Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Properties of Pseudo-1D S=1/2 AF-F Alternating Chains under Magnetic Fields

Satoshi Kokado [a] & Naoshi Suzuki [a b]

[a] Division of Materials Physics, Department of Physical Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka, 560-8531, Japan

[b] "Research" Area CREST, Japan Science and Technology Corporation

Version of record first published: 24 Sep 2006

To cite this article: Satoshi Kokado & Naoshi Suzuki (1999): Magnetic Properties of Pseudo-1D S=1/2 AF-F Alternating Chains under Magnetic Fields, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 153-162

To link to this article: http://dx.doi.org/10.1080/10587259908028859

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 153-162
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Properties of Pseudo-1D S=1/2 AF–F Alternating Chains under Magnetic Fields

SATOSHI KOKADO[a] and NAOSHI SUZUKI[ab]

[a]*Division of Materials Physics, Department of Physical Science, Graduate School of Engineering Science, Osaka University, 1–3 Machikaneyama-cho, Toyonaka, Osaka 560–8531, Japan and* [b]*"Research" Area CREST, Japan Science and Technology Corporation*

Magnetic properties of pseudo-1D S=1/2 AF–F exchange alternating systems under magnetic fields are investigated by the combined method of pair dynamical correlated-effective-field approximation (Pair-DCEFA) and mean field approximation. The results are applied to pseudo-1D S=1/2 AF-F alternating chain $(CH_3)_2CHNH_3CuCl_3$, and the exchange integrals of this system have been estimated as follows: J_{AF}=–47.0 K, J_F=94.0 K for intrachain couplings and $|J'|$=0.125 K for coupling between the adjacent chains. Further, it is shown that the observed nuclear spin-lattice relaxation time can be explained fairly well on the basis of the susceptibility calculated by the Pair-DCEFA.

Keywords: S=1/2 AF–F alternating chain; Pair-DCEFA; effect of inter-chain coupling; nuclear spin-lattice relaxation time

INTRODUCTION

Magnetic properties of one-dimensional (1D) $S=1/2$ antiferromagnetic-ferromagnetic (AF–F) alternating chains, which have a gap between the singlet ground state and triplet excited states, have been studied extensively both experimentally[1,2] and theoretically[3,4]. Recently, magnetic phase transitions have been observed in a couple of organic pseudo-1D $S=1/2$ AF–F alternating chains, and the importance of interchain couplings has been suggested. We have previously studied the effects of interchain couplings in these organic systems by using the

combined method in which the intrachain and interchain couplings are treated by the pair dynamical correlated-effective-field approximation (Pair-DCEFA) and the mean field approximation (MFA), respectively[3]. This Pair-DCEFA has advantages of being able to calculate easily the q- and ω-dependent susceptibility and its temperature dependence and also being applicable to three dimensional systems without difficulty.

Quite recently, by specific heat measurements Manaka *et al.*[5] have observed magnetic phase transitions under magnetic fields in a pseudo-1D S=1/2 AF F alternating chain $(CH_3)_2CHNH_3CuCl_3$ which does not order in zero field. In this paper, we extend the combined method[3] of Pair-DCEFA and MFA to the case under magnetic fields, and investigate the magnetic phase transition observed in $(CH_3)_2CHNH_3CuCl_3$. We also analyze by Pair-DCEFA the temperature dependence of nuclear spin-lattice relaxation time T_1 of this system, which has been measured by T. Kubo *et al.*[6].

PAIR-DCEFA UNDER MAGNETIC FIELDS

We first consider a single S=1/2 AF F alternating chain under magnetic fields along the z-axis. The relevant Hamiltonian is expressed as,

$$\mathcal{H} = -\sum_i \left[J_1 \boldsymbol{S}_{i,1} \cdot \boldsymbol{S}_{i,2} + J_2 \boldsymbol{S}_{i-1,2} \cdot \boldsymbol{S}_{i,1} - g\mu_B H (S^z_{i,1} + S^z_{i,2}) \right]. \quad (1)$$

