Magnetic susceptibility of $(VO)_2P_2O_7$: A one-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet with a ladder spin configuration and a singlet ground state

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Powder magnetic susceptibility data between 1.3 and 350 K are presented for the orthorhombic compound $(VO)_2P_2O_7$, containing a one-dimensional ladder configuration of spins $\frac{1}{2}$. Perhaps surprisingly, the data are accurately fitted, both as to shape and magnitude, by theoretical predictions of Bonner, Blöte, Bray, and Jacobs for the spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chain, with $J_1/k_B=-65.7$ K, $J_2/k_B=-46.0$ K, and $g=2.00$, where J_1 and J_2 are the two alternating exchange-interaction constants and g is the Landé g factor.

INTRODUCTION

Calculating the ground-state energy, excitation spectra, dynamics, and thermodynamics (magnetic susceptibility χ, heat capacity) of macroscopic quantum Heisenberg spin systems versus temperature T has been a challenge for decades and is still not amenable to exact solution in general. The situation is somewhat ameliorated in one dimension, where accurate solutions were obtained by Bonner and Fisher[1] for the uniform spin-$\frac{1}{2}$ chain. These results were obtained by exact solution of finite rings and chains containing $N\leq 11$ spins and extrapolation to $N=\infty$.

More recently, Bonner and others have examined theoretically the properties of the quantum spin-$\frac{1}{2}$ alternating antiferromagnetic chain, in which the exchange constant J between successive pairs of spins alternates between two values J_1 and J_2.[2-6] The Hamiltonian for this case is

$$\mathscr{H}=-2J_1\sum_i(\mathbf{s}_{2i}\cdot\mathbf{s}_{2i+1}+\alpha\mathbf{s}_{2i}\cdot\mathbf{s}_{2i-1}),$$

where $\alpha=J_2/J_1$ $(0\leq\alpha\leq 1)$, the number of spins is assumed to be even, and J_1 and J_2 are negative for antiferromagnetic interaction. This problem is important in several different areas as discussed in Ref. 3. As $\alpha\rightarrow 0$, one approaches the isolated dimer limit as in spin-exciton systems,[7] whereas as $\alpha\rightarrow 1$, one regains the uniform Heisenberg chain. For all $\alpha\neq 1$, there exists an energy gap between the nonmagnetic singlet ground state and the lowest triplet excited states, with the gap decreasing monotonically to zero with increasing α.[3,6] For $\alpha\neq 1$, $\chi(T)$ is predicted to increase from zero at $T=0$, reach a maximum at $T^{\max}\approx 1.2J_1/k_B$, then decrease monotonically with T; the precise shape of $\chi^{\rm calc}(T)$ depends on the value of α.[2,4,5] A special case of the alternating antiferromagnetic chain is the spin-Peierls system in which the chain is uniform above the spin-Peierls transition temperature and is progressively dimerized below;[8] in these systems, α is inherently temperature dependent.

There exist roughly twenty compounds for which the theoretical predictions for the physical properties of the alternating Heisenberg antiferromagnetic chain have been confirmed[8-12] (mainly for χ), a large fraction of which contain Cu^{2+} as the magnetic species. Several Cu^{2+} compounds are known from crystallographic studies at room temperature to form related one-dimensional spin ladder configurations.[10,13] Herein, we report $\chi(T)$ data for the orthorhombic compound $(VO)_2P_2O_7$ (vanadyl pyrophosphate) containing a spin ladder of V^{4+} ions, which are fitted very well by the $\chi(T)$ prediction of Ref. 2 from 10 to 200 K, a temperature range widely spanning the temperature $T^{\max}=80$ K. This temperature range also nearly exhausts the range over which the predictions were made $(0<T\leq 2.5T^{\max})$.

