Valence-Bond Crystal in a Pyrochlore Antiferromagnet with Orbital Degeneracy

S. Di Matteo,[1,2] G. Jackeli,[3,*] C. Lacroix,[4] and N. B. Perkins[1,5]

[1]*Laboratori Nazionali di Frascati INFN, via E. Fermi 40, C.P. 13, I-00044 Frascati (Roma) Italy*
[2]*Dipartimento di Fisica, Università di Roma III, via della Vasca Navale 84, I-00146 Roma Italy*
[3]*Institut Laue Langevin, B.P. 156, F-38042, Grenoble, France*
[4]*Laboratoire L. Néel, CNRS, B.P. 166, 38042 Grenoble Cedex 09, France*
[5]*Bogoliubov Laboratory of Theoretical Physics, JINR, 141980, Dubna, Russia*

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We discuss the ground state of a pyrochlore lattice of threefold orbitally degenerate $S = 1/2$ magnetic ions. We derive an effective spin-orbital Hamiltonian and show that the orbital degrees of freedom can modulate the spin exchange, removing the infinite spin-degeneracy characteristic of pyrochlore structures. The resulting state is a collection of spin-singlet dimers, with a residual degeneracy due to their relative orientation. This latter is lifted by a magnetoelastic interaction, induced in the spin-singlet phase space, that forces a tetragonal distortion. Such a theory provides an explanation for the helical spin-singlet pattern observed in the B spinel $MgTi_2O_4$.

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Geometrically frustrated antiferromagnets have gained increasing interest in the past decade [1]. The reason is that their ground states are highly degenerate and can evolve in a variety of ways: they can remain liquid down to the lowest temperatures [2], or lift their degeneracy via the order-out-of-disorder mechanism [3] or through a phase transition that lowers the local symmetry of the lattice [4,5]. In this Letter we want to point out and discuss another scenario, one that can appear when magnetic ions of frustrated lattices also possess an orbital degeneracy. The physical behavior of such systems may be drastically different from that of pure spin models, as the occurrence of an orbital ordering can modulate the spin exchange, thus lifting the geometrical degeneracy of the underlying lattice. In the following we focus on a system with threefold orbitally degenerate $S = 1/2$ magnetic ions in a corner-sharing tetrahedral (pyrochlore) lattice. This model is suitable to describe d^1-type transition-metal compounds, like the B spinel $MgTi_2O_4$. Here the magnetically active Ti^{3+} ions form a pyrochlore lattice and are characterized by one single electron in the threefold degenerate t_{2g} manifold. $MgTi_2O_4$ undergoes a metal-to-insulator transition on cooling below 260 K, with an associated cubic-to-tetragonal lowering of the symmetry [6]. At the transition the magnetic susceptibility continuously decreases and saturates, in the insulating phase to a value which is anomalously small for spin-1/2 local moments: For this reason the insulating phase has been interpreted as a spin singlet. Subsequent synchrotron and neutron powder diffraction experiments have revealed that the low-temperature crystal structure is made of alternating short and long Ti-Ti bonds forming a helix about the tetragonal c axis [7]. These findings have suggested a removal of the pyrochlore degeneracy by a one-dimensional (1D) helical dimerization of the spin pattern, with spin singlets located on short bonds. This phase can be regarded as a valence-bond crystal (VBC) since the long-range order of spin singlets (dimers) extends throughout the whole pyrochlore lattice.

Here we describe the microscopic theory behind the stabilization of this VBC ground state. We argue that, remarkably, such a novel phase can be realized on a pyrochlore lattice because of orbital degeneracy, without invoking any exotic interactions. The existence of an orbitally driven VBC had been suggested for a cubic lattice of d^9 compounds [8]. For d^2 compounds with frustrated lattices, the orbital order is shown to induce a spin-singlet ground state for triangular lattices [9], or a spin ordered one for pyrochlore lattices [10]. Yet, the peculiar case of d^1 spinel compounds leads to new results: the onset of an orbitally driven VBC state on the pyrochlore lattice.

