Entropy and specific heat of ferroics described by the transverse Ising model with different spins and its application for CoNb$_2$O$_6$

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Abstract

The entropy and specific heat dependence of ferroics on temperature and transverse fields especially in the quantum paramagnetic state (QPa) is investigated by using the transverse Ising model (TIM) with different spin values within mean field and Gaussian spin fluctuation approximations. An enhancement of a maximum peak in the temperature dependence of the specific heat curves due to spin fluctuations in the QPa phase is illustrated. This maximum peak shifts to the higher temperature region and its magnitude reduces with increasing the transverse field. In addition, the temperature corresponding to this maximum linearly depends on the deviation of the transverse field from its critical value. The obtained specific heat is found qualitatively in agreement with the experimental observations for the quasi one-dimensional (1D) Ising ferromagnet CoNb$_2$O$_6$ in the QPa phase. It is shown that the spin-1/2 three dimensional (3D) TIM better describes the specific heat of CoNb$_2$O$_6$ than the 1D-TIM does in the QPa phase near the critical temperature but the spin-3/2 3D-TIM is more adequate than the spin-1/2 3D-TIM for describing the thermal behavior of CoNb$_2$O$_6$ at high
temperatures and at high transverse fields.

Keywords: Transverse Ising model, specific heat, quantum para-magnetic state, Gaussian approximation

1. Introduction

Recently, the finite temperature thermodynamic characteristics such as entropy, heat capacity, susceptibility of the ferroic materials (ferromagnets or ferro-electrics) having quantum phase transitions (QPT) are studied intensively to comprehend the specific nature of this phenomenon. Quantum criticality near the quantum critical point (QCP) observed firstly in ferro-electrics where the ferro-electric transition temperature is suppressed to zero due to tuning parameters \[1\]. The tuning parameters, which bring systems through ordered phase to quantum para-magnetic (QPa) or quantum para-electric states in different cases, can be hydro-static pressure, atomic substitution, transverse magnetic or electric fields, etc. In this paper, the transverse field (TrF) implies the magnetic field inside ferromagnets or electric field inside ferro-electrics.

Rowley and Spalek et al \[2\] have shown that the non-classical behavior of the inverse susceptibility of SrTiO\(_3\) and related compounds, \(\chi^{-1}\) (equivalent to the inverse dielectric function, \(\epsilon^{-1}\)) has been proportional to \(T^2\) close to the QCP. In order to convince of the weight of the finite temperature quantum criticality proved by Sachdev \[3\], Kinross et al \[4\] has specified the quantum critical properties of the quasi-one dimensional (1D) Ising ferromagnet CoNb\(_2\)O\(_6\) sustaining up to high temperature (\(T \approx 4J\) with \(J\) the exchange interaction between nearest neighbor spins). Besides, Tian Lang et
al [5] has observed a prominent peak at the QCP in the heat capacity curve of the CoNb$_2$O$_6$. These authors have applied the exact solution [6, 7] for 1D transverse Ising model (TIM) with spin $s = 1/2$ to explain this observation and to provide evidences for the gap-less fermion-like excitation in a narrow interval of the transverse magnetic field below the QCP.

Even though those results are interesting, their explanation is not unique and need more discussions. The anisotropy of the heat capacity and the susceptibility of CoNb$_2$O$_6$ have been also investigated experimentally since 1994 by Hanawa et al. [8] who confirms that the magnetic moment of Co in this compound is $5.05 \, \mu_B$ and Co$^{+2}$ (3d$^7$) ions prefer a high spin (HS) state with $s=3/2$ rather than a low spin (LS) state with $s=1/2$, which is normally used in the exact fermion solution for the TIM. Recent first-principle calculations of Molla and Rahaman [9] have found that the magnetic moment at the Cobalt site is $2.89 \, \mu_B$, which favors the HS state. What is the relevance of the HS model for its description of the thermodynamics of the spin system in the varying TrF? The specific heat of CoNb$_2$O$_6$ clearly exhibits the maximum peak in the QPa states (Fig. 5 of Ref. [5]) which gradually reduces and moves to higher temperature while increasing TrF. There is a big discrepancy between the experimental data and the theoretical QPa specific heat curves given by the exact fermion solution for CoNb$_2$O$_6$, which requires additional theoretical investigation.

