Dopant-Bound Spinons in Cu$_{1-x}$Zn$_x$GeO$_3$

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Dedicated to Prof. J. Zittartz, on the occasion of his 60th birthday

Abstract. – Polarized inelastic light scattering experiments on Cu$_{1-x}$Zn$_x$GeO$_3$ (0 ≤ x ≤ 0.045) single crystals show for $x \neq 0$ a new distinct mode at nearly half the energy of the singlet response below the spin-Peierls transition. The temperature, magnetic field, polarization, and doping dependencies of this mode are similar to those of the singlet bound state. The data are interpreted in terms of a spinon-assisted light scattering process. Position and form of the peak provide strong evidence for the presence of dopant-bound spinons in Cu$_{1-x}$Zn$_x$GeO$_3$.

The discovery of the spin-Peierls (SP) transition in CuGeO$_3$ [1] led to a tremendous progress in our knowledge of one-dimensional antiferromagnetic Heisenberg spin-1/2 systems coupled to lattice degrees of freedom [2]. The substitution of Si for Ge [3] and Zn for Cu [4] made it possible to study changes of the superexchange mechanism and of the chain lengths, respectively, and their effects on the SP transition temperature $T_{SP}$ and on the singlet-triplet gap $\Delta_{trip}$. Susceptibility [3] [4] and specific heat [5] experiments showed a decrease of $T_{SP}$ upon increasing doping. Above a certain doping level the SP phase is replaced by an antiferromagnetically ordered phase below a Néel temperature $T_N$. For intermediate dopings, e.g. 2% Zn-doping, a coexistence of SP and Néel phase is observed. Recent investigations indicated a coexistence of both phases for a broad interval of dopings [6] [7] [8].

Inelastic light scattering (ILS) is a sensitive technique to study magnetic excitations in pure [9] [10] [11] [12] [13] [14] and doped CuGeO$_3$ [15] [16] [17]. It is the aim of the present Letter to show the existence of a so far unobserved type of magnetic scattering process in
doped gapful low-dimensional spin systems which arises due to the presence of dopant-bound spinons (DBS). This novel scattering process was observed in temperature, magnetic field, and doping-dependent polarized ILS experiments in the SP phase of Cu$_{1-x}$Zn$_x$GeO$_3$ for $x \neq 0$.

The ILS experiments were performed, using a Sandercock-type tandem Fabry-Perot interferometer, as described in [14]. The temperatures $T_{SP}$ and $T_N$ were checked by dc susceptibility measurements using a commercial SQUID magnetometer.

Fig. 1 presents ILS spectra of Cu$_{1-x}$Zn$_x$GeO$_3$ measured at $T=2.2$ K for various Zn concentrations. For pure CuGeO$_3$ one observes the well known singlet bound state (SBS), with the two-magnon continuum starting on its high frequency side. For higher temperatures a thermally activated excitation has been observed as a shoulder at roughly 18 cm$^{-1}$ on the low frequency side of the SBS [14]. The substitution of Zn for Cu dramatically changes the observed ILS spectra. With increasing substitution the SBS shifts to lower energies (see Fig. 1, filled circles in lower inset), in agreement with the decreasing $T_{SP}$. Simultaneously the SBS rapidly loses its intensity (see Fig. 1, filled circles in upper inset), broadens and its shape becomes more and more symmetric. Additionally, a new well-defined excitation can be observed for all doped samples ($x \neq 0$) at nearly half the frequency of the SBS [18]. Both excitations show the same asymmetric line shape for low doping concentrations. On increasing doping the integrated peak intensity rises up to $x = 1\%$; then it decreases up to $x = 3.3\%$ (see Fig. 1, open squares in upper inset). For the $x = 4.5\%$ sample no qualitative difference is observed compared to the $x = 3.3\%$ sample. Similar to the SBS the new mode broadens, becomes more symmetric, and shifts to lower energies upon increasing the doping (see Fig. 1, open squares in lower inset). The new excitation is also fully (ZZ) polarized with Z$\parallel$c-axis and shows no magnetic field dependence. Anticipating our interpretation we will attribute the new mode to a dopant-bound spinon (DBS).

Fig. 2 shows the temperature dependence for the $x = 0.66\%$ sample. At 2.2 K the SBS at 30 cm$^{-1}$ and the mode at 15 cm$^{-1}$ can be discerned. Both peaks show a clear asymmetric line shape. On increasing the temperature up to $T_{SP}$ both peaks display a similar behaviour. First, the integrated intensity decreases starting from a maximum value at roughly 3 K (Fig. 2, upper inset). This is accompanied by a broadening of the peaks and by a symmetrisation of their shapes. Furthermore, the peak positions shift to lower frequencies (Fig. 2, lower inset), with a similar behaviour as in the undoped sample [14] but with reduced $T_{SP}$.