$(VO)_2P_2O_7$ contains $(V=O)^{2+}$ (vanadyl) cations, which means that the vanadium atoms are in the 4+ oxidation state and therefore possess a single unpaired electron per atom (spin $\frac{1}{2}$). The structure[14,15] is composed of vanadyl cations and pyrophosphate $(P_2O_7)^{2-}$ groups (see Fig. 1). Within a layer perpendicular to the a axis reside magnetically isolated pairs of V^{4+} ions with an interatomic distance $d_{V\text{-}V}=3.19(1)$ Å. Each V atom is octahedrally coordinated by oxygen atoms and the V-V pairs are formed by sharing of an octahedral edge parallel to the layers. An infinite spin ladder is formed along the a axis

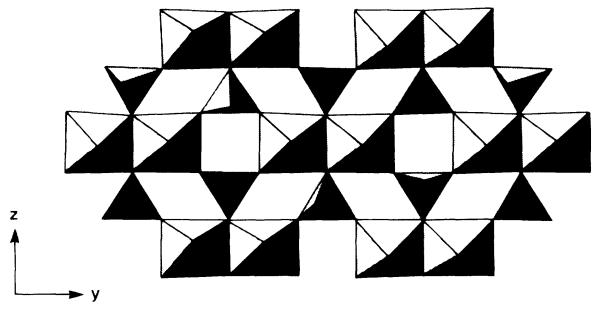

FIG. 1. Structure of $(VO)_2P_2O_7$. The octahedra contain the V^{4+} ions, the tetrahedra contain the phosphorus atoms, and the vertices represent oxygen atoms.

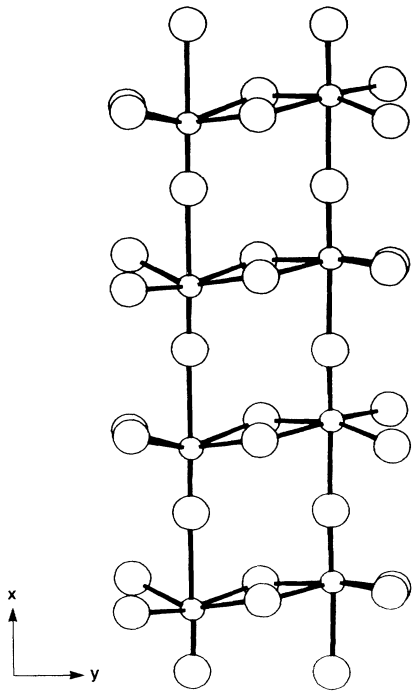

FIG. 2. The ladder of V^{4+} ions perpendicular to the layers in $(VO)_2P_2O_7$. The smaller circles represent vanadium atoms and the larger circles represent oxygen atoms.

by corner sharing of V-containing octahedra as shown in Fig. 2; the distance between the rungs of the ladder (the interlayer distance) is $d_{V\text{-}V}=3.864(2)$ Å.

EXPERIMENTAL DETAILS

Our polycrystalline sample of $(VO)_2P_2O_7$ was synthesized by dehydrating the crystalline precursor vanadyl phosphate hemihydrate $VO(HPO_4)\cdot\frac{1}{2}H_2O$ under flowing He gas at 1063 K for 19 h, followed by annealing in a sealed and evacuated quartz tube at 1048 K for 49 d.[16] The precursor was made with the highest-purity commerically available starting materials.[17] The intralayer structure of $VO(HPO_4)\cdot\frac{1}{2}H_2O$ ($d_{V\text{-}V}=3.10$ Å) is essentially the same as in $(VO)_2P_2O_7$, but $d_{V\text{-}V}=5.70$ Å perpendicular to the layers, far larger than in $(VO)_2P_2O_7$. Thus, we expected and found[17] that the magnetic properties of the precursor were those of isolated V^{4+}-V^{4+} dimers ($\alpha=0$). In particular, $\chi(T)$ was precisely fitted by assuming that the V-V intradimer exchange coupling was isotropic (Heisenberg-like), with a Landé g factor $g\approx 2$, similar to our findings for $(VO)_2P_2O_7$ below.

Magnetic susceptibility data for $(VO)_2P_2O_7$ were obtained from 4 to 350 K using a George Associates Faraday magnetometer in a magnetic field H of up to 6.3 kG at temperature sweep rates of 0.5—1 K/min.[16] Additional data above 1.3 K were subsequently obtained using a PAR vibrating-sample magnetometer in fields up to 5 kG. The data presented here have been corrected for the contributions of ferromagnetic impurities (<20 ppm), which were determined independently via magnetization versus H isotherms at selected temperatures.

