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Field-induced structural evolution in the spin-Peierls compound $CuGeO_3$: High-field ESR study

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The dimerized-incommensurate phase transition in the spin-Peierls compound $CuGeO_3$ is probed using the tunable-frequency high-resolution electron spin resonance technique in magnetic fields up to 17 T. A field-induced development of the solitonlike incommensurate superstructure is clearly indicated as a pronounced increase of the magnon spin resonance linewidth ΔB, with a ΔB_{max} at $B_c \sim 13.8$ T. The anomaly is explained in terms of the magnon-soliton scattering and suggests that the solitonlike phase exists close to the boundary of the dimerized-incommensurate phase transition. In addition, magnetic excitation spectra in 0.8% Si-doped $CuGeO_3$ are studied. Suppression of the ΔB anomaly observed in the doped samples suggests a collapse of the long-range-ordered soliton states upon doping, which is consistent with high-field neutron experiments.

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The discovery of a spin-Peierls transition in the inorganic compound $CuGeO_3$ (Ref. 1) has stimulated significant interest in experimental and theoretical studies of low-dimensional materials. A lattice dimerization, which is one of the most characteristic features in the spin-Peierls transition, was found to take place below $T_{SP} \sim 14$ K. In the dimerized phase the ground state is a spin singlet, separated from the first excited triplet by an energy gap. Application of an external magnetic field tends to suppress quantum fluctuations and eventually collapses the energy gap. By increasing the magnetic field above the threshold field $B_{DI} \sim 12.5$ T, $CuGeO_3$ undergoes a transition from the dimerized spin liquid commensurate to the incommensurate phase, where the periodicity of the spin polarization and lattice deformation is incommensurate with crystallographic lattice parameters. The low-field incommensurate region can be described by the formation of a regular array of domain walls (solitons). If the concentration of solitons is high enough, interactions between them result in a long-range-ordered soliton lattice, observed experimentally.[2] A further increase in field induces a plane-wave-modulated (harmonic) incommensurate state,[3,4] where the modulation phase is a harmonic function of the space coordinate in the direction of the modulation.

The rich magnetic phase diagram of $CuGeO_3$ has been a subject of many intensive high-field investigations. The high-frequency high-field electron spin resonance (ESR) technique was employed for studying magnetic excitation spectra in $CuGeO_3$.[5–9] These investigations provide valuable information on the size of the energy gaps in $CuGeO_3$ in the dimerized phase, on the g factors, and on the exchange coupling. Like nuclear magnetic resonance methods, high-resolution ESR is a very powerful tool to study local spin environments in solids. It was successfully used for investigating structural incommensurability in various materials.[10] Since the dimerized-incommensurate phase transition in $CuGeO_3$ has a magnetic origin, probing magnetic excitations in a broad range of magnetic fields (and frequencies) can provide important information on the field-induced structural evolution of $CuGeO_3$. The main motivation of this investigation was to study the peculiarities of the dimerized-incommensurate phase transition in $CuGeO_3$, using variable-frequency high-field high-resolution ESR.

In this work, we present a systematic study of the ESR linewidth (spin-triplet excitations) obtained in pure and 0.8% Si-doped $CuGeO_3$ single crystals, in the quasicontinuously covered frequency range of 175–510 GHz and magnetic fields up to 17 T. To the best of our knowledge, this is the first high-resolution ESR investigation of the commensurate-incommensurate phase transition in $CuGeO_3$, which is not driven by temperature, but by the magnetic field.

Experiments were performed using the high-field millimeter- and submillimeter-wave spectroscopy facility at the National High Magnetic Fields Laboratory, Tallahassee, FL. A key feature of the facility is a set of easily tunable millimeter- and submillimeter-wave radiation sources, backward wave oscillators (BWO's), operating in the frequency range of 140–700 GHz ($\sim$4.6–23.3 cm^{-1}). BWO's are classic vacuum-tube microwave devices, which (unlike other sources of millimeter- and submillimeter-wave radiation) possess an important distinguishing characteristic: they are tunable over a very wide frequency range—up to 30% from their central frequency. Due to this important property, high-field tunable-frequency BWO ESR spectroscopy gives a remarkable opportunity to probe magnetic excitations in a broad, quasicontinuously covered range of frequencies and magnetic fields[11,12] (unlike conventional ESR methods, which employ one constant frequency or a set of frequencies). The BWO's, in combination with a highly homogeneous (12 ppm/cm DSV) magnetic field provided by a 25-T hysteresis-free resistive magnet, make the facility a very powerful tool for systematic high-resolution ESR investigations of field-induced phenomena in $CuGeO_3$ and other magnetic materials.

