Quantum spin liquid in $\text{Sr}_2\text{CuO}_3$ induced by Acoustic Phonons

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We have carried out theoretical studies of the phonons and spinons excitation spectra of $\text{Sr}_2\text{CuO}_3$ in term of a one-dimensional model with non-adiabatic interaction magnetic and elastic subsystems using continuous time Monte Carlo method. Two gaps in triplet excitation spectrum are found. The bond defects concentration estimated is well agreement with the experimental data. The formation of magnetic moment on site at low temperature $T_N \sim 5K$ is caused by freezing quantum spin liquid with correlation radius of antiferromagnetic ordering $\xi/a \sim 300 - 500$.

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1. Introduction

Quasi-one-dimensional spin systems with antiferromagnetic interactions have received considerable attention because of a number of basic physical phenomena in low dimensions, such as the existence of a spin gap depending on the spin value or the frustration antiferromagnetic exchange, spin Peierls transitions, accompanied by the structural symmetry breaking. Orthorhombic compound $\text{Sr}_2\text{CuO}_3$ is considered as quasi-1D antiferromagnetic system. However, Raman studies reported that extra peaks were observed along the Cu-O chain directions [1] which implies that there might be some structural instabilities. This effect is confirmed by polarization-dependent infrared-active phonon spectra which have shown splitting of the stretching mode in the Cu-O chain direction about $20 \text{cm}^{-1}$ and became evident as $T$ decreases [2]. These unusual behavior are not expected by the previous theoretical calculations.

Another unclear behavior is the uniform spin susceptibility $\chi'(q = 0)$ have decreased steeply below $T \sim 33K$ without the signature of three-dimensional short range order approaching the Neel state by NMR Knight shift at the in-chain oxygen. The nuclear spin-lattice relaxation rate offsets the $\sim 1/T$ increase of the staggered spin susceptibility down to $10K$ and depends on frequency. The $q = 0$ mode of spin transport is ballistic and a diffusion-like contribution at $T << J$ [3]. The bulk susceptibility the measurements have shown decreasing above $\sim 10K$ [4]. The NMR lineshape have been changed in a very specific way, giving rise to "features", which have been explained by the chain edges and the presence of mobile bond-defects. A "defect" is defined as a local change in the magnetic bond coupling. As the translational symmetry of the spin system is broken, a local alternating magnetization develops around the defects in the direction of the applied field. The density of bond-defects decreases linearly with $T$. The source of the bond-defects might be related to the interstitial excess oxygen. However, at the lowest temperature, $T = 20K$, the density of bond-defects $\rho \sim 2.8 \cdot 10^{-3}$ remains more than ten times larger than the concentration of the residual spin-1/2 impurities ($\sim 1.3 \cdot 10^{-4}$) after annealing and the observed $T$ dependence of $\rho$ is not a constant [5].
The concept of mobile ”bond-defects” have been used for explanation of the temperature dependence and the anisotropy of the thermal conductivity below 50 K as the main source of spinon scattering at low temperatures [3]. The calculated mean distance between two neighboring bond defects, consistent with the NMR data between 20 and 60 K. The results of the specific heat measurements have been fit to the data above 4 K using the approximation $C = \gamma T + \beta T^3 + \delta T^5$. The linear in $T$ contribution is due to spinons excitations of a 1D Heisenberg spin-1/2 antiferromagnetic system with exchange $J = 2620 \pm 100$ which is 18% larger value than $J \approx 2200$ deduced from magnetic susceptibility data [4] and NMR data [5]. The Neel temperature $T_N$ depends on the measurement time and shifted to lower temperature with increasing time. So Neel temperature is $T_N = 5.4K$ from neutron scattering [7], 4.15K by $\mu SR$ [8] and 3.5K from the anomalies of the specific heat [3]. Possibly, here it is nonequilibrium process. Physical origin of the bond-defects remains unclear also as abrupt changes in susceptibility at different temperatures determined by NMR and by external magnetic field.

In the paper we try to answer on these questions basing on non-adiabatic interaction between spins. Numerical methods, such as exact diagonalization and density-matrix renormalization group, face the potential difficulty in dealing with a very large Hilbert space of the phonons. Here, we use Monte Carlo approaches restricted to finite chains $L = 100, 200$ but without any adiabatic approximation and the truncation of the infinite phonon Hilbert space. The method [9] is based on a path-integral representation for discrete system in which we work directly in the Euclidean time continuous. All the configuration update procedures contain no small parameters. Being based on local updates only, it allows to work with the grand canonical ensemble and to calculate any dynamical correlation function, expectation values.