Effective Hamiltonian.—We first derive a superexchange spin-orbital Hamiltonian similar to the Kugel-Khomskii model [11] for threefold orbitally degenerate d^1 ions on a pyrochlore lattice. We assume that the low-temperature insulating phase of $MgTi_2O_4$ is of the Mott-Hubbard type. We work in the cubic crystal class and look for possible instabilities towards symmetry reductions. Our parameters are the nearest-neighbor (NN) hopping term t, the Coulomb on-site repulsions U_1 (within the same orbital) and U_2 (among different orbitals), and the Hund's exchange, J_H. For t_{2g} wave functions the relation $U_1 = U_2 + 2J_H$ holds due to rotational symmetry in real space. The orbital occupancies of t_{2g} orbitals, $n_{\alpha\beta}$ ($\alpha, \beta = x, y, z$), are expressed in terms of the pseudospin $\vec{\tau} = 1$, with the correspondence: $\tau^z = -1 \rightarrow |yz\rangle$, $\tau^z = 0 \rightarrow |xy\rangle$, and $\tau^z = 1 \rightarrow |xz\rangle$. At first, we consider only the leading part of the hopping term, due to the largest $dd\sigma$ element, and discuss later the effects of smaller contributions (e.g., $dd\pi$). The $dd\sigma$ overlap in the $\alpha\beta$ plane connects only the corresponding orbitals of the same $\alpha\beta$

type. Thus, the total number of electrons in each orbital state is a conserved quantity and the orbital part of the effective Hamiltonian $H_{\rm eff}$ is Ising-like:

$$H_{\rm eff} = -J_1\sum_{\langle ij\rangle}[\vec{S}_i\cdot\vec{S}_j + 3/4]O_{ij} + J_2\sum_{\langle ij\rangle}[\vec{S}_i\cdot\vec{S}_j - 1/4]O_{ij} + J_3\sum_{\langle ij\rangle}[\vec{S}_i\cdot\vec{S}_j - 1/4]\tilde{O}_{ij}, \qquad (1)$$

where the sum is restricted to the NN sites. Introducing the projectors on the orbital states of site i, $P_{i,xz} = \frac{1}{2}\tau_{iz}(1+\tau_{iz})$, $P_{i,xy} = (1-\tau_{iz})(1+\tau_{iz})$, and $P_{i,yz} = -\frac{1}{2}\tau_{iz}(1-\tau_{iz})$, the orbital contributions along the bond ij in the $\alpha\beta$ plane is given by $O_{ij} = P_{i,\alpha\beta}(1-P_{j,\alpha\beta}) + P_{j,\alpha\beta}(1-P_{i,\alpha\beta})$ and $\tilde{O}_{ij} = P_{i,\alpha\beta}P_{j,\alpha\beta}$. The first and second terms in $H_{\rm eff}$ describe the ferro-magnetic (FM) $J_1 = t^2/(U_2 - J_H)$ and the antiferro-magnetic (AFM) $J_2 = t^2/(U_2 + J_H)$ interactions, respectively, and are active only when the two sites involved are occupied by different orbitals. The last term is AFM, with $J_3 = \frac{4}{3}t^2[2/(U_2 + J_H) + 1/(U_2 + 4J_H)]$, and is nonzero only when the two sites have the same orbital occupancy. At this point it is useful to have an idea of the energy scales that play a role in the Hamiltonian (1). We estimate $t \equiv t_\sigma \simeq 0.32$ eV, $J_H \simeq 0.64$ eV, and $U_2 \simeq 4.1$ eV [12]. Thus $\eta = J_H/U_2 \simeq 0.15 \ll 1$ and, just in order to present the results in a more transparent form, we expand the exchange energies around $\eta = 0$. We get $J_1 \simeq J(1+\eta)$, $J_2 \simeq J(1-\eta)$, and $J_3 \simeq 4J(1-2\eta)$, where $J = t^2/U_2 \simeq 25$ meV represents the overall energy scale. In the following we measure all energies in units of J.

The main aspect of $H_{\rm eff}$ is that, due to $dd\sigma$ character of the hopping terms, only some orbital configurations contribute to the energy: every bond ij in the $\alpha\beta$ plane has zero energy gain unless at least one of the two sites i and j has an occupied $\alpha\beta$ orbital. The strength, as well as the sign, of spin-exchange energy associated with two NN sites i and j depends on their orbital occupations and the direction of the ij bond. The strongest bond in the generic $\alpha\beta$ plane is characterized by both sites with $\alpha\beta$ occupancy: We shall call it b_0. Its exchange interaction is AFM and its spin Hamiltonian is given by $H_{b_0} = -1 + 2\eta + 4[1-2\eta]\vec{S}_i\cdot\vec{S}_j$.

