Frustration induced Raman scattering in CuGeO$_3$

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We present experimental data for the Raman intensity in the spin-Peierls compound CuGeO$_3$ and theoretical calculations from a one-dimensional frustrated spin model. The theory is based on (a) exact diagonalization and (b) a recently developed solitonic mean field theory. We find good agreement between the 1D-theory in the homogeneous phase and evidence for a novel dimerization of the Raman operator in the spin-Peierls state. Finally we present evidence for a coupling between the interchain exchange, the spin-Peierls order parameter and the magnetic excitations along the chains.

42.65.-k,78.20.-e,78.20.Ls

Low-dimensional spin systems exhibit many unusual properties resulting from quantum and dimensionality effects. An example is the continuum of spin-wave excitations in quantum one-dimensional (1D) spin systems which has been predicted for a long time [1] and has recently been confirmed by neutron scattering experiments [2] on KCuF$_3$.

Quantum 1D spin systems also show a variety of instabilities. Of particular interest is the spin-Peierls (SP) phase due to residual magnetoelastic couplings [3], which leads to the opening of a gap in the spin excitation spectrum. The discovery [4] of the spin-Peierls transition below $T_{SP} = 14$ K in an inorganic compound, CuGeO$_3$, has attracted widespread attention. This compound consists of chains of spin-$1/2$ Cu$^{2+}$ ions coupled by antiferromagnetic superexchange via the oxygen orbitals [5]. The Cu ions lie along the crystallographic c-axis and the exchange along the chains can be modeled by the 1D Hamiltonian

$$H = J \sum_i [(1 + \delta(-1)^i)S_i \cdot S_{i+1} + \alpha S_i \cdot S_{i+2}],$$

where $\delta$ is the dimerization parameter that vanishes above $T_{SP}$ [2]. The special geometry [2] of the superexchange path in CuGeO$_3$ leads to a small value of the exchange integral $J \approx 150$K and a substantial n.n.n. frustration term $\sim \alpha$ which competes with the n.n. antiferromagnetic exchange. The interchain couplings have been estimated to be small, $J_a \approx 0.1 J$ and $J_b \approx -0.01 J$ for the interchain exchange constants along a- and b-directions, respectively [2].

The phase diagram of $H$ in Eq. (1) has been calculated using the density-matrix renormalization-group method [2]. For $\delta = 0$ and $\alpha < \alpha_c \approx 0.2411$, the ground state is gapless and renormalizes to the Heisenberg fixed point. For $\alpha = 0.5$ and $\delta = 0$, the ground state is given by a valence-bond state and a gap of order $J/2$ induced by frustration is present. While the evaluation of the dynamical properties of (1) is a challenge to theory, the rich phase diagram can be explored by a variety of interesting experiments. In this context, the substantial value of the n.n.n. exchange integral in CuGeO$_3$ allows the experimental investigation of the effects of competing interactions in a low dimensional magnet, both in the uniform and in the spin-Peierls state.

An experimental method particularly suited for the study of magnetic excitations in an antiferromagnet is two magnon Raman scattering. For CuGeO$_3$, the Raman operator in $A_{1g}$ symmetry [6] is proportional to

$$H_R = \sum_i (1 + \gamma(-1)^i) S_i \cdot S_{i+1}. \quad (2)$$

In the homogeneous state ($\delta = \gamma = 0$) the interaction Hamiltonian commutes with the Heisenberg Hamiltonian for the case $\alpha = 0$ and there would be no Raman scattering. However when $\alpha \neq 0$, the model (1) leads to magnetic Raman scattering due to the presence of competing interactions which can be observed experimentally. Previous fits to experiments [7] based on (1) assumed $\alpha = 0$. Next, we note the presence of the factor $\gamma$ in Eq. (2) which appears because the exchange integral is sensitive to the inter-ionic distance.

Both features mentioned above are taken into consideration in this Letter where we present experimental data as well as the first theoretical results for the Raman intensity in one-dimensional spin systems obtained from (a) exact diagonalization studies of chains with $N_s \leq 28$ sites and (b) a newly developed solitonic mean field theory. Our results for $T > T_{SP}$ are obtained with $\delta = 0$ in Eq. (1), where the mean field theory provides an analytical framework to obtain expressions for the Raman intensity at finite temperatures. Below $T_{SP}$, we present first experimental evidence for a qualitative change in the Raman operator at the SP transition through the appearance of the factor $\gamma$ in Eq. (2). Here, we do not attempt to calculate $\gamma$ microscopically, but by comparing with experiment. We find that $\gamma \approx 0.12$ and this value of $\gamma$ affects the shape of the Raman spectrum in
the SP phase dramatically. Indeed, we find that the experimental results for $T < T_{SP}$ cannot be explained by Eq. (1) assuming $\gamma \to 0$. A detailed comparison of experiment and theory, both below and above the SP transition, is presented.