Here we have assumed the nearest neighbor (n.n.) exchange couplings J_1 (< 0) and J_2 (> 0). H represents the strength of the magnetic field and $\boldsymbol{S}_{i,\mu}$ denotes the spin μ in the unit cell i with μ being 1 or 2. Within the framework of Pair-DCEFA[3] the first and the third terms in Eq.(1), *i.e.* the antiferromagnetic coupling spin-pair, is treated exactly, and for the second term $J_2 \boldsymbol{S}_{i-1,2} \cdot \boldsymbol{S}_{i,1}$ in Eq.(1), *i.e.* the interaction between the pairs, the following decoupling is adopted:

$$J_2 \left[\boldsymbol{S}_{i-1,2} \cdot (\langle \boldsymbol{S}_{i,1} \rangle - \alpha \langle \boldsymbol{S}_{i-1,2} \rangle) + \boldsymbol{S}_{i,1} \cdot (\langle \boldsymbol{S}_{i-1,2} \rangle - \alpha \langle \boldsymbol{S}_{i,1} \rangle) \right], \quad (2)$$

where $\langle \boldsymbol{S} \rangle$ denotes the field-induced spin moment and α represents a correlation parameter which should be determined self-consistently[7].

The effective spin-pair Hamiltonian for the unit cell i is now given by

$$\mathcal{H}_i^{\text{eff}} = -J_1 \boldsymbol{S}_{i,1} \cdot \boldsymbol{S}_{i,2} + H'(S^z_{i,1} + S^z_{i,2}), \quad (3)$$

with

$$H' = g\mu_B H - J_2 \langle S^z \rangle (1 - \alpha),$$

where $\langle S^z \rangle$ ($\equiv \langle S^z_{i,1} \rangle = \langle S^z_{i,2} \rangle$) denotes the site-independent spin moment induced by the uniform external filed. By using the eigenvalues and eigenstates of the above effective Hamiltonian and in the spirit of the DCEFA[7] we can calculate the transverse susceptibility tensor $\tilde{\chi}^{+-}(q,\omega)$ of the whole system. The final expression of $\tilde{\chi}^{+-}(q,\omega)$ is written as follows:

$$\begin{pmatrix} \chi^{+-}_{11}(q,\omega) & \chi^{+-}_{12}(q,\omega) \\ \chi^{+-}_{21}(q,\omega) & \chi^{+-}_{22}(q,\omega) \end{pmatrix} = (hh^* - kk^*)^{-1} \times \begin{pmatrix} h^*\phi^{+-}_{11} - k\phi^{+-}_{12}\mathrm{e}^{-\mathrm{i}qc} & h^*\phi^{+-}_{12}\mathrm{e}^{\mathrm{i}qc} - k\phi^{+-}_{11} \\ -k^*\phi^{+-}_{11} + h\phi^{+-}_{12}\mathrm{e}^{-\mathrm{i}qc} & -k^*\phi^{+-}_{12}\mathrm{e}^{\mathrm{i}qc} + h\phi^{+-}_{11} \end{pmatrix}, \tag{4}$$

with

$$h = 1 + \frac{1}{2}J_2\left(\alpha\phi^{+-}_{11} - \phi^{+-}_{12}\mathrm{e}^{\mathrm{i}q(c+c')}\right),$$

$$k = -\frac{1}{2}J_2\left(\phi^{+-}_{11}\mathrm{e}^{-\mathrm{i}qc'} - \alpha\phi^{+-}_{12}\mathrm{e}^{\mathrm{i}qc}\right),$$

$$\phi^{+-}_{11} = \frac{1}{2}\left(\frac{\rho_\mathrm{s} - \rho_{\mathrm{t},1}}{\omega - J_1 + H'} + \frac{\rho_{\mathrm{t},-1} - \rho_\mathrm{s}}{\omega + J_1 + H'} + \frac{\rho_{\mathrm{t},-1} - \rho_{\mathrm{t},1}}{\omega + H'}\right),$$

$$\phi^{+-}_{12} = \frac{1}{2}\left(\frac{\rho_{\mathrm{t},1} - \rho_\mathrm{s}}{\omega - J_1 + H'} + \frac{\rho_\mathrm{s} - \rho_{\mathrm{t},-1}}{\omega + J_1 + H'} + \frac{\rho_{\mathrm{t},-1} - \rho_{\mathrm{t},1}}{\omega + H'}\right),$$

where c and c' represent the bond length for AF and F interactions, respectively, and $\rho_\mathrm{s} = \mathrm{e}^{-\beta J_1}/Z$ and $\rho_{\mathrm{t},m} = \mathrm{e}^{-\beta H' m}/Z$ (m=−1, 0, 1) with $Z = \mathrm{e}^{-\beta J_1} + \mathrm{e}^{\beta H'} + 1 + \mathrm{e}^{-\beta H'}$ and $\beta = 1/k_\mathrm{B}T$.

