Existence of massive singlet excitations in an antiferromagnetic alternating chain with $S=\frac{1}{2}$

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The one-dimensional Heisenberg model with alternating antiferromagnetic bond and spin-1/2 has been studied by the Monte Carlo method. The thermodynamic characteristics, spin-spin, and four spin-correlation function have been calculated. From several maxima of the correlation radius of the four spin-correlation function and sharp slopes of the dimer order parameter, a longitudinal component of the total spin square as a function of temperature and magnetic field, the existence of two mass singlet excitation branches with $\Delta S^z=0$ and one triplet with $\Delta S^z=1$ is suggested. Critical temperatures and fields related to singlet filled bands have been estimated. From these results low-temperature ($T<T_{SP}$) properties of spin-Peierls (SP) compounds $CuGeO_3$ and NaV_2O_5 have been explained.

I. INTRODUCTION

One-dimensional spin systems with antiferromagnetic interactions have been of great interest to researchers since exact solutions can be derived and take into account possible kinds of interactions. In particular, the interaction between an electron and a phonon can lead to phase transition at the same temperature, the so-called spin-Peierls transition.[1,2] Magnetic properties of these systems are analyzed in terms of Hubbard[3] and Heisenberg[4] models with the alternating parameters t and J. The low-energy-lying triplet excitations are suggested to exist. The mass gap (Δ) is proportional to the bond alternation of $\delta=J_i-J_{i+1}$ as $\Delta\sim\delta^5$ or $\Delta\sim\delta^{2/3}$.[2]

The model of the antiferromagnetic alternating spin-1/2 chain has been studied in the continuous limit[6–8] where it is equivalent to the exactly solvable sine-Gordon model. Affleck[6,7] derived an exact solution for massive spin waves with changes of S^z by ±1 for a nonzero topological angle. Essler and Tsvelik,[8] using a sine-Gordon Hamiltonian, calculated form factors for cos and sin and a mass gap which depends on the value of the bond alternation linearly. The authors derived two breathers: the first one has some mass M (triplet) and the second one has the mass equal to $\sqrt{3}M$ (singlet). To determine the mass gap, one needs to know two parameters: a dimensionless (nonuniversal) parameter λ and the spin-phonon coupling constant. Parameters, taken for $CuGeO_3$, give a larger value of energy of the two-particle continuum, which is in disagreement with the experiment. The main difficulties of these exactly solvable models are transition to the continium limit which is uncontrolled and some information can be lost. On the other hand, it is difficult to derive relations between parameters in the lattice and sine-Gordon models.

The exact solution of the uniform antiferromagnetic spin-1/2 Heisenberg chain shows that the low-lying excitations are spin-1/2 objects[9] (now called spinons), quite different from standard spin waves. The same excitations involve intermediate states where the z component of the magnetization has increased by $\Delta S^z=1$ and the other is not changed, i.e., $\Delta S^z=0$. Such excitations are quasidegenerated in the uniform case. The bond alternation may eliminate this degeneration and two kinks may make up the bound singlet low-energy state with $\Delta S^z=0$. From this assumption the strange low-temperature phenomenon can be explained in a singlet state of the spin-Peierls compounds of $CuGeO_3$ and predicted for NaV_2O_5. Spin-Peierls temperature in $CuGeO_3$ is $T_{sp}=14$ K, triplet gap is $\Delta=2$ meV (Ref. 10) and critical magnetic field is $H_c=13.6$ T.[11] However, from nonelastic magnetic scattering the singlet gap has been observed at $\Delta\sim1$ meV.[12] Thermal conductivity in the magnetic field has revealed two maxima in $CuGeO_3$ at the $T_1\approx5.5$ K, $T_2\approx22$ K,[13] which disappeared under the magnetic field $H=14$ T. Ultrasound scattering also exhibits maxima at $H=6$ T and at the critical field $H_c=13.6$ T.[14]

In the present paper we show that the antiferromagnetic chain with alternating exchange exhibits three critical temperatures and several critical fields associated with different spectrum branches of pair spin excitations both as a singlet with $\Delta S^z=0$ and a triplet with $\Delta S^z=1$. We give nontrivial quantitative predictions for static and dynamic quantities for NaV_2O_5 and successfully compare them with the results on $CuGeO_3$.