We first give a brief account of the theoretical and experimental methods before discussing the experimental data. The Raman intensity at zero temperature is given by

$$I_R(\omega) = -\frac{2}{\pi} Im \langle 0|H_R\frac{1}{\omega + i\epsilon - (H - E_0)}H_R|0\rangle,$$  \hspace{1cm} (3)

where $E_0$ is the ground-state energy, $H$ the Hamiltonian given by Eq. (1), and $\epsilon \to 0_+$. For a numerical evaluation of Eq. (3), we scale the Hamiltonian $H = cX + d$ such that the eigenvalues of the rescaled Hamiltonian $X$ are in the interval $[-1, 1]$. We define a rescaled energy and frequency by $E_0 = c\pi_0 + d$ and $\omega = c\pi + d$ and expand $I_R(x)$ in terms of Tschebyscheff polynomials, $T_i(x)$: $I_R(x) = (1 - x^2)^{-1/2}\sum_{i=0}^{N_p} a_i T_i(x + \delta_0)$, with $a_i = (2 - \delta_0)/\pi(0)|H_R T_i(X)H_R|0\rangle$ and $N_p \to \infty$. The quantities $a_i$ are evaluated recursively. This procedure, the kernel polynomial approximation, is an established and numerically stable method for the evaluation of the density of states [13]. For large values of $N_p$, the resulting spectral weight consists of a series of very sharp peaks that become delta-functions in the limit $N_p \to \infty$. Generally we find $N_p = 100$ convenient for comparison with experiment.

We also calculate the Raman intensity above $T_{SP}$ using a solitonic mean field theory. This method, originally suggested for the n.n. Heisenberg chain [13], is based on a transformation of the Heisenberg Hamiltonian to a Hamiltonian describing the dynamics of antiferromagnetic domain walls (solitons or spinon excitations) and a subsequent Jordan-Wigner transformation. The method reproduces the exact solutions at both the Ising and XY-limits. For the Heisenberg model it leads to correct asymptotic behavior of dynamical correlation functions. The solitonic mean field theory leads to a ground state described by the Hamiltonian $H_S = \sum_k E_k c_k^\dagger c_k$, where the $c_k$’s are quasiparticle (spinon) operators that are linear combinations of the soliton operators. The mean field dispersion relation $E_k = (1 + \frac{2}{\gamma})J/|\cos ka|$ compares very well with the des Cloizeaux-Pearson spectrum $\frac{2}{\gamma}J/|\cos ka|$ obtained from Bethe ansatz [13]. We generalize this method to the case of the n.n.n. chain.

The absence of Raman scattering in the n.n.n. chain is understood as $H_S$ conserving the number of spinons. This picture changes when $\alpha \neq 0$. We find that the inclusion of the n.n.n. term generates the following processes: (i) two-spinon scattering terms that lead to a renormalization of the spinon velocity and (ii) four-spinon creation terms that generate two-magnon Raman scattering in the n.n.n. chain. A perturbative treatment of the four-spinon terms allows us to obtain expressions for the Raman intensity $I_R(\omega)$ in the homogeneous phase at all temperatures.

The experiments were performed using the excitation line $\lambda = 514.5$-nm of an Ar-laser with a laser power of 2.7mW. We ensured that the incident radiation does not increase the temperature of the sample by more than 1.5 K. We used a DILOR-XY spectrometer and a nitrogen cooled CCD (back illuminated) as a detector in a quasi backscattering geometry with the polarization of incident and scattered light parallel to the c-axis and the Cu-O chains, respectively. Details of the experiment will be published elsewhere [14].

