Magnetic properties of (VO)$_2$P$_2$O$_7$: two-plane structure and spin-phonon interactions

G. S. Uhrig$^1$ and B. Normand$^2$

$^1$Institut für Theoretische Physik, Universität zu Köln, D-50937 Köln, Germany.
$^2$Theoretische Physik III, Universität Augsburg, D-86135 Augsburg, Germany.

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Detailed experiments on single-crystal (VO)$_2$P$_2$O$_7$ continue to reveal new and unexpected features. We show that a model composed of two, independent planes of spin chains with frustrated magnetic coupling is consistent with nuclear magnetic resonance and inelastic neutron scattering measurements. The pivotal role of PO$_4$ groups in mediating intrachain exchange interactions explains both the presence of two chain types and their extreme sensitivity to certain lattice vibrations, which results in the strong magnetoelastic coupling observed by light scattering. We compute the respective modifications of the spin and phonon dynamics due to this coupling, and illustrate their observable consequences on the phonon frequencies, magnon dispersions, static susceptibility and specific heat.

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I. INTRODUCTION

Vanadyl pyrophosphate (VOPO) presents a quantum magnetic system of $S = \frac{1}{2}$ V$^{4+}$ ions, whose antiferromagnetic (AF) Heisenberg superexchange interactions give a singlet ground state, with spin gap $\Delta = 3.1$meV. While early powder susceptibility and inelastic neutron scattering (INS) experiments were consistent with both spin-ladder and alternating-chain models, the first INS measurements on aligned single crystals confirmed the magnetic structure to be of alternating-chain conformation. In conjunction with observations on the structurally related material VODPO$_4 \propto$D$_2$O, the following picture was verified: the strongest exchange path ($J_1$) is the double V-O-P-O-V link through two phosphate groups along $\hat{b}$; the next strongest ($J_2$) is the double V-O-V link between edge-sharing VO$_5$ square pyramids, also along $\hat{b}$; the structurally dimerized chains have coupling ratio $\lambda = J_2/J_1 \approx 0.5$. The V-O-V bond along $\hat{a}$ is very weak. These results are consistent with the single electron on V$^{4+}$ occupying the d$_{xy}$ or t$_{2g}$ orbital (bc plane).

The same experiments obtained detailed measurements of a second, low-lying, triplet excitation with gap 5.7meV and significant intensity over at least half of the Brillouin zone, while in addition the coupling between dimerized chains was found to be weakly ferromagnetic (FM). Interpretation of the latter features was offered in terms of a frustrated coupling of the dimerized chains, via the long but presumably not insignificant V-O-P-O-V-P-O-V pathway, which would promote a triplet, two-magnon bound state. Although VOPO has a complicated structure which contains 8 V atoms per unit cell, the almost identical interatomic distances d$_{VV}$ suggested a model treating all dimers as identical magnetic unit cells.

Since the proposal of this picture, three important, additional experiments have been conducted on VOPO single crystals, namely further inelastic neutron scattering (INS) measurements, Nuclear Magnetic Resonance (NMR) studies and Raman light scattering. Each has offered new, and sometimes surprising, additional information concerning the physics of VOPO. The purpose of this work is to review these results and provide a new, minimal model which encapsulates all of the observed effects. We proceed in Sec. II with a discussion of INS and NMR results which lead to a two-plane description. In Sec. III we consider the strong magnetoelastic coupling observed by Raman scattering, and present a theoretical treatment of the coupled magnon-phonon system by the flow-equation method. The consequences of this coupling are illustrated for a variety of experimentally measurable quantities in Sec. IV. Sec. V contains a summary and conclusions.

II. NMR AND BILAYER STRUCTURE

Contrary to the expectation of magnetically identical V$^{4+}$ ions, NMR measurements of the Knight Shift and relaxation rate $1/T_1$ give clear evidence for two distinct species of $^{31}$P and $^{51}$V nuclei in VOPO. While results for both atomic species were not fully consistent, the presence of separate magnetic environments is quite unambiguous. An interpretation requires two distinct planes of coupled, dimerized chains, with different exchange constants ($J_1$, $J_2$)$_{A,B}$, resulting in different spin gaps $\Delta_{0A}$ and $\Delta_{0B}$.

This deduction is consistent with the structure, where 8 inequivalent V atoms occupy 2 dimers per chain and 2 chains per cell: despite the very small differences in V-V separations, these dimer units are clearly not identical. The very weak c-axis coupling, observed in the INS dispersion, acts to isolate the differing planes of coupled chains. The two triplet branches measured by INS have the simple interpretation of two one-magnon dispersion curves, one from each plane: this explains why their intensities have very similar $\mathbf{q}$-dependences. The reported gaps $\Delta_{0B} = 35K$ and $\Delta_{0A} = 68K$ are in excellent agreement with the results of Ref.