2. Model and method

The ratio interchain to intrachain exchange in $Sr_2CuO_4$ is an extremely small $\sim 10^{-3}$ and demonstrates a good one-dimensionality. The structural fluctuation were only observed along in chain at low temperature. As a result a spin-phonon interaction were considered along chain. The model Hamiltonian of an spin-phonon system takes the form:

$$H = \sum_{i=1}^{L} [J + \alpha(u_i - u_{i+1})][S_i^z S_{i+1}^z + (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) / 2] + M\dot{u}_i^2 / 2 + K(u_i - u_{i+1})^2 / 2. \quad (1)$$

Here $S_i^{z, \pm}$ are a spin operator components associated with the site $i$, $J > 0$ is the usual antiferromagnetic exchange integral, $\alpha$ is the spin-phonon coupling constant, $u_i$ is the displacement in the $z$-direction, $M$ is the mass of the ion and $K$ the spring constant. Using the quantum representation for phonon operators $b, b^\dagger$, the Hamiltonian becomes

$$H = \sum_{q} \sum_{i=1}^{L} [J + \alpha \sqrt{\frac{2h}{M\omega_0}} \sin \frac{q}{2} \cos (q(i - 0.5))(b_q + b_q^\dagger)][S_i^z S_{i+1}^z + (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) / 2] \quad (2)$$

$$+ \sum_{q} \hbar \Omega(q)b_q^\dagger b_q, \quad \Omega(q) = 2\sqrt{\frac{K}{M}} \sin \left(\frac{q}{2}\right), \quad \omega_0 = 2\sqrt{\frac{K}{M}}, \quad q = 2\pi n / L, n = 1, 2, ...L$$

The phonon frequency ($\omega_0$), spin-phonon coupling ($\alpha$), energy $E$, temperature $T$ are normalized on the exchange $J$ and $\hbar = 1, M = 1$. The temperature used in calculation is $\beta = J/T = 25$. Our system consists of the two subsystem interacted. The elastic subsystem is described by phonons with the number occupation $n_{ph} = 0, 1, 2...$ and magnetic subsystem
is characterized by the number occupation $n_m = 0, 1$ and Pauli operators $a, a^\dagger$ which coincide with $S$ spin operators. We start with the standard Green function of the phonon in the momentum $q$-imaginary-time $\tau$ representation:

$$\begin{align*}
g(q, \tau) &= \langle \text{vac}|b_q(\tau)b_q^\dagger(0)|\text{vac}\rangle, \quad \tau \geq 0, b_q(\tau) = \exp(H\tau)b_q\exp(-H\tau). \tag{3}
\end{align*}$$

$$\begin{align*}
g(q, \tau) &= \sum_\nu |\langle \nu|b_q^\dagger|\text{vac}\rangle|^2 \exp \left[ -(E_\nu(q) - E_0)\tau \right]
\end{align*}$$

where $|\nu\rangle$ is a complete set of the Hamiltonian $H$ in the sector of given $q$, $H|\nu(q)\rangle = E_\nu(q)|\nu(q)\rangle$, $H|\text{vac}\rangle = E_0|\text{vac}\rangle$, $E_0 = 0$. Rewriting Eq.(3) as

$$\begin{align*}
g(q, \tau) &= \int_0^\infty d\omega A(q, \omega) \exp(-\omega\tau), A(q, \omega) = \sum_\nu \delta(\omega - E_\nu(q)) |\langle \nu|b_q^\dagger|\text{vac}\rangle|^2 \tag{4}
\end{align*}$$

one defines the spectral function $A(q, \omega)$. We calculate a one-particle spin Green function

$$\begin{align*}
\langle a(\tau)a^\dagger(0)\rangle &= \int_0^\infty d\omega \rho_\nu(\omega) \exp(-\omega\tau), \tag{5}
\end{align*}$$

where $\rho_\nu(\omega)$ -spectral density function. Correlation functions are determined on the basis of a complete set of eigenvector of the Hamiltonian:

$$\begin{align*}
\langle O \rangle &= \frac{\sum_\nu \langle \nu|O|\nu_j\rangle}{\sum_\nu \langle \nu_i|\nu_j\rangle}, \tag{6}
\end{align*}$$

where $O$ is the longitudinal spin-spin correlation function $<S_i^zS_{i+\hbar}^z>$ and the phonon density-density $<n_{ph}(q)n_{ph}(q+p)>$. The distribution of phonons number $n_{ph}(q)$ and the magnons number $n_m(k)$ as a function of momentum are simulated.

