The quantum spin chains have been the subject of many theoretical and experimental studies since the conjecture was made by Haldane [1] that the antiferromagnetic Heisenberg model has a finite excitation gap for integer spins. The model, which has been intensively used to investigate the physics behind the Haldane’s conjecture, is the isotropic spin-one Heisenberg Hamiltonian with both bilinear and biquadratic spin interactions:

\[ H = J \sum_i [S_i \cdot S_{i+1} + \gamma (S_i \cdot S_{i+1})^2] \]  

(1)

For most of the existing quasi-one-dimensional (1D) S = 1 materials, the biquadratic term is very small compared with the bilinear term as well as the uniaxial anisotropy. This model was therefore generally thought to be of purely theoretical interest. However, recently Millet et al. [2] found that the magnetic susceptibility of a new quasi-1D S = 1 system, LiVGe₂O₆, shows a few interesting features which are absent in other S = 1 materials. They argued that both the interchain coupling and the uniaxial anisotropy are too small to create these features and suggested that the biquadratic term plays an important role in this material.

In this paper, we present a theoretical study for the thermodynamics of the Hamiltonian (1) with \( J > 0 \). We have calculated the magnetic susceptibility and specific heat of this model using the transfer matrix renormalization group (TMRG) method [3–6]. By comparing with the experimental data of LiVGe₂O₆, we find that the measured susceptibility, after subtracting the impurity contribution, can be quantitatively fitted by the numerical result with susceptibility, after subtracting the impurity contribution, can be quantitatively explained with this model. The biquadratic exchange interaction in this material is found to be ferromagnetic, i.e., with a positive coupling constant.

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The thermodynamics of this model can be understood from the valence bond solid model [9]. In this model, each site on the chain is occupied by two \( S = \frac{1}{2} \) spins and the ground state is formed by the bonding of two \( S = \frac{1}{2} \) spins from adjacent sites. These singlet bonds must be broken in order to excite the system, and this leads to a nonzero energy gap in the low-lying spectrum. This picture has been confirmed experimentally [10,11] as well as numerically [12]. At \( \gamma_{ic} \), the ground state undergoes a commensurate-incommensurate transition and the critical exponent for the magnetization changes from 1/2 below \( \gamma_{ic} \) to 1/4 above \( \gamma_{ic} \) [13,14]. Between \( \gamma_{ic} \) and 1, the system is in the incommensurate phase, and the incommensurate peak in the spin form factor \( S(q) \) of the ground state moves continuously from \( \pi \) to \( 2\pi/3 \) as \( \gamma \) increases from \( \gamma_{ic} \) to 1 [15]. Above \( \gamma = 1 \), the true nature of the ground state is still controversial [15,16]. Some works [15] suggest that it might be in a trimerized phase. When \( \gamma < -1 \), the ground state is doubly degenerate and dimerized.

The TMRG is a finite temperature extension of the powerful density matrix renormalization group method [17]. A detailed introduction to this method can be found in Refs. [3–6]. The TMRG method handles directly infinite spin chains and thus there is no finite system size effects. To calculate the spin susceptibility, we first evaluate the magnetization \( M \) of the system with a small external field \( B \), and then from the ratio \( M/B \) we obtain the value of the susceptibility. The specific heat is evaluated from the numerical derivative of the internal energy with respect to temperature. At low temperatures, since the specific heat is very small, the relative error of the specific heat may become quite large. In most of our calculations 100 states are retained.

Figure 1 shows the zero-field spin susceptibility \( \chi(T) \) normalized by its peak value \( \chi_{peak} \) as a function of the normalized temperature \( T/T_{peak} \) for a set of \( \gamma \), where \( T_{peak} \) is the temperature of \( \chi_{peak} \). Above \( T_{peak} \), \( \chi(T)/\chi_{peak} \) behaves similarly for all the curves shown in the figure. When \( \gamma \) is positive, \( \chi(T) \) drops quickly below \( T_{peak} \). This is because the energy gap in this parameter regime is very large. As \( \gamma \) becomes negative, \( \chi(T) \) just below \( T_{peak} \) tends to become flatter. At \( \gamma = -1 \), there is no gap in the
excitation spectrum, and $\chi(T)$ shows a small positive curvature at low temperatures, as in the $S = 1/2$ Heisenberg chain.