In the previous work [10], we have shown the existence of the gap-less long-wavelength spin excitation at the QCP of the mono-spin layer using the XZ quantum Heisenberg model with an arbitrary spin value under the TrF. Thus, there is another way to interpret the finite temperature experimental results.
using TIM with different spin values beside the famous spin-1/2 TIM given in literature (see for example, Ref. [11]). A coupling between spin chains, which plays an essential role in the formation of the isosceles triangular plane lattices of CoNb$_2$O$_6$ is also necessary to be taken into account in the 3D spin model used by Cabrera et al. [12]. The specific heat in transverse Ising thin films has been studied in Ref. [13] using the mean field (MF) and the effective mean field theory but the TrF dependence of the specific heat has not been considered.

In this paper, we aim to use the TIM with different spin values to describe the temperature and transverse field dependence of the entropy and the specific heat of ferroics. Our calculations are carried out within the mean field & Gaussian spin fluctuation approximations beyond the critical region. We also pay attention to the thermodynamic properties in the QPa states of ferromagnets and compare our results with the experimental specific heat of CoNb$_2$O$_6$ measured in Ref. [5].

Our paper includes four sections. In section II, the expressions of some thermodynamic quantities with the MF and Gaussian approximation in the QPa states are given explicitly using the TIM model with arbitrary spin values. Section III presents a comparison with the specific heat experiment for CoNb$_2$O$_6$ in the QPa regime and gives detail discussions. A conclusion is provided in the last section. Throughout this paper, we use a natural unit system with $\hbar = 1; k_B = 1$. 
2. The transverse Ising model and thermodynamic quantities

2.1. Model and free energy calculation in the Gaussian approximation

The crystal structure of CoNb$_2$O$_6$ belongs to the space group $Pbcn$ whose lattice parameters of an orthorhombic unit cell are $a=14.1337\;\text{Å}$, $b=5.7019\;\text{Å}$, $c=5.0382\;\text{Å}$\cite{14}. In order to describe the magnetic behavior of the quasi-1D magnet CoNb$_2$O$_6$, we use a 3-dimensional (3D) TIM instead of the quasi-2D model of Ref.\cite{15}. The three basis vectors of the unit cell of the 3D spin lattice are chosen similarly to Ref.\cite{12} where $a_1=b$, $a_2=(a-b)/2$, $a_3=c/2$. A spin position is defined by a three-component spin lattice vector $R_j$. The z-axis of the crystallographic coordinate Oxz system is parallel to the $c$ vector direction and the external TrF directs along the x-axis which is parallel to the $b$ vector. Denoting $s^z_j, s^x_j$ as spin operator components on the Ox, Oz coordinate axes, the Hamiltonian of the TIM is written by

$$H = -h_0 \sum_j s^z_j - \Omega_0 \sum_j s^x_j - \frac{1}{2} \sum_{jj'} J_{jj'} s^z_j s^z_{jj'}.$$ \hspace{1cm} (1)

Here the external longitudinal $h_0$ and the transverse field $\Omega_0$ are given in the energy unit like the exchange interaction, $J_{jj'} = J(|R_j - R_{jj'}|)$ and temperature $\tau$. Separating $H$ into mean field $H_0$ and spin fluctuation $H_{\text{int}}$ parts and using a unitary rotation to transform spin operators $s^z_j, s^x_j$ to $S^z_j, S^x_j$ in the new OXYZ coordinate system\cite{10}, we can derive a transformed Hamiltonian of the spin system, $H = H_0 + H_{\text{int}}$, where

$$H_0 = \frac{N}{2} J(0)m^2_z - \gamma \sum_j S^Z_j,$$ \hspace{1cm} (2)