To answer the question of why the $J$ values in the two
planes are so different, we note that the previous treatment of all dimers as identical magnetic unit cells was based on the fact that differences in $d_{V\chi}$ are $O(10^{-3})$ of the unit cell dimensions. However, inspection of the structural parameters reveals that differences in the locations of P atoms, and thus in the interatomic P-V distances $d_{P\chi}$, are $O(10^{-2})$. The PO$_4$ group is the essential element mediating the dominant superexchange path V-O-P-O-V. While quantitative accuracy is still lacking in ab initio superexchange calculations, particularly for V systems, the interaction magnitude is well known to have a very strong dependence on both interatomic spacings and bond angles. Thus one may expect a strong difference between values $J_{1A}$ and $J_{1B}$, but similar values of $J_{2A}$ and $J_{2B}$.

![Schematic representation of the VOPO system](image)

**FIG. 1.** Schematic representation of the VOPO system; A and B denote the two decoupled types of plane.

Retaining the basic framework of Ref. 7, we consider thus a model of two independent types of planes of alternating chains (Fig. 1). We begin by fitting the two independent magnon branches to determine the appropriate, effective superexchange constants. This is performed within a “static model”, by which is meant one with temperature-independent effective interactions, in contrast with the situation in Sec. IV where we will consider a model with phonon dynamics. The magnons are described by mobile triplet excitations and the fitting procedure differs from that presented for the single-plane model in two minor respects. First, as mentioned in that work, we fit the square of each dispersion curve,

$$\omega^2_\gamma(q) = J^2_{1\gamma} \sum_{ij} u_{ij\gamma} \cos(iq_y) \cos(jq_x),$$

(1)

because this smoother quantity gives a superior fit to the same order of expansion. The parameters $u_{ij\gamma}$ for $\gamma = A, B$, are determined to third order from the quantities $t_{ij}$ in Eq. (1) of Ref. 7 as

$$u_{00} = 1 + 7\lambda^3/32 + 2\nu^2 + 3\mu^2/4 - 2\lambda \alpha + 2\alpha^2 - (15\lambda^2\alpha + 6\lambda\alpha^2 - 12\alpha^3)/16$$

$$u_{10} = -\lambda - \lambda^2/2 + \mu^2/2 + 2\alpha + 5\lambda^3/32$$

$$-7\lambda^2\alpha/16 - 9\alpha^2/8 + 3\alpha^3/4$$

$$u_{01} = 2\mu_+ + 3\mu^2/4 - \lambda^2\mu_+ - 3\lambda^3/16$$

$$u_{20} = (\lambda^3 - 2\lambda^2\alpha + 4\alpha^2 - 8\alpha^3)/16$$

(2)

$$u_{02} = -\mu^2/2$$

$$u_{11} = -3\lambda^2\mu_+ - 4\alpha^2 - \lambda_+\mu_+ - 2\alpha_+\mu_+.$$

Here $\lambda = J_2/J_1$ (Fig. 1), $\mu_+ = (J_a + J_b)/J_1$ and $\mu_- = (J_a - J_b)/J_1$. The transverse part of the dispersion $\omega_\gamma(q)$ is very sensitive to the difference $\mu_-\gamma$. The parameter $\alpha = J_f/J_1$ denotes a frustrating, next-neighbor interaction $(J_f)$ along the spin chains. It is not present in our minimal model (Fig. 1) and is not used in the fits presented in this section, but is included here for reference from Sec. IV, where such a term is generated within the dynamical model. The second difference from Ref. 7 is that we do not determine $\mu_-\gamma$ from the condition on the Curie temperature deduced from the magnetic susceptibility, as this procedure may no longer be applicable in the presence of phonons coupled strongly to the spin subsystem (below). Instead we deduce the values $\mu_-\gamma$ from the maximum $\chi_{\max}$ of the measured susceptibility curve.

![Fitted dispersion relations](image)

**FIG. 2.** Fitted dispersion relations for the two elementary magnons, (a) in chain direction at $q_a = 0$ and (b) transverse to chains at $q_b = 0$. Data from Refs. 3 and 15.

The fit (Fig. 2) yields the following effective parameters:

$$(J_{1A}, J_{2A}, J_{3A}, J_{4A}) = (144.9K, 95.5K, 11.6K, 16.4K)$$

$$(J_{1B}, J_{2B}, J_{3B}, J_{4B}) = (122.9K, 95.0K, 13.4K, 18.6K).$$

(3)

The dimerization parameters $\lambda_A = 0.659$ and $\lambda_B = 0.772$ are rather different in each set of chains, but the values of
$J_2$ are similar, as expected from the considerations above (V-O-V superexchange). These static-model results for the chain couplings $J_1$ and $J_2$ are very close to those of the NMR experiment and are also in accord with values obtained recently by a detailed fit based on uncoupled, dimerized chains. In comparison with the latter, the present procedure has the advantage of containing the true dimensionality of the magnon dispersion, so that no discrepancy occurs between a gap from a chain fit and a gap including interchain coupling. Furthermore, we find that non-crossing magnon dispersion curves have a better physical justification due to the similarity of $J_2$ superexchange paths in both types of plane. Pressure-dependent measurements and comparative ab initio studies would be required to shed further light on the variation of superexchange parameters with atomic positions.