When the two sites of bond ij in the $\alpha\beta$ plane are occupied by one $\alpha\gamma$ and one $\alpha\beta$ orbitals $\gamma \neq \beta$ (bond b_1), one gets a weak FM interaction: $H_{b_1} = -1 - \eta/2 - 2\eta\vec{S}_i\cdot\vec{S}_j$.

Finally, the two sites of bond ij in the $\alpha\beta$ plane can be occupied by one $\alpha\gamma$ and one $\beta\gamma$ orbital (bond b_2), or by two $\alpha\gamma$ (or $\beta\gamma$) orbitals (bond b_3). These bonds are noninteracting, as far as only $dd\sigma$ overlap is considered.

Single tetrahedron.—In one tetrahedron there are basically three possible orbital configurations to be considered (see Fig. 1): (A) All four sites have the same orbital occupancy (say xy) and thus only the two bonds in the xy plane [shown by solid lines in Fig. 1(a)] give a nonzero energy contribution. (B) The two sites in one $\alpha\beta$ plane, e.g., xz, are both occupied by xz orbitals, while at least one of the two sites in the other xz plane is occupied by xy or yz orbitals [Fig. 1(b)]. (C) No bonds ij in the plane $\alpha\beta$ of the tetrahedron is such as to have both sites occupied by the $\alpha\beta$ orbital [Fig. 1(c)]. These three configurations are the bricks that allow the orbital pattern to be built throughout the whole pyrochlore lattice. Because of the Ising form of orbital interactions, in the following we can focus simply on these three cases, relying on the fact that configurations with a linear superposition of orbitals on each site must have a higher energy. We shall do only one exception to study a case with a particular physical meaning, i.e., that of a "cubic" symmetry, where each site is occupied by a linear superposition with equal weights of the three orbitals $\frac{1}{\sqrt{3}}[|xy\rangle + |xz\rangle + |yz\rangle]$ (case D).

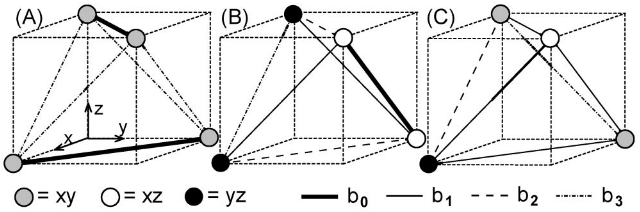

FIG. 1. Orbital and bond arrangements on a tetrahedron (a) case (A), (b) case (B), and (c) case (C).

Pyrochlore lattice.—Here we consider possible coverings of the lattice through the various tetrahedra.

(i) Heisenberg chains: When all tetrahedra of a pyrochlore lattice are of type (A) (ferro-orbital ordering) then the effective Hamiltonian (1) can be mapped into a set of one-dimensional decoupled Heisenberg chains. If, for example, all occupied orbitals are of xy type, all chains in $(1, \pm 1, 0)$ cubic directions [see Fig. 1(a)] are decoupled. The only interactions are due to AFM b_0 bonds described above. Thus, the ground-state energy per site can be evaluated exactly by using the results for a Heisenberg 1D chain [13]: $E_A = -2.77(1-2\eta)$.

