PHYSICAL REVIEW B VOLUME 55, NUMBER 10 1 MARCH 1997-II

Unusual antiferromagnetic state in Si-doped $CuGeO_3$ single crystals studied by specific-heat measurements in magnetic fields

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(Received 21 October 1996; revised manuscript received 27 December 1996)

We report the results of specific-heat measurements of $CuGe_{1-x}Si_xO_3$ ($x=0$, 0.01, 0.02) single crystals in magnetic fields up to 15 T. For $x=0.02$, a sharp transition was observed at the Néel temperature $T_N=4.8$ K, which is almost constant up to 15 T. For $x=0.01$, two broad transitions were observed at the spin-Peierls transition temperature $T_{SP}=10.8$ K and $T_N=2.5$ K in zero magnetic field. The antiferromagnetic state is changed drastically by the magnetic field and the magnetic-field-induced magnetic state was observed by specific-heat measurements. The magnetic phase diagram of $CuGe_{1-x}Si_xO_3$ was determined from specific-heat, thermal-expansion, and magnetization measurements. [S0163-1829(97)51510-4]

$CuGeO_3$ has been extensively studied since the discovery of the spin-Peierls (SP) transition by Hase, Terasaki, and Uchinokura.[1] In contrast with the organic SP compounds, $CuGeO_3$ can be obtained in a large and high-quality single crystal and is of great advantage for the examination of the cationic site substitution effect on the SP transition. In $CuGeO_3$, the intrachain and interchain exchange interactions were obtained as $J_c \sim 10$ meV, $J_b \sim 0.1 J_c$, and $J_a \sim -0.01 J_c$.[2] One of the interchain exchange interactions J_b is rather large compared to that in the organic SP compounds.[3] By substituting the cationic site, the lattice and the exchange interaction between Cu^{2+} spins should be modified and the interesting phenomena are expected, which are caused by the competition between the lattice dimerization and the three-dimensional (3D) antiferromagnetic (AF) ordering.[4] Such a substitution effect was studied in $Cu_{1-x}Zn_xGeO_3$.[5] The recent studies on $CuGe_{1-x}Si_xO_3$ single crystals showed that the SP transition temperature T_{SP} decreases monotonously and the AF ordering develops with increasing x and in a small x region ($0.005<x<0.02$) both SP transition and AF transition were observed.[6] These behaviors are similar to those in $Cu_{1-x}Zn_xGeO_3$.[5] Recent neutron scattering experiments indicate that in a sample with $x=0.007$, both AF and spin-Peierls states coexist below the Néel temperature T_N.[7] This is surprising because these two states are considered to be exclusive. Recently, it was proposed that the coexistence of both long-range lattice dimerization and antiferromagnetism, which is induced by the disorder due to cationic site substitution, is possible.[8]

In order to clarify the role of the substitution which causes the coexistence of the lattice dimerization and AF ordering, it is important to study the nature of the AF state below T_{SP} and to study how such an AF state is changed by the magnetic field. In this paper, we show the results of the systematic specific-heat measurements of $CuGe_{1-x}Si_xO_3$ ($x=0$, 0.01, 0.02) single crystals in magnetic fields parallel to the a axis and show the magnetic phase diagram up to 15 T. We chose these three samples because these samples with $x=0$, 0.01, and 0.02 show one SP transition, both SP and AF transitions, and one AF transition, respectively.

The single crystals of $CuGe_{1-x}Si_xO_3$ ($x=0$, 0.01, 0.02, 0.03) were prepared by the floating-zone method. The Si concentration x was determined by the inductivity coupled plasma emission spectrometry analysis. The specific heat was measured by the usual adiabatic heat pulse method. The temperature was measured by a carbon glass thermometer, which was calibrated in magnetic fields with a field insensitive capacitance thermometer in separate measurements. The sample weight was typically ~400 mg.