II. MODEL AND METHOD

We consider a one-dimensional (1D) Heisenberg model with negative interactions between nearest neighbors in the chain with $S=1/2$ directed along an external field along the axis $OZ-$. The alternating bonds are taken in terms of $I=J+\delta$ and $K=J-\delta$. The Hamiltonian is

$$H=-\sum_{i=1}^{L/2} I_{2i,2i-1}S_{2i}S_{2i-1}-\sum_{i=1}^{L/2} K_{2i,2i+1}S_{2i}S_{2i+1}-\sum_{i=1}^{L} h^z S_i^z,$$

where $I<0$, $K<0$, h^z is an external magnetic field and L is the size of the lattice.

The algorithm and the Monte Carlo (MC) method were earlier considered in detail.[15,16] MC simulations are made on the basis of the Trotter formula[17] using a parameter m called the ''Trotter number.'' The MC simulations were performed

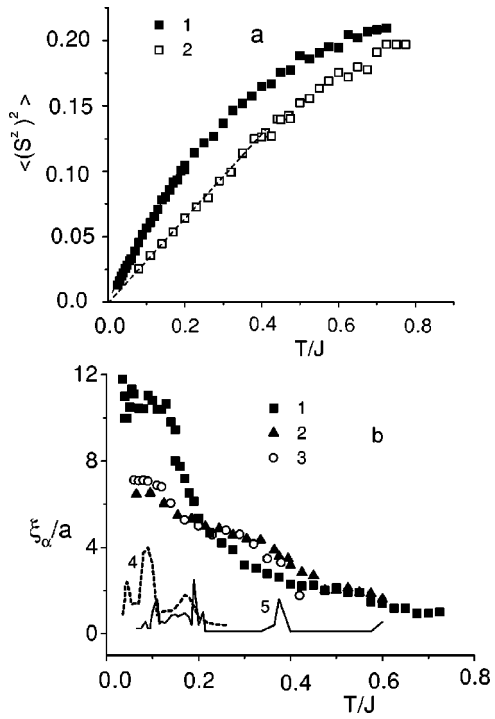

FIG. 1. The longitudinal component of total spin square $\langle (S^z)^2 \rangle$ vs temperature for $\delta = 0,1$ (1), $\delta = 0.6$ (2) (a). Correlation radius of spin-spin correlation function for $\delta = 0.1$ (1), 0.3 (2,3) and $m = 64$ (2), 124 (3) and correlation radius of four spin-correlation functions for $\delta = 0.1$ (4), 0.3 (5) vs temperature (b).

for several sizes of chains $L = 100$, 200, 400, and $m = 32$, 64, 124, 200 with a periodic boundary condition. For each chain we used from 4000 to 7000 MC steps to equilibrate and another 2000–5000 steps to calculate the averages. One MC step is determined by a turn of all spins on the lattice $L \times 2m$. The autocorrelation time (τ) needed to equilibrate is estimated from the relationship $\ln \tau = amT/J$ (T—temperature).[18] A systematic error due to quantum fluctuations yields an estimate $\sim 1/(mT/J)^2$ and for minimal temperature $T/J = 0.025$ it is approximately equal to 4%. The root-mean-square error of the energy is within the range of (0.1–0.6)%, susceptibility (6–11)%, correlation radius $\sim 10\%$. The errors due to the finite size of a chain can be minimized since we made simulations for $\xi < L/2$.

We shall consider possible excitations in this model. The extended resonance valence bond model includes coupling on all possible spins pairs and uncoupling of any pair can lead to excitation. Two sublattices with different spin stiffnesses arise from bond alternation in a chain. Then we might assume that the main density of spin excitations is due to uncoupling of the nearest spins. As a result, we can take as an order parameter the four spin-correlation functions $\langle S_0 S_1 S_r S_{r+1} \rangle$ and the difference of the functions calculated in sublattices with strong I and weak K exchanges, the so-called dimer order parameter

$$q^\alpha = 4/L \sum_{i=2}^{L/4} (\langle S_0^\alpha S_1^\alpha S_{2i-2}^\alpha S_{2i-1}^\alpha \rangle - \langle S_1^\alpha S_2^\alpha S_{2i-1}^\alpha S_{2i}^\alpha \rangle),$$