### 3. Results and discussion

The upper boundary of acoustic phonon band $\omega_0$ is in direct proportion to Debye temperature of $\Theta_{Sr_2CuO_3} = 441 \pm 10K$ [3] in term of Debye approximation. Using known data for $CuGeO_3$, $\Theta_{CuGeO_3} = 330K$ [4], $\omega_{0,Ge} \approx 1440K$ [1] we estimate $\omega_0 \approx 2100K$ for $Sr_2CuO_3$. The ratio of $\omega_0/J \approx 0.95$ will be used for calculation of dynamical characteristics. The spectral density of triplet excitations are shown in Fig.1. At the critical value of spin-phonon coupling $\alpha_{c1}$ the spectral density $\rho_\nu = 0$ for $E < \Delta$, were $\Delta$ is the gap in the triplet excitation spectrum. The gaps energies presented in inset of Fig.1 fit satisfactorily on the straight line $\Delta = -0.17(2) + 1.16(5)\alpha$ in the range of $\alpha_{c1} < \alpha < \alpha_{c2}$ with $\alpha_{c1} = 0.15(1)$.

For small spin-phonon coupling $\alpha < \alpha_{c1}$ the composite quasiparticle consisted spinon and phonon are formed. The inelastic interaction between spinon with momentum $k$ and phonon with $q$ lead to new quasiparticle with energy $E = E_q + E_k$ and momentum $k+q$. It follow from the distribution of the phonon number versus momentum as plotted in Fig.2a. The density of spinon excitations exhibits the singularity at the $E(k = \pi/2)$ and phonon excitations at the $E(q = \pi)$ and summered momentum agrees with MC result $N_{ph}(q \approx 4.5) \neq 0$. Quasiparticles with $q-k$ are absent. It may be attributed to the repulsion spin-phonon quasiparticle with momentum $q-k$ from spinon with the same energy $E = E_k - E_q$. Whereas the density
of spinon excitations tends to zero for energies $E = E_g + E_k$. The number of spin-phonon quasiparticles is increased against $\alpha$ as illustrated in Fig.2 and the bound states of spin-phonon quasiparticles are formed at $\alpha > \alpha_{c1}$ that are similar to bipolaron with the symbolic kind $< b^+_q \sum_i n_i b^+_p \sum_i \Pi_i^{n_i+n_2} S^z_i >$.

The correlation function of the phonon numbers $< N_{ph}(k)N_{ph}(k + q) >$, presented in Fig.3a, is nonzero at the certain wavenumber $q \sim 0.1$ and $q \sim \pi/3$ for $\alpha \simeq \alpha_{c1}$ and for all $q$ at the condition $\alpha > \alpha_{c2}$. The distribution of phonon numbers becomes continuum at the $\alpha > \alpha_{c2}$ with one sharp maximum at the wave vector of structure being in the range of $\pi < Q < 2\pi$, as plotted in Fig.2b. The value $\alpha_{c2} = 0.4 \pm 0.02$ is similar to a critical concentration when the dressed phonons effectively "percolate" along the three low-lying bands. The correlation function $< N_{ph}(k)N_{ph}(k + q) >$ is not equal to zero for all momentums as shown in Fig.3.

The transition from one state with localized phonons to delocalized is like to Anderson’s transition in disordered systems. The spin density in chain allocates random and nonuniform that follow from the normalized spin-spin correlation function shown in Fig.3b. The estimated values fit by exponential approximation $|< S^z_0 S^z_r > - < S^z_0 S^z_r >_{AF}| \sim A \exp (-r/\xi)$, where $\xi$ is a correlation radius of inhomogeneity. The magnons number distribution function exhibits also the random oscillations (Fig.4c). The transition to delocalized phonons is accompanied by strong increasing of the mean-square amplitude of ions vibration as presented in Fig.5b. At $\alpha = \alpha_{c1}$ the function $< u^2 > (\alpha)$ reveals also a some peculiarity. The average number of phonons, plotted in Fig.5a, increases vs. $\alpha$ according to the power law

$$N_{av} = 0.0012 (\frac{\alpha}{\alpha_{c2}})^{1.75(6)} (7)$$

From the spectral density of phonons shown in Fig.6 and spin excitations it may be stated that the coherent nonlinear bound excitations of phonon and magnon exist at $\alpha > \alpha_{c1}$. It may be interpreted as a standing vibration with the spin kink in sites. The disjoint vibrations are performed at the condition that the wave length is changed in two times $l/a = 2; 4; 8; 16; ...$ $c k = \pi/l$, $E = w_0 \sin(k/2)$. These estimates of energy are in good agreement with Monte Carlo results up to $l/a = 32$ because the temperature fluctuations ($T = 0.04$) cut the kinks interaction radius.