In comparison with the single-plane model, the frustrated interchain coupling is significantly weaker: in obvious notation, $\mu_{aA} = 0.080$, $\mu_{aB} = 0.109$, $\mu_{bA} = 0.113$, $\mu_{bB} = 0.151$. Any bound states of the elementary magnons can be expected to be at best only very weakly bound, and in addition to have very low weight. Another significant difference comes in calculating the static susceptibility $\chi(T)$ in the two-plane model: the fit to single-crystal susceptibility data is much improved in terms of $T_{\text{max}}$ (see Fig. 3). This arises because of the contribution of the higher-energy magnon band. Because the calculation of $\chi(T)$ is approximate, in that it involves only one-magnon contributions with interaction effects on a mean-field level, remaining discrepancies between theory and experiment are not unexpected. However, this last point cannot account for the inconsistency observed in the high-temperature regime, where the moments should behave independently, and we return to this issue below.

Two features remain the same as the previous framework. First, we contend that two, mutually frustrating AF interactions between the alternating chains remain the most likely scenario to account for the form of the FM $\omega$-axis dispersion. This is fitted appropriately by the weaker values ($J_a$, $J_b$) above. Although this may only be treated qualitatively, the condition on the Curie temperature, $\Theta_{\text{CW}} = -\frac{1}{8} \sum_\gamma \left[ J_{1\gamma} + J_{2\gamma} + 2(J_{0\gamma} + J_{0\gamma}) \right]$, $\Theta_{\text{CW}} = -\frac{1}{8} \sum_\gamma \left[ J_{1\gamma} + J_{2\gamma} + 2(J_{0\gamma} + J_{0\gamma}) \right]$, (4) provides further support for frustrated couplings, because the chain couplings alone remain unable to satisfy this sum. Second, the two-dimensional dispersion relation in $(q_0, q_0)$, with logarithmic singularities in the density of states, remains essential to explain the temperature scales of thermodynamic properties such as $\chi(T)$ and the electron spin resonance absorption.

### III. SPIN-PHONON INTERACTIONS

Recent Raman light-scattering experiments on single crystals of VOPO$_4$ have shown two important new features. One is a strong anharmonicity, in the form of a hardening (frequency increase) with decreasing temperature, of certain phonons, and the other a strong quasielastic scattering of magnetic origin. Both features are clear, qualitative evidence for magnetoelastic coupling. In the phonon system, the frequencies and polarizations of strongly renormalized phonons indicate oscillations of the phosphate (PO$_4$) groups. In particular, the 123cm$^{-1}$ phonon observed in $aa$ polarization (in-plane motion transverse to the chains, expected to have the strongest coupling) loses intensity very rapidly to the spin degrees of freedom. In the spin system, quasielastic scattering originates in energy fluctuations of the spins, which are strongly enhanced by temperature due to phonon coupling. In addition, the observed 2-magnon intensity falls rapidly with temperature; this feature seems to correspond to the onset of a continuum at $\omega = 2\Delta_{0B}$, rather than to a singlet bound state as suggested in Ref. 17.

At the qualitative level, this spin-phonon coupling is considerably stronger than that observed in the spin-Peierls system CuGeO$_3$. We also note here that the authors of Ref. 17 do not observe magnetic scattering at $\omega = 2\Delta_{0A}$ and state that this invalidates the 2-plane scenario. We suggest from i) the weakness of the $\omega = 2\Delta_{0B}$ feature and ii) the low intensities associated with any calculation of bound states in the current parameter regime, that the onset of the second continuum is simply too weak to have been detected here. The reported observation of this feature in further Raman experiment verifies this hypothesis.

We wish to provide a theoretical description for the consequences of a significant magnetoelastic coupling, in terms of those phonons most strongly coupled to a spin system represented by the above, minimal model of triplet magnon excitations. Spin-phonon coupling effects may readily be envisaged within a conventional, diagrammatic treatment where perturbative inclusion of a magnon-phonon vertex with coefficient $g$ would lead to $O(g^2)$ self-energy corrections to the phonons due to the presence of magnons, and conversely. However, this type of approach would appear to be precluded here by the difficulties inherent in expressing a propagator for hardcore bosons, and in substituting frequency summations with constrained thermal occupation functions. This approach has been applied to consider spin-phonon coupling in a two-chain ladder by the introduction of an infinite but fictitious repulsion term for triplet excitations on the same bond. In addition to this weakness, the bond-operator method appears to be applicable at the quantitative level only for very strongly dimerized systems. Here we will instead reproduce the mutual renormalization of phonons and magnons by a flow-equation method particularly suitable for local spin-phonon problems in which a unitary transformation is applied to the Hamiltonian of the coupled system to eliminate the coupling term.

