

Thermodynamics of ferrimagnetic double chains with z-z nearest-neighbor interactions

J. Curély and R. Georges

Laboratoire de Chimie du Solide, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence CEDEX, France

M. Drillon, M. Belaiche, and K. Benkhouja

Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 Rue Blaise Pascal, 67008 Strasbourg CEDEX, France

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We propose a general treatment involving the transfer-matrix method for solving ferrimagnetic double chains made up of two spin sublattices $(s, s')_N$ showing a z-z exchange coupling between nearest neighbors for several types of unit cell (for practical purpose we shall consider $s = \frac{1}{2}$). The whole physics of the infinite chain is contained in the largest-modulus eigenvalue v_1 of the 4×4 transfer matrix. When $s' > \frac{1}{2}$ we develop in the zero-field limit the secular polynomial (depending on v_1 and the field B) up to the B^2 term. By equating it to zero, we get the parallel magnetic susceptibility. When $s' = \frac{1}{2}$ the secular polynomial is simpler, and it is possible to obtain closed forms by using a differentiation method. We study successively the influence of intrachain and interchain nearest-neighbor interaction on the magnetic behavior for two types of unit cell. Some results appear to be of interest for the discussion of weak-interacting-chain lattices. This model is then applied to the one-dimensional compound $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$, which exhibits $(\frac{1}{2}, \frac{1}{2})_N$ double chains coupled by a zigzag interaction path and shows frustration effects.

I. INTRODUCTION

In the past few years, a lot of work has been devoted to the magnetic behavior of so-called ferrimagnetic chains made up of two sublattices that do not compensate each other.¹⁻⁴

Such chain systems may exhibit striking phenomena, such as the occurrence of a compensation temperature, well known for ferrimagnetic garnets, at nonzero temperature.⁵ Likewise, it was recently emphasized that nonuniform one-dimensional (1D) systems exhibiting a subtle stacking of the metal ions, as, for instance ladderlike, branched or trimerized chains, etc., may show unusual behavior.⁶ Some exotic stackings are illustrated in Fig. 1,

where only magnetic sites and exchange interaction pathways are indicated.

Determination of the effective spin Hamiltonian is an important aim when studying 1D physics. It also presents significant interest for chemists since the exchange interaction mechanisms are intimately linked with the nature of the chemical bond. Accordingly, much effort has focused on so-called "1D magnetic lattice engineering" to stabilize exotic systems. Ladderlike and frustrated chains (types A and B in Fig. 1) were isolated in the phosphates $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$,^{7,8} the nitrates $A(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ with $A = \text{Co}(\text{II}), \text{Ni}(\text{II})$,⁹ and molecular complexes such as the hydrazinium copper (II) chloride.¹⁰ Further, the properties of branch chains (type C), i.e., $\text{CoCu}(\text{pbaOH})(\text{H}_2\text{O})_3 \cdot n\text{H}_2\text{O}$,¹¹ and chains of discrete trimers (type D), i.e., $\text{Ca}_3\text{Cu}_3(\text{PO}_4)_4$ (Ref. 12) or $\text{Cu}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 2\text{TMSO}_2$,¹³ were thoroughly investigated, where TMSO_2 is tetramethylene sulfane.

Both the symmetry of interacting spins (z-z, Heisenberg, etc.) and the competition between different exchange pathways are relevant factors for the analysis of magnetic properties. From detailed structural and magnetic studies, it has been possible to determine trends for some 1D systems, but there is not yet any theoretical report on the physics of double chains. This paper is devoted to the discussion of the thermodynamics of ferrimagnetic double chains made of Ising-like interaction ions (z-z couplings) with different spin sublattices. Moreover, we shall use the exact results obtained with this model to show that, in a weakly interacting chain lattice, the short-range-order temperature domain is conveniently described by a model involving quasirigid blocks, the length of which is equal to the correlation length of an isolated chain.

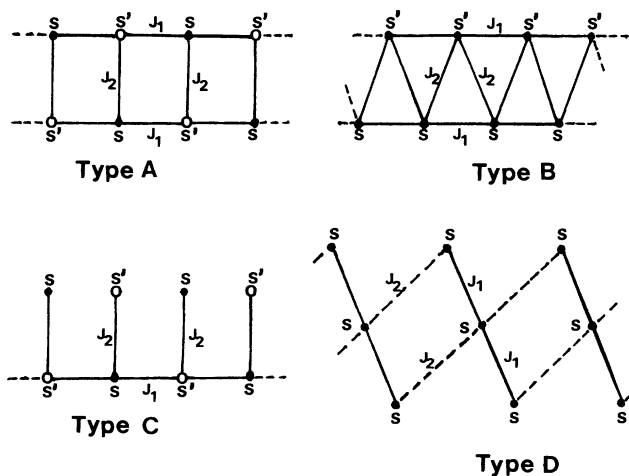


FIG. 1. Structure of type-A, -B, -C, and -D double chains.