(ii) Dimer phase: This state is made of (B)-type tetrahedra. We distinguish three types of such tetrahedra. All three are characterized by one strong b_0 bond, in an $\alpha\beta$ plane. The other two ions in the opposite $\alpha\beta$ plane can either be occupied by two $\alpha\gamma$ ($\beta\gamma$) orbitals forming a b_3 bond [case B_1, the one shown in Fig. 1(b)], or by one $\alpha\gamma$ and one $\alpha\beta$ orbital, linked in a b_1 bond (case B_2), or, finally, by one $\alpha\gamma$ and one $\beta\gamma$ orbital, forming a b_2 bond (case B_3). Since b_2 and b_3 bonds do not contribute to the energy, this latter depends only on the number, n_{b_0} and n_{b_1}, of b_0 and b_1 bonds in the unit cell. As all three B_i configurations are characterized by $n_{b_0} = 1$ and $n_{b_1} = 2$, all possible coverings of the pyrochlore lattice by B_i tetrahedra have the same energy, even if (n_{b_2}, n_{b_3}) are different for three B_i tetrahedra [(2,1) for B_1, (1,2) for B_2, (3,0) for B_3]. When the pyrochlore lattice is covered by B_i-type tetrahedra (two possible coverings are shown in Fig. 2), each spin is engaged in one strong AFM b_0 bond and two weak FM b_1 bonds. Such coverings form a degenerate manifold and the corresponding energy can be calculated as follows. In the limit $\eta \rightarrow 0$, the spin-only Hamiltonian can be solved exactly, as it can be decomposed into a sum of spin-uncoupled b_0 bonds. In this case the energy minimum is reached when the Heisenberg term of the b_0 bond is the lowest, i.e., for a pure quantum spin singlet ($\vec{S}_i \cdot \vec{S}_j = -3/4$). Remarkably, such spin-singlet (dimer) states, in the limit $\eta \rightarrow 0$, are also exact eigenstates of the full Hamiltonian (1). As $\eta \ll 1$, the dimer state is stable against the weak FM interdimer interaction. In this case the magnetic contribution along the FM b_1 bond is zero ($\langle \vec{S}_i \cdot \vec{S}_j \rangle = 0$ for i and j belonging to different dimers) and we are led to an energy per site given by $E_B = E_{b_0}/2 + E_{b_1} = -3 + \frac{7}{2}\eta$. Here $E_{b_{0(1)}}$ is the energy of the bond $b_{0(1)}$.

(iii) FM order: Consider the state where all tetrahedra are of type (C) [see Fig. 1(c)]. There are four interacting FM b_1 bonds and two noninteracting bonds (b_2 and b_3) per tetrahedron. The ground state for this case is, thus, ferromagnetic with an energy $E_C = 2E_{b_1} = -2(1 + \eta)$.

(iv) Frustrated AFM: The realization of this phase restores the full pyrochlore lattice symmetry, thus describing an ideal cubic phase. All bonds are equivalent and by averaging Eq. (1) over the orbital configurations on neighboring sites i and j, we obtain the spin Heisenberg Hamiltonian on the pyrochlore lattice: $H_D = \sum_{\langle ij \rangle}(-5/9 + [4/9 - 16\eta/9]\vec{S}_i \cdot \vec{S}_j)$. The system is thus highly frustrated and its ground state is a spin liquid [2], whose energy per site is $E_D \simeq -1.89 + 0.89\eta$. Here we have used the ground-state energy estimated $(1/N)\sum_{ij}\vec{S}_i \cdot \vec{S}_j \simeq -0.5$ on the pyrochlore lattice [14].

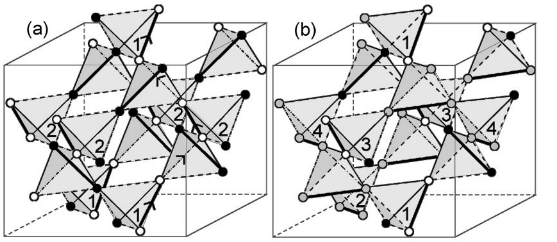

FIG. 2. Two different coverings of the unit cubic cell through dimers, phase (ii). The same notations as in Fig. 1 are used. Locations of singlets are represented by thick links. Different numbers correspond to inequivalent tetrahedra. (a) The experimental phase of $MgTi_2O_4$: the helical dimerization pattern (indicated by arrows) is formed by alternating short b_0 and long b_3 bonds. All tetrahedra are in phase B_1. (b) a different covering of the cubic cell through all B_i tetrahedra. The inclusion of the magnetoelastic coupling pushes these states higher in energy.