Motivated by the qualitative observation concerning the importance of the PO$_4$ groups, which is further sup-
ported by experimental observation on the phonon modes involved, in VOPO and related compounds\[7\] we will consider the previous model with phonon coupling only to the dominant dimer bonds $J_{1A}, J_{1B}$. We begin with the Hamiltonian in the form

$$H = \sum_{\gamma=A,B} \sum_{i,j} \left\{ J_{17} S_{i,j}^1 S_{i+1,j}^1 + J_{27} S_{i,j}^2 S_{i+1,j}^2 \right\} + \sum_{m=1,2} \left[ J_{f7} S_{i,j}^m S_{i+1,j}^m + J_{b7} S_{i,j}^m S_{i+1,j}^{m+1} \right]$$

$$+ \omega_0 b_i^\dagger b_i + G(b_i + b_i^\dagger) S_{i,j}^1 S_{i,j}^2 \}$$

(5)

where $i$ and $j$ are respectively indices for the dimer bonds ($J_1$) along and across the chains in each decoupled plane, and $m = 1, 2$ denotes the left or right spin in each dimer. The phonons $\{b_i\}$ are introduced as local, Einstein modes of fixed frequency $\omega_0$ at each dimer bond $i$; in reciprocal space these are nondispersive, and have the same weight at all wave vectors $q$. Because these phonon modes involve motion of the PO$_4$ groups, and not of the magnetic ($V^{4+}$) ions themselves, correlations between displacements may safely be neglected, and the approximation of Einstein phonons justified. The spin-phonon coupling constant $G$ is a free parameter to be fixed from experiment, but may in principle be very large: comparison with CuGeO$_2$ suggests that values exceeding 0.3$J_{1A}$ are not excluded.\[2,3\] The term in $J_{f7}$ describes a frustrating, next-neighbor coupling along the dimerized spin chains; this is zero in the bare model (Sec. II), but is generated at second order in $G$ by the unitary transformation which eliminates the final term to leave only phonon terms bilinear in $\{b_i\}$ in the resulting, effective Hamiltonian. A systematic discussion of the transformation procedure is presented in Ref.\[2,3\].

In deriving the effective Hamiltonian we retain only the leading order in $G/\omega_0$, which is $(G/\omega_0)^2$; omission of next-order terms $(G/\omega_0)^4$ can be expected to be well justified. The transformation also involves an expansion in $J/\omega_0$, where terms $O(J/\omega_0)$ are retained but those $O((J/\omega_0)^2)$ omitted; the validity of this approximation is not apparent in VOPO, which from the values of $J_{1\gamma}$ and $\omega_0$ is not well in the anti-adiabatic limit, but is motivated by the good, semi-quantitative agreement with simulations for a similar model by Bursill et al.\[4,5\] and may also be justified \textit{a posteriori}. The general form of the effective Hamiltonian may be represented as

$$H = H_{\text{spin}} + H_{\text{phonon}} + \Delta H_X + \Delta H_Y + \Delta H_Z,$$

in which $H_{\text{spin}}$ and $H_{\text{phonon}}$ denote respectively the pure spin and phonon parts of Eq. (5). The coupling term is transformed into two correction terms in the spin sector, following the notation of Ref.\[23\] we write as

$$\Delta H_X = -\frac{1}{\omega_0} \sum_{i,j} A_{i,j}^1 A_{i,j}$$

and

$$\Delta H_Y = \frac{1}{2\omega_0} \coth \left( \frac{\omega_0}{2T} \right) \sum_{i,j} \left[ A_{i,j}^1, L A_{i,j} \right].$$

(8)

Here $A_{i,j}$ denotes the local coupling, which we have taken as $G S_{i,j}^1 S_{i,j}^2$ and $L A = [H S, A]$ denotes the commutator of the quantity $A$ with the spin-only part $H_S$ of the starting Hamiltonian (Eq. (5)). A further correction term arises for the phonon sector,

$$\Delta H_Z = \frac{1}{\omega_0} \sum_{i,j} b_{i,j}^{\dagger} b_{i,j} \left[ A_{i,j}^1, L A_{i,j} \right] S,$$

(9)

where the expectation value $\langle \ldots \rangle_S$ is computed for the spin sector. This last contribution was not considered in Ref.\[2,3\] where the focus was on the spin sector, and arises in the phonon sector from a mean-field treatment of the terms in Eq. (9e) of that work.

Explicit evaluation of the additional terms generated by the transformation (Eqs. (12)) yields

$$\Delta H_X = -\frac{G^2}{\omega_0} \sum_{i,j} (S_{i,j}^1 S_{i,j}^2)^2 = \frac{G^2}{2\omega_0} \sum_{i,j} (S_{i,j}^1 S_{i,j}^2),$$

(10)

to within a constant, using that for spins $S = 1/2$, $(S_1 S_2 + 3/4)^2 = S_1 S_2 + 3/4$ because the eigenvalues of the right-hand side are 0 and 1. $\Delta H_Y$ and $\Delta H_Z$ are calculated from the result

$$\left[ A_{i,j}^1, L A_{i,j} \right] = \frac{1}{2} G^2 \left\{ J_2 (S_{i+1,j}^1 - S_{i-1,j}^1) (S_{i,j}^1 - S_{i,j}^2) - (J_a - J_b) (S_{i,j}^1 - S_{i,j}^2) \times [(S_{i+1,j}^1 - S_{i,j}^2) + (S_{i,j}^1 - S_{i-1,j}^1)] \right\},$$