II. THEORETICAL ASPECTS

A. Type-A double chains

We first consider the 1D magnetic system shown in Fig. 2. It may be described as a pair of elementary ferrimagnetic chains linked together by interchain interactions in order to constitute a so-called double chain. Only the nearest-neighbor couplings are taken into account, and they are assumed to be relevant between s^z components of the spin operators only. Two kinds of spins are involved, s_k and s'_k ($k = 1, \dots, 2N$), with spin quantum numbers s and s' and Landé factors g and g' , respectively. The present study¹⁴ has been initially motivated, as far as we are concerned with this kind of chain, by the synthesis and experimental work⁷⁻¹⁵ on several low-dimensional phosphates, such as $(\text{VO})_2\text{P}_2\text{O}_7$. The crystal structure of this pyrophosphate exhibits well-isolated double chains of spin- $\frac{1}{2}$ $(\text{VO})^{2+}$ ions (see below). The corresponding Hamiltonian may be written

$$\mathcal{H} = \sum_{i=0}^N (H_i^{\text{ex}} + H_i^{\text{mag}}), \quad (1)$$

with

$$H_i^{\text{ex}} = J_1 [(s_{2i-1}^z + s_{2i+1}^z) s_{2i}^z + (s'_{2i-1}{}^z + s'_{2i+1}{}^z) s_{2i}^z] \\ + J_2 (s_{2i-1}^z s'_{2i-1}{}^z + s_{2i}^z s'_{2i}{}^z), \quad (2)$$

$$H_i^{\text{mag}} = -[g(s_{2i}^z + s'_{2i+1}{}^z) + g'(s'_{2i}{}^z + s_{2i-1}^z)] B. \quad (3)$$

In these expressions J_1 and J_2 refer to intrachain and interchain nearest-neighbor interactions, respectively; note that a few terms are to be dropped from the boundary contributions H_0^{ex} , H_N^{ex} , H_0^{mag} , and H_N^{mag} ; B is the intensity of the magnetic field (assumed to be applied along the z direction).

Let $Z_N(B)$ be the partition for the chain beginning at (s'_1, s'_2) and ending at (s_{2N}, s_{2N+1}) . Let $Z_N(B)$ be the vec-

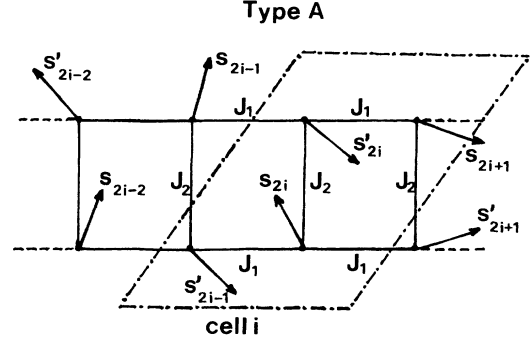


FIG. 2. Structure of the unit cell for a type-A double chain.

tor defined as follows: m_N represents the current state of the pair (s_{2N}, s_{2N+1}) characterized by the values of s_{2N}^z and s_{2N+1}^z . Among all the states of the chain contributing to the sum $Z_N(B)$, we consider those for which the last pair (s_{2N}, s_{2N+1}) is associated with m_N . The corresponding part of the summation gives the component $Z_N^{m_N}(B)$. As a result, the vector $Z_N(B)$ has $d = (2s + 1)(2s' + 1)$ components and we can write

$$Z_N(B) = \sum_{m_N} Z_N^{m_N}(B). \quad (4)$$

We can similarly define the quantities $Z_{N-1}(B)$, $Z_{N-1}^{m_{N-1}}(B)$, and $Z_{N-1}^{m_{N-1}-1}(B)$ related to a chain beginning again at (s'_1, s'_2) but ending at (s_{2N-2}, s_{2N-1}) . It is easily shown that $Z_N(B)$ and $Z_0(B)$ are related by the relationship

$$Z_N(B) = (\mathcal{T})^N Z_0(B), \quad (5)$$

where (\mathcal{T}) is a square $d \times d$ matrix (transfer matrix). Its current element $(\mathcal{T})_{m_i m_{i-1}}$ is given by

$$(\mathcal{T})_{m_i m_{i-1}} = \exp[\beta g B (s_{2i}^z + s'_{2i+1}{}^z)] \frac{\sinh\{(\beta/2)(2s' + 1)[J_1(s_{2i-1}^z + s_{2i+1}^z) + J_2 s_{2i}^z - g' B]\}}{\sinh\{(\beta/2)[J_1(s_{2i-1}^z + s_{2i+1}^z) + J_2 s_{2i}^z - g' B]\}} \\ \times \frac{\sinh\{(\beta/2)(2s + 1)[J_1(s_{2i-2}^z + s_{2i}^z) + J_2 s_{2i-1}^z - g B]\}}{\sinh\{(\beta/2)[J_1(s_{2i-2}^z + s_{2i}^z) + J_2 s_{2i-1}^z - g B]\}} \quad (6)$$