$$H_{\text{int}} = -\frac{1}{2} \sum_{k,\alpha\alpha'} I^{\alpha\alpha'}(k)\delta S^\alpha(k)\delta S^{\alpha'}(-k),$$ \hspace{1cm} (3)
where $\alpha = X, Z$, $J(0)$ is a Fourier component of exchange interaction at $\mathbf{k} = 0$ given by Eq. (8), $m_z = \langle s^z \rangle$ and $m_x = \langle s^x \rangle$, the thermodynamic average of the magnetic moments per site. Since the OZ axis of the rotated OXYZ coordinate system is chosen parallel to the direction of the net field $\gamma$, only statistical average value of the longitudinal spin component differs from zero ($\langle S_z^j \rangle \neq 0$ and $\langle S_y^j \rangle = 0$). The total field $\gamma$ is composed of the longitudinal $h$ and the transverse $\Omega_0$ components, which are $\gamma = \sqrt{h^2 + \Omega_0^2}$ and $h = h_0 + J(0)m_z$. The 2x2 exchange interaction symmetric matrix $\hat{I}(\mathbf{k})$ with the matrix elements appeared in the Eq. (3) is defined by

$$\hat{I}(\mathbf{k}) = \begin{bmatrix} I^{XX}(\mathbf{k}) & I^{XZ}(\mathbf{k}) \\ I^{ZX}(\mathbf{k}) & I^{ZZ}(\mathbf{k}) \end{bmatrix} = \frac{J(\mathbf{k})}{\gamma^2} \begin{bmatrix} \Omega_0^2 & -\Omega_0 h \\ -\Omega_0 h & h^2 \end{bmatrix} \quad (4)$$

with the Fourier images of the exchange interaction $J(\mathbf{k}) = \sum R_j J(R_j)e^{i\mathbf{k}R_j}$. The lattice vectors $\mathbf{R}_j$ points out the position of the $j^{th}$ spin and is presented by three basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. The wave vector $\mathbf{k}$ is given in the reciprocal lattice of the orthohombic crystal lattice. Using the similar intra-chain and inter-chain nearest (NN), next-nearest neighbor (NNN) exchange couplings for CoNb$_2$O$_6$ to those in Ref. [12], a Fourier image $J(\mathbf{k})$ can be written in the following form,

$$J(\mathbf{k}) = \sum_{\Delta} J'_2 e^{i\mathbf{k}\Delta} + \sum_{\Delta_1} J_2 e^{i\mathbf{k}\Delta_1} + \sum_{\Delta_2} J_1 e^{i\mathbf{k}\Delta_2} + \sum_{\Delta_3} J_2 e^{i\mathbf{k}\Delta_3}, \quad (5)$$

$$\Delta = \pm c; \Delta_1 = \pm c/2; \Delta_2 = \pm b; \Delta_3 = \pm (a \pm b)/2, \quad (6)$$

where $J_2 > 0 (J'_2 < 0)$ is a ferromagnetic-FM (anti-ferromagnetic-AF) intra-chain exchange coupling between NN (NNN) spins along the $z$ direction of the crystallographic coordinate system. $J_1, J_2$ are inter-chain anti-ferromagnetic NN (NNN) exchange couplings between spins in the $xy$-plane, respectively. In
the rest of our paper (except for, in the part III), all dimensionless quantities such as the Fourier image of the exchange coupling $J(k)$, field strengths $\gamma$, $h$, $\Omega_0$, temperature $\tau$, free energy and spin wave frequency are given in the scale of the exchange coupling $J_z$. For example, $\tau = T/J_z$ and

$$J(k) = 2[\cos(k_x c/2) + J'_z \cos(k_x c) + J_1 \cos(k_y b)] + 2J_2 \cos(k_x a/2) \cos(k_y b/2)], \quad (7)$$

$$J(0) = 2(1 + J'_z + J_1 + 2J_2) \quad (8)$$

Since we are interested in the role of the TrF, the external longitudinal field is turned off ($h_0 = 0$) and we have only intrinsic longitudinal field, $h = J(0)m_z$. Using the functional integral method and the MF & Gaussian approximations similarly to the work of Ref. [10], we get the free energy per spin $f$, which consists of the mean field part $f_0$ and the fluctuation part $f_1$.