(11)

where four-spin terms are neglected. With due attention to the number of neighboring chains, the additional terms $\Delta H_X, \Delta H_Y, \text{ and } \Delta H_Z$ may be transcribed into the form of the initial Hamiltonian (5), as corrections to the couplings $\{J\}$,

$$\Delta J_{1\gamma} = \frac{G^2}{2\omega_0},$$

(12a)

$$\Delta J_{2\gamma} = -\frac{G^2}{2\omega_0} J_{2\gamma} \coth \left( \frac{\omega_0}{2T} \right),$$

(12b)

$$\Delta J_{f7} = \frac{G^2}{4\omega_0} J_{f7} \coth \left( \frac{\omega_0}{2T} \right),$$

(12c)

$$\Delta J_{a\gamma} = -\frac{G^2}{2\omega_0} (J_a - J_b) \coth \left( \frac{\omega_0}{2T} \right),$$

(12d)

$$\Delta J_{b\gamma} = \frac{G^2}{2\omega_0} (J_a - J_b) \coth \left( \frac{\omega_0}{2T} \right),$$

(12e)
and as a correction to the phonon frequency in each plane of
\[
\Delta \omega_{0\gamma} = \frac{G^2}{a_0^2} J_{2\gamma} \left( \langle S_i^z S_{i+1}^z \rangle - \langle S_i^z S_i^z \rangle \right). \tag{13}
\]
The latter result was obtained by neglecting additional interchain coupling terms, on the grounds that both the coupling constants \(|J_a - J_b| \ll J_2\) and the spin expectation values are much smaller between the chains than within them. The expectation values in Eq. (13) may be computed for independent chains by a high-temperature expansion in combination with the known \(T = 0\) behavior as described in App. A.

These values are all finite at zero temperature. In order to perform a self-consistent calculation, we deduce the appropriate bare values of the coupling constants such that their renormalized values correspond to the experimental data. Thus the fitting parameters provided in the previous section are effective quantities already containing the low-\(T\) renormalization. We now discuss the quantitative properties of these corrections in the context of phonon anharmonicity, magnon thermal renormalization, and thermodynamic properties.

IV. EXPERIMENTAL CONSEQUENCES

A. Phonon anharmonicity

One observes from Eq. (13) that \(\Delta \omega_0 > 0\), because for an AF system \(\langle S_i^z S_{i+1}^z \rangle\) is negative. Further, one expects that \(\Delta \omega_0 \to 0\) as temperature becomes very large and the expectation values vanish. Both of these features are consistent with experiment. More interestingly still, \(\Delta \omega_0\) does not vary monotonically with temperature, as \(\langle S_i S_j \rangle\) for nearest neighbors increases in magnitude at low temperatures; this result is exactly in accord with the small, initial increase observed with temperature for both 70cm\(^{-1}\) and 123cm\(^{-1}\) phonons.

Fig. 3 shows the thermal renormalization effect for an Einstein phonon of bare frequency \(\omega_0 = 118.4\text{cm}^{-1}\) (14.68meV). The bare frequency value is chosen such that the effective frequency including corrections contains the low-\(T\) renormalization. The resulting value of 0.58 for \(G = 6.6\text{meV}\) was chosen to reproduce the initial upturn seen in cc polarization. Note that we do not wish to imply a connection between the two plane types and the two polarizations: each polarization measures some combination of the contributions from each plane type, determined by possibly different coupling constants to each. However, the results in Fig. 3 provide a good indication of general magnetoelastic coupling effects, and of the splitting in energy of a single phonon mode when further couplings are neglected, which from comparison with experiment appears realistic. For completeness, we add here that the results in Fig. 3 were computed with the bare coupling constants
\[
(J_{1A}, J_{2A}, J_{1b}, J_{2b}) = (132K, 112K, 10.9K, 17.1K).
\]

\[
(J_{1B}, J_{2B}, J_{1b}, J_{2b}) = (111K, 110K, 12.5K, 19.5K). \tag{14}
\]

Comparison with Fig. 3 shows that the coupling \(G\) has a strong effect on the chain superexchange parameters \(J_1\) and \(J_2\), but does not alter strongly the interchain values \(J_a\) and \(J_b\), whose sum we have determined as in Sec. II.

![Fig. 3. Thermal renormalization due to magnons, for a phonon of frequency \(\omega_0 = 118.4\text{cm}^{-1}\) with coupling \(G = 6.6\text{meV}\). Symbols are experimental data in cc and bb polarizations, from Ref. 17.](image-url)
B. Magnon renormalization

Inspection of the renormalized coupling constants (Eqs. (12)) reveals the following qualitative features. i) the strong interaction constant $J_1$ has a temperature-independent enhancement; ii) the weaker bond $J_2$ is suppressed with increasing temperature; iii) in-chain frustration $J_f$ is introduced, and rises with increasing $T$; iv) the interchain coupling diminishes as temperature rises. Based on these observations, one expects a band flattening effect of thermal renormalization, shown by the strong interaction constant $J_1$, and increases with increasing temperature, whereas the difference between the extrema, $ω_{max} - ω_{min}$, depends mostly on $J_2$ (and partly on $J_f$), and decreases with increasing temperature.