$$(\alpha = x, y, z).$$

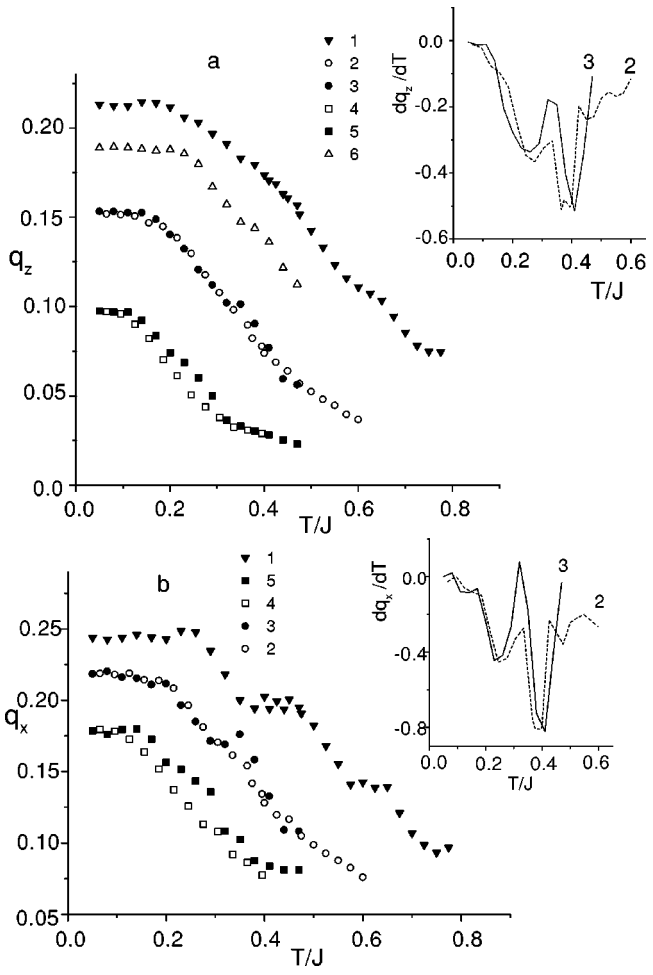

FIG. 2. Temperature dependence of dimer order parameter for longitudinal q_z (a) and transverse q_x (b) spin components for $\delta = 0.15$ (4,5), 0.3 (2,3), 0.45 (6), 0.6 (1) and $m = 64$ (1,3,5), $m = 124$ (2,4,6). Inset shows dq_z/dT (a) and dq_x/dT (b) vs temperature for $\delta = 0.3$.

The correlation radius ξ_4 and the parameter η_4 were determined from the fit of the four spin-correlation functions

$$\langle S_0^z S_1^z S_{r-1}^z S_r^z \rangle = A/r^{\eta_4} \exp(-r/\xi_4),$$

where $r = 2i+1$, $i = 1,2,3 \ldots$. The following quantities were calculated: energy, magnetization, susceptibility in an external field $\chi = M/H$, and spin-spin correlation functions of the longitudinal spin components $\langle S^z(0) S^z(r) \rangle$, their Fourier transform in magnetic field. The correlation radius ξ_2 and the parameter η_2 were determined from the fit of the spin-spin-correlation function

$$\langle S^z(0) S^z(r) \rangle = B/r^{\eta_2} \exp(-r/\xi_2).$$

The single state can be different from the paramagnet (PM) on the basis of the calculation of the longitudinal component of the total spin square $\langle (S^z)^2 \rangle$ which is equal to zero in the single state and $\langle (S^z)^2 \rangle = S(S+1)/3$ in PM.

III. RESULTS

We calculated the above characteristic temperature dependences for a number of alternation values $\delta = 0.1$, 0.15, 0.2,

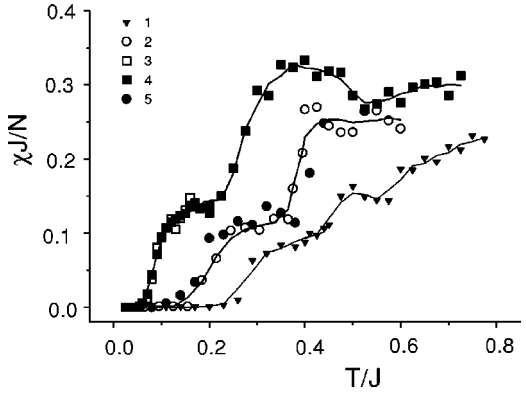

FIG. 3. Susceptibility χ for $\delta=0.1$ (3,4), 0.3 (2,5), 0.6 (1), $m=64$ (2,4), $m=124$ (3,5) versus temperature.

