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 frequency-tunable high-resolution electron spin resonance (ESR) technique, in magnetic fields up to 17 T. A field-induced development of the soliton-like incommensurate superstructure is clearly indicated as a pronounced increase of the magnon spin resonance linewidth $\Delta B$, with a $\Delta B_{\text{max}}$ at $B_c \sim 13.8$ T. The anomaly is explained in terms of the magnon-soliton scattering, and suggests that the soliton-like 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 $\Delta B$ anomaly observed in the doped samples suggests a collapse of the long-range-ordered soliton states upon doping, that is consistent with high-field neutron experiments.

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The discovery of a spin-Peierls transition in an inorganic compound CuGeO$_3$ 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 $T_{\text{SP}} \sim 14$ K. In the dimerized phase the ground state is a spin singlet, separated from the first excited triplet by an energy gap. Application of external magnetic field tends to suppress quantum fluctuations, and eventually collapses the energy gap. By increasing the magnetic field above the threshold field, $B_{\text{TH}} \sim 12.5$ 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 a 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. A further increase in field induces a plane-wave modulated (harmonic) incommensurate state, where the modulation phase is a linear 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/field electron spin resonance (ESR) technique was employed for studying magnetic excitation spectra in CuGeO$_3$. 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. 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 field-induced structural evolution of CuGeO$_3$. The main motivation of this investigation was to study peculiarities of the dimerized-incommensurate phase transition in CuGeO$_3$, using multifrequency 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 quasi-continuously 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 Field Laboratory, Tallahassee, FL. A key feature of the facility is a set of easily-tunable millimeter and sub-millimeter wave radiation sources, Backward Wave Oscillators (BWOs), operating in the frequency range of 140-700 GHz ($\sim 4.6 - 23.3$ cm$^{-1}$). BWOs 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 BWO ESR spectroscopy provides a remarkable possi-
bility to probe magnetic excitations in a broad, quasi-continuously-covered range of frequencies and magnetic fields\textsuperscript{11,12} (unlike conventional ESR methods, which employ one constant frequency, or a set of frequencies). The BWOs, in combination with 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\textsubscript{3} and other magnetic materials.

The spectrometer works in transmission mode and employs oversized cylindrical waveguides. An extremely low-noise, 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 a direct detection of the absorption/transmission and provides better sensitivity for broader resonance lines. The spectrometer operates in the 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\textsubscript{3} single crystals with a typical thickness of 0.2 mm were used. The experiment was performed in the Faraday geometry with 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\textsubscript{3} at higher fields (in the plane-wave modulated phase) is beyond the current consideration and will be reported elsewhere\textsuperscript{13}.

Before going ahead with experimental data, let us briefly characterize low-energy spin excitations in CuGeO\textsubscript{3}. Above $T_{SP}$, CuGeO\textsubscript{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\textsubscript{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\textsuperscript{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\textsubscript{3}\textsuperscript{35,7}. In the soliton-like 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\textsubscript{3} in the soliton-like phase\textsuperscript{36}. Magnetic bound states, which are a general feature of many low-dimensional spin systems (see for instance\textsuperscript{16,17}), manifest themselves in CuGeO\textsubscript{3} in the far-infrared region\textsuperscript{18}, and can be an interesting subject for high-frequency/field ESR studies.

The first ESR investigation of the high-field, incommensurate phase in CuGeO\textsubscript{3} was performed by Palme et al.\textsuperscript{19}, who observed magnetic field hysteresis effects in the incommensurate phase. Drastic changes were noted on 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\textsuperscript{10}, which can be explained in terms of pinning of the microscopic 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\textsuperscript{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 soliton-like 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 line is microscopically modulated, that removes the equivalence of the ESR active sites and causes spreading of the ESR absorption into a quasi-continuous distribution of local resonance lines. 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 a frequency and a linewidth vs 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 linewidth 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. However, a drastic change in the ESR linewidth $\Delta B$ is observed at the transition from the dimerized to incommensurate 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 low-temperature magnetic properties of CuGeO$_3$, creating defects and enhancing three-dimensional antiferromagnetic correlations in the dimerized phase. It was found also that even a very small doping had a drastic effect on the shape of the lattice modulation. 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 coupling from antiferromagnetic to ferromagnetic. If the doping exceeds some critical concentration a long-range order in the soliton lattice can be completely suppressed. High-field neutron scattering experiments 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), that 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 SQUID magnetometer. The susceptibility of doped crystals exhibits a minimum at $T \sim 7.7$ K (an evidence of the coexisting dimer liquid state and enhanced three-dimensional short-range-order 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. on 0.8%Si-doped CuGeO$_3$.