In Fig. 1, we present the data for the two-magnon Raman continuum in the homogeneous state at $T = 20$ K. Phonon lines [4] at 184 cm$^{-1}$ and at 330 cm$^{-1}$ are subtracted from the experimental data (squares). The shoulder observed at $\sim 390$cm$^{-1}$ is presently not understood. We interpret the two-magnon continuum as scattering intensity caused by the creation of four spinon excitations. The Raman intensity from such a scattering process calculated from our solitonic mean field theory is shown in Fig. 1 (dashed-dotted line), where we use $J = 150$ K $\sim$ 104 cm$^{-1}$ and $\alpha = 0.24$ [4]. The maximum theoretical value of the Raman intensity is normalized to the experimental value from which a Rayleigh tail and a uniform background of 50 counts are subtracted. The maximum of the experimental data is situated at slightly larger energies, which could be a consequence of a slight misfit of the parameters used. For instance, we find that $J = 160$ K and $\alpha = 0.2$ (dotted line) improves the agreement between theory and experiment. The data presented in Fig. 1 provide substantial evidence that a 1D Hamiltonian of type (1) can indeed account for the observed Raman continuum owing to the presence of the n.n.n. frustration term. This continuum should also be seen in neutron scattering experiments above $T_{SP}$.

In Fig. 2 we present the numerical results for the dimerized state, $\delta = 0.03$ [3], and a finite-size analysis (in the inset). The numerical result for $\gamma = 0$ (upper curve, dashed line) is surprisingly flat and can be approximated (upper curve, solid line) by the expression

$$I_R(\gamma = 0, \omega) = A\theta(\omega - 2\Delta)(1 - \tanh(2(\omega - \omega_0))),$$  \hspace{1cm} (4)

with the values of the parameters $2\Delta \approx 30$cm$^{-1}$, $\omega_0 \approx 312$cm$^{-1}$ being determined by a fit to the numerical data (A is a normalization constant). Below $T_{SP}$, a gap opens up and the DOS has a singularity at the lower edge [14,7]. Therefore, one expects a peak arising from this singularity. However, this singularity is removed by matrix element effects arising from the Raman operator [5].

The $\gamma$-dependence of the Raman intensity is strong, as can be seen in Fig. 2, where we plot the data for $\gamma = 0.12$ (lower curves) In order to understand this large matrix-element effect we have examined in detail (for $N_p = 1000$)
the relative weight \( \rho(\gamma, E_i) \) of the individual poles (at energies \( E_i \)) contributing to the Raman intensity for systems of size \( N_s = 20, 24 \) and 28. We have found that the basis of the observed matrix-element effect lies in the remarkable fact that for each pole there is a certain \( \gamma_0(E_i) \) at which the intensity of the pole actually vanishes, i.e.

\[
\rho(\gamma, E_i) = \frac{I_{\gamma=0}}{I_{\gamma}} \left( \frac{\gamma - \gamma_0(E_i)}{\gamma_0(E_i)} \right)^2, \tag{5}
\]

where \( I_{\gamma} \) is a normalization constant defined by \( \int_0^\infty d\omega \rho(\gamma, \omega) = 1 \) (we choose \( \omega_c = 6J \)). From the numerical data we found that \( \gamma_0(E_i) \) can be approximated by \( \gamma_0(E_i) \approx \delta + \kappa E_i \), where \( \kappa \approx 4/3000 \text{cm}^{-1} \).

Combining (4) and (5), we obtain an analytic approximation for the Raman intensity in the dimerized state,

\[
I_R(\gamma, \omega) \approx \rho(\gamma, \omega)I_R(0, \omega) \tag{6}
\]

This formula reproduces the numerical results well (see Fig. 3).

In Fig. 3, we present data for the spin-Peierls phase at \( T = 5 \text{K} \). Let us first discuss the line at 30 cm\(^{-1} \). We find that the analytic curve for \( \gamma = 0.12 \) reproduces this peak well (solid line in Fig. 3). Note that here \( \gamma \) is the only free parameter in the theory. Choosing \( \gamma = 0 \) instead would result in a complete disagreement with experiment (compare Fig. 3). The line at 30 cm\(^{-1} \) is known to be of 1D magnetic origin (the value 30 cm\(^{-1} \) is indeed twice the one-magnon gap obtained from neutron scattering [5]). This suggests that this peak arises from the spin-Peierls Hamiltonian [1] in combination with matrix-element effects of the Raman operator [12]. Therefore we conclude that Fig. 3 provides strong evidence for the dimerization of \( H_R \) below \( T_{SP} \) leading to substantial matrix-element effects.