Figure 1 shows the specific heat of $CuGe_{1-x}Si_xO_3$ single crystals ($x=0$, 0.01, 0.02) in the form of $C/T-T$. For $x=0$, a sharp peak is observed at $T_{SP}=14.2$ K, which is consistent with those reported previously.[9–12] The specific heat below ~6 K can be fitted by $C=\beta T^3+\alpha \exp(-\Delta/k_B T)$ and we obtained $\beta \sim 0.4$–0.5 mJ/mol K^4 and $\Delta/k_B \sim 20$–23 K.

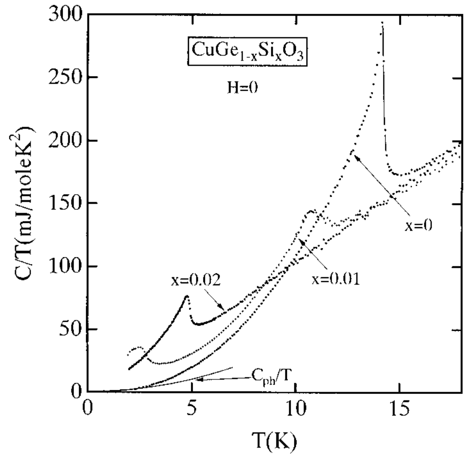

FIG. 1. Temperature dependence of $CuGe_{1-x}Si_xO_3$ ($x=0$, 0.01, 0.02) single crystals in the form of $C/T-T$. The phonon specific heat is also shown by a solid line assuming the simplest form of $C_{ph}=\beta T^3$ with β=0.4 mJ/mol K^4 in the form of $C_{ph}/T-T$ up to 7 K.

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Similar values were obtained in Ref. 10 and the value of Δ agrees with that obtained by neutron diffraction.[2] In Fig. 1, the phonon part of the specific heat C_{ph} is also shown in the form of $C_{\mathrm{ph}}/T-T$ up to 7 K, where $C_{\mathrm{ph}}=\beta T^3$ with $\beta=0.4$ mJ/mol K^4, corresponding to the Debye temperature of 290 K. At temperatures higher than 6–7 K, it is difficult to expect the above simple form of βT^3 to be the phonon specific heat because if we assume the above simple form for C_{ph}, the temperature dependence of the magnetic specific heat $C_m=C-\beta T^3$ for $x=0.02$ at high temperatures becomes unlikely for one-dimensional AF with a large J_c. C_{ph} at high temperatures may not be so simple, which is expected from the unusual thermal expansion at high temperatures.[13,14] For $x=0.02$, a sharp peak was observed at 4.8 K, which is ascribed to the AF magnetic transition. A similar result was obtained for $x=0.03$, where T_N was 4.5 K. For $x=0.01$, two peaks were observed at 10.8 and 2.5 K. The former peak is associated with the SP transition and the latter with the AF transition. Both peaks are rather broad compared with those at T_{SP} for $x=0$ and T_N for $x=0.02$, respectively. It was discussed by Regnault *et al.* that the broad transition at T_{SP} may be due to the sample inhomogeneity caused by the Si doping for the sample with $x=0.007$.[7] This suggests that the broad transition at T_N may also be due to the sample inhomogeneity. However, we consider that it is intrinsic in this compound, as will be discussed later. The broad specific-heat peak at T_N and the existence of a long tail of the specific heat up to ~6 K for $x=0.01$ indicate that the AF short-range order above T_N seems to be larger for $x=0.01$ than for $x=0.02$. The results of the thermal expansion also indicate the short-range order effect above T_N in $H=0$.[15] The coexistence of the AF short-range order with the dimerization in a temperature range between T_N and T_{SP} was reported by neutron scattering in a sample with $T_{\mathrm{SP}}=9$ K and $T_N=4$ K.[7]