RESULTS

Our previous study of the influence of the annealing conditions in the preparation of $(VO)_2P_2O_7$ on $\chi(T)$ between 4 and 350 K indicated that $\chi(T)$ is the sum of two distinct terms:[16]

$$\chi(T)=f\chi^{\text{defect}}(T)+(1-f)\chi^{\text{bulk}}(T)\ ,$$

where $\chi^{\text{defect}}(T)=C/(T-\Theta)$ is the contribution from V^{4+} spin-$\frac{1}{2}$ defects and $\chi^{\text{bulk}}(T)$ is the bulk term of as-yet unidentified origin. The defect concentration f decreases with increasing severity of the anneal, and both $\chi^{\text{bulk}}(T)$ and $\chi^{\text{defect}}(T)$ are nearly independent of f. Shown in Fig. 3 are $\chi(T)$ data obtained more recently in the vibrating sample magnetometer below 80 K for sample 3 of Ref. 16. Because these data extend to lower temperatures (1.3 K) than in Ref. 16 (4 K), we have been able to better confirm that the lowest temperature data converge to $f\chi^{\text{defect}}(T)$ [i.e., that $\chi^{\text{bulk}}(T\to 0)\to 0$], as shown in Fig. 4; here, $f=0.0225$ and $\Theta=-3.8$ K, in agreement with the values

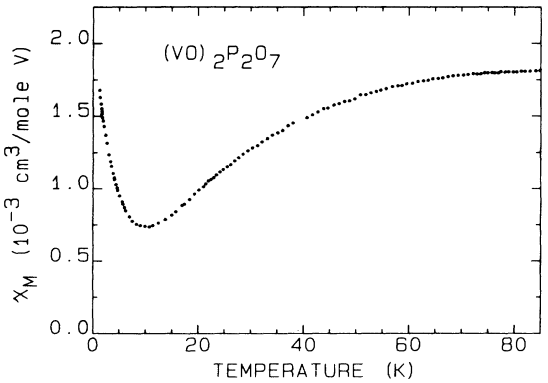

FIG. 3. Measured molar magnetic susceptibility χ_M versus temperature for $(VO)_2P_2O_7$ (sample 3 in Ref. 16) from 1.3 to 85 K in a magnetic field of 5 kG.

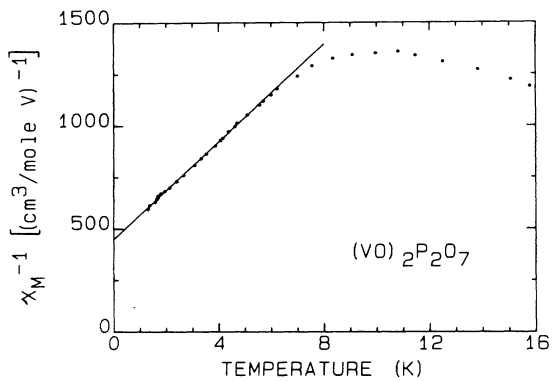

FIG. 4. Inverse molar magnetic susceptibility χ_M^{-1} versus temperature from the data in Fig. 3 between 1.3 and 16 K. The solid line is a linear least-squares fit to the data below 5 K.

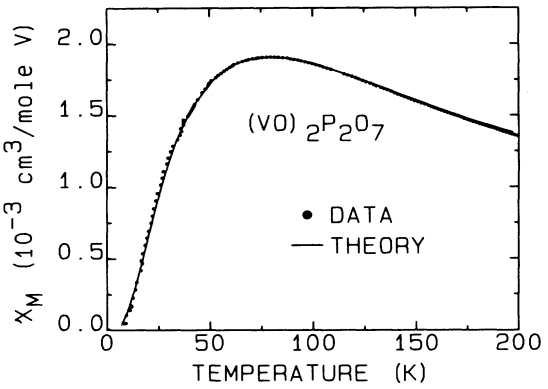

FIG. 5. Molar magnetic susceptibility χ_M versus temperature for bulk $(VO)_2P_2O_7$, derived from the Faraday magnetometer data in Ref. 16. The solid curve is a prediction for a spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chain, as discussed in the text.

deduced from the higher temperature Faraday magnetometer data in Ref. 16.