Before turning to the discussion of the DBS, we first discuss several other possible origins of the new mode. The temperature dependence of the intensity of the new mode (Fig. 2, upper inset) is quite different from the one we observed for the thermally activated three-magnon process in undoped CuGeO$_3$ [14]. Hence we exclude a scattering process starting from an excited state. We also exclude that the new mode is simply due to a dopant-induced phonon scattering for two reasons. First, the scattering intensity should be more or less proportional to the doping concentration which is obviously not the case. Second, a dopant-induced phonon scattering process does not conserve momentum. Hence it should yield a rather broad feature, contrary to the observed one.

The similarities between the new mode and the SBS (same peak shapes, similar $T$ dependence of the peak positions and intensities (Fig. 2, insets), qualitatively similar doping dependence of the peak positions (Fig. 1, lower inset) suggest that the new mode is also of magnetic origin and linked to a bound state. The energy of the new excitation almost equals the triplet gap energy $\Delta_{trip} = 2.1$ meV ($\approx 16.8$ cm$^{-1}$) [14]. Thus one might think of a one-magnon process. The experiments, however, show that the DBS mode is fully (ZZ) polarized and shows neither a splitting nor a shift in magnetic fields. The interpretation for the DBS peak given previously [14, 17] is not consistent with these observations. On these grounds, we exclude a simple one-magnon scattering process based on spin-orbit coupling [2].
The discussion of the origin of the DBS will be done in the framework of a simple model presented now. Let us view the ground state of the spin chains without doping as Resonating Valence Bond (RVB) state with singlets of various lengths. The dimerization which is imposed on a single chain by its adjacent chains strongly favors nearest-neighbour singlets on the strong bonds. Locally the ground state is close to a product of such singlets as in the limit of strong dimerization \[21\]. The introduction of a non-magnetic dopant like Zn breaks one of the singlets since one singlet partner is lacking. In this way, a magnetically free strong dimerization \[21\]. The introduction of a non-magnetic dopant like Zn breaks one of the bonds. Locally the ground state is close to a product of such singlets as in the limit of strong dimerization \[21\].

Doping of Si does not alter the scenario decisively. Replacing Ge by Si affects two adjacent chains; it is believed to cut them \[24\]. Since the dimerization pattern alternates from chain to chain \[25, 26\] each cut breaks one weak and one strong bond. The breaking of the strong bonds introduces two \(S = 1/2\) spinons because two chain ends with weak bonds at the ends are generated like Zn-doping introduces one chain end with a weak bond. This is in perfect agreement with the results of Sekine et al. who observe DBS peaks in Zn- as in Si-doped CuGeO\(_3\) samples.

Focusing on low doping concentration, we treat the spinons introduced by the dopants as independent from one another. They are, however, bound to their generating dopants \[27\]. Let us assume that the singlet pairs are at sites \((2i - 1, 2i)\) for integer \(i\) and that a dopant is present at site 1 so that the spinon is at site 2. The spinon might move without changing the number of singlets but changing their position. If the spinon moves to site \(2j\) there are singlets at the bonds \((2i', 2i' + 1)\) for \(0 < i' < j\). For a single chain this configuration can be considered equivalent to the one with a spinon at site 2. For the three-dimensional ensemble of elastically coupled chains, however, the motion of the spinon costs energy which increases with the distance \(l\) between spinon and dopant. If there is a sufficiently large next-nearest neighbour coupling \(J_2\), namely \(\alpha := J_2/J_1 > \alpha_c \approx 0.241 \[28, 29\], this increase is linear in \(l\) \[30\]. Otherwise, it is sublinear \[31\]. Since there is strong evidence in CuGeO\(_3\) that the frustration is above \(\alpha_c \[22, 33\) we adopt the linear potential \[2\]. For \(\alpha > \alpha_c\) the spinons also have a finite mass and their kinetic energy displays a quadratic minimum in \(k\)-space.

