High-Field Electron Spin Resonance and Magnetization in the Dimerized Phase of $CuGeO_3$

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ESR and magnetization measurements have been performed up to 14 T in the compound $CuGeO_3$. Two kinds of magnetic transitions are observed, between excited states and from the ground state. The former result essentially from a Zeeman splitting of the $S = 1$ magnetic triplet state characterizing the spin Peierls gap which exists at the wave vector $\mathbf{Q} = [1, 1, 1]$ of the magnetic Brillouin zone. The latter provide the first evidence of a Zeeman splitting on a spin Peierls gap. It is observed at $\mathbf{Q} = [0, 0, 0]$.

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The recent observation of a spin Peierls (SP) transition in the inorganic compound $CuGeO_3$ [1] has renewed the interest in the study of $s = \frac{1}{2}$ Heisenberg antiferromagnetic chains ($\frac{1}{2}$HAFC). In such isotropic spin systems, the diverging of the magnetic fluctuations as $T \to 0$ is expected to yield a dimerization of the lattice—this is the SP transition—at a well-defined temperature T_{SP} [2]. However, such an effect is rarely observed due to the occurrence of three-dimensional ordering which, typically, stabilizes the spin chain before T_{SP} is reached. When the dimerized phase is realized, i.e., below T_{SP}, the spin system is characterized by a $S = 0$ nonmagnetic singlet ground state (GS) and a $S = 1$ magnetic excited triplet state separated from the GS by an energy gap (the "SP gap" E_{SP}) [2]. At this point it is worthwhile making the comparison with Haldane spin chains (HSC), since the same predictions are usually given for that spin system [3]. However, in a HSC, which is the integer-spin analog of the $\frac{1}{2}$HAFC, the energy gap does not result from a dimerization but from the occurrence of nonlinear quantum fluctuations in the GS. Although the physics of $\frac{1}{2}$HAFC and of HSC are completely different, the recent experimental investigations of HSC may serve as a guide and as a point of comparison. For instance, in HSC the effect of a magnetic field has been shown to split the excited $S = 1$ triplet state at the "quantum" gap, which is known to open at the wave-vector value $q = 1$ of the one-dimensional reciprocal lattice. [In this Letter, the wave vectors refer to the magnetic Brillouin zone and are expressed in reciprocal lattice unit (rlu).] This Zeeman effect gives rise to three distinct energy branches characterized by different magnetic states [4]. As shown by high-field ESR measurements, magnetic $\Delta m = 1$ transitions can be induced directly between these split states around $q = 1$ [5]. The purpose of the present Letter is to report on a similar high-field ESR investigation—including magnetization measurements—of the dimerized phase of $CuGeO_3$. Such a high-field study will be shown to provide new insights on the dimerized phase and a better understanding of the low-field ESR experiments performed previously on "spin Peierls" compounds [6,7].

The cyrstallographic structure of $CuGeO_3$ belongs to the orthorhombic system defined by orthogonal axes $\mathbf{a}, \mathbf{b}, \mathbf{c}$ [8]. The magnetic chains are formed by the Cu^{2+} ions disposed along $\mathbf{c}$. Our experimental investigation was carried out on a single crystal of volume $5 \times 5 \times 2$ mm^3. It was cleaved along (100) planes from a larger cylindrical crystal, grown from the melt by a floating zone technique associated with an image furnace [9]. Susceptibility measurements in low field have revealed a well-defined SP transition in that crystal at $T_{SP} = 14$ K. The observed ESR lines to be discussed are obtained from the absorption of the unpolarized light, delivered by an optically pumped far-infrared (FIR) waveguide laser in the range 160–1627 GHz [5]. The recorded signals are the derivative of the light absorption. Measurements have also been made at lower frequencies (down to 55 GHz) by using microwave solid-state diode sources. The magnetization was measured using the extraction method. In both kinds of measurements, the external magnetic field H was applied along $\mathbf{a}$, i.e., perpendicular to the chain direction. It could be varied from 0 up to 14 T. Two distinct classes of ESR transitions have to be considered: the "low-frequency" (LF) lines observed below 500 GHz, and the "high-frequency" (HF) lines above 1000 GHz.