(v) Mixed (A) and (C) configuration: It is possible to cover the pyrochlore lattice also by means of a mixed configuration with (A)- and (C)-type tetrahedra. It can be visualized from Fig. 2(b) if, e.g., the four labeled tetrahedra would be of (A) type, with two spin singlets on strong b_0 bonds and three different orbital occupancies, and the four unlabeled tetrahedra of (C) type with no spin singlets. This dimer configuration is degenerate with the dimer phase (ii) as far as only $dd\sigma$ overlap is considered, as, on average, $n_{b_0} = 1$ and $n_{b_1} = 2$. Yet, in this case $n_{b_2} = 1/2$ and $n_{b_3} = 5/2$, and the degeneracy is removed by $dd\pi$ overlap in favor of the dimer phase (ii) (for which $n_{b_2} \geq 1$), as the energy gain of the b_2 bond is $-t_\pi^2/[4t^2]$ (in units of J), while that of the b_3 bond is $-t_\pi^2/[8t^2]$.

Ground-state manifold.—On the basis of the previous energy considerations, a simple phase diagram can be derived, in terms of η, the only free parameter available. For $\eta = 0$ the lowest ground-state energy is that of phase (ii). With increasing η we find only one phase transition at $\eta_c = 2/11 \simeq 0.18$, between the dimer phase (ii) and the FM phase (iii). As η_c is above our estimated value of $\eta \simeq 0.15$, we can conclude that the ground state of $MgTi_2O_4$ is described by phase (ii) and is characterized by a frozen pattern of spin singlets throughout the whole pyrochlore lattice that removes the original spin degeneracy. Nonetheless, there is still a remaining degeneracy to be lifted. It is related to the freedom in the choice of the two orbitals on the tetrahedron bond opposite the one of the singlet. Different choices of these orbitals give rise to inequivalent covering patterns of the pyrochlore lattice with one dimer per tetrahedron (see Fig. 2). This degeneracy is given by the number of such dimer coverings and the corresponding number of states can be estimated to grow with the system size as $\mathcal{N} \sim 3^{N_T} = \sqrt{3}^N$ [15]. Here $N_T = N/2$ is the number of tetrahedra and we have ignored the contributions coming from closed loops (hexagons) on the pyrochlore lattice. This ground-state manifold is different from a resonating valence-bond state, since each dimer covering is frozen in an exact eigenstate of the Hamiltonian (1) for $\eta = 0$. For finite η the different dimer patterns are not connected by the Hamiltonian: The bond corresponding to the dimer in each tetrahedron is fixed, being determined by orbital pattern, and orbital degrees of freedom are Ising-like variables.

Lifting of degeneracy.—The above discussed degeneracy cannot be removed within the Kugel-Khomskii-type model, not even introducing $dd\pi$ and $dd\delta$ overlaps. The reason is related to the fact that the energy gain depends only on the total number of each type of bond (n_{b_0}, n_{b_1}, n_{b_2}, n_{b_3}) in the unit cell and, in order to fill the whole crystal with a periodicity not lower than the one of the primitive cubic cell shown in Fig. 2, the average number of bonds n_{b_i} per tetrahedron is the same, whichever of the three building blocks B_1, B_2, or B_3 is used. It is given by $n_{b_0} = 1$, $n_{b_1} = 2$, $n_{b_2} = 2$, $n_{b_3} = 1$, and it corresponds to the value of case B_1, which is the only one that allows coverage of the whole cubic cell without mixing other configurations [see Fig. 2(a)]. Associated with the B_1 phase, we have the minimal cell enlarging (doubling instead of quadrupling), and the maximal space subgroup ($P4_12_12$) of the original face-centered $Fd\bar{3}m$ cubic cell.

