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Magnetic phase diagram of the spin-Peierls cuprate $CuGeO_3$

Masashi Hase, Ichiro Terasaki,* and Kunimitsu Uchinokura
Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Masashi Tokunaga and Noboru Miura
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Haruhiko Obara
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba-shi, Ibaraki 305, Japan

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The magnetization of the spin-Peierls cuprate $CuGeO_3$ was measured in magnetic fields up to 25 T at constant temperatures from 3.5 to 20.3 K. The transition temperature without the field is 14.0 K. The characteristic nonlinearity of the magnetization was observed below 13.4 K, which means the transition was from a dimerized phase to other phases. This transition is of first and second order below and above 10.0 K, respectively. The critical field of the transition between dimerized and magnetic phases is 12–13 T. The magnetic phase diagram of $CuGeO_3$ agrees qualitatively with both experimental results of typical organic spin-Peierls materials and a theoretical calculation.

The spin-Peierls (SP) transition is one of the most interesting phenomena observed in low-dimensional quantum spin systems. In the SP system, as the temperature is lowered, a phase with $S = \frac{1}{2}$ uniform Heisenberg antiferromagnetic linear chains (U phase) changes into a phase with dimerized or alternating chains (D phase) at the transition temperature (T_{SP}). Below T_{SP}, the ground state is a spin singlet (nonmagnetic), and a finite energy gap opens in an excitation spectrum. The SP transition has been known so far to occur only in a very few organic materials such as tetrathiafulvalinium bis-*cis*-(1,2-perfluoromethylethylene-1-2-dithiolato)-copper [TTF-$CuS_4C_4(CF_3)_4$, denoted TTF-CuBDT] (Refs. 1 and 2) and methylethylmorpholinium ditetracyanoquinodimethane $[MEM(TCNQ)]_2$.[3]

Among many experimental and theoretical works of the SP system, an investigation of this system in magnetic fields (H) is one of the most stimulative studies, because the organic SP materials exhibit characteristic properties in H below $T_{SP}(0)$ (T_{SP} without H).[4–11] In the absence of H, the wave vector of a lattice distortion (q) is π/a (a is a lattice spacing in a chain), which causes the lattice dimerization. When the magnetic field is applied to the SP system, the value of q sticks at π/a in low magnetic fields on account of Umklapp effects. However, another magnetic phase (M phase) appears above a critical field (H_c) and is considered to be another commensurate, discommensurate (a magnetic soliton), or incommensurate phase. A consensus about the M phase has not been established. For example, Bonner *et al.* have doubted whether the soliton picture is valid for the M phase because the experimental value of H_c is larger than the value theoretically estimated from the soliton picture.[11] On the other hand, Hijmans, Brom, and de Jongh have asserted that their results of NMR experiments can be explained in terms of a soliton-lattice model.[9]

It was claimed that typical organic SP materials show a universal behavior for the magnetic phase diagrams represented in terms of reduced variables $T/T_{SP}(0)$ and $H/T_{SP}(0)$.[7] The experimentally obtained phase boundaries between U and the other phases are of second order, and are consistent with the theoretical result of Cross.[12] On the other hand, the transition between D and M phases (DM transition) is of first order in a low-temperature region [$T/T_{SP}(0) \leq 0.5$–0.7]. Although some theories[12–17] predicted the existence of the first-order phase transition, there is no consensus of the DM transition.

