state is spin singlet (nonmagnetic), and a finite energy gap opens in the excitation spectrum. In such a case, the susceptibilities exponentially drop to small constant values below T_{sp}.

In fact, the magnetic susceptibility of p-CyDOV above 15 K can be well described by the 1D Heisenberg linear chain model ($\alpha = 1$) with AFM exchange of $2J/k = -84$ K between neighboring spins, as shown in Fig. 3. The small increase in the susceptibility below 5.6 K was observed which will be attributable to isolated monoradicals and/or broken-chain effects.[9] The residual paramagnetic radical concentration, calculated from the susceptibility at 4.2 K and assuming validity of the Curie law, is only 1.3%.

The field dependence of the magnetization (M) of polycrystalline p-CyDOV has been measured. The measurements were performed at 4.2 K for increasing and decreasing mode of pulsed magnetic field (H) up to 35 T. M and dM/dH vs. H plots are shown in Fig. 4. We observed a characteristic nonlinearity of magnetization, which means the transitions from dimerized to the other magnetic phase.[13-17] The hysteresis of magnetization for increasing and decreasing H was observed. Critical field (H_c) which is defined as the field of the peak position in the dM/dH curve is indicated by an arrow in Fig. 4 (b). The values of H_c^{up} and H_c^{down} measured in increasing and decreasing field are 25 T and 11 T, respectively. The former is 14 T larger than the latter. Thus the transition is of first order. Similar nonlinearity and hysteresis of magnetization have also been reported in organic and inorganic spin-Peierls materials, such as TTF-CuBDT,[13,14] MEM-(TCNQ)$_2$[15] and CuGeO$_3$.[17] Such a magnetic behavior is considered to be common features of the spin-Peierls system.

The susceptibility data of p-CyDOV were analyzed following the method of Bray et al.[1,2] Above the SP transition temperature (T_{sp}), the chains are uniform, and χ_M is fit by

TABLE I Magnetic properties of 3-(4-R-phenyl)-1,5-dimethyl-6-oxoverdazyl radicals.

Radical	T_{max}	Exchange Interaction	Alternation Parameter
PDOV	50 ± 1 K	$2J_1/k$ = -83 K $2J_2/k$ = -42 K	α =0.5
p-MDOV	33 ± 1K	$2J_1/k$ = -55 K $2J_2/k$ = -27 K	α =0.5
p-MeDOV	19 ± 1K	$2J/k$ = -29 K	α =1.0
p-CyDOV	54 ± 2 K	$2J/k$ = -84 K Spin Peierls Transition at T_{SP} = 15 K	α =1.0
p-NDOV	——	θ = -(2.0 ± 0.2) K	Curie-Weiss

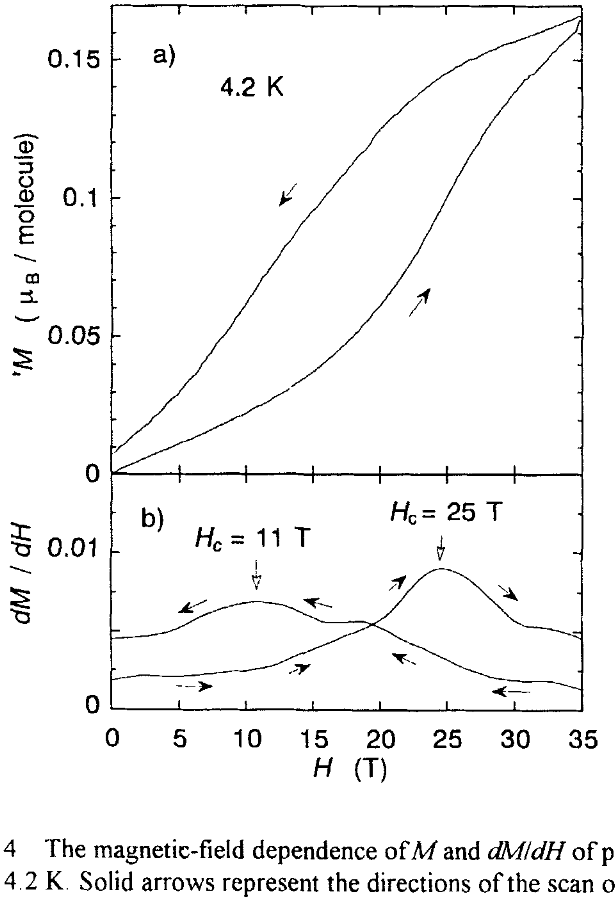


FIGURE 4 The magnetic-field dependence of M and dM/dH of p-CyDOV crystal at 4.2 K. Solid arrows represent the directions of the scan of the magnetic-field.