$$f = f_0 + f_1, \quad (9)$$

$$f_0 = \frac{1}{2}J(0)m_z^2 - \frac{1}{\beta} \ln \frac{\sh((s + 1/2)y)}{\sh(y/2)}, \quad (10)$$

$$f_1 = \frac{1}{2N\beta} \sum_k \ln \left\{ \frac{1 - \beta I_{ZZ}(k)\gamma b_s'(y)}{\omega(k)} \right\}$$

$$+ \frac{1}{2\beta N} \sum_k \ln \left\{ \frac{\sh(\beta \omega(k)/2)}{\sh(y/2)} \right\}, \quad (11)$$

$$y = \beta \gamma \quad (12)$$

where $\beta = \tau^{-1}$ and $\omega(k) = \gamma - I_{XX}(k)b_s(y)$, the temperature-dependent energy of the elementary excitation obtained in Ref. [10].

2.2. Thermodynamics quantities of the TIM in the mean field approximation

In the lowest approximation, the finite temperature behavior of the spin system can be described using the mean field approximation (MFA), where
Figure 1: Temperature dependence of the components $m_x$, $m_z$ and the total $m$ magnetic moment per site for spin (a) $s=1/2$ and (b) $s=3/2$ cases with $J(0)=1.0$ at different transverse field values. The SR temperature $\tau_R$ and the Curie temperature $\tau_C$ are indicated by arrows. The parameters $J(0)$, $\Omega_0$, $\tau_R$, $\tau_C$ are given in unit of NN exchange integral $J_z$.

Figure 2: The dependence of the SR temperature $\tau_R$ on the transverse field $\Omega_0$ for spin (a) $s=1/2$, (b) $s=3/2$ cases.
the spin fluctuation term $H_{\text{int}}$ (Eq. (3)) is omitted. The entropy $S_0$, the internal energy $E_0$, the specific heat $C_0$ per spin is obtained in the MFA by taking derivatives of Eq. (10) with respect to temperature, which give

$$S_0 = -\frac{\partial f_0}{\partial \tau} = -y b_s(y) + \ln \frac{\sinh[(s + 1/2)y]}{\sinh(y/2)},$$

(13)

$$E_0 = f_0 + \tau S_0 = \frac{1}{2}J(0)m_z^2 - \tau y b_s(y),$$

(14)

$$C_0 = -\frac{\tau}{\partial S_0/\partial \tau} = y^2 b'(y) \left\{ 1 - \frac{J(0)\hbar^2 y b'(y)}{\gamma^3 - J(0)\Omega_0^2 b_s(y)} \right\}^{-1},$$

(15)

where $b_s(y)$ and $b'_s(y)$ are the Brillouin function and its derivative respectively, which are

$$b_s(y) = (s + \frac{1}{2}) \operatorname{ch} \left[ \left( s + \frac{1}{2} \right) y \right] - \frac{1}{2} \operatorname{ch} \frac{y}{2},$$

(16)

$$b'_s(y) = \frac{1}{4 \sinh^2 \left( \frac{y}{2} \right)} - \frac{(s + \frac{1}{2})^2}{\sinh^2 [(s + \frac{1}{2})y]}.$$

(17)

The critical temperature $\tau_R$ (spin reorientation temperature referred to Ref. [10]) is found by solving the following equation, which is

$$b_s \left( \frac{\Omega_0}{\tau_R} \right) = \frac{\Omega_0}{J(0)},$$

(18)

If $\tau_R(\Omega_{0c}) = 0$, the critical TrF is deduced from Eq. (18), which is

$$\Omega_{0c} = sJ(0).$$

(19)

We list temperature regimes, where magnetization components are followed by different rules below.

i/ If $\tau < \tau_R$,

$$m_x = \frac{\Omega_0}{J(0)}; \quad m_z = \sqrt{b_s^2(\gamma/\tau) - m_x^2}$$

(20)

where $\gamma = J(0)b_s(\gamma/\tau)$. 

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ii/ If $\tau \geq \tau_R$,

$$m_z = 0; \quad m_x = b_s(\gamma/\tau)$$

(21)

where $\gamma = \Omega_0$.