Recently Hase, Terasaki, and Uchinokura have discovered that an insulating cuprate $CuGeO_3$ exhibits the SP transition.[18] Antiferromagnetic chains consist of Cu^{2+} and O^{2-} ions and are separated from one another by Ge-O chains.[19] The values of $T_{SP}(0)$ and an intrachain exchange interaction[20] above $T_{SP}(0)$ were estimated to be about 14.0 and 88.0 K, respectively, from the temperature dependence of the magnetic susceptibility [$\chi(T)$] measured by a superconducting quantum interference device (SQUID) magnetometer.[18]

This cuprate is a unique SP system. Localized d electrons of Cu^{2+} are responsible for $S=1/2$ in $CuGeO_3$. On the other hand, local spins are due to unpaired electrons located in π orbits of planar complexes such as TTF^+ or $TCNQ^-$ in ordinary organic SP systems. As a result, there occur some differences between this cuprate and organic SP materials. For example, an average g value of $CuGeO_3$ (2.18) (Ref. 21) is larger than 2, which is considered to be due to the spin-orbit interaction of d electrons, while the g value of organic SP compounds is nearly equal to 2.[1–3] This difference may cause the material dependence of magnetic properties because the magnetization is finite in the M phase. Therefore, it is important to examine whether the above-mentioned universality is valid for $CuGeO_3$ or not. Thus, we measured high-field magnetizations of this cuprate and compared our result with the known data of organic SP materials and the theory of Cross.

We synthesized polycrystalline $CuGeO_3$ by an ordinary solid-state reaction method. Magnetization (M) was obtained as a function of H in pulsed magnetic fields up to 25 T with a duration time of about 12 ms. The data of dM/dt and dH/dt were detected using an induction method and the values of M and H were numerically calculated. The pick-up coil of M consists of two coaxial coils wound in the opposite direction to cancel the voltage induced by the external magnetic field when a sample is removed. The length of the pick-up coil of M is about 7 mm. The inner coil, with a radius of 2 mm has 400-turn windings, and the outer coil, with a radius of 3 mm, has 180-turn windings. The powder sample (about 137 mg) was stuffed into the inner coil. The pick-up coil of H is located near the pick-up coil of M. The measurement was performed at various temperatures from 3.5 to 20.3 K.

Typical data of M and dM/dH are shown in Fig. 1. Let us begin with the data at 4.2 K. We observed a characteristic nonlinearity of M associated with a phase transition, and the hysteresis between M's for increasing and decreasing H, which indicates the first-order phase transition. In the following discussion, we define H_c related to the phase transition as the field of the peak position in the dM/dH curve, which is indicated by triangles in Fig. 1. The value of H_c measured in increasing field ($H_c^{\rm up}$) is slightly larger than that measured in decreasing field ($H_c^{\rm down}$). As the temperature is raised, the nonlinearity becomes less evident up to 13.4 K, and M is a linear function of H up to 25 T above 13.8 K. The hysteresis decreases with increasing temperature and disappears above 10.0 K. Thus the transition is of first and second order below and above 10.0 K, respectively. Below 13.8 K, the slope of M changes outside the region where the nonlinearity appears, that is, the slope in a high-field region is larger than that in a low-field region. It means that the transition from a phase with a small susceptibility to that with a large susceptibility occurs with increasing H. As is indicated by dashed lines in Fig. 1, an extrapolated line of the magnetization from the high-field region intersects the left-hand ordinate at $M \sim 0$. Similar nonlinearity and hysteresis of M have been also reported in organic SP materials and are common features of the SP system.[4–7]

We show the magnetic phase diagram expressed in terms of the reduced variables h [$=gH/2T_{\rm SP}(0)$] and t [$=T/T_{\rm SP}(0)$] in Fig. 2. Since the Zeeman energy depends on the g value as well as H itself, we use $gH/2T_{\rm SP}(0)$ instead of $H/T_{\rm SP}(0)$, which was used in Ref. 7. The average g values are 2.18, 1.97, 2.05, and 2.00 for $CuGeO_3$,[21] TTF-CuBDT,[1] TTF-AuBDT,[2] and MEM(TCNQ)$_2$,[3], respectively. Open circles and triangles represent $h_c^{\rm up}$ [$=gH_c^{\rm up}/2T_{\rm SP}(0)$] and $h_c^{\rm down}$ [$=gH_c^{\rm down}/2T_{\rm SP}(0)$] in the region of the first-order phase transition, respectively, and closed squares h_c [$=gH_c/2T_{\rm SP}(0)$] in the region of the second-order phase transition. Closed diamonds represent the magnetic field dependence of $T_{\rm SP}$ [$T_{\rm SP}(H)$] determined from $\chi(T)$'s, which were measured in constant fields up to 5 T by a SQUID magnetometer in our previous work.[18] The data of typical organic SP materials are also included in this figure.[5–7] Solid and dashed curves, which have been calculated by Cross,[12] denote phase boundaries between D and U phases and between