In order to substantiate these geometrical considerations, we need to find the physical mechanism that removes the B-manifold degeneracy in favor of the B_1 state. From the above discussion it follows that only correlations between bonds can lift it. These correlations naturally appear if the magnetoelastic contribution to the energy is considered, as the orbitally driven modulations of the spin-exchange energies distort the underlying lattice through the spin-Peierls mechanism. In the degenerate B manifold, every tetrahedron is characterized by a strong exchange on the bond b_0 where the singlet is located. A reduction of the bond length enlarges the energy gain, because of the increase in the $dd\sigma$ overlap. This selects the triplet-T deformation mode from the irreducible representations of the tetrahedron group, which is the only one that singles out one shorter bond [16]. This mode generates a tetragonal distortion of the tetrahedron, with short and long bonds located opposite each other and four intermediate bonds. Because of this mechanism, the position of the two b_1 bonds in the tetrahedron is uniquely determined: In order to maximize the superexchange energy gain by keeping the highest value for t_σ, the intermediate-strength b_1 bonds are not allowed to lie on the long bond opposite to the singlet b_0. The elongation of the weak bonds of b_3 type is energetically more favorable. It is possible to check that the only possibility to have such a constraint for the whole cell is realized for the state B_1 [Fig. 2(a)]. On the contrary, both cases B_2 and B_3 [Fig. 2(b)] do not allow coverage of the cell without at least one b_1 bond lying opposite to the singlet edge [e.g., tetrahedron 4 in Fig. 2(b)], thus with an extra-energy cost. Hence, the energy is minimized when all tetrahedra are of B_1 kind, with a T-type tetragonal distortion. In this state all dimers are condensed in the ordered helical pattern shown in Fig. 2(a) and form a VBC. This dimerization pattern exactly reproduces the one observed in the insulating phase of $MgTi_2O_4$ [7]. The present theory also predicts a peculiar orbital ordering in the dimerized phase: a ferro-orbital order along the helices with antiferro-orbital order between them [see Fig. 2(a)]. This orbital ordering can undergo an experimental test through Ti K edge natural circular dichroism, which is sensitive to the chirality of a t_{2g} orbital order along the helix, when x rays are shone along the helical axis.

Within the present scenario two transition temperatures are expected. The highest T_{c_1}, determined by the exchange coupling within the singlet ($T_{c_1} \sim J_3 \simeq 4J \simeq 1000$ K), corresponds to the transition from a paramagnet to a spin gap (dimer) state, with a ferro-orbital order on each dimer. This state can be regarded as a weakly interacting gas of dimers and is highly degenerate with respect to the dimers orientation. At the lowest transition temperature, given by the magnetoelastic coupling, this degeneracy is lifted through the spin-Peierls distortion. At this temperature dimers condense and form the VBC shown in Fig. 2(a). The entropy involved in this transition is estimated to be $\sim \ln[\mathcal{N}]/N = \ln\sqrt{3}$. In the case of $MgTi_2O_4$, it is known [6] that, with increasing temperature, this compound goes from an insulating to a metallic phase at $T_{c_2} \simeq 260$ K. The transition to the metallic state rules out the possibility of a high-temperature spin-singlet state with disordered dimers and does not allow evaluation of the order of magnitude of the magnetoelastic coupling. We can just estimate its lower limit as about $1/4(\simeq T_{c_2}/T_{c_1})$ of the singlet-binding energy.

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*Also at E. Andronikashvili Institute of Physics, Georgian Academy of Sciences, Tbilisi, Georgia

[1] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 2001).
[2] B. Canals and C. Lacroix, Phys. Rev. Lett. **80**, 2933 (1998); H. Tsunetsugu, Phys. Rev. B **65**, 024415, (2001).
[3] J. Villain *et al.*, J. Phys. (Paris) **41**, 1263 (1980).
[4] Y. Yamashita and K. Ueda, Phys. Rev. Lett. **85**, 4960 (2000).
[5] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. B **66**, 064403 (2002).
[6] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **71**, 1848 (2002).
[7] M. Schmidt *et al.*, Phys. Rev. Lett. **92**, 056402 (2004).
[8] L. F. Feiner, A. M. Oles, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).
[9] H. F. Pen *et al.*, Phys. Rev. Lett. **78**, 1323 (1997).
[10] H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405(R) (2003); O. Tchernyshyov, cond-mat/0401203.
[11] K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **231**, 25 (1982)].
[12] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996); J. Matsuno, A. Fujimori, and L. F. Mattheiss, *ibid.* **60**, 1607 (1999).
[13] M. Takhashi, *Thermodynamics of One-Dimensional Solvable Models* (Cambridge University Press, Cambridge, England, 1999).
[14] B. Canals and C. Lacroix, Phys. Rev. B **61**, 1149 (2000).
[15] When a singlet is located on a given tetrahedron then each neighboring tetrahedron is left with only three possible choices for a singlet location.
[16] For a simple spin Hamiltonian it is the doublet E-mode that removes the local degeneracy of the tetrahedron [4].