Figures 2(a) and 2(b) show the specific heat of $\mathrm{CuGe_{0.99}Si_{0.01}O_3}$ in magnetic fields $H\|a$ axis in the form of $C/T-T$. T_{SP} decreases with increasing field as in $\mathrm{CuGeO_3}$. The peak shape of the specific heat at T_N is changed drastically by the magnetic field. In $H=0$, a peak is broad but pronounced. With increasing field, it is rapidly suppressed and almost disappears at ~7 T, while the temperature of a peak is not shifted up to ~7 T. However, for $H=8$ T, a small kink appears at $T\sim3$ K and the temperature of this kink increases and becomes clearer with further increase of field. At present, we do not know whether below the temperature of a small kink above ~8 T, the AF ordering survives or not. The neutron scattering experiment is desired to clarify how the AF state is changed by the magnetic field. In this paper, we consider tentatively that the AF order survives above ~8 T. The change of the peak shape at T_N is more clearly seen in Fig. 2(b). The point at $T\sim3$ K and $C/T\sim25$ mJ/mol K^2 looks like a fixed point. The magnetic entropy below T_N is much smaller above ~8 T than that in a low field. The nature of the AF state is very different below and above ~7 T. Here, we discuss the origin of the broad transition at T_N in $H=0$ for $x=0.01$. We consider that it is not extrinsic due to the sample inhomogeneity induced by the Si doping but intrinsic for the following reasons. One is that while the peak of the specific heat at T_N in a small field region is broad, it becomes clear above ~8 T. The other is that the peak at T_N for $x=0.02$ is much sharper than that for $x=0.01$ in $H=0$. If the sample inhomogeneity is the reason for the broad peak at T_N, it should be insensitive to the magnetic field and should be broader for $x=0.02$ than for $x=0.01$, which contradicts the present result. Furthermore, our recent thermal expansion measurements along the a axis for $x=0.01$ in longitudinal magnetic fields up to 15 T showed that a clear shrinkage was observed below T_N in low and high magnetic field regions, while a shrinkage was small around 7 T.[15] Thus, the broad transition at T_N for $x=0.01$ in a small field is considered to be one of the intrinsic characteristics of the unusual AF state in the dimerized (D) phase.

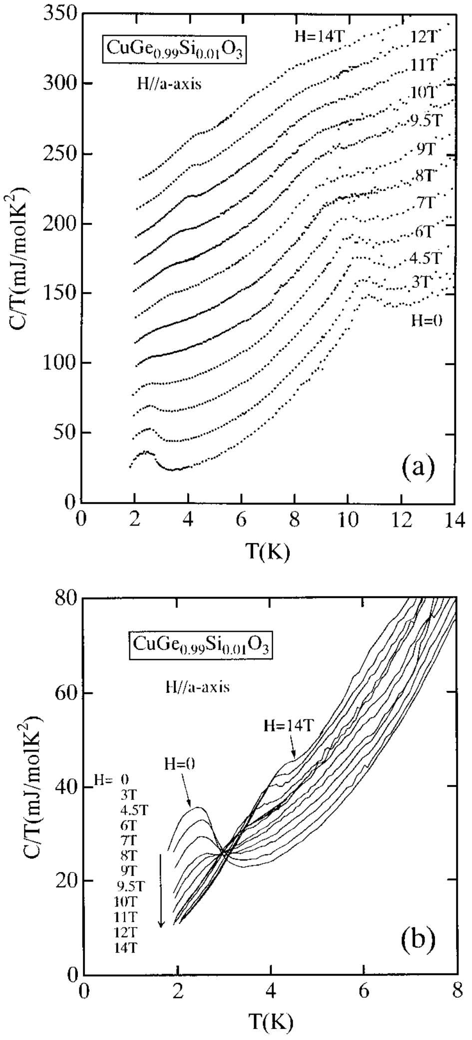

FIG. 2. Temperature dependence of the specific heat of $\mathrm{CuGe_{0.99}Si_{0.01}O_3}$ under the magnetic field parallel to the a axis in the form of $C/T-T$. In (a), the origin of the vertical axis is shifted by 20 mJ/mol K^2. In (b), it is common to all the curves.