Fig. 1 shows the MFA temperature dependence of the total magnetic moment per site $m$ and its components $m_z$, $m_x$ with two spin-1/2 and -3/2 cases. The spin system is in the QPa state if $\tau > \tau_R$, where only the magnetic component along the transverse field $m_x$ exists. The Curie temperature determines an order-disorder phase transition without the external TrF ($\Omega_0 = 0$). The critical temperature used in the TIM is practically identical with the spin reorientation (SR) temperature $\tau_R$, which is reduced with increasing TrF and $\tau_R(\Omega_0) \leq \tau_C$. In addition, we can see that both the magnetic moment and the SR temperature are enhanced while increasing the spin value $s$. 

Figure 3: Temperature dependence of the MF magnetic entropy $S_0$ for spin cases: (a) $s=1/2$ and (b) $s=3/2$ cases. We choose $J(0)=1.2$ for $s=1/2$ and $J(0)=0.3$ for spin $s=3/2$ systems. The values of critical field $\Omega_0c$ are given in the figure.
The dependence of the SR temperature on the TrF is also illustrated in Fig. 2. It is found out that the \( \tau_R \) value and the critical transverse field \( \Omega_0c \) are proportional to the internal exchange parameter \( J(0) \) for both spin cases. However, for the same set of parameters, the \( \tau_c \) value for the HS case is always considerably larger than that of the LS case. It is obviously seen in Fig. 2, when the HS or LS model are applied for describing materials with a given Curie temperature \( \tau_c \) determined by \( J(0)s(s+1)/3 \) within the MFA, \( J(0) \) will be chosen smaller for the HS model than for the LS model. For this reason, \( J(0) \) is set to be 1.2 and 0.3 for the LS and HS cases in Fig. 3-6, respectively.

We plot in Fig. 3 the spin entropy \( S_0 \) as a function of temperature for two spin cases at different TrFs where the entropy is monotonically suppressed with increasing TrF and reaches the saturation value, \( \ln2 \) (\( \ln4 \)) for \( s = 1/2 \) (\( s = 3/2 \)) at high temperatures. The entropy data extracted from experi-
Figure 5: The dependence of the ratio $C/\tau$ on temperature for the LS system (a) $s=1/2$ and HS (b) $s=3/2$ for different transverse fields. The exchange interaction parameter $J(0)$ is chosen similarly as in Fig. 3.

Figure 6: Temperature dependence of the entropy systems in the QPa phase with $\Omega_0 > \Omega_{0c}$. The MF part and the total entropy including fluctuations are denoted by $S_0$ and $S$, respectively. The exchange parameters are $J(0)=1.2$, $J'_z = -0.2$, $J_1 = -0.1$, $J_2 = -0.05$ for the LS (a) and $J(0)=0.3$, $J'_z = -0.2$, $J_1 = -0.1$, $J_2 = -0.275$ for the HS (b) cases, respectively. The critical TrF value in the MFA is 0.6 (0.45) for the LS (HS) system.
mental results for CoNb$_2$O$_6$ has generally agreed with this tendency except for Fig. 4b of Ref. [5] which has shown an intriguing behavior that the spin entropy of CoNb$_2$O$_6$ at B = 5 T is larger than that at zero field. According to the general understanding, the spin entropy with the same HS or LS states at the same temperature should have been smaller in larger TrFs (see Fig. 3), hence, the entropy data at B = 5 T of Ref. [5] are seemingly peculiar, which requires further experimental verification.

The free energy of the LS and HS systems versus temperatures is also presented in Fig. 4 at different TrFs, which reveals that the HS system is more stable than the LS system at high TrFs and at low temperatures due to its lower free energy (see the curves for $s = 1/2$ and $3/2$ when $\Omega_0 = 2.0$ with $\tau < 0.4$). This observation is reasonably expected because the Zeeman energy has a role of stabilizing systems at high fields, hence this fact has to be taken into account for analyzing the experimental results.