the 1D AFM Heisenberg model. Below T_{sp}, the lattice progressively dimerizes, and two unequal and alternating J's are produced,

$$2J_{1,2}(T) = 2J[1+\delta(T)] \qquad (2)$$

The BCS theory predicts a relation (3).

$$\Delta(0)/T_{sp} = 1.76 \qquad (3)$$

where $\Delta(0)$ is $\Delta(T)$ at $T = 0$, and $\Delta(T)$ is the magnetic energy gap. $\Delta(T)$ follows a BCS-type temperature dependence. According to the mean-field theory of Pytte,[18] the relationship between $\delta(T)$ and the magnetic energy gap $\Delta(T)$ at temperature T is expressed as

$$\delta(T) = \Delta(T)/2p|J| \qquad (4)$$

where the value of p is 1.637. The spin-lattice system dimerizes (in zero field) at a temperature T_{sp} given by[1,2]

$$T_{sp} = 4.56p|J|\exp(-1/\lambda) \qquad (5)$$

where λ is the spin-lattice coupling constant. Substituting $T_{sp} = 15$ K and $2|J|/k = 84$ K from the high-temperature data into the above equations, we get

$$\Delta(0) = 26\text{ K}; \quad \delta(0) = 0.192; \quad \lambda = 0.33; \quad 2|J_1|/k = 101\text{ K}, \quad \alpha = 0.68. \qquad (6)$$

In the present work, we found that the magnetic susceptibility of p-CyDOV radical crystal exhibits the characteristic properties of the spin-Peierls transition. To our knowledge, this is the first example of spin-Peierls transition found for a genuine organic non-ionic radical crystal. The above values of $\Delta(0)$, $\delta(0)$ and λ observed for p-CyDOV (26 K, 0.192, 0.33) are close to corresponding those of ionic radical salts, such as TTF-CuBDT (21 K, 0.167, 0.32)[1,2] and MEM-(TCNQ)$_2$ (28 K, 0.164, 0.32),[3] and inorganic compound, CuGeO$_3$ (24 K, 0.167, 0.20),[4] respectively. The similarities in these values are very interesting, although the reason is not clear at present.

Effect of nonmagnetic impurities on the spin-Peierls transition of p-CyDOV

The magnetic susceptibilities of diluted p-CyDOV crystal, (p-CyDOV)$_{1-x}$(p-CyDOV-H)$_x$, were measured to study the effects of nonmagnetic impurities on the SP transition.

To study the effects of impurities, amine precursor of p-CyDOV (p-CyDOV-H) was chosen as the best dopant. First, p-CyDOV-H is expected to be substituted easily for p-CyDOV, because van der Waals radius of p-CyDOV-H is thought to be similar to that of p-CyDOV. Second, p-CyDOV-H molecules are nonmagnetic; that is, the magnetic susceptibility is determined by the p-CyDOV spins (S = 1/2).

The temperature dependence of the magnetic susceptibility per 1-mol p-CyDOV radical, χ_M, of (p-CyDOV)$_{1-x}$(p-CyDOV-H)$_x$ is shown in Fig. 5. The susceptibility of each diluted crystal increases monotonically with decreasing temperature below 300 K and shows a broad maximum at the temperature of T_{max}. The value of T_{max} decreases as the concentration x of p-CyDOV-H increases; T_{max}'s are 54 K for x = 0, 54 K for 0.01, 53 K for 0.03, 52 K for 0.05, 45 K for 0.07, and 42 K for 0.10. The SP transition indicated by a drop of χ_M near 12 ~ 15 K was observed in the samples with $x \leq 0.05$. The value of T_{sp} defined as the onset temperature of the drop reduces with substitution of p-CyDOV-H and disappears around x = 0.07. The x dependence of T_{sp} is shown in Fig. 6. The value of $T_{sp}(x)/T_{sp}(0)$ linearly reduces up to $x \leq 0.05$, which is expressed as 1 - 4.2x. This means that the value of T_{sp} rapidly decreases by a small amount of p-CyDOV-H substitution. As described above, the strong x dependence was observed in χ_M below 80 K. The result indicates that p-CyDOV-H homogeneously distributes in the AFM chains in each sample.