The inset of Fig. 1 shows the $\gamma$ dependence of $\chi_{\text{peak}}$ and $T_{\text{peak}}$. The increase of $\chi_{\text{peak}}$ with $\gamma$ indicates that the susceptibility becomes larger when $\gamma$ moves from the dimerized phase to the Haldane phase. This is consistent with the picture that in the dimerized phase the spin is frozen by forming a rather rigid spin singlet, while in the Haldane phase the spin is relatively free above the Haldane gap. The peak temperature $T_{\text{peak}}^4$ drops almost linearly with $\gamma$. The slope of this drop is about 1.6$J$ per unit $\gamma$.

In a gapped phase, the low-lying excitation has approximately the energy dispersion $\epsilon_k = \Delta + \nu^2/3(k - k_0)^2 + O[(k - k_0)^3]$, where $k_0$ is the wave vector of the excitation minimum, $\Delta$ is the energy gap, and $\nu$ is the spin velocity. When $T \ll \Delta$, $\chi(T)$ has the form [18]

$$\chi(T) = \lambda \sqrt{\frac{\Delta}{T}} e^{-\Delta/T},$$

where $\lambda$ is a $T$-independent parameter. From the fit of the low temperature TMRG results of $\chi(T)$ with this equation, we can estimate the value of $\Delta$. The result of $\Delta$ we obtained is shown in Fig. 2. The maximum energy gap is $\sim 2J/3$, located at $\gamma = 1/3$. Our results agree with other numerical studies [16,19].

Figure 3 shows the temperature dependence of the specific heat $C(T)$ for a set of $\gamma$. The inset of the figure shows the $\gamma$ dependence of the peak value of the specific heat, $C_{\text{peak}}$, and the peak temperature $T_{\text{peak}}$. Compared with $T_{\text{peak}}^4$, $T_{\text{peak}}$ behaves quite differently. It drops with increasing $\gamma$ when $\gamma < 1/2$ and becomes almost a constant when $\gamma > 1/2$. Below the peak temperature, $C/C_{\text{peak}}$ shows quite similar behavior for all the curves shown in the figure except at very low temperatures. Since there is no energy gap at $\gamma = \pm 1$, $C(T)$ at these two points approaches zero linearly with decreasing $T$. However, for other cases, $C(T)$ decays exponentially at low temperatures. For the two exact solvable points $\gamma = \pm 1$, exact results are available [20], and the specific heat vanishes linearly at low temperature. However, due to large errors at low temperatures, our results do not show this behavior clearly. Above the peak temperature, $C/C_{\text{peak}}$ drops quickly for negative $\gamma$. However, when $\gamma$ becomes bigger, in particular in the incommensurate phase ($\gamma = 2/3$ and 1), $C(T)$ shows a weak and broadened peak above $T_{\text{peak}}^4$. It seems that there is a new excitation mode accumulated at low energies in the incommensurate state.

Now let us compare the numerical results with the spin susceptibility data $\chi_{\text{exp}}$ of LiVGe$_2$O$_6$ measured by Millet et al. on a powder sample [2]. As mentioned in [2], two extraordinary features appear in $\chi_{\text{exp}}$. One is the slow drop of $\chi_{\text{exp}}$ on both sides of the susceptibility peak, and the other is the abrupt drop of $\chi_{\text{exp}}$ below 22 K with a sharp upturn below 15 K. The first feature, in particular the slow drop of $\chi_{\text{exp}}$ below the peak temperature, is reminiscent of a gapless system. The second feature of $\chi_{\text{exp}}$ is typical of a spin-Peierls system with impurities, such as in Zn doped CuGeO$_3$ [21]. These features have led Millet et al. to interpret LiVGe$_2$O$_6$ as a nearly gapless $S = 1$ spin chain with the spin-Peierls instability. However, whether the abrupt drop of $\chi_{\text{exp}}$ at 22 K is really due to a spin-Peierls transition is still an open question.

The sharp upturn of $\chi_{\text{exp}}$ at low temperatures indicates that the impurity contribution is strong. To see how strong the impurity effect is, let us first do a comparison without subtracting the impurity contribution in $\chi_{\text{exp}}$. In Fig. 1, the measured susceptibility $\chi_{\text{exp}}$, normalized by its peak value at about 47 K is compared with the TMRG results discussed previously. The disagreement between the theoretical and experimental results indicates that the impurity effect is too strong to be ignored even at high temperatures.
By fitting the low temperature experimental data below 15 K with this equation, we find that $C' = 0.115 \text{ cm}^3\text{K/mol}$, $\theta' = 14.1 \text{ K}$, $\alpha = 2.18 \text{ K}^2$, $\lambda = 0.0063 \text{ cm}^3\text{K/mol}$, and $\Delta = 36 \text{ K}$. These parameters show that not only the contribution from impurities to $\chi_{\text{exp}}$ is large as expected, but also the interaction among impurities is strong at low temperatures. There is no simple explanation for such a strong correlation among impurities. Clearly this is an important problem which should be further investigated both theoretically and experimentally.