$\chi^{\text{bulk}}(T)$ was determined by subtracting the above defect contribution from the observed $\chi(T)$ data, and the results are plotted in Fig. 5. From here on, $\chi^{\text{defect}}(T)$ will not be further discussed, and $\chi^{\text{bulk}}(T)$ will be simply denoted by $\chi(T)$. The inverse of χ is plotted for 20—350 K in Fig. 6. From Fig. 5, χ increases from a value near zero at the lowest temperatures to a rounded maximum at $T^{\max}=79.6$ K, then monotonically decreases at higher temperatures. A qualitative discussion of these data in terms of a model in which spin-$\frac{1}{2}$ dimers interact in the molecular-field approximation was given previously.[16] The lowest temperature data indicate a nonmagnetic singlet ground state for bulk $(VO)_2P_2O_7$, whereas the shape of $\chi(T)$ at higher T suggests that short-range antiferromagnetic ordering occurs over a broad temperature range. No evidence of long-range magnetic ordering is seen at any temperature above 1.3 K. From Fig. 6, $\chi(T)$ asymptotically approaches Curie-Weiss behavior $[\chi=C/(T-\Theta)]$ with increasing temperature. A linear fit to the data in Fig. 6 between 250 and 350 K (solid line in Fig. 6) yields the Curie constant $C=0.386$ cm^{3}K/mole V and the Weiss temperature $\Theta=-84.1$ K; thus, $|\Theta|\approx T^{\max}$. The sign of Θ confirms antiferromagnetic coupling between the spins. The value of C is close to that (0.375 cm^{3}K/mole V) expected for a spin-$\frac{1}{2}$, $g=2$ system and consistent with isotropic interspin exchange coupling.

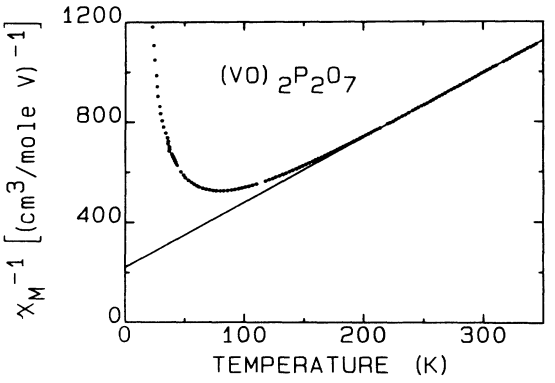

FIG. 6. Inverse molar magnetic susceptibility χ_M^{-1} versus temperature for bulk $(VO)_2P_2O_7$, from Fig. 5. The straight line is a fit to the data between 250 and 350 K; essentially the same fit is obtained by fitting to the data between 300 and 350 K.

DATA MODELING AND DISCUSSION

As noted above, there is reason to believe that the exchange interactions between the spins $\frac{1}{2}$ in $(VO)_2P_2O_7$ are isotropic. Further, the shape of $\chi(T)$ is similar to that predicted for spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chains.[2] Although the structural considerations above show that the spin configuration is a ladder rather than a chain, there exist no published theoretical predictions for $\chi(T)$ for the former case for various values of α. However, for the α values ($\sim$0.3) for which a theoretical comparison has been attempted, the thermodynamic properties have been found to be very similar for the two configurations.[18,19] Therefore, we attempt to fit our $\chi(T)$ data with the predictions of Ref. 2 for the spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chain.

To facilitate determination of the parameter $\alpha=J_2/J_1$, we have plotted in Fig. 7 the reduced susceptibility $\chi(T)/\chi^{\max}$ versus reduced temperature $T/T^{\max}$ from Fig. 5, where $\chi^{\max}=1.907\times10^{-3}$ cm^3/mole V and $T^{\max}=79.6$ K. Also plotted are the predictions of Ref. 2 for $0<\alpha<1$ ($\alpha=0.4$, 0.6, 0.8, and 0.9). The two calculated curves for $\alpha=0.6$ and 0.8 bracket the experimental data. By linearly interpolating between the curves for these two α values, we obtained a good fit with $\alpha=0.7$, as shown in Fig. 7. Using the relation $J_1=k_B T^{\max}/1.212$ appropriate to