In order to determine $\langle S^z \rangle$ and α simultaneously, we impose the following self-consistency conditions:

$$\langle S^z \rangle = \mathrm{Tr}[S^z_{i1}\exp(-\beta\mathcal{H}^{\mathrm{eff}}_i)]/\mathrm{Tr}[\exp(-\beta\mathcal{H}^{\mathrm{eff}}_i)], \tag{5}$$

$$\langle\{S^+_1, S^-_1\}\rangle = \frac{2}{N}\sum_q \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \coth(\frac{\beta\omega}{2})\,\mathrm{Im}\chi^{+-}_{11}(q,\omega + \mathrm{i}s), \tag{6}$$

where N denotes the total number of spins and $\langle\{S^+_1, S^-_1\}\rangle \equiv \langle S^+_1 S^-_1 + S^-_1 S^+_1\rangle = 2\{S(S+1) - \langle(S^z)^2\rangle\}$ represents the on-site spin correlation calculated by using the effective spin-pair Hamiltonian Eq.(3). Equation (5) represents the usual self-consistency condition for $\langle S^z \rangle$. Equation (6) is required from the fluctuation-dissipation theorem, and its implication is that the on-site spin correlation calculated from the dynamical susceptibility (the right-hand side of Eq.(6)) should be equal to that calculated from the effective spin-pair Hamiltonian.

Equation (5) is expressed more explicitly as

$$\langle S^z \rangle = \frac{1}{2}(\rho_{\mathrm{t},1} - \rho_{\mathrm{t},-1}). \tag{7}$$

The actual calculational procedure of the righthand side of Eq.(6) is as follows. We first solve $hh^*-kk^*=0$ to obtain poles $\omega_i(q)$ $(i=1\sim3)$ of $\chi_{11}^{+-}(q,\omega)$. Then, by using these $\omega_i(q)$, $\chi_{11}^{+-}(q,\omega)$ is transformed as

$$\chi_{11}^{+-}(q,\omega)=\sum_{i=1}^{3}\frac{\gamma_i(q)}{\omega-\omega_i(q)}, \tag{8}$$

with

$$\gamma_l(q)=G(q,\omega_l(q))\prod_{i=1}^{3}(\omega_l(q)+x_i)/\prod_{\substack{m,n=1\\(m\neq n)}}^{3}(\omega_m(q)-\omega_n(q)), \tag{9}$$

where

$$G(q,\omega)=h^*\phi_{11}^{+-}-k\phi_{12}^{+-}e^{-iqc},$$
$$x_1=-J_1+H',\quad x_2=J_1+H',\quad x_3=H'.$$

Inserting Eq.(8) into the righthand side of Eq.(6) we can rewrite Eq.(6) in the following form:

$$\langle(S^z)^2\rangle-\frac{3}{4}=\frac{1}{N}\sum_q\left[\sum_{i=1}^{3}\gamma_i(q)\coth(\beta\omega_i(q)/2)\right]. \tag{10}$$

From Eq.(7) and Eq.(10), $\langle S^z\rangle$ and α are determined self-consistently.

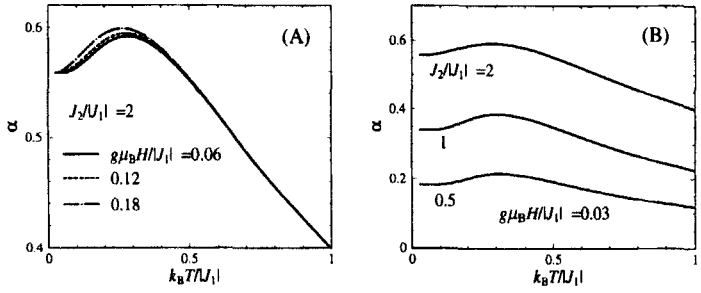

FIGURE 1 (A) The temperature dependence of the correlation parameter α for $g\mu_BH/|J_1|$=0.06, 0.12, 0.18 and $J_2/|J_1|$=2. (B) The temperature dependence of the correlation parameter α for $J_2/|J_1|$=0.5, 1, 2 and $g\mu_BH/|J_1|$=0.03.