0.3, 0.45, 0.6, 0.75. The longitudinal component of the total spin square $\langle (S^z)^2 \rangle$ is shown in Fig. 1. The temperature dependence is well approximated by the linear function $\langle (S^z)^2 \rangle = A + BT$ with $A=0$ in the range of $0<T<T_{c3}$, which indicates the existence of single state in the ground state. Temperature dependence of the correlation radius ξ_4 shows maxima [Fig. 1(b)] at T_{ci} $(i=1,2,3)$. The correlation radius ξ_2 and the dimer order parameter q decrease at the same temperature. We plotted in Fig. 2 the dimer order parameter for several values of bond alternation and different Trotter numbers. The derivative of dq/dT reveals minima at T_{c2} and T_{c3} which are independent of the Trotter number within the calculation errors, as shown in inset of Fig. 2. Susceptibility is equal to zero at low temperatures $T \leqslant T_{c1}$ and the derivative of $d\chi/dT$ exhibits a maximum at T_{c2} and a minimum at T_{c3}. Some temperature dependences are plotted in Fig. 3.

From the results we can propose the following picture of excitations. The degeneration of two-particle singlet and triplet excitations in a uniform antiferromagnetic (AF) chain is taken off as a result of bond alternation and two kinks with $s=1/2$ and $s=-1/2$ can form bound singlet states in the sublattice of weak K exchanges. There are also singlet pairs coupled denoted as circles. The wave functions of excitation can be presented as $\psi_1 \propto |\bigcirc\uparrow\uparrow\bigcirc\cdots\downarrow\downarrow\bigcirc\rangle + |\bigcirc\downarrow\downarrow\bigcirc\cdots\uparrow\uparrow\bigcirc\rangle$. The energy associated with the maximum of density of these excitations is in proportion to the

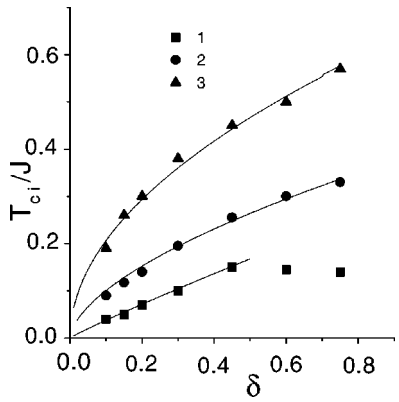

FIG. 4. Critical temperatures T_{ci}/J $[i=1$ (1), 2 (2), 3 (3)] as a function of bond alternation. Power-law fit is $T_{ci}=A_i\delta^{\beta_i}$ marked by solid line.

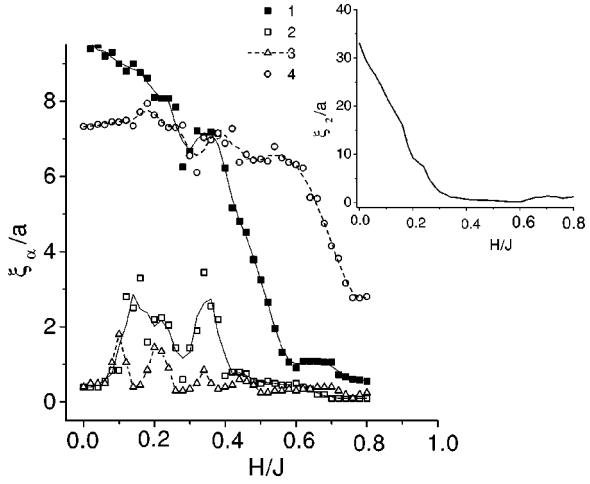

FIG. 5. Magnetic-field dependence of the correlation radius of spin-spin correlation function ξ_2 (1,4, inset) and four spin-correlation functions ξ_4 (2,3) for $\delta=0.15$ (1,3), 0.3 (2,4). Inset shows ξ_2 of the AF chain for $\delta=0$, $T/J=0.035$.

first critical temperature T_{c1}. When temperature exceeds T_{c1}, triplet excitations with $\Delta S^z=1$ exist throughout the whole chain including a sublattice with the strong bond I. It is derived from $\chi>0$ and a decrease of the dimer order parameter. The wave function may be given by $\psi_2 \propto |\bigcirc\uparrow\uparrow\downarrow\uparrow\uparrow\bigcirc\rangle$. On the basis of a sharp decrease of the dimer order parameter and slow change of susceptibility, an assumption is made that singlet excitations with $\Delta S^z=0$ are