![Graph](image1)

**FIG. 4.** (a) Thermal (phonon) renormalization of elementary magnon modes at $q_a = 0$, illustrated for an Einstein phonon with frequency $ω_0 = 118.4 cm^{-1}$ and coupling $G = 6.6 meV$, at temperatures of 10K and 300K. (b) Band-flattening effect of thermal renormalization, shown by thermal evolution of $Δω = ω(0, π) - ω(0, 0)$, the difference between dispersion extrema.

The magnon thermal renormalization arising as a result of spin-phonon coupling should be manifest in corrections to thermodynamic quantities at high temperatures. Considering first the static susceptibility $χ(T)$, this may be computed by integration over the available magnon modes. $χ(T)$ grows initially with temperature, its behavior governed exponentially by the gaps, has a maximum on the order of the dominant energy scales $J_1$, and converges at high-$T$ to Curie-Weiss behavior. Fig. 5 compares the single-crystal experimental susceptibility with the single-plane model predictions, the two-plane, static model for the parameters fitted in Eqs. (3), and the two-plane, dynamical model with thermally renormalized magnon dispersions (Eqs. (14)). In the last case, one Einstein phonon mode per bond ($ω_0 = 118.4 cm^{-1}$, $G = 6.6 meV$) is used, as in the calculations of the previous section.

![Graph](image2)

**FIG. 5.** Comparison of experimental susceptibility $χ(T)$ (circles) with single-plane model (dashed), static, two-plane model (dot-dashed), and dynamical, two-plane model containing renormalizing effects of an Einstein phonon with frequency $ω_0 = 118.4 cm^{-1}$ and coupling $G = 6.6 meV$ (solid). Experimental data from Ref. [14].
As noted in Sec. II, the two-plane, static model gives a rather good account of the low-temperature regime and the maximum, and remains quite satisfactory at higher temperatures. It is perhaps surprising in view of the large coupling constant $G$ that the effects of dynamical phonons are so small. However, it is also evident that the model including thermal renormalization of the superexchange parameters provides excellent agreement in all three temperature regimes, including high-$T$. This result not only confirms the consistency of the method, and of the value of $G$ deduced from the phonon anharmonicity, but has a profound consequence for interpretation of high-$T$ susceptibility data in terms of a Curie-Weiss temperature in the presence of phonons. The effects of a spin-phonon coupling on $\Theta_{\text{CW}}$ may be computed rigorously, as shown in App. B. It is found that the value of $\Theta_{\text{CW}}$ including spin-phonon coupling corresponds to that given in Eq. (4) if the renormalization of $J_{17}$ due to $\Delta H_X$ (8) is taken into account. Corrections due to $\Delta H_Y$ (7) are found to cancel. We note finally that in the real material, several types of phonon mode contribute to a susceptibility renormalization. However, because their effects are proportional to the square of the corresponding coupling constant, contributions beyond that from the dominant phonon mode may be weak.

![Graph](image)

**FIG. 6.** Specific heat of magnetic system, comparing static (solid) and dynamical (dashed) two-plane models. Dot-dashed line is for dynamical model in a magnetic field of 24T. Points are experimental data from Ref. 17. Dynamical models contain one Einstein phonon of frequency $\omega_0 = 118.4 \text{cm}^{-1}$ and coupling $G = 6.6 \text{meV}$.

We close this section by computing a further experimentally accessible quantity which is expected to illustrate thermal renormalization due to magnetoelastic coupling. The specific heat of the spin system alone is difficult to isolate from phonon contributions, and to date has been deduced only indirectly from quasielastic Raman scattering. The calculation proceeds as for the magnetic susceptibility, but with integration in reciprocal space over the magnon contributions to the second temperature derivative of the free energy, and may be readily extended to finite magnetic fields. The results presented in Fig. 6 demonstrate again both the utility of the static model and the small but significant upward renormalization offered by the dynamical model at high $T$. Both sets of data are close to the results of calculations for a single dimerized chain with appropriate $\lambda$, indicating that interchain coupling effects have only a small effect on the overall features of thermodynamic quantities. By contrast, a strong magnetic field is most effective at low $T$, where it acts to reduce the gap, and at intermediate $T$ where the peak value of $C(T)$ is suppressed. The experimental data show too much scatter to be of particular utility, and we await more refined measurements of this quantity.

**V. SUMMARY**

In conclusion, we have analyzed a two-plane model for VOPO, which is fully consistent with the known crystal structure, and emphasize the key role of the PO$_4$ groups mediating the dominant superexchange path. A full understanding of the magnetic properties is not possible without considering the strong magnetoelastic coupling effects observed in Raman light-scattering experiments. We account for these qualitatively in terms of phonon modes of the phosphate groups, and quantitatively by using the flow-equation method. Phonon hardening is found to have contributions from both spin coupling and lattice anharmonicity, although only the former can account for the observed low-temperature softening, which provides an estimate of the spin-phonon coupling constants.