In Figures 1(A) and (B) we show examples of temperature and magnetic-field dependencies of α. As seen from Figure 1(A), with decreasing temperature from high temperatures, α increases monotonously, takes a maximum around the temperature corresponding to about $0.3|J_1|$, and then approaches to a finite value toward T=0 K. Further, α becomes large when H increases. Figure 1(B) shows that the smaller the value of $J_2/|J_1|$ takes, the smaller α becomes. Most of these characteristic behaviors of α can be understood by considering that spin correlation between the spin pairs become strong for large J_2 and also they develop with decreasing temperature or increasing magnetic fields. However, the physical origin of the maximum of α as a function of temperature is not clear at present. As to the temperature and magnetic-field dependencies of $\langle S^z \rangle$ we simply note that it takes rather small values in the whole temperature range for magnetic fields smaller than the gap energy. Once $\langle S^z \rangle$ and α are determined, the dynamical susceptibility tensor $\tilde{\chi}^{+-}(q,\omega)$ is fixed and we can calculate various physical quantities from $\tilde{\chi}^{+-}(q,\omega)$[3].

Effect of Interchain Coupling

Recently, magnetic phase transitions under magnetic fields have been observed in an organic pseudo-1D S=1/2 AF F exchange alternating chain $(CH_3)_2CHNH_3CuCl_3$[5] which does not order at zero field. Motivated by this experimental results, we have investigated the effect of interchain coupling on the magnetic phase transition under magnetic fields. For this purpose we have adopted the combined method[3] of Pair-DCEFA and the mean-field approximation (MFA), that is, we use Pair-DCEFA for intrachain coupling and MFA for interchain coupling. According to this method the generalized susceptibility for the whole three dimensional system can be obtained in terms of the interchain coupling and the susceptibility of a single chain obtained by Pair-DCEFA. Occurrence of phase transitions is generally determined from the condition of divergence of the generalized susceptibility and in the present case the condition is expressed as[3],

$$[(1/|2J'|) - \lambda_+(q,H,T)][(1/|2J'|) - \lambda_-(q,H,T)] = 0, \tag{11}$$

where J' denotes the n.n. interchain exchange integral (the number of n.n. spins is assumed to be four), and $\lambda_\pm(q,H,T)$ denote $\lambda_{11}^{+-}(q,\omega) \pm |\lambda_{12}^{+-}(q,\omega)|$ which are the two eigenvalues of the static susceptibility tensor $\tilde{\chi}^{+-}(q,0)$ of a single chain. It is noted here that $\lambda_-(0,0,T)$ corresponds to the uniform static susceptibility of a single chain. In Figure 2, we show as an example q- and temperature dependence of $\lambda_+(q,H,T)$ for $J_2/|J_1| = 2$ and $g\mu_B H/|J_1|$=0.03. To be important, for AF F chains $\lambda_+(q,H,T)$ is larger than $\lambda_-(q,H,T)$ for any value of q. Furthermore,

at each temperature for a given field $\chi_+(q,H,T)$ takes the maximum value at $q = \pi$ as a function of q, and this behavior can be explained by considering that the gap has the minimum value at $q=\pi$. It should be also noted that for a given temperature the value of $\chi_+(q,H,T)$ increases with increasing H.

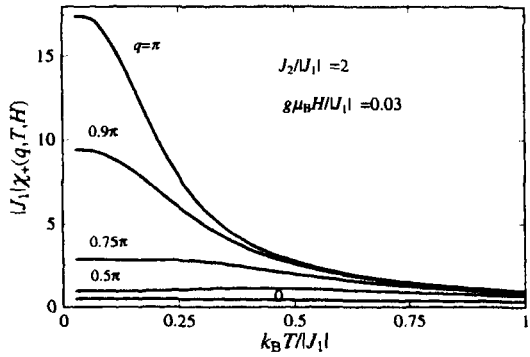

FIGURE 2 The temperature dependence of $\chi_+(q,H,T)$ calculated for several values of q by fixing $J_2/|J_1|$ and $g\mu_B H/|J_1|$ to 2 and 0.03, respectively. The unit of q is $1/(c+c')$.