The spectrometer works in transmission mode and employs oversized cylindrical waveguides. An extremely lownoise, wide-frequency-range, InSb hot electron bolometer, operated at liquid-He temperature, serves as a detector. The spectrometer allows for experiments to be carried out over a range of temperatures from 1.5 to 300 K. The spectra are recorded while sweeping the magnetic field. Two kinds of signal modulation are possible. While modulation of the magnetic field gives a better signal-to-noise ratio for narrower lines, modulation of the radiation power using a chopper (optical modulation) allows direct detection of the absorption and transmission and provides better sensitivity for broader resonance lines. The spectrometer operates in Faraday or Voigt geometry (propagation vector of the radiation parallel or perpendicular to the external magnetic field, respectively).

In order to detect the real shape of the absorption with a minimum of experimental error, optical modulation of the radiation power was used in our experiments. Pure and 0.8% Si-doped $CuGeO_3$ single crystals with a typical thickness of 0.2 mm were used. The experiment was performed in Faraday geometry with the magnetic field applied in the direction of the *a* axis. In this work we focused on studying the dimerized-incommensurate phase transition, and thus only results obtained in fields up to 17 T are presented. ESR investigation of the magnetic excitations in $CuGeO_3$ at higher fields (in the plane-wave-modulated phase) is beyond the current consideration and will be reported elsewhere.[13]

Before going ahead with experimental data, let us briefly characterize low-energy spin excitations in $CuGeO_3$. Above T_{SP}, $CuGeO_3$ is in the commensurate phase and can be regarded as an $S=1/2$ uniform Heisenberg antiferromagnet, with a gapless spin-singlet ground state. Triplet excitations in this phase can be described as massless domain wall-like $S=1/2$ fermion-type excitations, spinons. Below T_{SP}, $CuGeO_3$ is in the dimerized phase; the ESR spectrum is basically formed by transitions between the excited Zeeman-split triplet states; these massive boson-type excitations can be defined as magnons and the corresponding resonance as a magnon spin resonance.[14] With dimerization the spinons are confined into magnon excitations; as a result, the two-spinon continuum in the dimerized phase is significantly modified. Transitions from the ground states are normally forbidden in low-dimensional gapped spin systems. However, breaking translational symmetry (due to the Dzyaloshinskii-Moriya interactions or staggered field effects, for instance) can allow ground-state excitations. These transitions occur at the center of the Brillouin zone; the observation of these transitions using ESR provides direct and accurate information on energy gaps in $CuGeO_3$.[5,7] In the solitonlike incommensurate phase there are two types of competing excitations. Magnetic excitations within the spin-dimerized domains can be ascribed to the magnon subsystem (magnons), while soliton-type excitations originate from transitions within the soliton subsystems. The soliton subsystem appears to strongly contribute to the bulk magnetization and the excitation spectrum of the $CuGeO_3$ in the solitonlike phase.[15] Magnetic bound states, which are a general feature of many low-dimensional spin systems (see, for instance, Refs. 16 and 17), manifest themselves in $CuGeO_3$ in the far-infrared region[18] and can be an interesting subject for high-frequency and high-field ESR studies.

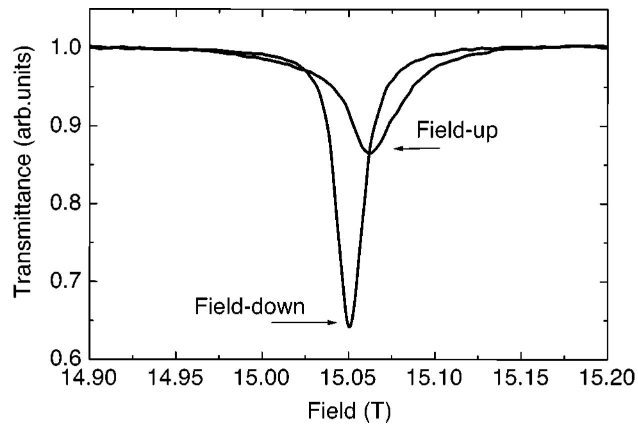

FIG. 1. The ESR spectrum in $CuGeO_3$ taken at a frequency of 431.8 GHz in ascending and descending fields ($T=4.2$ K). The spectrum clearly indicates a magnetic field hysteresis.