We next show in Fig. 5 the ratio of MF heat capacity and temperature for different spin values. While increasing the TrF $\Omega_0$ from zero up to the critical value $\Omega_{0c}$, the maximum peak of this curve shifts to the lower temperature. The spin system exists in the QPa state from zero temperature beyond the critical TrF where the maximum peak moves to the opposite direction. When $\Omega_0 > \Omega_{0c}$, the maximum peak of the $C_0/\tau$ curve and its shift tendency are characterized for the QPa order which are also experimentally observed [5] but its nature has not been unveiled. We believe that the maximum peak originates from two opposite tendencies where the transverse field enhances the transverse order while thermal fluctuations suppress it. Although the MFA result is kindly simple, it presents precisely the qualitative behavior of
the C₀/τ curve.

2.3. Quantum paramagnetic states

We are interested in the QPa states when the longitudinal component of the order parameter mₙ disappears and the system is completely characterized by the transverse order parameter mₓ = bₓ(Ω₀/τ) (see the Eq. (21)). Free energy f, entropy S and specific heat C in QPa states within the Gaussian approximation are successively given by

\[
\begin{align*}
\text{f} &= f₀ + \frac{1}{2βN} \sum_k \ln \frac{\text{sh}(βω_k/2)}{\text{sh}(y₀/2)} \\
\text{S} &= S₀ - \frac{1}{2N} \sum_k \ln \frac{\text{sh}(βω_k/2)}{\text{sh}(y₀/2)} \\
&+ \frac{1}{4N} \sum_k \left\{[βω_k - βJ(k)y₀b'_k(y₀)] \text{cth}(βω_k/2) - y₀ \text{cth}(y₀/2)\right\}
\end{align*}
\]

where

\[
\begin{align*}
f₀ &= -\frac{1}{β} \ln \frac{\text{sh}[(s + 1/2)y₀]}{\text{sh}(y₀/2)}, \\
S₀ &= -y₀b_k(y₀) + \ln \frac{\text{sh}[(s + 1/2)y₀]}{\text{sh}(y₀/2)}, \\
C &= C₀ + \frac{y₀^2}{8\text{sh}^2(y₀/2)} + \frac{β^2}{8N} \sum_k \frac{[ω_k - J(k)y₀b'_k(y₀)]^2}{\text{sh}^2(βω_k/2)}
\end{align*}
\]

where C₀ = y₀²b'(y₀) and the elementary excitation energy in the QPa state is

\[
\begin{align*}
ω_k &= Ω₀ - J(k)b_k(y₀), \\
y₀ &= βΩ₀.
\end{align*}
\]
The additional second term beyond the MFA in Eq. (22) for free energy is the contribution from elementary excitations at finite temperatures. Therefore, the thermodynamic properties of the spin system can be calculated numerically using Eqs. (22)-(28) where the summation taken over \( k \) values is replaced by the integration,

\[
\frac{1}{N} \sum_{k} \ldots \rightarrow \frac{1}{(4\pi)^3} \int_{-2\pi}^{2\pi} dk_x \int_{-2\pi}^{2\pi} dk_y \int_{-2\pi}^{2\pi} dk_z ,
\]

and

\[
J(k) = 2[J_z \cos(k_z/2) + J'_z \cos(k_z) + J_1 \cos(k_y) + 2J_2 \cos(k_x/2) \cos(k_y/2)].
\]

Fig. 6 shows the temperature dependence of the MFA entropy \( S_0 \) and the total fluctuating entropy \( S \) of the LS and HS systems in the QPa state at different TrFs. At very low temperatures, the quantum spin fluctuations have great influence on the entropy due to the Heisenberg principle in contrast with the suppression of thermal fluctuations. An increase of TrF \( \Omega_0 \) enhances the order parameter \( m_x \) in the QPa state, thus reduces the disorder and the spin entropy. At the same field near the critical value, a maximum peak of the entropy curve is more apparently observed at very low temperatures for the LS case and is suppressed with increasing TrFs (see Fig. 6a).