The actual transition temperature (Néel temperature T_N) is defined as the highest temperature which satisfies the condition (11). Hence, by taking into consideration the characteristic behaviors of $\chi_\pm(q,H,T)$ mentioned above the equation to determine T_N is expressed simply as

$$1/|2J'| - \chi_+(\pi,H,T) = 0. \tag{12}$$

It is easily recognized that T_N is practically determined from the crossing between the curve of $\chi_+(\pi,H,T)$ as a function of T and the straight line corresponding to $1/|2J'|$. Since $\chi_+(\pi,H,T)$ is a decreasing function of T, if $1/|2J'| > \chi_+(\pi,H,0)$ is satisfied, no crossing point is obtained, *i.e.* phase transition does not occur. In particular, if $1/|2J'| > \chi_+(\pi,0,0)$, it means that the system does not order at zero field. Even in that case, the phase transition is expected to occur for finite fields because $\chi_+(\pi,H,0)$ increases with increasing H and hence $1/|2J'| < \chi_+(\pi,H,0)$ may be fulfilled for H larger than some critical value.

In applying the above method to $(CH_3)_2CHNH_3CuCl_3$ we first analyzed by Pair-DCEFA the observed uniform static susceptibility[2] at

temperatures higher than T_N and estimated the intrachain exchange integrals as J_1=−47.0 K and J_2=94.0 K. The observed and the calculated uniform static susceptibilities as functions of temperature are shown in Figure 3(A). Next, by making use of $\chi_+(\pi, T, H)$ calculated with use of g=2.26[2] and the determined J_1 and J_2 we have estimated the magnitude of J' so as to reproduce the observed Néel temperature at H=10.2 T (see Figures 3(B) and (C)). The magnitude of interchain exchange coupling determined in this way is $|J'|$=0.125 K.

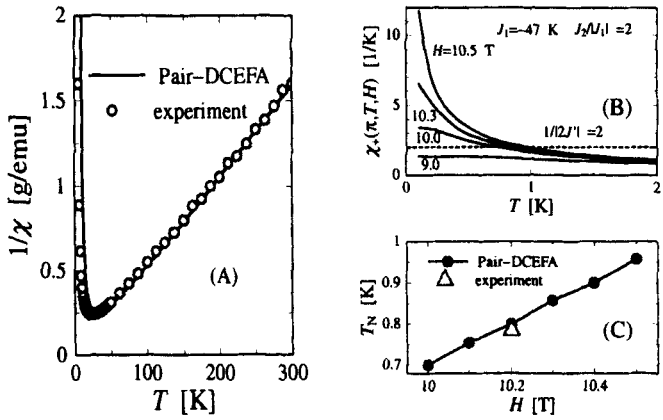

FIGURE 3 (A) The temperature dependence of inverse of the uniform susceptibility of $(CH_3)_2CHNH_3CuCl_3$. The circles denote the experimental data[2] and the full curve represents the theoretical results for a single AF–F chain obtained by Pair-DCEFA with use of J_1=−47.0 K and J_2=94.0 K. (B) The temperature dependence of $\chi_+(\pi, T, H)$ of $(CH_3)_2CHNH_3CuCl_3$ calculated for several values of H. The horizontal dotted line represents $1/|2J'| = 2$. (C) The magnetic-field dependence of T_N. The open triangles denote the experimental data[5] and the closed circles the theoretical results.

Nuclear Spin-Lattice Relaxation Time

Quite recently, T. Kubo *et al.*[6] have measured proton spin-lattice relaxation time T_1 of $(CH_3)_2CHNH_3CuCl_3$ under magnetic fields. According to their results $1/T_1$ shows at a low temperature region a behavior of activate energy type expressed as $\exp[-(\Delta - g\mu_B H)/k_B T]$, but its origin

is not clear. Hence, in this section we try to understand this behavior of $1/T_1$ by performing analysis with use of the susceptibility under magnetic fields obtained by Pair-DCEFA.

