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^{11}B-NMR study of low-temperature phase transition in CuB_2O_4

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Abstract
The material CuB_2O_4 presents a variety of phases in the B–T phase diagram, caused by the frustration and the Dzialoshinskii–Moriya interaction. In order to investigate the nature of the phase transitions, a ^{11}B-NMR experiment on CuB_2O_4 has been performed under an applied magnetic field along the a-axis down to 0.4 K. A new incommensurate–incommensurate phase transition has been found at 0.8 K under a field of 0.5 T. Further, another phase transition has been observed at 4.7 K under a field of about 2 T, which is consistent with the transition reported by the neutron diffraction experiment.

1. Introduction

In the usual three-dimensional magnet, the long-range ordering occurs around a temperature comparable with the exchange coupling energy divided by the Boltzmann constant. Below the ordering temperature, almost all magnetic entropy is lost. However, if geometrically competing antiferromagnetic coupling causes the frustrated spin system, and/or the Dzialoshinskii–Moriya interaction disturbs the spin system, then the magnetic entropy still remains, even below the ordering temperature, presenting a variety of magnetic phases. The copper metaborate CuB_2O_4 is one such magnet. This material has been studied using several experimental methods, such as magnetic susceptibility [1], specific heat [2], electron spin resonance (ESR) [3, 4], neutron diffraction [5–7], muon spin relaxation (μSR) [6], nonlinear optics [8], nuclear magnetic resonance (NMR) [9] and so on. Under a zero magnetic field, the successive phase transitions occur as follows. With decreasing temperature, the paramagnetic phase changes to the commensurate weak ferromagnetic phase at $T_N = 21$ K. The second magnetic phase transition at $T^* = 9.5$ K causes the incommensurate helix phase. At a temperature just below T^*, the formation of a magnetic soliton lattice has been reported from the higher-order magnetic satellite appearing in the neutron diffraction experiment [5]. At $T^{**} \simeq 1.8$ K, an additional

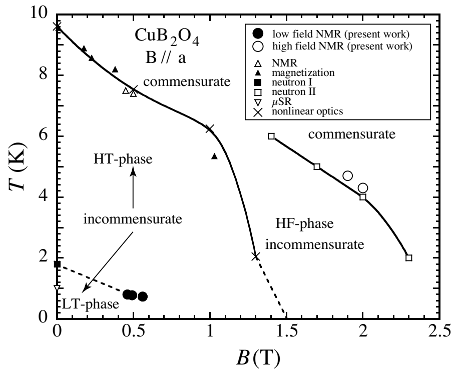

Figure 1. B–T phase diagram of CuB_2O_4: $B \parallel a$-axis. The diagram is determined by NMR [9], magnetizations [9], neutron diffraction I [6], neutron diffraction II [10], μSR [6] and nonlinear optics [8] experiments. Solid and open circles are points determined by the present ^{11}B-NMR experiments. For details, see the text.

magnetic phase transition is suggested by neutron diffraction experiments [6]. Further, under an external magnetic field, CuB_2O_4 exhibits several magnetic phases in the B–T phase diagram. In order to investigate the properties of these phases in CuB_2O_4, NMR experiments were performed on the ^{11}B nucleus.

2. Experimental results and discussion

^{11}B-NMR experiments in CuB_2O_4 were performed using a piece of single crystal under an external magnetic field of $B \parallel a$-axis at a temperature from 10 K down to 0.4 K. The single crystal was grown at the Institute of Physics (SB RAS) in Krasnoyarsk. The material CuB_2O_4 belongs to tetragonal space group $I\bar{4}2d$ (D^{12}_{2d}) with the lattice parameters $a = 11.528$ Å and $c = 5.607$ Å [7]. The unit cell contains 12 formula units and Cu^{2+} ions occupy two different positions. The Cu(A) ions are located at site 4b (point symmetry S_4, $00\frac{1}{2}$), showing no magnetic frustrations or D–M interaction. Meanwhile, the Cu(B) ions are at site 8d (point symmetry C_2, $x\frac{1}{4}\frac{1}{8}$, $x = 0.0815$). These ions form four zigzag chains along the c-axis in the unit cell. Since both the nearest and the next-nearest interactions are considered to be antiferromagnetic, these chains are magnetically frustrated. From considerations of the inversion symmetry of the crystal, D–M interaction is expected between Cu(B)–Cu(B) as well as Cu(A)–Cu(B) interaction. For the convenience of the discussion below, the B–T phase diagram of CuB_2O_4 is shown in figure 1. The diagram has been determined under a magnetic field applied along the a-axis through experiments that have already been reported [6, 8–10].