Figure 3 shows the specific heat of $\mathrm{CuGe_{0.98}Si_{0.02}O_3}$ in magnetic fields $H\|a$ axis in the form of $C/T-T$. It is known that in the pseudo-1D Heisenberg AF, T_N is enhanced by applying the magnetic field because the reduced T_N in $H=0$ originates from the large AF spin fluctuation due to the low dimensionality, and this AF spin fluctuation is suppressed by the magnetic field.[16] However, in the present compound, T_N is almost constant up to 15 T and also the shape of the specific-heat peak at T_N is almost constant to the 15 T and

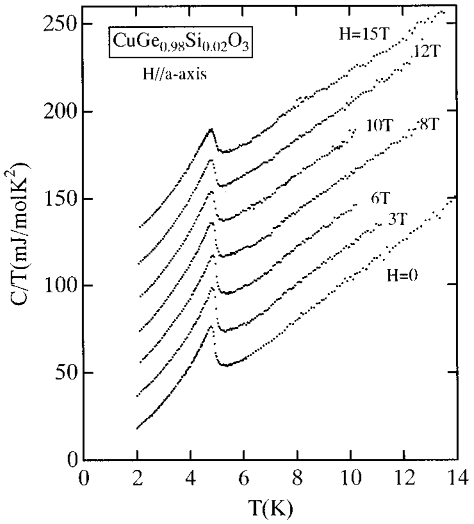

FIG. 3. Temperature dependence of the specific heat of $CuGe_{0.98}Si_{0.02}O_3$ under the magnetic field parallel to the a axis in the form of $C/T-T$. The origin of the vertical axis is shifted by 20 mJ/mol K^2 for each curve.

also the shape of the specific-heat peak at T_N is scarcely changed by the magnetic field. These suggest that the spin fluctuation above T_N is not large in this compound. This will be discussed later.

Figure 4 shows the magnetic phase diagram of $CuGe_{1-x}Si_xO_3$. As the peak shape at T_N is broad in a low field region for $x=0.01$, T_N was determined as a peak position of the specific heat. The phase boundary between the D and the high field magnetic (M) phases for $x=0.01$ was determined from the nonlinear increase of the magnetization,[17] as is observed in $CuGeO_3$.[18] However, this nonlinear increase is much smaller than that in $CuGeO_3$ and the phase boundary D-M is also much broader than that in $CuGeO_3$. This phase boundary is much broader than that in $CuGeO_3$.[18] The phase boundary between the uniform (U) and D phases shows nearly a parallel shift toward lower temperatures with increasing x. T_N for $x=0.02$ is almost constant, independent of the magnetic field up to 15 T. T_N for $x=0.01$ is almost constant up to ~7 T and increases with increasing field and T_N saturates to ~5 K with further increase of field. According to the results in a sample with $T_{SP}=9$ K and $T_N=4$ K in $H=0$ by Poirier *et al.*, two phase boundaries between U and D phases and D and AF phases coincide with each other above 9 T and the temperature of the phase boundary above 9 T is also ~5 K.[19] These results suggest that T_N saturates to ~5 K in the above three compounds. Further studies are necessary to clarify whether it is accidental or not. The increase of T_N with increasing field above ~8 T for $x=0.01$ is associated with the decrease of T_{SP}. Here, we make a few remarks on the specific heat in the magnetic field. The peak shape of the specific heat at T_N is very different between low and high field regions, as mentioned above. One of the reasons is that the excited triplet state which will be increased in a high magnetic field affects the peak shape of the specific heat. It is also interesting to point out that a peak shape of the specific heat at T_N in a high field region is very different between the samples with $x=0.01$ and 0.02, regardless of nearly the same T_N. We also note that the point at $T\sim4$ K and $H\sim11$ T looks like a tetracritical point. However, as the phase boundaries are broad, it is difficult to discuss such a possibility any further, at present. Further studies are necessary to clarify the unusual properties of the AF state in the D phase.

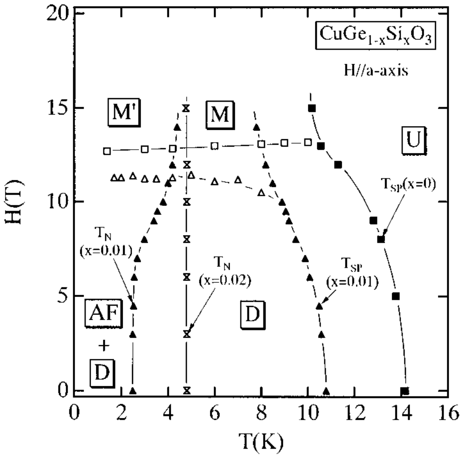

FIG. 4. Magnetic phase diagram of $CuGe_{1-x}Si_xO_3$ determined from the results of the specific heat. The phase boundary between D and M phases for $x=0.01$ (Δ) were determined from the magnetization measurement (Ref. 15); that for $x=0$ (☐) is cited in Ref. 16. The phases of U, D, M, M', and AF are cited for $x=0.01$. We tentatively define the phase above ~11 T and below ~4 K for $x=0.01$ as the M' phase.