The triplet excitation ("magnon") of a dimerized, sufficiently frustrated chain can be viewed as a bound pair of two spinons coupled to \(S = 1\) \[30\]. In the limit of small dimerization, this bound state is described by the continuum Schrödinger equation

\[
\Delta_{\text{trip}} \Psi(x) = -\frac{1}{2\mu} \left( \frac{\partial}{\partial x} \right)^2 \Psi(x) + A\delta x \Psi(x),
\]

with \(x \geq 0\) being the relative coordinate and \(A\) some constant. If we describe the single spinon bound to its generating dopant in the same way we write

\[
E_i \Psi(x) = -\frac{1}{2m} \left( \frac{\partial}{\partial x} \right)^2 \Psi(x) + A\delta x \Psi(x),
\]

where \(x \geq 0\) is the distance to the dopant. The only difference to \(1\) is the mass factor. For the relative motion in \(1\) we have \(\mu^{-1} = 2m^{-1}\) if \(m\) denotes the single spinon mass. By substituting \(x \rightarrow x/2^{1/3}\) in \[3\] we obtain \(E_0 = 2^{-1/3}\Delta_{\text{trip}}\) for the ground state contribution of the dopant-bound spinon. All the bound states of a linear potential are proportional to the negative zeros \(-a_i\) of the Airy function \[34\]. So we have for the first excited level \(E_1 = |a_2|/|a_1|2^{-1/3}\Delta_{\text{trip}}\), see also Fig. 3. The first excitation energy is \(\Delta_{\text{spinon}}/E_0 = (|a_2| - |a_1|)/|a_1|\), whence \(\Delta_{\text{spinon}}/\Delta_{\text{trip}} = 2^{-1/3}(|a_2| - |a_1|)/|a_1| \approx 0.6\). The corresponding excitation process is visualized by the solid arrow in Fig. 3. Calculations of \(\Delta_{\text{spinon}}/\Delta_{\text{trip}}\) in more elaborate models will be presented elsewhere \[31\].
Higher levels $E_{i>2}$ are not stable since they can decay into the levels $E_0$ or $E_1$ by producing a new pair of spinons coupled to a magnon as described by eq. (3). Such a magnon is not confined to a region in space since it does not disturb the dimerization pattern other than locally. Thus the ladder of dopant-bound spinons in Fig. 3 is discontinued after two levels by the magnon continuum. The dashed arrow indicates the possibility to create unconfined magnons. The corresponding continuum yields the asymmetric tail at higher energy of the lines experimentally observed.

The question is now whether a dopant-bound spinon in the ground state $E_0$ can be excited to a state $E_1$ by a photon in a light scattering experiment. Such a scattering can be described by the spin conserving Raman operator which has the following structure $R = \sum_i (1 - (-1)^i) S_i S_{i+1} + \gamma S_i S_{i+2}$, where the alternation $\delta$ is the same as in the Hamiltonian, whereas the frustration $\gamma$ generally differs from the one in the Hamiltonian [35]. The action of $R$ on the ground state is twofold. Besides the spinon the usual two-magnon process takes place [29, 34]. For the action of $R$ on the spinon let us assume that the spinon is at site $i$ in the RVB picture. Then the relevant part of $R$ (neglecting the small alternation $\delta$) is $R_1 + R_2$ with $R_1 = S_i (S_{i-1} + \gamma S_{i-2})$ and $R_2 = S_i (S_{i+1} + \gamma S_{i+2})$. Applying $R_t$ to the spinon at $i$ and the adjacent singlet at $(i+1,i+2)$ yields (see also Ref. [4])

$$R_t|\uparrow,s\rangle = (1 - \gamma) \left[ (1/4)|\uparrow,t_0\rangle - 1/(2\sqrt{2})|\downarrow,t_1\rangle \right], \tag{3}$$

where the arrows indicate the $S_z$ component of the spinon and $s$, $t_0$ or $t_\pm 1$ stand for a singlet, triplet with $S_z = 0$ or $S_z = \pm 1$ for the two spins at sites $i + 1$ and $i + 2$. Eq. (3) suggests that the Raman operator applied to the spinon creates solely an additional magnon (dashed arrow Fig. 3). Yet the state on the right hand side in (3) is not orthogonal to pure spinon states. It has 75% overlap with the state $|s,\uparrow\rangle$ where the spins at sites $i$ and $i + 1$ form a singlet and the spinon is at site $i + 2$. Thus the main effect of $R_t$ is to shift the spinon by one singlet spin pair to the right. In analogy $R_1$ shifts by one singlet spin pair to the left. Thus the Raman operator is indeed able to excite the ground state $E_0$ of the dopant-bound spinon corresponding to the solid arrow in Fig. 3. The remaining 25% effect of the action of $R$, which cannot be viewed as action within the single spinon subspace, are attributed to processes like spinon-assisted triplet creation (dashed arrow in Fig. 3). But note that the total spin of spinon and triplet remains always unchanged. This is in agreement with the absence of a magnetic field dependence.