Two regions of the phase diagram attract our attention. One is the region around the point $T^{**} \simeq 1.8$ K at zero field. The other is the region around 5 K and 2 T, where a new phase transition is reported from the recent neutron diffraction experiment [10]. The NMR experiments were performed in these two regions of the phase diagram. Hereafter we call them low-field NMR and high-field NMR, respectively.

2.1. Low-field NMR at liquid ^{3}He temperature

The temperature T^* of the commensurate–incommensurate phase transition decreases with increasing external magnetic field. By lowering the temperature, another phase transition has

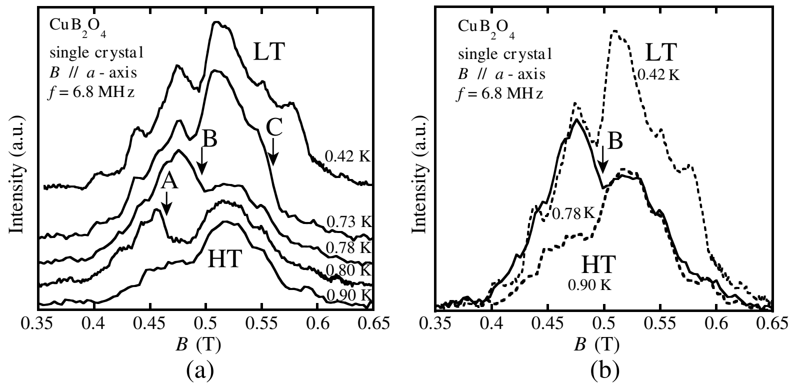

Figure 2. (a) Temperature dependence of the spin-echo spectrum of ^{11}B in CuB_2O_4: $B \parallel a$-axis. The arrows A, B and C indicate the fields where the transition in the spectrum occurs. (b) Superposition of the spectra at HT and LT and that at 0.78 K. A transition in the spectrum at 0.78 K is clearly seen at 0.49 T, marked as arrow B.

been reported to occur at $T^{**} \simeq 1.8$ K under zero magnetic field from a neutron diffraction experiment [6]. However, an NMR experiment for such low temperatures has not been reported.

In order to study the field dependence of T^{**}, a ^{11}B-NMR experiment on CuB_2O_4 was carried out at liquid ^{3}He temperatures down to 0.4 K. The temperature dependence of the spin-echo spectrum under an external magnetic field $B \parallel a$-axis is shown in figure 2(a). Each resonance line indicates a characteristic feature of the incommensurate phase—the so-called powder pattern. At a glance, the line structure changes gradually with the temperature variation. However, by inspecting the line shape in detail, we find a transition in the spectrum, as will be discussed below. We believe that the spectral transition is caused by the field-dependent phase transition.

The spectral pattern at 0.90 K seems to differ from that at 0.42 K. Since all the spectral pattern in figure 2(a) is the powder pattern, the transition may be an incommensurate–incommensurate phase transition. Here, we call the high-and low-temperature phases HT-phase and LT-phase, respectively. The spectral pattern at 0.90 K, marked as HT in figure 2(a), is considered to have the characteristic of the HT-phase, while that marked as LT at 0.42 K has the characteristic of the LT-phase. Then, for example, as shown in figure 2(b), the spectral pattern at 0.78 K coincides with the pattern of the LT-phase for the field region below 0.49 T, while it coincides with the pattern of the HT-phase for the field region above 0.49 T. Thus a transition in the spectral pattern occurs at 0.49 T, denoted by the arrow B in figures 2(a) and (b). Similarly, arrows A and C denote the transition fields for 0.80 and 0.73 K, respectively. The result is plotted as solid circles in figure 1. For the purpose of examining the nature of the HT-to LT-phase transition, the NMR spectrum was carefully observed around the transition field. Hysteresis appears in the spectrum; in other words, the spectral pattern depends on the sweep direction of the magnetic field. Then, the HT-to LT-phase transition may be the first-order phase transition.