Now we will apply our results to estimate spin-phonon coupling for the one-dimensional spin system $Sr_2CuO_3$ with intracharge $J = 2200K$, $\omega_0 = 2100K$. The abrupt change of the bulk susceptibility at $T \simeq 10K$ is associated with gap in the triplet excitation spectrum. Using typical ratio between gap and critical temperature, for example, for $CuGeO_3$, $\Delta/T_c \simeq 1.8$ we estimate $\alpha = 0.154$ from eq. 0.008 $= -0.17 + 1.16\alpha$. The average phonons number is $N_{ph} = 2.2 \cdot 10^{-4}$. These phonons are formed bound states with energy about $\sim 0.55 \ eV$, $0.76 \ eV$, $1 \ eV$ as followed from the spectral phonon density plotted in Fig.6 because maximum phonon energy with $n_q = 1$, $E = 0.95J \sim 0.18 \ eV$. This energy of elastic fluctuation is compared to the value of the experimental charge transfer gap $E_g = 1.5 \pm 0.3 eV$. Derived from He I ultraviolet photoemission combined with bremsstrahlung isochromat spec-
troscopy [12] and the on-site Coulomb interaction on oxygen site $U_p = 4.4eV$ [13]. The elastic fluctuation lead to change of the electron density on oxygen site and discontinuity of antiferromagnetic exchange that causes formation of the paramagnetic spin $1.3 \cdot 10^{-4}$ observed at low temperature $\sim 4K$.

There are spin-phonon quasiparticles with energy $E_{sp, ph} = 1040cm^{-1}, 562cm^{-1}, 287cm^{-1}, 144cm^{-1}, 72cm^{-1}, 36cm^{-1}, 18cm^{-1}$. The optic phonon mode observed at $\omega_1 = 550cm^{-1}$ corresponds to stretching mode and mode with $\omega_2 = 569cm^{-1}$ is attributed to spin-phonon quasiparticle with $k = \pi/4, \omega^{MC} = 562cm^{-1}$. The relaxation time (or lifetime) of the bond spin-phonon quasiparticle is decreased at heating and at $T \sim E^{MC} \sim 800K$ it is decomposed that qualitatively agrees with experimental data. The phonon width of optical conductivity spectrum is increased from $\gamma = 17.4cm^{-1}, T = 10K$ to $\gamma = 35.1cm^{-1}, T = 300K$ and the strength of the oscillator is decreased from $S = 0.09cm^{-1}, T = 10K$ to $S = 0.06cm^{-1}, T = 300K$. The phonon width and the strength of the oscillator of mode $\omega_1 = 550cm^{-1}$ don’t change in the range $10K < T < 300K$ [4].

The bond defects observed by NMR and heat transport arise from formation of the standing vibration sites. The density of bond defects $\rho \simeq 1/l$ is in direct proportional to wavevector of the standing vibration $k = \pi/l$ and estimated density is satisfactory fit with experimental data at $T = 20K, \rho^{MC} \simeq 5 \cdot 10^{-3}, \rho^{ex} \simeq 2.8 \cdot 10^{-3}$. If discrete spectrum of spin-phonon quasiparticles map to continuum the temperature dependence $\rho$ may be presented as $\rho \simeq 2T/\pi\omega_0$ which well agree with NMR data [4]. It is also explained the linear dependence of the specific heat at low temperatures. Interaction between loosely coupled phonon and spinon modes in the center of Brillouin band may be presented as $(k-\omega/v_{ph})(k-\omega/v_{sp}) = \tilde{\alpha}^2$, where $v_{ph} = \omega_0/2, v_{sp} = \pi/2J, \tilde{\alpha} = \alpha/\sqrt{\omega_0}$. It lead to repulse of these branches and formation of gap in the spinon spectrum with $\Delta(k = 0)/J = \alpha\sqrt{\pi}/2\sqrt{J} \simeq 0.019$. This gap $\Delta(k = 0) = 43K$ causes abrupt decrease of the dynamical spin susceptibility for $k = 0$ at $T \sim 33K$. The $k = 0$ mode of spin transport has a diffusion like contribution for $T << J$ as a result of the fact that the finite density of bound spin-phonon quasiparticles exists at $E = 0$.