where s_{2i}^z , s_{2i+1}^z , s_{2i-2}^z , and s_{2i-1}^z are given by m_i and m_{i-1} . Clearly, because of the regular structure of the chain (\mathcal{T}) appears to be independent of i . Let us now label $v_1(B)$, $v_2(B)$, \dots , the eigenvalues of the matrix (\mathcal{T}) , ordered in the decreasing modulus order, and $e_1(B)$, $e_2(B)$, \dots , the corresponding unitary eigenvectors. Let $Z_N^\mu(B)$ be the component of $Z_N(B)$ along $e_\mu(B)$. We may then write

$$Z_N(B) = \sum_{\mu=1}^d [v_\mu(B)]^N Z_0^\mu(B) e_\mu(B). \quad (7)$$

In the infinite-chain limit, only the contribution associat-

ed with the dominant (largest-modulus) eigenvalue $v_1(B)$ need be retained. As a result,

$$\ln[Z_N(B)] \underset{N \rightarrow +\infty}{\sim} N \ln[v_1(B)]. \quad (8)$$

Thus the whole physics of the infinite chain is involved in the dependence of the dominant transfer-matrix eigenvalue (or its logarithm) on the various relevant parameters. We immediately get, for the magnetization \mathcal{M}_\parallel and the zero-field susceptibility χ_\parallel referred to the unit cell (containing two s - and two s' -type spins),

$$\mathcal{M}_{\parallel} = \frac{1}{\beta} \frac{\partial \ln[v_1(B)]}{\partial B}, \quad (9)$$

$$\chi_{\parallel} = \frac{1}{\beta} \left[\frac{1}{v_1(B)} \frac{\partial^2 v_1(B)}{\partial B^2} \right]_{B=0}.$$

For $s = \frac{1}{2}$, (\mathcal{T}) is 4×4 matrix. In the zero-field limit, it is easily transformed into two 2×2 diagonal blocks, thus allowing for an analytical treatment. For nonvanishing magnetic field, the secular polynomial must be developed as a B power series up to the B^2 term:

$$P(v_1, B) = v_1(0)^4 + \left[a + \frac{a''}{2} B^2 \right] v_1(0)^3 + \left[b + \frac{b''}{2} B^2 \right] v_1(0)^2 + \left[c + \frac{c''}{2} B^2 \right] v_1(0) + d + \frac{d''}{2} B^2 \quad (10)$$

(the first power of B actually disappears as a result of the field-reversal symmetry of the system under consideration). It is then possible, equating this polynomial to zero, to express the B variation of v_1 up to second order. We then get the zero-field susceptibility

$$\chi_{\parallel} = - \frac{1}{\beta v_1(0)} \frac{a'' v_1(0)^3 + b'' v_1(0)^2 + c'' v_1(0) + d''}{4 v_1(0)^3 + 3 a v_1(0)^2 + 2 b v_1(0) + c}. \quad (11)$$

The detailed resulting expression is somewhat cumbersome and need not be reproduced *in extenso*. When both spins s and s' are equal to $\frac{1}{2}$, the magnetic susceptibility reduces to an expression that is easier to handle and which is given in the Appendix.

In order to have better insight, we shall essentially consider the $\chi_{\parallel} T$ product normalized to its infinite-temperature value (the Curie constant). This normalized value will be called $(\chi_{\parallel} T)_n$. In the low-temperature range, the parallel susceptibility is mainly related to the value of the magnetic moment per unit cell in the ground state, which depends on the sign of the exchange interaction constants J_1 and J_2 . This moment may vanish under various conditions: (i) The s and s' sublattices are separately antiferromagnetic (this occurs when the product $J_1 J_2$ is negative) and (ii) these sublattices are ferromagnetic, but they carry opposite moments which compensate exactly ($J_1 J_2$ is positive). Practically, such a situation may occur essentially when similar cations occupy both lattice sites.

The curves in Fig. 3 correspond to a type-A $(\frac{1}{2}, 1)$ chain with the ratio $r = g's'/gs$ taken equal to 2.5. They have been drawn assuming $|J_2|$ much smaller than $|J_1|$ in order to point out the influence of a weak interchain coupling which must never be completely ignored in so-called 1D magnetic substances. For the $(--)$ and $(-+)$ curves, J_1 is negative and the moments add together on each elementary chain considered separately.