A few examples of LF lines recorded at $\omega = 294$ GHz are shown in Fig. 1(a). The thin solid curves result from a numerical integration of the recorded ESR lines. Hence, they represent the actual light absorption spectra. At the lowest temperatures ($T \approx 4$ K) the LF resonance signal may be regarded as made of one single line. At $T = 9.8$ K, due to the two apparent peaks, it can be considered as essentially composed of two lines. Above $T \approx 12$ K, the complexity of the experimental ESR spectrum increases drastically (see the example for $T = 14.9$ K), and

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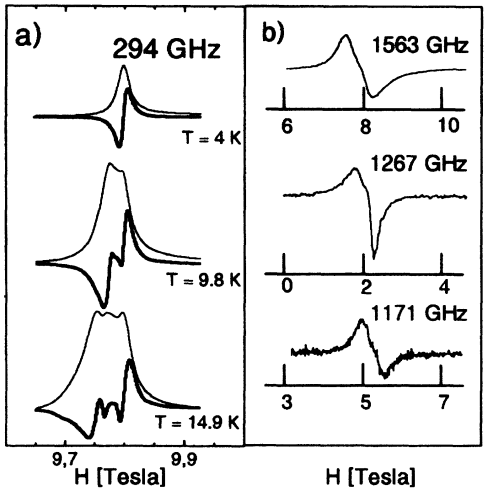

FIG. 1. (a) Low-frequency (LF) ESR signals (thick lines) in $CuGeO_3$ at different temperatures for $\omega = 294$ GHz. Thin lines are numerically integrated signals, showing the "experimental" absorption curves. (b) Examples of high-frequency (HF) ESR signals at $T = 4$ K.

such an analysis in terms of single lines cannot be developed further. However, since T_{SP} decreases with H—for $H \approx 10$ T, T_{SP} is only $T_{SP} \approx 12$ K—the ESR data of the dimerized phase are only those obtained for $T < T_{SP}$, and the two-line model sketched above can be used for the analysis. Assuming each line to have a Lorentzian shape [the dash-dotted lines (1) and (2) in Fig. 2(a)], one is able to reproduce the absorption spectra quite well: compare in Fig. 2(a) the dotted line which is the sum of (1) and (2), and the solid line describing the experimental

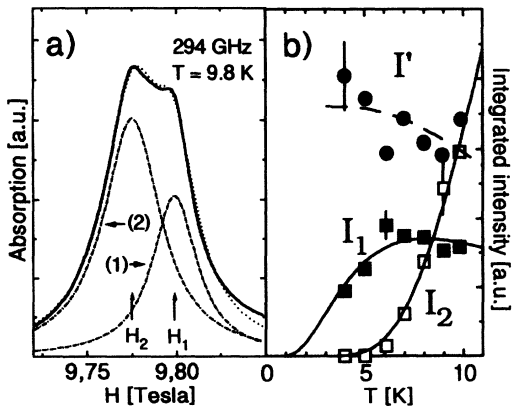

FIG. 2. (a) Detailed analysis of a LF absorption curve (solid line). Two dot-dashed Lorentzians (1) and (2), centered at H_1 and H_2, are least-squares fitted to the solid line to obtain the dotted curve. (b) Temperature dependence of integrated intensities I_1 (■), I_2 (□), and I' (●). I_1 and I_2 correspond to the two Lorentzians defined in (a). The solid lines are theoretical curves (see text). I' corresponds to HF transitions from the ground state at $\omega = 1267$ GHz. The dashed line is a guide to the eye.

light absorption. Further, a numerical fitting procedure allows us to determine for any temperature below T_{SP} both the resonance fields $H_{1,2}$, which correspond to the maximum of each Lorentzian, and their "integrated" intensities $I_{1,2}$. While the results for I_1 and I_2 as a function of temperature are shown in Fig. 2(b), the resonance frequency ω_1, which is temperature independent, is observed to agree very well with the Zeeman law $\omega_1 = g\mu_B H_1$ with $g = 2.136 \pm 0.002$ (μ_B is the Bohr magneton). This value of g compares well with previous determinations and we conclude that the LF resonance spectra observed here in high field correspond to the low-field ESR lines reported in the literature [6]. In high field, the ESR line is seen to be essentially composed of two lines. The temperature dependencies of I_1 and I_2, shown in Fig. 2(b), are typical of magnetic transitions induced between excited states (and not from the GS) [5]. Considering I_1 first, we assume that these states are those of a split $S = 1$ triplet associated with an energy gap E_{g1}. The corresponding energy diagram with $g = 2.136$ is represented as a function of field in Fig. 3(a) (the solid lines). The supposed $\Delta m = 1$ transitions are illustrated by the solid double-headed arrows. In that model, the integrated intensity I_1 is governed by the populations of the connected states.