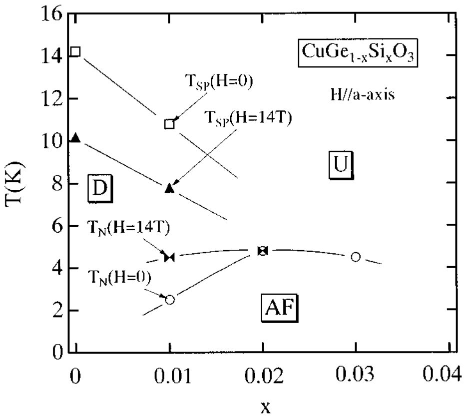

FIG. 5. T-x phase diagram of $CuGe_{1-x}Si_xO_3$ in $H=0$ and $H=14$ T.

Figure 5 shows the x dependence of T_{SP} and T_N in $H=0$ and 14 T. The results in $H=0$ are similar to those reported before.[6] The results in $H=14$ T show that T_{SP} is reduced and T_N is enhanced by the magnetic field and T_N for $x=0.01$ saturates to ~5 K. The increase of T_N with increasing x up to 0.02 is due to the destruction of the spin gap by the doping. The increase of T_N with increasing field may be due to the destruction of the spin gap by the magnetic field. The temperature of ~5 K looks like the maximum T_N in the $CuGe_{1-x}Si_xO_3$ system. We make the following remarks. When the gap Δ is destroyed by the magnetic field, we expect a decrease of Δ with increasing magnetic field. However, it is difficult to see such a change of Δ in the specific heat for $x=0.01$ in Fig. 2, where the data below T_{SP} seem to be parallel in field to the other curves. Our recent results of the thermal expansion show that the short-range order above T_N is observed in $H=0$ and becomes smaller with increasing magnetic field.[15] As for the magnetic field dependence of T_{SP}, it decreases with field. The changes of these three quantities of Δ, short-range order, and T_{SP} occur at the same time under the magnetic field. The specific heat contains all these contributions. This may be the reason why a change of Δ with magnetic field is difficult to see in the specific heat.

In conclusion, we obtained the results of the specific-heat measurements of $\mathrm{CuGe}_{1-x}\mathrm{Si}_x\mathrm{O}_3$ single crystals ($x=0$, 0.01, 0.02) in magnetic fields up to 15 T. In a sample with $x=0.02$, the transition to the AF-ordered state was observed and $T_N=4.8$ K is almost constant up to 15 T, which was discussed from the standpoint of the contribution of the two dimensionality of the exchange interaction. For $x=0.01$, two transitions are observed at $T_{\mathrm{SP}}=10.8$ K and $T_N=2.5$ K in $H=0$. In this sample, while the field dependence of T_{SP} is normal for $x=0$, that of T_N is very different from that for $x=0.02$. The peak shape of the specific heat at T_N is drastically changed by the magnetic field and the results suggest that the AF state is very different below and above ~7 T. Above ~7 T, T_N increases with field and seems to saturate to ~5 K, which coincides with $T_N=4.8$ K for $x=0.02$. Further studies are necessary to understand these unusual AF states in the D phase.

The authors would like to thank Professor I. Harada and Professor S. Inagaki for stimulating discussions. We thank T. Ohtomo, H. Miura, S. Tanno, and K. Hosokura of Tohoku University Cryogenic Center. This work was carried out in HFLSM, IMR, Tohoku University. The Aoyama-Gakuin group was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) and the Science Research Fund of Japan Private School Promotion Foundation.

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