As for the dynamics of the spin system, the nuclear spin–lattice relaxation rate T_1^{-1} was measured for ^{11}B in CuB_2O_4. The temperature dependence of T_1^{-1} measured under a magnetic field of about 0.5 T applied along the a-axis is shown in figure 3. Below T_N, the spin–lattice relaxation rate T_1^{-1} showed a small anomaly around $T^* \sim 7.5$ K, and then increased continuously below T^*. The most prominent anomaly of T_1^{-1} was found at $T^{**} \sim 0.8$ K, namely T_1^{-1} exhibited a pronounced jump. This jump in the temperature dependence of T_1^{-1}

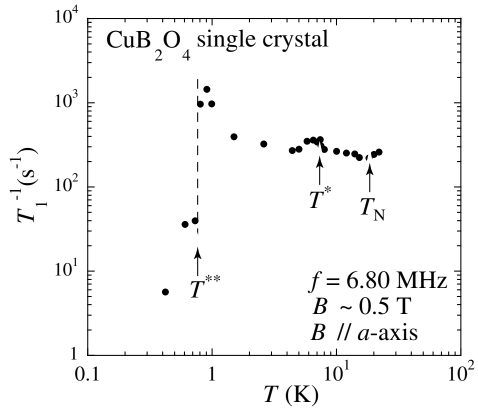

Figure 3. Temperature dependence of the nuclear spin–lattice relaxation rate T_1^{-1} of ^{11}B in CuB_2O_4: $B \parallel a$-axis. The arrows T_N, T^* and T^{**} denote the phase transition temperatures.

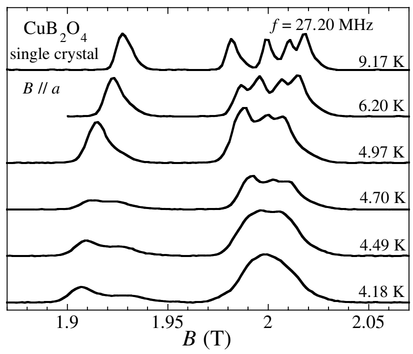

Figure 4. Temperature dependence of the spin-echo spectrum of ^{11}B in CuB_2O_4: $B \parallel a$-axis. The spectral pattern changes at about 4.7 K, suggesting a commensurate–incommensurate phase transition.

just corresponds to the jump in the spectral transition discussed above. Thus the jump in T_1^{-1} is considered to be caused by the HT-to LT-phase transition. Below T^{**}, the spin–lattice relaxation rate T_1^{-1} decreased steeply with decreasing temperature.

In summary of the low field NMR experiments, a new phase transition was found. This transition may correspond to the transition at 1.8 K without magnetic field reported by the experiment of the neutron diffraction [6].

2.2. High-field NMR

Recently, an additional phase transition in CuB_2O_4 around 5 K and 2 T has been reported from neutron diffraction experiments under a magnetic field applied along the a-axis [10]. We call this incommensurate high-field phase an HF-phase, indicated in figure 1. In order to confirm the existence of the new phase, a ^{11}B-NMR experiment was performed for an external magnetic field of around 2 T along the a-axis with an operating frequency of 27.20 MHz. The temperature dependence of the spin-echo spectrum is shown in figure 4. The spectrum is divided into two groups, namely the low-field group around 1.9 T and the high-field group around 2.0 T. The spectrum of the low-field group above 4.97 K consists of a single sharp line, indicating that the spin system is in the commensurate phase. Meanwhile, below 4.70 K this line becomes broad, showing the powder pattern. This fact suggests that at 1.9 T the magnetic phase changes from commensurate phase to incommensurate phase around 4.70 K, which is consistent with the result reported from the neutron diffraction experiment. As for the spectrum in the high-field group, it is suggested that, at around 2.0 T, the magnetic phase changes from commensurate phase to incommensurate phase at about 4.3 K. From the high-field NMR experiments discussed above, we have obtained the phase boundary under a magnetic field of nearly 2 T. These are plotted in figure 1 using open circles.

3. Conclusion

Pulsed NMR experiments were performed on the ^{11}B nucleus in CuB_2O_4 down to liquid ^3He temperatures with an external magnetic field along the a-axis at around 0.5 T. A new incommensurate–incommensurate phase transition was found at around 0.8 K under an applied magnetic field of 0.5 T. Another NMR experiment at around 5 K and 2 T revealed a phase transition consistent with that reported from the neutron diffraction experiments. The newly determined B–T phase diagram is summarized in figure 1.

Acknowledgments

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