In Fig. 3 we show a frequency and a linewidth vs field diagrams of the magnetic excitations in the 0.8%Si-doped CuGeO$_3$ samples. Similar to the 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 an evidence of the collapsing...
long-range ordered soliton-like lattice. Second, the $\Delta B$ anomaly found in the 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-order 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 six times smaller than that in the doped samples, Fig. 2 and Fig. 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 anisotropy found in the pure CuGeO$_3$ is observed at $B_c \sim 13.8$ T, that clearly indicates a pronounced development of the incommensurate soliton-like 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.

In conclusion, the field-induced structural evolution in the spin-Peierls compound CuGeO$_3$ is probed using frequency-tunable 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 soliton-like phase, and confirms that the soliton-like 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-order soliton correlations and corresponding magnon-soliton scattering. The use of the high-field frequency-tunable 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.

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1. M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. 70, 3051 (1993).
2. V. Kiryukhin, B. Keimer, J.P. Hill, and A. Vigliante, Phys. Rev. Lett. 76, 4608 (1996).
3. T. Lorenz, B. Bächner, P.H.M. van Loosdrecht, F. Schönfeld, G. Chouteau, A. Revcolevschi, and G. Dhalenne, Phys. Rev. Lett. 81, 148 (1998).
4. M. Horvatić, Y. Fagot-Revurat, C. Berthier, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. 83, 420 (1999).
5. T. M. Brill, J. P. Boucher, J. Voiron, G. Dhalenne, A. Revcolevschi, and J. P. Renard, Phys. Rev. Lett. 73, 1545 (1994).
6. H. Nojiri, Y. Shimamoto, N. Miura, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B 57, 10276 (1998).
7. H. Nojiri, H. Ohta, S. Okubo, O. Fujita, J. Akimitsu, and M. Motokawa, J. Phys. Soc. Japan 68, 3417 (1999).
8. Y. Yamamoto, H. Ohta, M. Motokawa, O. Fujita, and J. Akimitsu, J. Phys. Soc. Japan 66, 1115 (1997).
9. W. Palme, S. Schmidt, B. Lüthi, J.P. Boucher, M. Weiden, R. Hauptmann, C. Geibel, A. Revcolevschi, G. Dhalenne, Physica B 246, 32 (1998).
10. R. Blic, P. Prelović, V. Rutar, J. Seliger, and S. Žumer, in Incommensurate Phases in Dielectrics, Edited by R. Blic and A.P. Levanyuk (North-Holland Physics Publishing, Amsterdam, 1986).
11. V.M. Naumenko, V.V. Eremenko, A.V. Klochko, Instruments and Experimental Techniques 24, 933 (1981).
12. V.V. Eremenko, S.A. Zvyagin, V.V. Pishko, Yu.G. Pashkevich, V.V. Shahov, Soviet J. Low Temp. Physics 18, 175 (1992).
13. S.A. Zvyagin, et. al., unpublished.
14. J.-P. Boucher, L.-P. Regnault, and L.E. Lorenzo, RIKEN Review 24, 5 (1999).
15. M. Enderle, H.M. Ronnow, D.F. McMorrow, L.-P. Regnault, G. Dhalenne, A. Revcolevschi, P. Vorderwisch, H. Schneider, P. Smeibidl, and M. Meißner, Phys. Rev. Lett. 87, 177203 (2001).
16. M. Date and M. Motokawa, Phys. Rev. Lett. 16, 1111 (1966).
17. M. Orendáč, S. Zvyagin, A. Orendáčová, M. Sieling, B. Lüthi, A. Feher, and M.W. Meisel, Phys. Rev. B 60, 4170 (1999).
18. G. Els, P.H.M. van Loosdrecht, P. Lemmens, H. von Berg, G. Güntherodt, G.S. Uhrig, O. Fujita, J. Akimitsu, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. 79, 5138 (1997).
19. W. Palme, G. Ambert, J. P. Boucher, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. 76, 4817 (1996).
20. V. Kiryukhin, B. Keimer, J.P. Hill, S.M. Coad, and D. McPaul, Phys. Rev. B 54, 7269 (1996).
21. L.P. Regnault, J.P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. 32, 579 (1995).
22. R.J. Christianson, Y.J. Wang, S.C. LaMarra, R.J. Birgeneau, V. Kiryukhin, T. Masuda, I. Tsukada, K. Uchinokura, and B. Keimer, Phys. Rev. B 66, 174105 (2002).
23. W. Geertema and D. Khomskii, Phys. Rev. B 54, 3011 (1996).
24. B. Grenier, L.P. Regnault, J.E. Lorenzo, J. Voiron, J. Bossy, J.P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. 44, 511 (1998).
25. B. Grenier, J.-P. Renard, P. Veillet, C. Paulsen, R. Calemczuk, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B 57, 3444 (1998).
26. J.W. Bray, et. al., in Extended Linear Chain Compounds, edited by J.S. Miller (Plenum, New York, 1983).