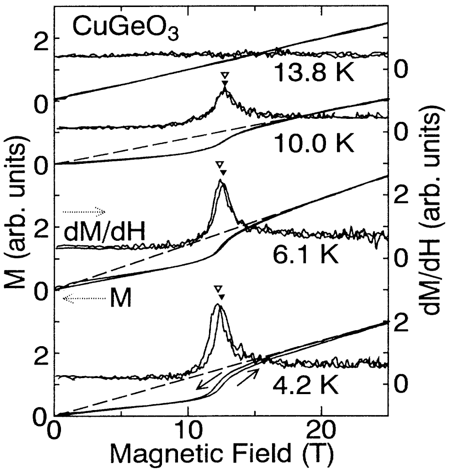

FIG. 1. The magnetic-field dependence of M and dM/dH of polycrystalline $CuGeO_3$ at 4.2, 6.1, 10.0, and 13.8 K. The vertical positions of M and dM/dH are shifted as indicated on the left-hand and right-hand sides of the figure, respectively. Closed and open triangles denote the peak position of dM/dH measured in increasing and decreasing fields, respectively. Solid arrows represent the directions of the scan of the field. Dashed lines mean the extrapolation of the magnetization from the high-field region to $H=0$.

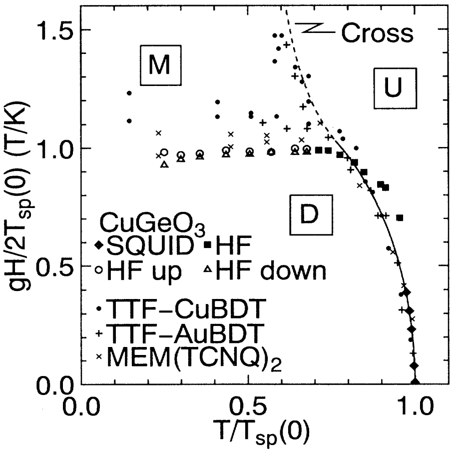

FIG. 2. The magnetic phase diagram of $CuGeO_3$. Open circles, open triangles, and closed squares represent the critical fields determined from the magnetizations measured in the high-magnetic fields up to 25 T, and closed diamonds spin-Peierls transition temperature derived from the susceptibilities measured by a SQUID magnetometer. This figure includes the data of typical organic spin-Peierls materials. Solid and dashed curves are theoretical ones. D, U, and M denote dimerized, uniform, and magnetic phases, respectively. References; TTF-CuBDT from Ref. 5, TTF-AuBDT from Ref. 7, MEM(TCNQ)$_2$ from Ref. 6 and theoretical curves from Ref. 12.

U and M phases, respectively.

The magnetic phase diagram of CuGeO$_3$ agrees qualitatively with both experimental results of organic SP systems and the theoretical prediction despite large differences in crystal structures. As a result, we could determine the boundary between D and the other phases in this work. The value of h_c decreases with increasing temperature above $t \sim 0.74$. In other words, the transition temperature is decreased by the field. The reduction of the transition temperature is due to the suppression of spin fluctuation and the increasing Zeeman energy. Especially below $h \sim 0.39$ ($H \sim 5$ T), the data of CuGeO$_3$ and theoretical curve exhibit an excellent agreement.[22] On the other hand, below $t \sim 0.74$, the value of $h_c^{\rm up}$ is nearly independent of temperature and that of $h_c^{\rm down}$ decreases slightly as temperature is lowered (the value of H_c is 12–13 T). The difference between the values of $h_c^{\rm up}$ and $h_c^{\rm down}$ increases with decreasing temperature, which qualitatively agrees with the results of organic SP materials.