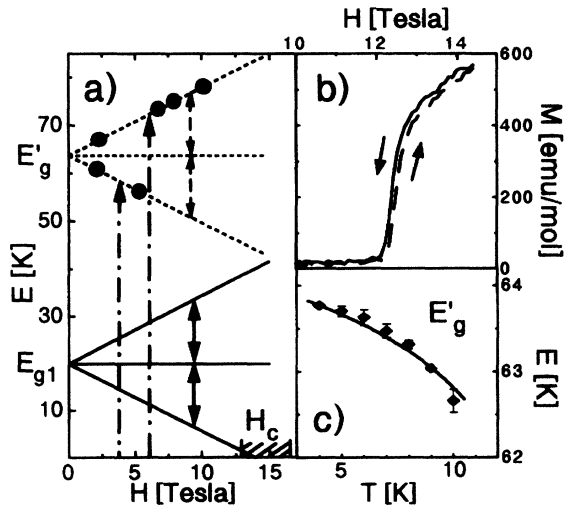

FIG. 3. (a) Energy level diagram as a function of field for ESR transitions in $CuGeO_3$. The Zeeman splitting of two triplet states with SP gaps E_{g1} and E'_g is shown as solid and dashed lines, respectively. These states are located at different points in the Brillouin zone (see text). LF transitions take place between excited states as shown by the solid and dashed double-headed arrows. The hatched area denotes the region for the critical field H_c, where the lowest gap closes. The single-headed dot-dashed arrows illustrate the HF transitions from the ground state. Observed HF resonances are shown as dots (●). (b) Magnetization as a function of field at $T = 1.53$ K, showing a jumplike behavior around H_c and a small hysteresis effect. (c) Temperature dependence of the SP gap E'_g. The solid line is a fit according to $64.13(1 - T/T_{SP})^{\beta}$, with $T_{SP} = 14$ K and $\beta = 0.016$.

Taking into account the above Zeeman effect, these populations depend, apart from a proportionality constant, on only one parameter, namely the energy gap in zero field E_{g1}. In Fig. 2(b) the solid line is the corresponding prediction for Boltzmann statistics fitted to the data. It leads to the value $E_{g1} = 22 \pm 5$ K. The good agreement of this value with previous evaluations of the "SP gap" in $CuGeO_3$ [1,6,10] supports our description proposed for the ESR lines of intensity I_1: they result from $\Delta m = 1$ transitions between the split states of the $S = 1$ triplet SP gap, i.e., $E_{g1} \equiv E_{SP}$. As seen in Fig. 3(a), this model predicts the gap of the lowest energy branch to close at a well-defined value of the field, H_c. We evaluate $H_c \approx 13-17$ T for $\mathbf{H}//\mathbf{a}$. According to Fig. 3(b) where the magnetization measurements are presented, these values actually correspond to the field range where the spin system regains a magnetic behavior. One may therefore ask the important question whether the closing of this gap plays a role in the critical transition observed in that field range [11]. Such an effect was observed in HSC, and in that case it is established that H_c is the critical field above which the spin system becomes magnetic [12]. In Fig. 3(b), it is also worth noting the hysteresis effect, which is a well-known property of an SP transition at low temperature [2]. For I_2 a similar analysis in terms of transitions between excited states associated with an energy gap E_{g2} can be performed. Because of the limited accuracy of the data in Fig. 2(b), only a rough evaluation of it can be given: $E_{g2} = 55 \pm 10$ K. However, this analysis allows us to predict the existence of a second energy gap in the dimerized phase of $CuGeO_3$. It is located at a higher energy than E_{g1}.

In an ideal dimerized chain, one expects, for reasons of symmetry, the SP gap to occur at two wave vectors: $q = 0$ and $q = 1$ in the magnetic Brillouin zone. This would not be the case in HSC, where the gap of the elementary excitation can only be seen at $q = 1$ [13]. At this point an important remark is in order. If a gap does exist at $q = 0$, it should be possible to also induce $\Delta m = 1$ transitions from the GS (which is a $S = 0$ state) to the gap excitation (which is a $S = 1$ state). In the energy range of the gap E_{g1} ($\pm$ the Zeeman splitting) no such transitions have been seen in our experiments. However, transitions from the GS have been observed at much higher energies. Examples of such HF lines are shown in Fig. 1(b). The main reason to argue that such lines are induced from the GS (and not between excited states) is given by the temperature dependence of their integrated intensity I'. An example of I' as a function of temperature for a HF line is reported in Fig. 2(b). As $T \to 0$, the intensity I' does not decrease, unlike the same quantities for the LF lines. The field dependence of the observed resonances at $T = 4$ K, shown as the full dots in Fig. 3(a), is also remarkable. The HF lines belong to two excitation branches, which are well interpreted as resulting from a Zeeman splitting of a $S = 1$ gap excitation [the straight dashed lines in Fig. 3(a) correspond to a gyromagnetic ratio $g' = 2.102 \pm 0.002$]. The gap value extrapolated to $H \to 0$ can be accurately determined: $E'_g = 63.77 \pm 0.05$ K at $T = 4$ K. We may notice the reasonable agreement of this value with our previous evaluation of E_{g2}, and, as a first approach, we shall identify in the following E'_g with E_{g2}: $E'_g \cong E_{g2}$. The temperature dependence of the gap E'_g can also be determined experimentally. As shown in Fig. 3(c), E'_g is observed to decrease rapidly as $T \to T_{SP}$.