By subtracting the impurity contribution from $\chi_{\text{exp}}$, we obtain the intrinsic susceptibility $\chi_{\text{intrinsic}}$ of LiVGe$_2$O$_6$. The result for $\chi_{\text{intrinsic}}$ together with the raw data $\chi_{\text{exp}}$ and $\chi_{\text{imp}}$ is shown in Fig. 4. After the subtraction, the abrupt drop of $\chi_{\text{exp}}$ at 22 K becomes less distinct, but the change in the slope is still visible. The most significant change of $\chi_{\text{intrinsic}}$ compared with $\chi_{\text{exp}}$ is that the peak shifts to a higher temperature and the drop below the peak temperature becomes more rapid. By comparing in detail the normalized $\chi_{\text{intrinsic}}$ with the theoretical results, we find that $\chi_{\text{intrinsic}}$ can be well fitted by the numerical curve with $\gamma = 1/6$ (Fig. 4). This shows that the biquadratic term in model (1) does have an important contribution to the low energy spin dynamics of LiVGe$_2$O$_6$, in agreement with Millet et al. [2]. However, the value of $\gamma$ which gives the best fit, in particular its sign, is different from that suggested in Ref. [2]. A detailed comparison indicates that $\chi_{\text{intrinsic}}$ lies between the theoretical curves for $\gamma = 1/4$ and $1/8$ in the whole temperature region. Thus the uncertainty in the value of $\gamma_c$ is very small. The result at $\gamma_c \sim 1$ suggested in Ref. [2] does not fit the experimental data.

At $\gamma = 1/6$, $T_{\text{peak}} = 1.025J$. Setting this $T_{\text{peak}}$ equal to the peak temperature of $\chi_{\text{intrinsic}}$, we find that $J \sim 73 \text{ K}$.
Compared with the gap value $\Delta = 36$ K obtained previously, we have $\Delta \sim 0.49 J$. This value of $\Delta$ is rather close to the Haldane gap, $0.54 J$, of the Hamiltonian (1) at $\gamma = 1/6$ (Fig. 2). This suggests that the low energy spin excitations are gapped and the change of the slope at 22 K is not due to a spin-Peierls transition.

We have also compared $\chi_{\text{intrinsic}}$ with the spin susceptibility of the $S = 1$ Heisenberg model with uniaxial single-ion anisotropy but without the biquadratic term [22], namely the model $H = J \sum_i [S_i \cdot S_{i+1} + D \sum_i S_i^2]$. However, in the parameter region which might be physically relevant, $-1/2 < D < 1/2$, we find that none of the numerical curves fits $\chi_{\text{intrinsic}}$ in the whole temperature range. This shows that the uniaxial anisotropy in LiVGe$_2$O$_6$ is indeed very small, in agreement with the analysis of Millet et al. [2].

The above analysis confirms the importance of the biquadratic exchange interaction in LiVGe$_2$O$_6$. On the other hand, it also raises some new questions. In the argument given by Millet et al., the biquadratic term comes from fourth order since at second order the antiferromagnetic and ferromagnetic terms partially cancel. However, the coefficient of this biquadratic term is negative (i.e., $\gamma < 0$) according to their calculation, in contrast with the result we obtain. To resolve this disagreement, further investigation into the electronic structure of LiVGe$_2$O$_6$ is needed. More detailed measurements with high quality single crystals would also help clarify the impurity effect as well as the nature of the anomaly at 22 K in this material. In a $S = 1$ Heisenberg chain, the localized nonmagnetic impurity may induce midgap states within the Haldane gap [23–25]. A better understanding of the physical properties of these midgap states would also be helpful for further understanding the thermodynamics of LiVGe$_2$O$_6$ at low temperatures.

In summary, the thermodynamic properties of the bilinear and biquadratic Heisenberg model have been studied and compared with the experiments. The measured susceptibility data of LiVGe$_2$O$_6$, after subtracting the impurity contribution, can be quantitatively explained by the model (1) with $\gamma = 1/6$.

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