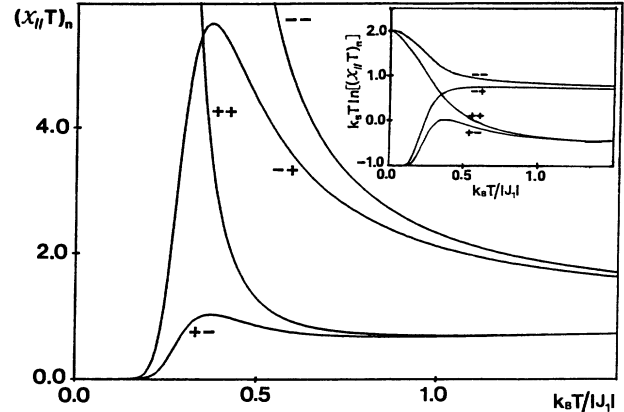


FIG. 3. $(\chi_{\parallel} T)_n$ product thermal variation for a type-A double chain ($s = \frac{1}{2}$, $s' = 1$, $g'/g = 2.5$, $|J_2| = 0.05|J_1|$); the signs which label the curves are those of J_1 and J_2 (inset, thermal variation of $k_B T \ln[(\chi_{\parallel} T)_n]$; note that positive exchange refers to antiferromagnetic coupling).

In the $(--)$ case, the chains are coupled ferromagnetically. This results in an enhancement of the low-temperature exponential divergence of the $(\chi_{\parallel} T)_n$ product. It has been shown in previous work^{16,17} that, in the low-temperature range, a chain behaves essentially as an assembly of independent rigid blocks with length ξ , where ξ is the correlation length. In the $(-+)$ case, the (nearly ferromagnetically ordered) elementary chains are coupled antiferromagnetically. Then the $(\chi_{\parallel} T)_n$ divergence is maintained down to the temperature at which the interchain exchange energy of two such blocks with length ξ becomes similar to $k_B T$. This crossover temperature T_0 thus appears to be solution of the equation

$$\frac{k_B T}{|J_2|} = \xi \left[\frac{k_B T}{|J_1|} \right]. \quad (12)$$

Solving this equation with the numerical values of Fig. 3, we get $k_B T_0 / |J_2| = 0.34$. This value exactly corresponds to the maximum of the $(-+)$ curve. The $(++)$ and $(+-)$ curves show similar behavior despite a less prominent maximum for $(+-)$ due to partial compensation of the moments (antiferromagnetic coupling) in each elementary chain.

The $(+-)$ and $(-+)$ curves are examples of case (i) (see above), where the magnetic moments of both sublattices vanish in the ground state. Let us now briefly examine case (ii) (compensation situation). It has been pointed out^{18,19} that for single ferrimagnetic chains, with spin alternation $\dots s, s', s, s', \dots$, and nearest-neighbor z - z antiferromagnetic coupling, the low-temperature magnetic susceptibility is essentially governed in the compensation case by the spin quantum numbers s and s' . This results from a subtle competition between long- and short-range correlations (more specifically, between the increase of the correlation length ξ and the decrease of the effective magnetic moment carried by the unit cell) as the temperature decreases.

TABLE I. Low-temperature behavior of a type-A double chain with z-z-type coupling (compensation case).

$s' \leq 1$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} 0$
$s' > 1$ $J_2/J_1 < 2(s'-1)$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} +\infty$
$J_2/J_1 = 2(s'-1)$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} \frac{2}{s'^2} \left(\frac{g}{2} \right)^2$
$J_2/J_1 > 2(s'-1)$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} 0$

In the present case, a detailed examination shows that similar, although more complex, effects are observed. Actually, it appears that the ratio between the exchange interactions, J_2/J_1 , is also of critical importance. The results (given for the $\chi_{\parallel} T$ product) are summarized in Table I and illustrated by Fig. 4.

B. Type-B double chains

We now turn to type-B chains. Such magnetic chains were observed in the phosphate $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$ and, more recently, in the nitrate $\text{Co}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$. In such systems the magnetic moments are carried by the $\frac{1}{2}$ spins associated with the $(\text{VO})^{2+}$ and Co^{2+} ions (see below).²⁰ For this type of chain, with the current cell now involving only two spins s_i and s'_i (Fig. 5), the Hamiltonian is given by (1), with now

$$H_i^{\text{ex}} = J_1 s_{i-1}^z s_i^z + J'_1 s'_{i-1}{}^z s'_i{}^z + J_2 s_i^z (s'_{i-1}{}^z + s'_i{}^z), \quad (13)$$

$$H_i^{\text{mag}} = -(g s_i^z + g' s'_i{}^z) B. \quad (14)$$

Note that similar remarks concerning the edge contributions ($i=0$ or N) are also relevant. Following the same procedure as previously, the typical term for the transfer