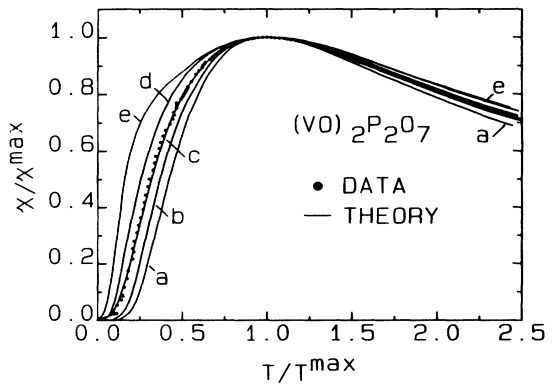

FIG. 7. Reduced magnetic susceptibility $\chi/\chi^{\max}$ versus reduced temperature $T/T^{\max}$ for $(VO)_2P_2O_7$. The solid curves *a*, *b*, *d* and *e* are theoretical predictions from Ref. 2 for α values of 0.4, 0.6, 0.8, and 0.9 for the spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chain, respectively, where $\alpha=J_2/J_1$ is the chain-alternation parameter. Curve *c* for $\alpha=0.7$ was obtained by interpolating between curves *b* and *d*.

$\alpha=0.7$, we get $J_1/k_B=-65.7$ K and $J_2/k_B=-46.0$ K. These values are both comparable with the value $J/k_B=-45.3$ K obtained[16,17] for the intradimer exchange constant in the precursor $VO(HPO_4)\cdot\frac{1}{2}H_2O$, and with the value ($-78$ K) (Ref. 20) in the layered compound CsV_2O_5 which also contains isolated pairs of V^{4+} ions in an intralayer structure[21] very similar to that of the precursor. Scaling the fit for $\alpha=0.7$ in Fig. 7 back to the data in Fig. 5 at T^{max}, one obtains the solid curve in Fig. 5. Using our value for J_1 and the relationship between $\chi^{max}|J_1|/Ng^2\mu_B^2$ and α in Ref. 22, where N is Avogadro's number and μ_B is the Bohr magneton, we find $g=2.00$, the free-electron g value, consistent with our assumption of isotropic exchange coupling between the spins in the sample and with the Curie constant found above from the high-temperature fit in Fig. 6. This g value is close to values (~ 1.97) found for V^{4+} by ESR in other vanadium phosphates.[23]

Because the calculated $\chi(T)$ curves in Ref. 2 were derived assuming an alternating chain rather than a ladder configuration for the spins, as is present crystallographically at room temperature in $(VO)_2P_2O_7$, the excellent agreement we obtain between the predicted and observed susceptibilities apparently confirms and extends previous statements based on theory for smaller $\alpha\sim 0.3$ that the thermodynamics of spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chains and ladders are almost indistinguishable;[18,19] however, the J_1 and J_2 values obtained from the latter two respective fits to the same data do differ somewhat.[18]

SUMMARY

We have shown that the bulk magnetic susceptibility of the one-dimensional spin ladder compound $(VO)_2P_2O_7$ is accurately described by the theoretical predictions of Bonner, Blöte, Bray, and Jacobs for the spin-$\frac{1}{2}$ alternating antiferromagnetic Heisenberg chain. Why this should be so in our case is not clear, since the thermodynamics of ladders and alternating chains are expected to diverge from each other as $\alpha\rightarrow 1$.[24] We hope that the present work will inspire explicit calculations of $\chi(T)$ of the spin-$\frac{1}{2}$ antiferromagnetic Heisenberg spin ladder, particularly for intermediate and large values of $\alpha(0.5\lesssim\alpha\lesssim 1)$. It is possible that although the crystallographic arrangement of the spins in $(VO)_2P_2O_7$ is a ladder configuration, the effective configuration defined by the actual exchange interactions between the spins is that of an alternating (possibly zig-zag) chain, as was ultimately found to be the case for $Cu(NO_3)_2\cdot 2\frac{1}{2}H_2O$.[10] The calculations for the ladder just suggested would hopefully help to distinguish between these two possibilities.

ACKNOWLEDGMENTS

We are grateful to J. C. Bonner and I. S. Jacobs for sending copies of Figs. 2 and 6 in Ref. 2; from the former figure, we digitized the theoretical $\chi(T)$ curves subsequently plotted in our Fig. 7, and from the latter obtained the relationship in Ref. 22. We thank J. F. Brody for preparing the sample.

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