The first ESR investigation of the high-field, incommensurate phase in $CuGeO_3$ was performed by Palme *et al.*,[19] who observed magnetic field hysteresis effects in the incommensurate phase. Drastic changes were noted in both the ESR linewidth and field, depending on the magnetic field sweep direction. Generally speaking, a hysteresis phenomenon is a quite common feature of incommensurate structures,[10] which can be explained in terms of pinning of the microscopical incommensurate superstructure on the discreteness of the crystal lattice and/or defects. If the incommensurability originates from an interplay of spin and lattice degrees of freedom (i.e., a magnetic structure is incommensurate with the crystallographic structure), the discreteness of the magnetic lattice and/or magnetic defects can strongly affect incommensurate superstructure.[20]

A typical ESR spectrum at the frequency of 431.8 GHz ($T=4.2$ K) is shown in Fig. 1. We confirm a hysteresis behavior of the absorption in $CuGeO_3$ in the incommensurate phase ($B>B_{DI}$). One can see that the ESR line is much narrower in the descending fields. Qualitatively, such a behavior can be explained as follows. The solitonlike phase consists of nearly commensurate regions separated by domain walls (solitons) where the phase of the order parameter changes rapidly. Because of that, a local field on Cu^{2+} sites in $CuGeO_3$ is microscopically modulated, which removes the equivalence of the ESR-active sites and causes spreading of the ESR absorption into a quasicontinuous distribution of local resonance lines. The magnetic field tends to polarize spins, making effective fields on the Cu^{2+} sites more homogenous. This results in the ESR line narrowing, as seen in descending fields.

In Fig. 2 we show frequency and linewidth versus magnetic field diagrams of the ESR in $CuGeO_3$ in ascending magnetic fields up to 17 T and in a frequency range of 175–510 GHz. The Lorentzian fit of absorptions was used to calculate the ESR linwidth at half-height. The g factor of excitations remains almost constant in the entire frequency-field range $g\sim 2.15$, which is consistent with pulsed-field ESR data.[6] However, a drastic change in the ESR linewidth ΔB is observed at the transition from the dimerized to incommen-

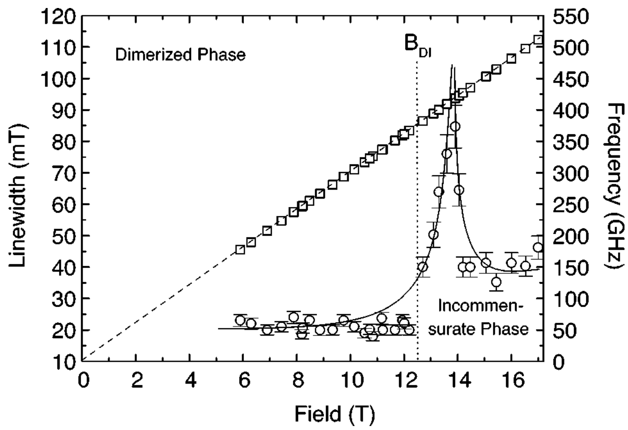

FIG. 2. The frequency-field (squares) and linewidth-field (circles) dependences of the ESR excitations in $CuGeO_3$ at $T = 4.2$ K. The data are shown for ascending fields. The dashed line is a frequency-field dependence of magnetic excitations with $g = 2.15$. The solid lines are guides for eyes. The dotted line denotes the dimerized-incommensurate phase transition boundary.

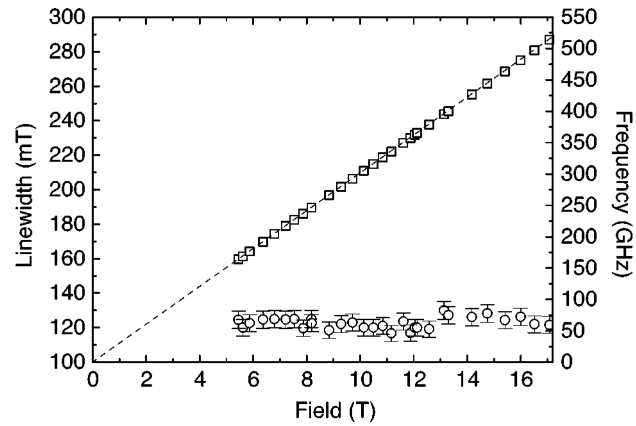

FIG. 3. The frequency-field (squares) and linewidth-field (circles) dependencies of the ESR excitations in 0.8% Si-doped $CuGeO_3$ at $T = 4.2$ K. The dashed line is a frequency-field dependence of magnetic excitations with $g = 2.15$.

surate phase. A maximum in the linewidth is found at $B_c \sim 13.8$ T.