From the above we conclude that the relatively sharp DBS mode visible in Figs. 1 and 2 is due to a spinon bound to the dopant. Its energy is below the triplet gap $\Delta_{\text{trip}}$ and its Raman line shape is asymmetric, since there is also a one-magnon continuum on its high frequency side belonging to it. It is possible to corroborate this picture also by a calculation in the strong dimerization limit yielding analogous results [31].

Albeit our theoretical picture explains qualitatively very well the experimental findings it is not yet quantitative. The experimentally observed sharp DBS mode is not at the theoretical value of $0.6\Delta_{\text{trip}}$, but just below $\Delta_{\text{trip}}$, and the DBS resonance and the one-magnon continuum are not separated. The same problem appears for the ratio of the singlet and the triplet gap for undoped CuGeO$_3$ [35] which is theoretically too low ($\approx 1.5$) compared to the experimental value $\approx 1.85$ (cf. the SBS at zero doping in Fig. 1 to $\Delta_{\text{trip}} \approx 2.1\text{meV}$ [4]). Binding energies depend decisively on the dimensionality. Generically a higher dimensionality lowers the density of states (DOS) at low energies. Passing from 1D to 2D to 3D, the DOS at the lower band edges passes from an inverse square root divergence to a steplike jump to a square root singularity. Thus the available phase space for the bound state is reduced and consequently also the binding energy which is the difference of the resonance peak position from the continuum onset. Hence it is plausible to attribute the too low experimental binding energies to the higher dimensional
character of the spin system in \( \text{CuGeO}_3 \) [37].

For higher dopings the dopant-bound spinons start to interact by exchanging \( S = 1 \) magnons. We expect that the appearance of antiferromagnetic order, while the dimerization persists (see, e.g., the shoulder close to the laser line for \( x = 3.3\% \) in Fig. 1), can be understood as an ordering of these \( S = 1/2 \) states due to their interaction [6, 27]. But this question is far from being settled.

In summary, we performed temperature, magnetic field, polarization, and doping dependent inelastic light scattering experiments in \( \text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3 \) with \( 0 \leq x \leq 4.5\% \). Besides the singlet-bound state, we observed a novel spinon-assisted excitation for all dopings \( (x \neq 0) \) below \( T_{SP} \). We interpret this new mode as evidence for dopant-bound spinons which we found theoretically in an effective spinon description.

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Fig. 1. – (ZZ) polarized ILS spectra of Cu$_{1-x}$Zn$_x$GeO$_3$ at $T = 2.2$ K for $0 \leq x \leq 3.3\%$ showing the singlet bound state (SBS) and the dopant-bound spinon (DBS). The curves are given an offset for clarity. The $x = 0\%$ spectrum is reduced by 1/6. The SBS mode at $x = 0.2\%$ is reduced by 1/5. The inset shows the concentration dependence of the integrated intensity (upper inset) and of the peak position (lower inset) of the SBS (filled circles) and the DBS (open squares).

Fig. 2. – (ZZ) polarized ILS spectra for $x = 0.66\%$ showing the temperature dependence of the singlet bound state (SBS) and the dopant-bound spinon (DBS). The curves are given an offset for clarity. The inset shows the temperature dependence of the integrated intensity (upper inset) and of the peak position (lower inset) of the SBS (filled circles) and of the DBS (open squares). Solid lines in the insets are guides to the eye.

Fig. 3. – Eigenenergies of the spinon confined to the dopant by a linear potential. The solid arrow corresponds to the sharp resonance at an energy below the triplet gap $\Delta_{\text{trip}}$; the dashed arrow corresponds to the high energy tail of the asymmetric dopant-bound spinon (DBS) peak.
Cu$_{1-x}$Zn$_x$GeO$_3$

$T=2.2K$

Int. vs Energy Shift

Zn-Concentration vs Energy Shift

Inset: DBS and SBS data for various Zn concentrations.
$\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$

$x = 0.66\%$

Intensity (a.u.) vs. Energy Shift (cm$^{-1}$) vs. Temperature (K)
\[ E \]

magnon continuum

\[ E_c \]
\[ E_1 \]
\[ E_0 \]

\[ \Delta_{\text{spinon}} \]
\[ \Delta_{\text{trip}} \]

distance from dopant