The first report of the effects of impurities on the spin-Peierls system was performed for CuGeO$_3$ system by Hase et al.[19] They synthesized polycrystalline Cu$_{1-x}$Zn$_x$GeO$_3$ and measured the magnetic susceptibilities to study the effects of nonmagnetic Zn^{2+} impurities on the spin-Peierls system. The SP transition temperature (T_{sp}) linearly reduces, following the equation $T_{sp}(x)/T_{sp}(0) = 1 - 13.7x$, and the SP state collapses around x = 0.03. Further, they discovered another phase transition in the samples with $0.02 \leq x \leq 0.08$ below 4.5 K. At beginning, it was reported that this phase transition is a spin-glass transition. However, it is revealed that an AFM order occurs instead of a spin-glass state by the measurements of magnetic susceptibility of single crystals[20] and specific heat of powder sample.[21] The appearance of AFM transition was explained as follows; the spin-Peierls order in CuGeO$_3$ is destroyed by Zn doping. The disappearance of the SP order leads to a development of the 1D AFM correlation in each chain, which is considered to play an important role in the appearance of AFM transition at low temperatures (T_N = 2 ~ 4.5 K) for the samples with x = 0.02 ~ 0.08. Theoretically, it has been suggested that Zn doping results in a collapse of the spin gap and the existence of a gapless SP state for Zn concentration $x \geq 0.03$.[22]

As described above, x dependence of T_{sp} and magnetic behavior of diluted p-CyDOV crystal is similar to that of Zn doped CuGeO$_3$ crystal. We could not observe AFM transition for diluted p-CyDOV crystal at low temperature. However, in the present work, the magnetic susceptibility measurements were performed at the temperature above 4.2 K. Therefore, at lower temperature, we can expect AFM transition for diluted p-CyDOV crystal. The measurements of magnetic susceptibility at lower temperatures below 4.2 K are now in progress in our laboratory.

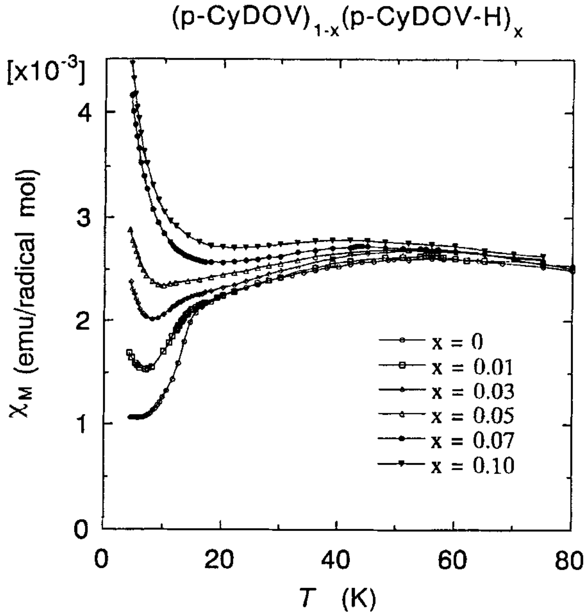


FIGURE 5 Paramagnetic molar susceptibility (χ_M) of diluted p-CyDOV crystal, $(p\text{-CyDOV})_{1-x}(p\text{-CyDOV-H})_x$ (x = 0, 0.01, 0.03, 0.05, 0.07, and 0.10), (4.2-80 K).

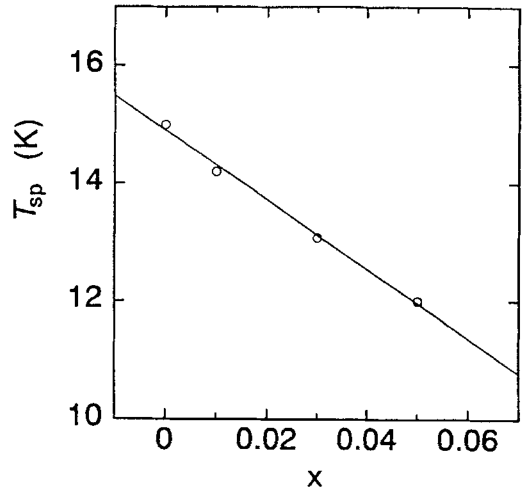


FIGURE 6 The x dependence of spin-Peierls transition temperature (T_{sp}) of diluted crystal $(p\text{-CyDOV})_{1-x}(p\text{-CyDOV-H})_x$.

ACKNOWLEDGMENTS

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