The inverse of nuclear spin-lattice relaxation time $1/T_1$ is written approximately as,

$$1/T_1 \propto T \sum_q \sum_{m,n=1}^{2} \left[(1/4) A^{\perp}_{mn}(q) \lambda^{+-}_{mn}(q) + A^{//}_{mn}(q) \lambda^{zz}_{mn}(q) \right], \tag{13}$$

where $A^{l}_{mn}(q)$ (m, n=1 or 2, l=$\perp$ or //) are the coefficients of hyperfine structure which are defined as the Fourier component of the product of two dipole-dipole interaction between electric spin S_i and nuclear spin[8]. Explicitly $A^{l}_{mn}(q)$ are given as follows:

$$A^{\perp}_{mn}(q) = \sum_{i,j} \frac{(1 - 3\cos^2\theta_{p,im})(1 - 3\cos^2\theta_{p,jn}) + 9\sin^2\theta_{p,im}\sin^2\theta_{p,jn}}{r^3_{p,im} r^3_{p,jn}} \times e^{iq(r_{im} - r_{jn})}, \tag{14}$$

$$A^{//}_{mn}(q) = \sum_{i,j} \frac{9\sin\theta_{p,im}\cos\theta_{p,im}\sin\theta_{p,jn}\cos\theta_{p,jn}}{r^3_{p,im} r^3_{p,jn}} e^{iq(r_{im} - r_{jn})}, \tag{15}$$

where r_{im} (r_{jn}) represents m (n) site in ith (jth) unit cell with m (n) being 1 or 2, and $r_{p,im}$ ($r_{p,jn}$) denotes the distance between proton site and r_{im} (r_{jn}). Further, the $\theta_{p,im}$ ($\theta_{p,jn}$) is defined as the angle between the direction of electric spin at r_{im} (r_{jn}) and that of proton spin.

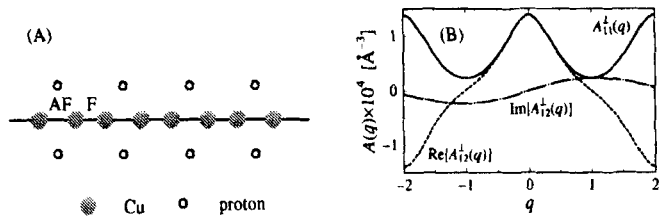

FIGURE 4 (A) The positions of protons in the vicinity of Cu ions in $(CH_3)_2CHNH_3CuCl_3$. (B) The q-dependencies of $A^{\perp}_{11}(q)$, $\mathrm{Re}[A^{\perp}_{12}(q)]$ and $\mathrm{Im}[A^{\perp}_{12}(q)]$ in $(CH_3)_2CHNH_3CuCl_3$ are shown by the solid, dotted and dot-dashed curves, respectively. The unit of q is $\pi/(c + c')$.

In actual calculation of $A^{l}_{mn}(q)$ we have assumed the proton and copper positions as shown in Figure 4(A) and the following distances are used: Cu-Cu [short] =3.417 Å, Cu-Cu [long] =3.506 Å[9], and distance between proton and Cu chain $\sim$ 6.0 Å. In Figure 4(B), q-dependencies of $A^{\perp}_{11}(q)$, $\mathrm{Re}[A^{\perp}_{12}(q)]$ and $\mathrm{Im}[A^{\perp}_{12}(q)]$ are shown by the solid, dotted and dot-dashed curves, respectively. As seen from Figure 4(B) $A^{\perp}_{11}(q)$ and $|\mathrm{Re}[A^{\perp}_{12}(q)]|$ have large values around q=0 and 2π, but they are small around q=π. Further the magnitude of $\mathrm{Im}[A^{\perp}_{12}(q)]$ is rather small compared with those of $A^{\perp}_{11}(q)$ and $\mathrm{Re}[A^{\perp}_{12}(q)]$, and it should be noted also that $A^{//}_{mn}(q)$ (m, n=1 or 2) have quite small magnitude for any value of q. Considering all of these characteristic features of $A^{l}_{mn}(q)$ we adopt the following drastic approximation, namely we take into account only $A^{\perp}_{11}(q)$ and $\mathrm{Re}[A^{\perp}_{12}(q)]$ for q=0 and 2π and neglect all of other $A^{l}_{mn}(q)$. Then $1/T_1$ is expressed simply as,