In order to explore the nature of the ESR linewidth anomaly and the possible role of the soliton subsystem in it, ESR on $CuGeO_3$ +0.8% Si (where a long-range-ordered incommensurate state appears to be completely suppressed by doping) was performed.

It was shown that doping can significantly affect the low-temperature magnetic properties of $CuGeO_3$, creating defects and enhancing three-dimensional antiferromagnetic correlations in the dimerized phase.[21] It was found also that even a very small doping had a drastic effect on the shape of the lattice modulation.[22] The effect is especially strong in the case of Si doping, when Si^{4+} substitutes Ge^{4+}. It distorts the lattice and the configuration of oxygens around the copper sites and may result in reversing the coupling from antiferromagnetic to ferromagnetic.[23] If the doping exceeds some critical concentration, a long-range order in the soliton lattice can be completely suppressed.[2] High-field neutron scattering experiments[24] revealed only a short-range ordering of solitons in 0.7% Si-doped samples (while a long-range-ordered soliton structure still persists in 0.3% Si-doped crystals), which suggests a threshold concentration of about 0.5%–0.6%.

The doped $CuGeO_3$ samples were initially characterized by measuring magnetic susceptibility at temperatures down to 1.8 K, using a superconducting quantum interference device (SQUID) magnetometer. The susceptibility of doped crystals exhibits a minimum at $T \sim 7.7$ K (evidence of the coexisting dimer liquid state and enhanced three-dimensional short-range-ordered antiferromagnetic correlations) and a pronounced peak, corresponding to an antiferromagnetic ordering with $T_N \sim 3.7$ K. The data are consistent with results obtained by Grenier *et al.*[25] on 0.8% Si-doped $CuGeO_3$.

In Fig. 3 we show frequency and linewidth versus field diagrams of the magnetic excitations in the 0.8% Si-doped $CuGeO_3$ samples. Similar to pure $CuGeO_3$, no drastic changes are found in the *g*-factor behavior. Instead, two distinguishing features in the ESR spectra are found. First, no hysteresis effects are observed in fields up to 17 T, which appears to be evidence of the collapsing long-range-ordered solitonlike lattice. Second, the ΔB anomaly found in pure $CuGeO_3$ at $B_c \sim 13.8$ T is completely suppressed in doped $CuGeO_3$.

Our observations clearly indicate the essential role of the long-range-ordered soliton correlations in the ESR linewidth anomaly in $CuGeO_3$. Like any structural imperfection in spin systems with a collective type of elementary excitations (note, for instance, that the ESR linewidth in the dimerized phase in pure $CuGeO_3$ is about 6 times smaller than that in the doped samples, Figs. 2 and 3), the soliton lattice in $CuGeO_3$ introduces additional scattering for magnons. As a result, an intensive magnon-soliton scattering manifests itself in the ESR line broadening. A maximum of the linewidth is observed at $B_c \sim 13.8$ T, which clearly indicates a pronounced development of the incommensurate solitonlike superstructure (and a corresponding enhancement of the scattering processes) close to the boundary of the dimerized-incommensurate phase transition, B_{DI}. This observation is consistent with high-field magnetostriction and thermal expansion experiments.[3]

In conclusion, the field-induced structural evolution in the spin-Peierls compound $CuGeO_3$ is probed using tunable-frequency high-resolution ESR in fields up to 17 T. Our studies reveal several important peculiarities of its high-field properties. The ESR linewidth anomaly strongly suggests the essential role of magnon-soliton scattering processes in the solitonlike phase and confirms that the solitonlike regime exists close to the boundary of the dimerized-incommensurate phase transition. Our data are consistent with high-field inelastic neutron scattering experiments, suggesting that doping significantly affects the solitonlike structure in $CuGeO_3$, suppressing long-range-ordered soliton correlations and corresponding magnon-soliton scattering. The use of the high-field tunable-frequency ESR approach (applied for an analysis of the ESR linewidth in a broad frequency-field range) can provide important information on field-induced structural evolutions in other spin-Peierls materials.[26]

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