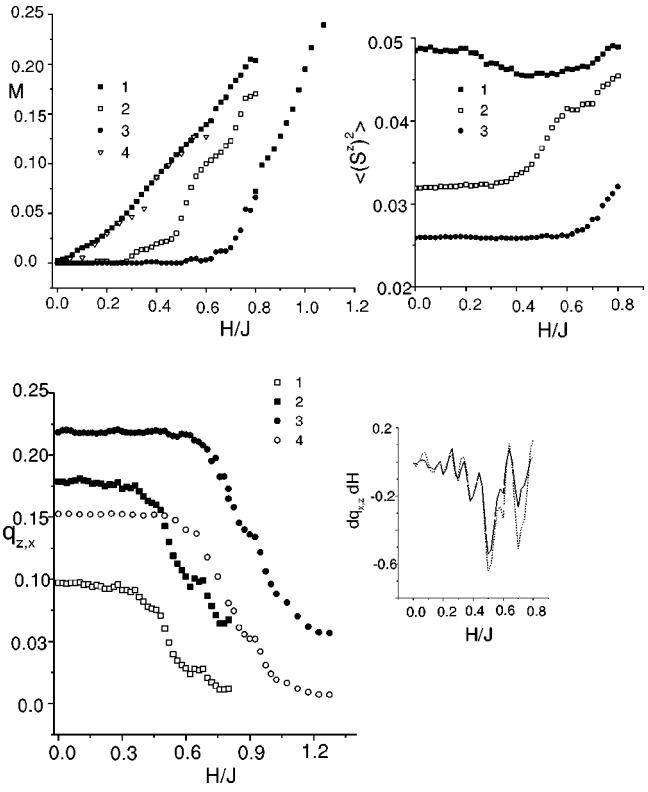

FIG. 6. Magnetization M, $\langle (S^z)^2 \rangle$ vs magnetic field for $\delta=0$ (1), 0.15 (2), 0.3 (3), 0.05 (4). Dimer order parameter q_α for longitudinal $\alpha=z$ (1,4) and transverse $\alpha=x$ (2,3) spin components for $\delta=0.15$ (1,2), 0.3 (3,4). Inset shows derivative dq_α/dH ($\alpha=z$ is the solid line, $\alpha=x$ is the dotted line) for $\delta=0.15$.

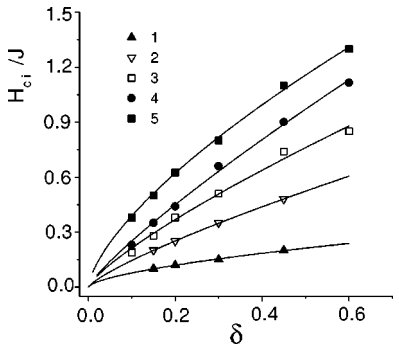

FIG. 7. Critical magnetic field H_{ci}/J $(i=1:5)$ as a function of bond alternation. Power-law fit is $H_{ci}=B_i\delta^{\gamma_i}$ marked by solid line.

formed in the sublattice with the strong bond I at T_{c3} and the wave function is similar to ψ_1. There is, of course, a one-particle singlet excitation[8] and a multiple-excitation, leading to additional contributions to susceptibility. We indicate the main possible excitations at these temperatures.

Critical temperatures determined on the basis of the ξ_4 maxima and dq/dT minima are shown in Fig. 4. We fitted the MC results for T_{ci} by the power law $T_{ci}=A_i\delta^{\beta_i}$ and obtained the following parameters for every critical temperature $A_1=0.32\pm0.06$, $\beta_1=1\pm0.08$, $A_2=0.41\pm0.11$, $\beta_2=0{,}65\pm0.07$, $A_3=0.66\pm0.12$, $\beta_3=0.5\pm0.06$.

The singlet excitation branch in the K sublattice is split into two in the magnetic fields H_{c1}, H_{c2}. The correlation radius ξ_4 plotted in Fig. 5 reveals two maxima at these fields. The correlation radius of the spin-spin correlation function does not quite depend on the magnetic field at $H<H_{c2}$ compared with ξ_2 in the uniform AF chain where it sharply decreases (inset in Fig. 5). The dimer order parameter exhibits small maxima at H_{c1},H_{c2}. It is particularly seen in the dq_x/dH derivative plotted by a dotted line in the inset of Fig. 6. From the $q_{x,z}$ variation versus field we infer that transverse and longitudinal kinks are excited accordingly at H_{c1},H_{c2}. Magnetization arises at H_{c3}, as shown in Fig. 6. The magnetic wave vector of the structure determined from the $S(k)$ maximum is varied in the range of $0<Q<\pi/a$ in the fields $H_{c3}<H<H_{c5}$, and a ferromagnetic long-range order exists at H_{c5}. The dimer order parameter is decreased at the critical fields H_{ci} $(i=3,4,5)$ and a derivative of dq/dH shows the minima (Fig. 6). The results provide evidence for triplet excitations in both IK sublattices. Some critical fields are shown in Fig. 7 and are fit by the power law $H_{ci}=B_i\delta^{\gamma_i}$ with the parameters presented in Table 1.