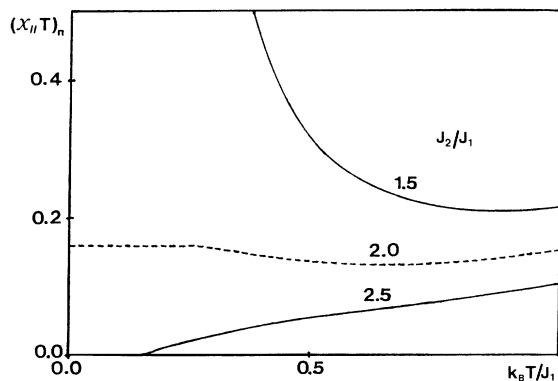


FIG. 4. Thermal variation of the $(\chi_{\parallel} T)_n$ product for a compensated $(\frac{1}{2}, 2)$ type-A double chain, for several values of the J_2/J_1 ratio ($J_1 > 0$).

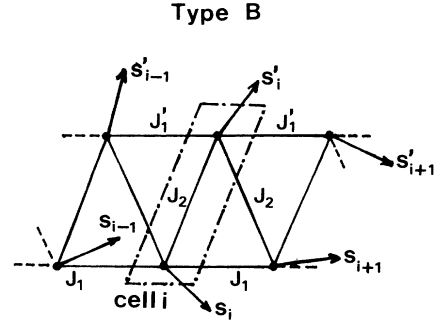


FIG. 5. Structure of the unit cell for a type-B double chain.

matrix is now given by

$$(\mathcal{T})_{m_i, m_{i-1}} = \exp\{ -\beta [J_1 s_{i-1}^z s_i^z + J'_1 s'_{i-1}{}^z s'_i{}^z + J_2 s_i^z (s'_{i-1}{}^z + s'_i{}^z) - (g s_i^z + g' s'_i{}^z) B] \}, \quad (15)$$

where $s_i^z, s'_i{}^z$ and $s_{i-1}^z, s'_{i-1}{}^z$ are given by m_i and m_{i-1} . The partition function and zero-field magnetic susceptibility are also calculated in a similar way. For the simple case of a double chain with $s' = s = \frac{1}{2}$, $g' = g$, and $J'_1 = J_1$, the magnetic susceptibility reduces to a closed expression (see Appendix). We discuss now the main difference between type-A and -B double chains: It concerns the possibility of frustration effects. We shall thus essentially consider the case of positive (antiferromagnetic) exchange interaction along both elementary chains (J_1).

For negative (ferromagnetic) J_1 , each elementary chain exhibits a ferromagnetic ground state and is magnetized ferromagnetically or antiferromagnetically with respect to the other one, depending on the sign of J_2 . For positive J_2 the overall ground state is antiferromagnetic and the $(\chi_{\parallel} T)_n$ product vanishes as $\exp(\beta(J_1 - J_2/2))$ on cooling down. For negative J_2 the overall ground state is ferromagnetic and the $(\chi_{\parallel} T)_n$ product diverges as $\exp[-\beta(J_1 + J_2/2)]$.

For positive J_1 frustration occurs whatever the sign of

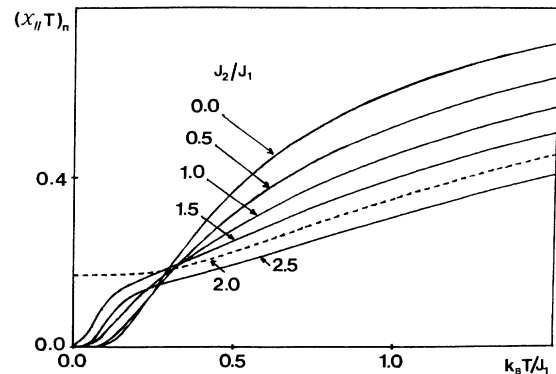


FIG. 6. Thermal variation of the $(\chi_{\parallel} T)_n$ product for a $(\frac{1}{2}, \frac{1}{2})$ type-B double chain, for $J_1 > 0$ and various positive J_2 values.

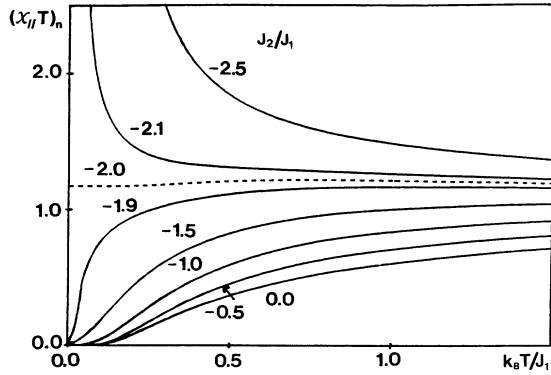


FIG. 7. Thermal variation of the $(\chi_{\parallel} T)_n$ product for a $(\frac{1}{2}, \frac{1}{2})$ type-B double chain, for $J_1 > 0$ and various negative J_2 values.