At low temperature the spin liquid with non-linear topological excitations having $S = 1/2$ is freezeed that lead to small magnetic moment on site and elastic neutrons scattering. So in compound $CuGeO_3$ having transition singlet-triplet at $T = 14K$ a long range order is observed at low temperatures when ions $Cu$ or $Ge$ are displaced by $Mg$ or $Sr$. Breaking a exchange between the nearest neighbors results in a finite spin density near breaking. Between the generated magnetic moments the interaction is existed per phonon field in 3D dimensional space. The critical field may be estimated by mean field (MF) approximation $T_N = 2Sc(J_0 + 2J_1)$, where $c$— impurities concentration, $S = 1/2, J_0$ and $J_1$ is accordingly intra- and interchain exchange in simple cubic lattice. The calculated critical temperatures for $Cu_{1-x}Mg_xGeO_3$ are in well agreement with experimental data $T_N^{MF} = 2.4K, T_N^{ex} = 2.5K, x = 0.016; T_N^{MF} = 3.2K, T_N^{ex} = 3K, x = 0.0216$ [14]. Using similar evaluation for $Sr_2CuO_3$ with concentration of bond defect at $T \simeq 6K, c \simeq 2 \cdot 10^{-3}$ we determined the critical temperature $T_N^{MF} \simeq 4.5K$ which is in well agreement with experiment $3.5K < T_N^{ex} < 5.4K$. Scatter of temperatures may be due to dependence of freezing bond defects from frequency. The average distance between bond defects is $\sim 2 \cdot 10^{3}A$ and the periodic local alternating magnetization exists which is observed by NMR at low temperatures. Mean square displacement is $< U^2 > \sim 10^{-6}$ that may give rise the structural deformation along chain $\delta a \sim \sqrt{< U^2 >} \sim 10^{-3}A$ for $a = 3.9A, M \simeq 10^{-22}g$. 


In summary, the spectrum of spinon excitations along chain is asymmetric relative wavenumber \( k = \pi / 2 \) with two gaps \( \Delta(k = 0) = 43K \) and \( \Delta(k = \pi) = 18K \) that account for steeply decrease of the bulk susceptibility and the dynamical spin susceptibility for \( k = 0 \) at the temperatures \( T \simeq 10K, T \simeq 33K \). The spectrum of bound spin-phonon excitations is due to bond defects the density of which is linearly increased against temperature. At low temperature \( T \sim 5K \) the non-linear spin-phonon excitations are freezed on the breaking exchange and induce magnetic moment on site with correlation radius of antiferromagnetic ordering 1200 – 2000\( \text{A} \). The magnetic properties of \( \text{Sr}_2\text{CuO}_3 \) are similar to \( \text{CuGeO}_3 \) with impurities having two transitions on temperature. The paramagnetic contribution in the bulk susceptibility at \( T < 4K \) result from a structural defects on oxygen ions due to spin-phonon coupling.

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Captions to Aplesnin paper “Quantum spin liquid in Sr$_2$CuO$_3$ induced by Acoustic Phonons”

Fig. 1 The spectral density of the one-particle excitations with $\omega_0 = 0.95, \alpha = 0.05(1), 0.15(2)$ (a); $\alpha = 0.2(1), 0.4(2)$ (b). In insert, the gap energy $\Delta$ in the excitation spectrum as a function of spin-phonon coupling.

Fig. 2 Distribution of phonon numbers versus momentum for $\alpha = 0.05(1), 0.2(2)$ (a); $\alpha = 0.4(1), 0.6(2)$ (b).

Fig. 3 The normalized correlation function of the phonon numbers versus wavenumber for $\alpha = 0.2(1), 0.4(2), 0.6(3)$ (a) and the spin-spin correlation function as a function of distance for $\alpha = 0.2(1), 0.6(2)$ (b). Solid line is shown the exponential dependence $Aexp(-r/\xi), A = 0.008(8), \xi = 9.1(9)$.

Fig. 4 Distribution of magnon numbers versus momentum for $\alpha = 0.05, 0 \leq k \leq \pi$ (a); $\alpha = 0.2, 0 < k < \pi$ (b); $\alpha = 0.6, 0 < k < \pi$ (c).

Fig. 5 The average phonons number $< N_{ph,av} >$ (a) and the mean-square displacement of ions $< u^2 >$ (b) versus $\alpha/\alpha_c$.

Fig. 6 The normalized spectral density of phonon excitations $\rho_{ph}/\rho_{ph,max}$ versus energy for the spin-phonon coupling $\alpha = 0.25(a); \alpha = 0.4(b); \alpha = 0.7(c)$.