Let us now consider the two lines at 226 cm\(^{-1} \) and at 104 cm\(^{-1} \) observed below \( T_{SP} \) (see Fig. 3). The assignment of the 104 cm\(^{-1} \) line is still controversial and will not be discussed here. The 226 cm\(^{-1} \) line has been assigned previously to be of magnetic origin [13]. A classical (non-interacting) spin-wave calculation, using the measured magnon dispersion in c-direction [12], produces a peak at 226 cm\(^{-1} \). However, it is well known that in ideal one-dimensional systems, magnons do not behave classically but form a continuum of excitations [12]. Consequently one would not expect a sharp peak, like the one observed at 226 cm\(^{-1} \) to occur in a one-dimensional system. This expectation is borne out by our numerical data (solid line in Fig. 3), which does not show the 226 cm\(^{-1} \) peak. It is clear that to explain the presence of this peak, one has to go beyond a one-dimensional spin model.

The magnitude of the interchain coupling \( J_b \) in CuGeO\(_3\) is comparable to the spin-Peierls temperature (14 K). One might therefore expect the chains to become correlated for temperatures around \( T_{SP} \approx J_b \), resulting in the appearance of a well defined magnon branch, which leads to the observed peak at 226 cm\(^{-1} \). In Fig. 3, we present the temperature dependence of the intensity of the 226 cm\(^{-1} \) line (for comparison we include in Fig. 3, two other Peierls-active Raman lines). One clearly sees that this line becomes active only below \( T_{SP} \). Thus we conclude that the interchain coupling becomes relevant only below \( T_{SP} \). This conclusion is in agreement with recently presented neutron scattering data [19], which shows a pronounced change in the spectrum below \( T_{SP} \).

In conclusion, we find good agreement between the experimental magnetic Raman spectrum in the homogeneous phase and the one-dimensional frustrated spin model for CuGeO\(_3\). The importance of the competing interactions for the occurrence of magnetic Raman intensity in the homogeneous phase has been pointed out and is consistent with the absence of inelastic Raman scattering in 1D spin compounds without frustration such as KCuF\(_3\) [20]. For the spin-Peierls state we find that observation of a sharp line at the spin-triplet excitation energy of 30 cm\(^{-1} \) indicates a dimerization of the Raman operator. Finally, the observed Peierls-active line at 226 cm\(^{-1} \) indicates the appearance of a well defined magnon branch below \( T_{SP} \).

acknowledgments

This work was supported through the Deutsche Forschungsgemeinschaft, the Graduiertenkolleg “Festkörper-spektroskopie”, SFB 341 and SFB 252, and by the BMBF 13N6586/8.

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FIG. 1. Experimental (squares) and theoretical results (lines) for the Raman intensity in the homogeneous phase of CuGeO$_3$ at $T = 20$ K. Shown are the results from the solitonic mean field theory at $T = 20$ K ($\delta = 0 = \gamma$) and for two sets of parameters (a) $J = 104$ cm$^{-1}$, $\alpha = 0.24$ [6] (dashed-dotted line), and (b) $J = 119$ cm$^{-1}$, $\alpha = 0.2$ (dotted line).

FIG. 2. The numerical results for $N_s = 28$ (dashed lines), $\delta = 0.03$, $\alpha = 0.24$, $N_p = 100$ and $\gamma = 0$ (upper curve) and $\gamma = 0.12$ (lower curve). The numerical results are compared with the analytic formula (2) (solid lines). Inset: A comparison of numerical results for $N_s = 28$ (dashed line) and $N_s = 24$ (dotted line) and $\gamma = 0$.

FIG. 3. Experimental data (squares) and the analytic approximation (Eq. 6, solid line) for the Raman intensity of CuGeO$_3$ in the spin-Peierls phase at $T = 5$ K. The phonon lines have been subtracted from the experimental data.

FIG. 4. Temperature dependence of the relative intensities of three Peierls-active Raman lines. The 30 cm$^{-1}$ line (squares), the 226 cm$^{-1}$ line (triangles) and the 369 cm$^{-1}$ line (circles, a folded phonon line) The intensities are normalized to their respective values at $T = 6$ K. The intensities at $T = 200$ K are subtracted for reference.
Raman shift in cm$^{-1}$

Raman intensity

T = 20 K
Normalized Raman intensity vs. Temperature (K)

- □ □ □ 30 cm\(^{-1}\)
- △ △ △ 226 cm\(^{-1}\)
- ■ ■ ■ 369 cm\(^{-1}\)