$$1/T_1 \propto T\{A^{\perp}_{11}(0)\chi^{+-}_{11}(0) + \mathrm{Re}[A^{\perp}_{12}(0)]\mathrm{Re}[\chi^{+-}_{12}(0)] + A^{\perp}_{11}(2\pi)\chi^{+-}_{11}(2\pi) + \mathrm{Re}[A^{\perp}_{12}(2\pi)]\mathrm{Re}[\chi^{+-}_{12}(2\pi)]\}. \quad (16)$$

From this equation we have calculated the temperature dependence of $1/T_1$ at H=3.5 T by using $\chi^{+-}_{11}(q)$ and $\mathrm{Re}[\chi^{+-}_{12}(q)]$ (q=0. 2π) obtained in the previous section. The results are shown in Figure 5 by the full curve. The obtained $1/T_1$ agrees fairly well with the experimental result[6].

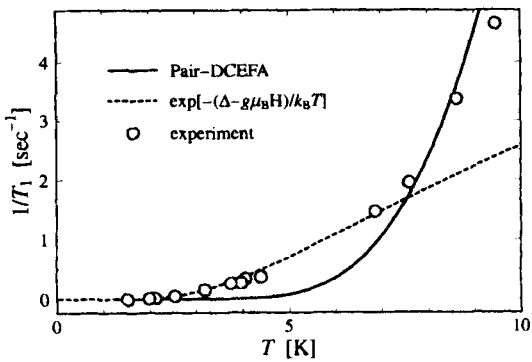

FIGURE 5 The temperature dependence of $1/T_1$ of $(CH_3)_2CHNH_3CuCl_3$ at H=3.5 T. The solid and dotted curves represent the results obtained by using Pair-DCEFA and by assuming the activate energy type, respectively. The circles denote the experimental data[6].

CONCLUSION

By extending Pair-DCEFA to the case under magnetic fields we have investigated the magnetic properties of $S=1/2$ AF–F alternating chains under magnetic fields. We also studied the effects of interchain coupling on the magnetic phase transition under magnetic fields by adopting the combined method of Pair-DCEFA and MFA. Applying the combined method to a pseudo-1D $S=1/2$ AF F chain $(CH_3)_2CHNH_3CuCl_3$ we have evaluated the interchain exchange coupling as well as intrachain exchange coupling. Finally, by using the susceptibilities calculated by Pair-DCEFA we have succeeded to explain the observed temperature dependence of nuclear spin-lattice relaxation time of $(CH_3)_2CHNH_3CuCl_3$.

Acknowledgments

We would like to thank Dr. H. Manaka of Chiba University and Prof. T. Kubo and Mr. T. Waketa of Nara University of Education for useful discussion and showing us their experimental data prior to publication.

References

[1] M. Hagiwara, Y. Narumi, K. Kindo, T.C. Kobayashi, H. Yamakage, K. Amaya and G. Schimauch, *J. Phys. Soc.Jpn.*, **66,** 1792 (1997).
[2] H. Manaka, I. Yamada and K. Yamaguchi, *J. Phys. Soc. Jpn.*, **66,** 564 (1997).
[3] S. Kokado and N. Suzuki, *J. Phys. Soc. Jpn.*, **66,** 3605 (1997).
[4] J.J. Borrás-Almenar, E. Coronado, J. Curely, R. Georges and J. C. Gianduzzo, *Inorg. Chem.*, **33,** 5171 (1994).
[5] H. Manaka, I. Yamada, Z. Honda. H.A. Katori and K. Katsuniata, to be published in *J. Phys. Soc. Jpn.*
[6] T. Kubo and T. Waketa, private communications.
[7] N. Suzuki, *J. Phys. Soc.Jpn.*, **45,** 1791 (1978).
[8] D. Hone, C. Scherer and F. Borsa, *Phys. Rev. B,* **9,** 965 (1974).
[9] S.A. Roberts. D.R. Bloomquist, R.D. Willett and H.W. Dodgen, *J. Am. Chem. Soc.*, **103,** 2603 (1981).