J_2 . In any case the ground-state configuration depends on the sign of $|J_2| - 2J_1$. If this quantity is positive, J_2 prevails and the structure is ferromagnetic or antiferromagnetic along the zigzag path, depending on the sign of J_2 . At low temperature the $(\chi_{\parallel} T)_n$ product diverges or vanishes according to the laws $\exp[-\beta(J_1 + J_2/2)]$ and $\exp[\beta(J_1 - J_2/2)]$, respectively (Figs. 6 and 7). In that case J_1 is always frustrated at low temperature. For weaker J_2 values, J_1 prevails. Each elementary chain is antiferromagnetic at low temperature, showing a decrease of the $(\chi_{\parallel} T)_n$ product according to $\exp[-\beta(J_1 - |J_2|/2)]$. The occurrence of $|J_2|$ in the exponent clearly indicates that J_2 , whatever its sign, tends to destabilize the ground-state arrangement (Figs. 6 and 7). For the critical case ($|J_2| = 2J_1$), the $(\chi_{\parallel} T)_n$ product reaches a finite value at low temperature, which actually depends on the sign of J_2 (the results given for the $\chi_{\parallel} T$ product are summarized in Table II).

Of course, it is not realistic to imagine experimental situations for which $|J_2|$ exactly equals $2J_1$. But this condition could be approached in some real compounds. In that case, as observed in Fig. 7 for negative J_2 , the $(\chi_{\parallel} T)_n$ product should be almost temperature independent down to temperatures close to $|J_2 + 2J_1|/k_B$. Such temperatures may be low enough for the material to behave like a pure or weakly interacting paramagnet in the whole experimental temperature range, thus sustaining possible erroneous interpretations.

TABLE II. Low-temperature behavior of a type-B double chain with z - z type coupling in the critical frustration case.

$J_1 > 0, J_2 = 2J_1$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} \frac{1}{4} \left(\frac{3}{\sqrt{5}} - 1 \right) \left(\frac{g}{2} \right)^2$
$J_1 > 0, J_2 = -2J_1$	$\chi_{\parallel} T \xrightarrow{T \rightarrow 0} \frac{1}{4} \left(\frac{3}{\sqrt{5}} + 1 \right) \left(\frac{g}{2} \right)^2$

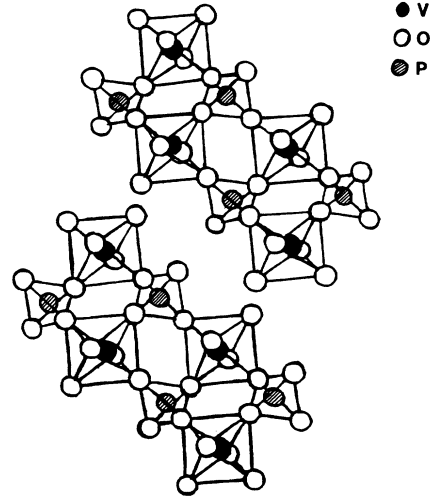


FIG. 8. Structure of the compound $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$.

III. DOUBLE CHAIN $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$

A. Structure description

The crystal structure of $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$, solved by Leonowicz *et al.*,⁸ is triclinic with space group P_{-1} and unit-cell parameters $a = 8.38 \text{ \AA}$, $b = 8.92 \text{ \AA}$, $c = 13.46 \text{ \AA}$, $\alpha = 79.9^\circ$, $\beta = 76.3^\circ$, and $\gamma = 71.0^\circ$.

It can be described from the stacking of (VO_6) octahedra and (PO_4) tetrahedra, which form infinite double chains parallel to the crystallographic a direction (Fig. 8). The nearest-neighbor interactions between vanadium ions involve one bridging species (PO_4) along a single chain and two bridging species in the other direction (Fig. 9). The double chains are related by lattice translation in the b direction, thus forming rippled sheets connected to each other through hydrogen bonds of water molecules.

The local surrounding of metal ions shows that vanadyl species, characterized by a short V-O bond ($d = 1.6 \text{ \AA}$), are stabilized. Accordingly, the above phosphate may be viewed as a collection of type-B double chains made of $s = \frac{1}{2}$ spins. It represents a good example to investigate frustration effects in a 1D system, although z - z exchange couplings are questionable for vanadyl ions.

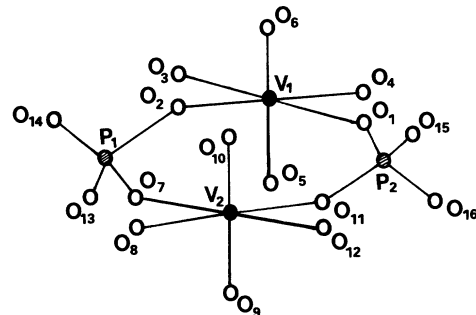


FIG. 9. Structure of the $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$ unit cell.