In order to appreciate the influence of the spin fluctuations on \( C/\tau \) and \( C_0/\tau \), we display simultaneously these quantities in Fig. 7 with and without considering the spin fluctuations. We can assess the spin fluctuation effect from the deviation of the specific heat from its MFA value, i.e. \( \Delta C = C - C_0 \). The spin fluctuations strongly affect on the spin systems in the low temperature regime, which is characterized by the maximum peak of the curve in the QPa state. The amplitude of this peak is larger when the TrF
Figure 7: The temperature dependence of $C/\tau$ in the QPa phase with $\Omega_0 > \Omega_{0c}$. The MF part and the total entropy including fluctuations, are denoted by $C_0$ and $C$. The exchange parameters $J(0)$, $J_z$, $J_1$, $J_2$ for the LS (a) and for the HS (b) cases are correspondingly chosen similarly to Fig. 6. Insets show the linear dependence of the characteristic temperature $\tau^*$ on the field difference $\Omega_0 - \Omega_{0c}$. 
Figure 8: The dependence of $C/\tau$ on temperature $\tau$ with various NN in-plane AF exchange and NNN intra-chain exchange integrals for spins (a) $s=1/2$ and (b) $s=3/2$. The TrF is set as $\Omega_0 = 1.0$.

is closer to the critical field $\Omega_{0c}$. The temperature $\tau^*$ corresponding to the maximum of the curve can be estimated in the zero temperature limit of the Eq. (26) where analytic calculations show that the specific heat tends to zero following by the exponential law $\exp\left[-(\Omega_0 - \Omega_{0c})/\tau^2\right]$ and the maximum of $C/\tau$ curve occurs at $\tau^* \approx (\Omega_0 - \Omega_{0c})/2$ with $\Omega_{0c} = J(0)s$. Insets in Fig. 7 well describe the linear dependence of $\tau^*$ on the deviation from the critical transverse field $\Omega_{0c}$.

We also investigate the modification of specific heat on the in-plane inter-chain couplings. Fig. 8(a) shows that for the LS model, the antiferromagnetic NN inter-chain exchange couplings, $J_1, J_2$, insignificantly affect the shape and the magnitude of the temperature dependence of the heat capacity at the same sufficiently large value of $J(0)=1.2$. In the HS case, a significant change and a shift of the maximum peak of the $C/\tau$ curve to the
higher temperature are observed when $J_1$ and $J_2$ values are comparable with the exchange parameter $J(0)=0.3$ (see Fig. (8b)). In the HS 3D-TIM, the AF inter-chain in-plane exchange couplings $J_1$, $J_2$ play a key role in the formation of the isosceles triangular spin lattice and they have a noticeable effect on the heat capacity at the temperatures near the critical temperature.

3. Specific heat of CoNb$_2$O$_6$ in quantum paramagnetic states

In this part, the thermodynamic properties of typical 1D Ising ferromagnet CoNb$_2$O$_6$ in the QPa state are numerically calculated and discussed in the framework of the Gaussian spin fluctuation approximation.

The phase transition temperature and the critical $T_{cF}$ derived from the field dependent specific heat experiment are about $T_c = 2.85$ K (0.246 meV) and $B_c = 5.24$ T (0.61 meV), respectively. One can use these data to estimate the order of the exchange coupling parameter $J(0)$ defined by Eq. (29). Within the MFA, the Curie temperature $T_c$ is evaluated by $J(0)s(s+1)/3$. Taking $T_c = 2.85$K, we can obtain the exchange parameter $J(0) = 1.039$ meV (0.197 meV) for the LS (HS) model.

Table 1 lists the exchange couplings parameters $J_z$, $J'_z$, $J_1$, $J(0)$ of the TIM for the CoNb$_2$O$_6$ spin system in the QPa states, which are determined from neutron experiments at 7 T and from the density functional theory (DFT) calculation. Comparing data given in Table 1, we note that the value $J(0) = 3.66$ meV estimated from the neutron experiment is three (ten) times larger than the value derived from the specific heat experiment results $J(0) = 1.039$ meV (0.197 meV) evaluated within the LS (HS) model. The signs of intra-chain couplings $J_z$, $J'_z$ obtained by the DFT calculations.
Figure 9: Experimental and theoretical temperature dependence of the specific heat data of CoNb$_2$O$_6$ at 5.4 T. The dashed (solid) line corresponds to the 1D (3D) TIM with exchange coupling parameters given in Table 1.