The low-field ESR lines of the dimerized phase in $\frac{1}{2}$HAFC are usually analyzed by referring to susceptibility measurements [6,7]. The present high-field study allows us to refer directly to the elementary excitations of the spin system. In the case of $CuGeO_3$, where the interchain magnetic couplings are not negligible, the excitation spectrum has to be considered within the three-dimensional reciprocal lattice. In such a description any wave vector is represented as $\mathbf{Q} = [h,k,l]$, where h, k, and l are the components (expressed in rlu) along the reciprocal axes $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$. Neutron inelastic scattering (NIS) measurements preformed in $CuGeO_3$ have established that the SP gap E_{SP} opens at $\mathbf{Q} = [1,1,1]$ [10]. As shown above, we can identify E_{g1} with E_{SP} ($E_{g1} \equiv E_{SP}$). As a consequence, we may infer that the splitting represented in the lower half of Fig. 3(a) by the solid lines describes the effect of a field at that specific wave vector. Therefore, we have to conclude that the LF line of intensity I_1 results from magnetic transitions induced at the same wave vector of the Brillouin zone. Since ESR is restricted to a momentum transfer of $\Delta q = 0$, transitions from the GS at $\mathbf{Q} = [0,0,0]$ to the lowest lying triplet at $\mathbf{Q} = [1,1,1]$ cannot be excited directly. The LF transitions are represented by the solid double-headed arrows in Fig. 3(a). In $CuGeO_3$, the interchain couplings give rise to an appreciable dispersion of the excitation spectrum, in particular along $\mathbf{b}^*$. As a result, another gap ($E'_{SP} \approx 65$ K) has been observed by NIS at $\mathbf{Q} = [0,0,1]$ [10]. The value of E'_{SP} agrees very well with our determination of E'_g, i.e., $E'_g \equiv E'_{SP}$. Therefore, the splitting represented in the upper half of Fig. 3(a) by the dashed lines describes the effect of a field at that other point of the reciprocal space. The dashed double-headed arrows are the $\Delta m = 1$ transitions, which could explain the observed LF lines of intensity I_2. As also shown by NIS, the energy dispersion along $\mathbf{a}^*$ is very small. In that direction $(h,1,1)$ the excitation branch is flat [10] and no additional gap needs to be considered. Since the HF lines result from transitions induced from the GS, they are known to be associated with the uniform wave vector $\mathbf{Q} = [0,0,0]$. This point (or any equivalent point) of the reciprocal space has not been explored by NIS. However, since the magnetic coupling between the dimerized pairs develops preferentially along $\mathbf{c}$, we can predict, for reasons of symmetry, that the gaps at $\mathbf{Q} = [0,0,0]$ and at $\mathbf{Q} = [0,0,1]$ should be the same. Since E'_g agrees so well

with E'_{SP}, this prediction is consequently well supported by the present ESR investigation. The splitting shown in the upper half of Fig. 3(a) also describes the effect of a magnetic field on the gap E'_g, located at $\mathbf{Q} = [0,0,0]$. In the same figure, the dot-dashed arrows represent the actual magnetic transitions induced from the GS, which explain the HF lines.

In summary, two kinds of ESR lines have been observed. On the one hand, there are the LF lines, which correspond to transitions between excited states. For the lines of intensity I_1, these transitions develop around $\mathbf{Q} = [1,1,1]$ and, more generally, around any wave vectors $\mathbf{Q} = [h,1,1]$. They are associated with the gap E_{SP} ($\equiv E_{g1}$). For the lines of intensity I_2, the transitions are probably associated with the gap E'_{SP} ($\cong E_{g2}$). For this reason, they can be predicted to occur near $\mathbf{Q} = [0,0,1]$ and, more generally, near any wave vectors $\mathbf{Q} = [h,0,1]$. For symmetry reasons, they can also be induced between the excited states of the split gap E'_g, seen at $\mathbf{Q} = [0,0,0]$. On the other hand, there are the HF lines, which correspond to transitions from the GS, i.e., at $\mathbf{Q} = [0,0,0]$. They are associated with the second gap E'_{SP} ($\equiv E'_g$), which is also a consequence of the dimerization effect. It differs from E_{SP} only because of the interchain coupling. For this reason, E'_{SP} can be considered as an SP gap. The temperature dependence of E'_g, shown in Fig. 3(c), follows the renormalization behavior of an SP gap, as $T \rightarrow T_{SP}$ with a critical exponent $\beta = 0.016 \pm 0.002$. This value is smaller than $\beta = 0.093$, determined by NIS in Ref. [10] for the smaller gap at $\mathbf{Q} = [0,1,1]$. Finally, the HF lines are seen to provide direct evidence for the splitting of an SP gap in a dimerized phase. They prove that an SP gap is indeed associated with a $S = 1$ magnetic triplet state.

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