The above results for critical temperatures and magnetic fields are now compared with experimental results with spin-Peierls compounds NaV_2O_5 (Refs. 19 and 20) and $CuGeO_3$ (Refs. 10, 21, and 22). The spin-Peierls temperature in NaV_2O_5 is $T_{sp}/J=35.3$ K/440 K≈0.08, the triplet gap $\Delta/J\approx0.25$[19]. Additional singularities are determined by infrared reflectivity at the $E_1/J=280$ K/440 K≈0.6, $E_2/J=520$ K/440 K≈1.2 (Ref. 20) along the dimerization axis. From the comparison of T_{sp}^{ex} with T_{c2}^{MC} the alternation value is $\delta\approx0.08$. Critical temperatures of singlet excitations are estimated as $T_{c1}\approx14$ K and $T_{c3}\approx84$ K. If the relationship between the gap Δ and T_{sp} is $\Delta/T_{sp}\sim3$, and it is to be valid for other critical temperatures, then energy E_1 is associated with the maximum of singlet excitation density in the range of energy $\sim(3.5$–$5)$meV. Multiparticle excitation may cause infrared reflectivity at $E_2=45$ meV. The second nontrivial prediction of the present calculation is the existence of a small specific-heat maximum in NaV_2O_5 at the $T\simeq20$ K.

TABLE I. Fitting parameters for power dependences of critical magnetic fields versus bond alternation $H_{ci}=B_i\delta^{\gamma_i}$.

i	1	2	3	4	5
B_i	0.33 ± 0.04	0.9 ± 0.06	1.3 ± 0.16	1.7 ± 0.2	1.8 ± 0.12
γ_i	0.63 ± 0.05	0.8 ± 0.05	0.8 ± 0.1	0.84 ± 0.09	0.67 ± 0.04

From the experimental results, the spin-Peierls temperature in $CuGeO_3$ is $T_{sp}=14$ K,[11] the exchange $J=120$ K,[10] the critical magnetic field $H_c=13.6$ T,[11] we find the alternation value to be $\delta=0.14$. The values calculated by Monte Carlo simulations are $T_{sp}^{MC}=13.5$ K, $T_{c1}=5.4$ K, $H_{c1}=8.9$ T, $H_{c2}=16.4$ T. Overestimation of the critical field, compared with the experimental value, is caused by the strong magnetostriction of the $CuGeO_3$ compound,[21,22] which can lead to disappearance of lattice dimerization and $\delta\to0$. It can be inferred that the maximum of the magnetic heat conductivity at $T=5.5$ K,[13] the singlet gap observed by nonelastic neutron scattering around ~1 meV at $Q=(0,\pi/b,\pi/c)$,[12] and the strong scattering ultrasound in the magnetic field $H=6$ T,[14] can be attributed to mass singlet excitations in the spin-Peierls phase with $T_c^{MC}=5.4$ K critical temperature of the filled band. The interchain coupling $(J_\perp=0.1J)$ for $CuGeO_3$ (Ref. 10) can be ignored, because the correlation radius of the spin-spin correlation function calculated in the 2D anisotropic Heisenberg model[23] along the c chain is much larger than in the transverse direction for the singlet state $\xi_\parallel\gg\xi_\perp$. On the basis of this, spin excitations in a chain give the main contribution to the thermodynamic quantities, critical temperatures. The allowance of interchain couplings in a singlet state is due to a small split of the singlet excitation branch into transverse and longitudinal modes and this is the second-order value effect.[24]

Summarizing our results, we calculated three critical temperatures, two of which are associated with the energy of filled singlet bands with $\Delta S^z=0$, and one triplet with $\Delta S^z=1$ in an antiferromagnetic alternating chain. Singlet and triplet excitation branches are split accordingly into two and three branches in the same critical magnetic fields, which fit well the power law $H_{ci}=B_i\delta^{\gamma_i}$ $(i=1:5)$. From our results, the low-temperature $(T<T_{sp})$ behavior of the spin-Peierls compounds is explained in $CuGeO_3$ and predicted in NaV_2O_5.

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