In the following paragraphs, we discuss the material dependence of the magnetic phase diagram, which is observed in the transition region between the D and M phases. The value of h_c indicating the DM transition (h_c^{DM}) varies in all the compounds, which had been considered to be almost the same.[7] The difference between the values of $h_c^{\rm up}$ and $h_c^{\rm down}$ in CuGeO$_3$ is smaller than that in TTF-CuBDT (Ref. 5) or MEM(TCNQ)$_2$.[6] The value of t, below which the transition is of first order, is about 0.71 in CuGeO$_3$, which is close to the value obtained in MEM(TCNQ)$_2$ (0.67) and slightly larger than the values obtained in TTF-CuBDT and TTF-AuBDT (Ref. 9) (0.50 and 0.50, respectively).

It is commonly considered that the interchain exchange interaction affects the properties of the M phase because the magnetization is finite in the M phase. Inagaki and Fukuyama have obtained the phase diagram at 0 K in the presence of the magnetic field for the quasi-one-dimensional Heisenberg antiferromagnet coupled with the lattice distortion.[27] According to their theory, the value of h_c^{DM} is lowered by the existence of the interchain exchange interaction. Although the value of this interaction cannot be estimated at present, we think that the small variation of h_c^{DM} in SP materials is caused by the interchain exchange interaction, which may depend on crystal structures.

In this work, we could not obtain a phase boundary between U and M phases. For a further comparison between CuGeO$_3$ and organic SP materials or theories, it is necessary to determine this phase boundary by differential susceptibility or specific heat. A preliminary measurement of the temperature dependence of the differential susceptibility clearly shows the peak structure due to this phase transition,[28] which will be reported separately. In addition to the determination of this phase boundary, it is important that the M phase is studied by microscopic probe such as neutron-scattering measurement for more accurate discussion of the DM transition.

In summary, we measured the field dependence of the magnetizations of polycrystalline CuGeO$_3$, which exhibits the spin-Peierls transition around 14.0 K in the absence of the magnetic field. The measurements were performed at constant temperatures from 3.5 to 20.3 K in pulsed magnetic fields up to 25 T. The nonlinearity of the magnetization was observed below 13.4 K, which means the transitions from dimerized to the other phases. The hysteresis between the magnetization measured in increasing and decreasing fields was observed below 10.0 K. The critical field of the transition between dimerized and magnetic phases is about 12–13 T. If the magnetic phase diagram is expressed by reduced variables $gH/2T_{\rm SP}(0)$ and $T/T_{\rm SP}(0)$, the diagram of CuGeO$_3$ qualitatively agrees with both the results of typical organic spin-Peierls systems and the theoretical curve calculated by Cross.

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[*] Present address: Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku, Tokyo 135, Japan.

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was compared with the theoretical values 0.44, 0.44, and 0.38 of Bray (Ref. 23), Bulaevskii, Buzdin, and Khomskii (Ref. 24), and Cross (Ref. 12), respectively. In view of the present paper, the horizontal axis and the equation, which defines α, should be modified as $[g\mu_B H/2k_B T_{\mathrm{SP}}(0)]^2$ and $1 - T_{\mathrm{SP}}(H)/T_{\mathrm{SP}}(0) \sim \alpha[g\mu_B H/2k_B T_{\mathrm{SP}}(0)]^2$. Then we obtained α=0.39, which is in excellent agreement with 0.38 of Cross (Ref. 12). This means that the Luther-Peschel-type treatment (Ref. 25) of Cross and Fisher (Ref. 13) and the phase Hamiltonian method of Nakano and Fukuyama (Ref. 26), both of which properly took into account the Umklapp effects in zero magnetic field, give more suitable ground for understanding the spin-Peierls transition in the magnetic field than the Hartree-Fock treatment, on which Refs. 23 and 24 are based.

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