We obtain an excellent fit to the magnon dispersion data for the two triplet modes observed by INS, and find complete agreement with the parameters deduced from NMR studies. In addition, there is a strong thermal renormalization of the magnon dispersions due to phonons, in the form of a band flattening, which should be clearly visible in INS measurements performed as a function of temperature. We show further that, while the static two-plane model parameters give a good account of static susceptibility and specific heat data, the renormalization effects of dynamical phonons lead to additional corrections which are required to reproduce the high-temperature limit. However, we have found that even for very strong coupling, the influence of phonons on thermodynamic magnetic properties is rather small, and such quantities may be quite well described by a static model. Unambiguous evidence of phonon effects is provided only by dynamical properties, such as Raman spectra and triplet dispersions.
VI. ACKNOWLEDGEMENTS

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APPENDIX A: DLOG-PADÉ EXTRAPOLATION OF EXPECTATION VALUES

In this appendix we present details of the computation of expectation values such as \( \langle S_{i,j}^1 S_{i,j}^2 \rangle \), as functions of temperature. The basic physical consideration is straightforward for a gapped spin system, and we will demonstrate it for the expectation value \( A(T) = \langle S_{i,j}^1 S_{i,j}^2 \rangle \) of the spin correlation function for the strong bond in a dimerized spin chain (i is the dimer index). At zero temperature, \( A(T) \) has the finite, negative value \( A_0 \). At small but finite temperature, \( A(T) \) will deviate from \( A_0 \), with an exponentially small deviation due to the presence of the spin gap. It is plausible to take this deviation to be positive, \( A(T) - A_0 \geq 0 \), and so one expects (cf. Fig. 5)

\[
A(T) \approx A_0 + A_1 T^\nu \exp(-\Delta/T) \quad \text{for } T \text{ small}
\]

\[
A(T) \propto 1/T \quad \text{for } T \text{ large}
\]

where \( \Delta \) is the spin gap. The exponent \( \nu = d/2 \) is determined for a dispersion with quadratic minima only by the dimensionality \( d \). For the quantitative computation we use two sources of input, namely i) an expansion at zero temperature about the dimer limit, such as that given in Ref. 31, and ii) a high temperature expansion such as that presented in Refs. 24-27.

From (i) one may deduce the values of \( A_0 \) and \( \Delta \). For a sufficiently dimerized system such as \((\text{VO})_2\text{P}_2\text{O}_7\), the plain truncated series can be used. The value of \( A_0 \) is obtained from the expansion of the ground state energy as a function of the strong-bond coupling \( J_1 \), the weak-bond coupling \( J_2 \), and the next-nearest-neighbor coupling \( J_f \), by partial differentiation with respect to \( J_1 \).

The extrapolation is performed using a Dlog-Padé approximant for \( A(T) - A_0 \) in the following manner. Expansion in \( \beta \) up to 9th order is used to describe

\[
a := \partial_\beta A(1/\beta)/A(1/\beta) - A_0.
\]

Then, because we expect regular behavior in the limit \( \beta \to \infty \), it is appropriate to change to variable \( u = \beta/(1 + \beta) \) (whence \( \beta = u/(1 - u) \)). Because \( u \propto \beta \) for small values of \( u \) and \( \beta \), an expansion of \( a \) in terms of \( u \) is available up to order 8. This is used to set up a [8, 2] Padé approximant \( P_8/Q_2 \) in \( u \), where the subscripts stand for the degree of the polynomial in \( u \). The missing constants for order 9 and 10 are determined from the
known asymptotic behavior. From Eq. (A1a) we have $a = -\Delta - d/(2\beta) + \mathcal{O}(\beta^{-2})$, which yields

$$P_s/Q_2\bigg|_{u=1} = -\Delta$$

(A3)

$$\partial_u(P_s/Q_2)\bigg|_{u=1} = 1/2$$

(A4)

for chain geometry. In this way, reliable and non-defective interpolations between the zero-temperature result and the high-temperature behavior can be obtained, as illustrated in Fig. 7.

**APPENDIX B: CURIE-WEISS TEMPERATURE AND SPIN-PHONON COUPLING**

In this appendix we derive the effect of a magnetoelastic coupling on the Curie-Weiss temperature, $\Theta_{\text{CW}}$. Because at high temperatures one assumes $\chi(T) \propto (T - \Theta_{\text{CW}})^{-1}$, this procedure involves computing the subleading $1/T$ behavior in $(T - \Theta_{\text{CW}})^{-1} = 1/T + \Theta_{\text{CW}}/T^2 + \mathcal{O}(T^{-3})$. We consider first a uniform spin chain coupled to Einstein phonons,

$$H = J \sum_i S_i S_{i+1}(1 + g(b_i + b_i^\dagger)) + \omega b_i^\dagger b_i .$$

(B1)

Direct expansion in $1/T$ of the partition function $\text{Tr}[\exp(-\beta H)]$ is not possible due to the infinite-dimensional bosonic Hilbert space, and we employ instead an expansion in $J$.