Table 1: Exchange coupling parameters (meV)

| TIM     | Exchange coupling parameters (meV) | Ref.       |
|---------|------------------------------------|------------|
| S=0.5   | J$_z$ | J$'_z$ | J$_1$ | J$_2$ | J(0) |                   |
|         | 2.19  | -0.29  | -0.03 | -0.02 | 3.66 | [12]        |
|         | -0.152 | 0.332  | -0.106 | -0.280 | NA | [9]           |
| S=0.5   | 0.519 | 0      | 0      | 0      | 1.039 | Current work 1D-TIM |
|         | 0.950 | -0.043 | -0.043 | -0.172 | 1.039 | Current work 3D-TIM |
| S=1.5   | 0.357 | -0.443 | -0.172 | -0.22 | 0.197 | Current work 3D-TIM |
Figure 10: The temperature dependence of the experimental specific heat data [5] at B = 5.4 (a), 6.5 (b) and 8 T (c) by the LS (dashed lines) and the HS (solid lines) 3D-TIM. The exchange coupling parameters of the models are given in the last two rows of Table 1.
seem to be opposite to what have been used in Ref. [12], but the magnitude of these exchange parameters is a few tens of meV, which are in agreement with the magnitude of the parameters extracted from the specific heat measurement. The temperature dependence of the specific heat of CoNb$_2$O$_6$ has been investigated when $B > B_c$ (5.24 T) in Ref. [5], which shows that the spin system exists in the QPa from zero temperature.

Fig. 9 shows the comparison between our results and the specific heat data of CoNb$_2$O$_6$ at $B = 5.4$ T [5] in the framework of the spin-1/2 TIM. The values of exchange coupling parameters in the 1D and 3D TIM are shown in the Table 1. We also notice that the fitted data using exact fermion solution for the TIM chain (or 1D case) does not show the sharp peak near the critical field [5]. Meanwhile, the theoretical curves of the 1D and 3D TIM does clearly present a sharp peak near the critical field and the 3D-TIM (dashed line) is better to describe the magnitude of this anomaly close to the critical temperature. This improvement is due to the inclusion of the exchange couplings $J_1$, $J_2$ in 3D-TIM with HS and their magnitude comparable with the exchange coupling parameter $J(0)$ (see Table 1.)

Fig. 10 exhibits the fit using the 3D-LS and -HS TIM for the specific heat data of CoNb$_2$O$_6$ at $B = 5.4, 6.5$ and 8 T. The specific heat behavior near $T_c$ is well described by the 3D-LS model but the 3D-HS model is quantitatively closer to the experimental values at the high temperature. Since the lower spin model ($s=1/2$) is more ”quantum”, it is more appropriate to describe the thermodynamic properties near zero temperature (the critical temperature in the QPa state). However, at high temperatures and at high fields, the thermal excited states have such an important contribution of higher energy
state that the spin-3/2 model is more adequate to explain the thermodynamic behaviors of CoNb₂O₆. It also implies that the possible spin crossing effect (the change of spin states from s=1/2 to s=3/2 or to other spin states) with increasing TrFs and its influence on the thermodynamics of the ferroics having QPT are still opening questions for further study.

4. Conclusions

The thermodynamics of ferroics having quantum phase transition are examined using the TIM with different spins in the framework of the mean field and the Gaussian spin fluctuation approximations. The suppression and the shift of the specific heat maximum by increasing the transverse magnetic field in the QPa state experimentally observed in the 1D Ising ferromagnet CoNb₂O₆ are well illustrated by the TIM model with various spin values. It is shown that the maximum peak of the specific heat in the QPa phase near zero temperature is vividly described by using the 3D TIM with spin-1/2 while the spin-3/2 3D-TIM is more suitable to present the temperature dependent curve of the specific heat of CoNb₂O₆ in the QPa state at high temperatures and at high fields.

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