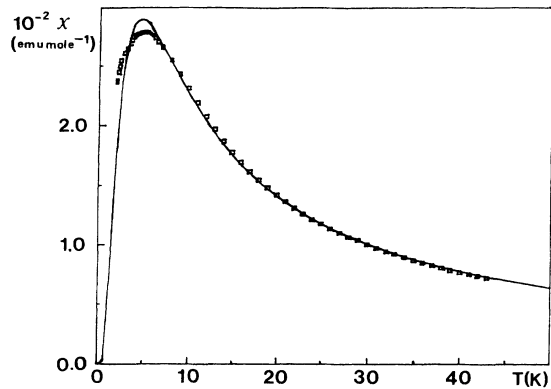


FIG. 10. Experimental results (dotted line, $J_1=9.3$ K, $J_2=-1.7$ K, $g=1.9$) and theoretical curve for the parallel susceptibility of the compound $\text{VO}(\text{HPO}_4)\cdot 4\text{H}_2\text{O}$.

B. Discussion of magnetic results

The temperature dependence of the magnetic susceptibility is plotted in Fig. 10. At high temperature $\chi(T)$ obeys the Curie-Weiss law for $s=\frac{1}{2}$ and a Landé factor close to 1.9. At low temperature a maximum of susceptibility is observed around 5 K; then $\chi(T)$ decreases on further cooling. Such a behavior is typical of a regular antiferromagnetic 1D system with weak exchange coupling between nearest neighbors.

On close examination of the exchange pathways, it appears that intrachain and interchain interactions involve both phosphate groups, but with different bond angles. As a result, the sign and magnitude of both exchange constants J_1 and J_2 may differ, since magnetic couplings are strongly dependent on structural features.

Using the type-B double-chain model investigated above, we have fitted the experimental data by letting J_1 and J_2 vary. The best agreement between theory and experiment, displayed in Fig. 10, corresponds to the parameters $J_1=9.3$ K, $J_2=-1.7$ K, and $g=1.9$. It can be noted that the agreement with experiment is good, except in the vicinity of the $\chi(T)$ maximum, where some discrepancy occurs. Such a disagreement is probably related to the nature of exchange interactions, which are the most likely Heisenberg-like, while an anisotropic model was assumed for simplification.

Focusing now on the values of the exchange parameters, it appears that J_1 (intrachain) is antiferromagnetic while J_2 (interchain) is ferromagnetic, thus promoting a frustrated spin configuration in the ground state. As discussed above, the system reduces, for $|J_2| \ll 2J_1$, to two weakly coupled antiferromagnetic chains, and whatever the sign of J_2 , a maximum of susceptibility must be ob-

served. For positive or negative J_2 , the same number of frustrated pathways is obtained, so that the value of this parameter may be questionable.

IV. CONCLUSION

It must be emphasized that the temperature below which the interchain coupling begins significantly to operate should be higher than that at which tridimensional long-range ordering sets in. To some extent this distinction is similar to that delimiting short- and long-range order in two-dimensional networks, since the chain structure may actually be viewed as a two-dimensional array of chains. As is well known, the short-range temperature ordering domain is very large in two-dimensional systems. In the present case, as long as one excludes the vicinity of the long-range ordering domain, most of the results obtained in this paper may be used for analyzing the thermodynamical behavior. Specifically, at temperature T , the chain system may be considered as an assembly of giant magnetic moments, each one with magnitude $M\xi(T)$ (where M is the magnitude of the magnetic moment per unit cell), coupled together by the interaction $J_2\xi(T)$.¹⁷ The exact calculations presented in this work confirm this point of view with a very good accuracy in the case of the double z-z chain. This provides us with further proof that this temperature-dependent parameter $J_2\xi(T)$ can be introduced into a standard molecular-field process, involving the number \mathcal{N} of chains interacting with a given one.²¹⁻²³

APPENDIX

For the simplest case of a type-A or -B double chain with $s=s'=\frac{1}{2}$, it is possible to obtain a closed-form expression for the parallel magnetic susceptibility. For the type-A double chain, the unit cell reduces to a couple of spins ($s_i \cdot s'_i$), each one belonging to a single chain; the corresponding Hamiltonian may be written

$$H_i^{\text{ex}, A} = J_1(\sigma_i \sigma_{i+1} + \sigma'_i \sigma'_{i+1}) + J_2 \sigma_i \sigma'_i, \quad (\text{A1})$$

$$H_i^{\text{mag}, A} = -g(\sigma_i + \sigma'_i),$$

where $\sigma = \sigma' = \frac{1}{2}$; for the type-B double chain, expressions (13) and (14) remain valid.