The first two terms read

$$\text{Tr}[\exp(-\beta H)] = \mathcal{O}(J^3) + Z_0^N.$$ $$(1 + NJ^2\text{Tr}_{\text{spins1,2}}[\{S_1 S_2\}^3](\beta^2/2! + g^2 f_1/Z_0)) ,$$

(B2)

with $Z_0 = (1 - e^{-\beta \omega})^{-1}$ the bosonic partition function and the coefficient $f_1$ given by

$$f_1 = \int_0^\beta \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 d\beta_3 \delta(\beta - \beta_1 - \beta_2 - \beta_3).$$

$$\text{Tr}_{\text{boson}}[e^{-\beta_1 \omega b_i^\dagger b_i} e^{-\beta_2 \omega b_i^\dagger b_i} e^{-\beta_3 \omega b_i^\dagger b_i}] ,$$

(B3)

where $u$ denotes $b + b^\dagger$. The coefficients $f_m$ are the generalization of (B3) to $2m$ $\beta$-ordered factors of $u$. The evaluation of $\text{Tr}_{\text{spins1,2}}[\{S_1 S_2\}^2]$ is straightforward, and yields $3/16$. The evaluation of $f$ is possible by explicit calculation, or more easily by the observation that $f$ equals the second coefficient in $\lambda$ in an expansion of $Z(\lambda)$, where

$$Z(\lambda) = Z_0 + \sum_m \lambda^{2m} f_m .$$

(B4)

is the partition function of $H = \omega b_i^\dagger b_i + \lambda u$. Transforming to shifted bosons $\tilde{b} = b + \lambda / \omega$, the shifted partition sum is easily found to be $Z(\lambda) = Z_0 \exp(\beta \lambda^2 / \omega)$, whence it follows directly that $f_m = Z_0(\beta / \omega)^m / m!$. Because $f_m$ is of order $\beta^m Z_0$, the general phononic contribution in Eq. (B2) is of order $J^{2m}(\beta / \omega)^m$, or higher in $\beta$. Hence one obtains a systematic high-temperature expansion circumventing the problem of the infinite-dimensional bosonic Hilbert space, which is cut off by the factor $e^{-\beta \omega b_i^\dagger b_i}$.

In analogy to the expansion (B2), the variance of the magnetization $M := \sum_i S_i^z$ is given by

$$\frac{1}{N} \text{Tr} [M^2 \exp(-\beta H)] = \frac{1}{4} R_1 + R_2 + \mathcal{O}(J^3),$$

(B5)

where $R_1$ is the partition sum (B2) and $R_2$.
\[ R_2 = 2Z_0^N \left( -\beta J \text{Tr}_{\text{spins}1,2} [S^z_1 S^z_2(S_1 \cdot S_2)] + J^2 \text{Tr}_{\text{spins}1,2} \left[ S^z_1 S^z_2 (S_1 \cdot S_2)^2 \right] \left( \beta^2 / 2 + g^2 f_1 / Z_0 \right) \right). \]  

(B6)

The susceptibility \( \chi(T) \) is the ratio of Eqs. (B5) and (B2) to order \( J^2 \),

\[ 4T \chi = 1 - \frac{\beta J}{2} - \frac{\beta^2 J^2}{8} - \frac{\beta g^2 J^2}{4\omega} + O(J^3 \beta^2) \]  

(B7)

\[ = 1 - \beta \left( \frac{J}{2} + \frac{g^2 J^2}{4\omega} \right) + O(\beta^2), \]  

(B8)

from which follows

\[ \Theta_{\text{CW}} = - \left( \frac{J}{2} + \frac{g^2 J^2}{4\omega} \right). \]  

(B9)

This result implies quite generally that the Curie-Weiss temperature is lowered by spin-phonon interactions, i.e. in AF systems the modulus of \( \Theta_{\text{CW}} \) increases. For Einstein phonons the contribution of spin-phonon coupling to the Curie-Weiss temperature amounts to \(-G^2/(8\omega)\) per bond linked to each site with coupling \( G = gJ \). This is exactly the same effect as the renormalization contained in \( \Delta H_X \) (Eq. (5)), a fact which corroborates the validity and utility of the flow-equation approach.

To conclude this appendix, we have for the model (5) a change of \( \Theta_{\text{CW}} \) due to spin-phonon interactions given by

\[ \Theta_{\text{CW};\text{total}} = \Theta_{\text{CW};\text{bare}} - \frac{G^2}{8\omega} \]  

(B10)

where \( \Theta_{\text{CW};\text{bare}} \) is the value given in Eq. (4). The expansions of Eqs. (B2,B5) provide an interesting and systematic extension to higher orders in \( J \). Generally, a calculation in \( J^{2m} \) will provide results for a high-temperature expansion up to \( \beta^m \).