Using the unitary transformation matrix

$$(\mathcal{V}) = (\mathcal{V})^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix}, \quad (\text{A2})$$

now both types of transfer matrix can be worked out in a similar framework:

$$(\mathcal{T}) = \begin{pmatrix} X_1 \cosh(2L) & Y_3 \cosh(2L) & Y_4 \sinh(2L) & X_4 \sinh(2L) \\ Y_1 & X_2 & 0 & 0 \\ 0 & 0 & X_3 & Y_2 \\ X_1 \sinh(2L) & Y_3 \sinh(2L) & Y_4 \cosh(2L) & X_4 \cosh(2L) \end{pmatrix}, \quad (\text{A3})$$

where

	Type A	Type B	
X_1	$b(a + a^{-1})$	$ab^2 + a^{-1}$	(A4)
X_2	$b^{-1}(a + a^{-1})$	$ab^{-2} + a^{-1}$	
X_3	$b^{-1}(a - a^{-1})$	$ab^{-2} - a^{-1}$	
X_4	$b(a - a^{-1})$	$ab^2 - a^{-1}$	
Y_1	$b^2 + 1$	$2b$	
Y_2	$b^2 - 1$	0	
Y_3	$b^{-2} + 1$	$2b^{-1}$	
Y_4	$b^{-2} - 1$	0	

and

$$a = \exp\left[-\frac{\beta J_1}{2}\right], \quad b = \exp\left[-\frac{\beta J_2}{4}\right], \quad L = \beta \frac{g}{2} B. \quad (\text{A5})$$

In the zero-field limit, (T') reduces to two 2×2 diagonal blocks and the eigenvalues can be easily calculated:

$$\begin{bmatrix} v_1(0) \\ v_2(0) \end{bmatrix} = \frac{1}{2}(X_1 + X_2 \pm R), \quad \begin{bmatrix} v_3(0) \\ v_4(0) \end{bmatrix} = \frac{1}{2}(X_3 + X_4 \pm R'), \quad (\text{A6})$$

where

$$R = [(X_1 - X_2)^2 + 4Y_1 Y_3]^{1/2}, \quad R' = [(X_3 - X_4)^2 + 4Y_2 Y_4]^{1/2}. \quad (\text{A7})$$

For a nonvanishing magnetic field, the secular polynomial $P(v, B)$ is

$$\begin{aligned} P(v, B) = & v^4 - v^3[X_2 + X_3 + (X_1 + X_4)W] + v^2[\{(X_1 + X_4)(X_2 + X_3) - Y_1 Y_3 - Y_2 Y_4\}W + X_1 X_4 + X_2 X_3] \\ & - v[X_1 X_2 X_4 W^2 + \{X_3(X_1 X_2 - Y_1 Y_3) + X_2(X_3 X_4 - Y_2 Y_4)\}W \\ & + X_1(X_3 X_4 - Y_2 Y_4) - X_4 Y_1 Y_3] + (X_1 X_2 - Y_1 Y_3)(X_3 X_4 - Y_2 Y_4), \end{aligned} \quad (\text{A8})$$

where

$$W = \cosh(\beta g B). \quad (\text{A9})$$

It has no evident roots. However, after differentiation, we get the parallel magnetic susceptibility

$$\chi_{\parallel} = -\frac{1}{2\beta v_1(0)} \left[\frac{\partial^2 W}{\partial B^2} \right]_{B=0} \frac{[\partial P(v_1, W(B))/\partial W]_{B=0}}{[\partial P(v, W(0))/\partial v]_{v=v_1(0)}}. \quad (\text{A10})$$

In this expression the factors $[\partial P(v_1, W(b))/\partial W]_{B=0}$ and $(\partial^2 W/\partial B^2)_{B=0}$ are rapidly deduced from Eqs. (A8) and (A9); we note that the term $[\partial P(v, W(0))/\partial v]_{v=v_1(0)}$ is also the product

$$[v_1(0) - v_2(0)][v_1(0) - v_3(0)][v_1(0) - v_4(0)].$$

Then (A10) becomes

$$\begin{aligned} \chi_{\parallel} = & \beta \left[\frac{g}{2} \right]^2 (ER)^{-1} \{ (X_1 + X_4)[v_1(0)]^2 + [Y_1 Y_3 + Y_2 Y_4 - (X_1 + X_4)(X_2 + X_3)]v_1(0) \\ & + X_3(X_1 X_2 - Y_1 Y_3) + X_2(X_3 X_4 - Y_2 Y_4) \}. \end{aligned} \quad (\text{A11})$$

where

$$E = 2a^{-2}U^2 + a^{-1}RU + 2V \quad (\text{A12})$$

and

Type A	Type B	
$U \cosh(\beta J_2/4)$	1	(A13)
$V \cosh^2(\beta J_2/4)$	$\cosh(\beta J_2/4)$	

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