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Magnetic behaviour of the two-dimensional Heisenberg ferromagnet Cs_2CuF_4 under high pressure: a sensitive magnetic measurement in a diamond-anvil cell to 26 GPa

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Abstract

The isomorphous compounds A_2CuF_4 ($A = K$, Rb, Cs) are two-dimensional Heisenberg ferromagnets with the Curie temperatures of 6.25, 6.05 and 4.55 K, respectively. Previous studies showed that pressure-induced magnetic phase transitions occur in K_2CuF_4 and Rb_2CuF_4 at around 10 GPa, above which the ferromagnetic behaviour disappears as a result of the structural change from antiferrodistortive to ferrodistortive order of the CuF_6 octahedra in the basal plane. For Cs_2CuF_4 it was revealed that the interlayer exchange interaction changes from ferromagnetic to antiferromagnetic at a certain pressure below 2.2 GPa. Motivated by this unexpected result, we have carried out magnetic measurements on Cs_2CuF_4 in a diamond-anvil cell at various pressures up to 26 GPa by using a superconducting quantum interference device vibrating coil magnetometer. It was found that the Néel temperature increases with pressure at a rate of 0.3 K GPa^{-1} up to 17 GPa, reaches a maximum of about 9 K at around 17 GPa and then decreases rapidly to zero. At pressures above 21 GPa the magnetic susceptibility decreases to the background level, strongly suggesting that a structural change similar to those observed for the other two compounds occurs for Cs_2CuF_4 at around this pressure.

1. Introduction

It is of interest to make magnetic studies under pressures much higher than those that a piston–cylinder cell can generate. A diamond-anvil cell (DAC) is a possible device for use for this purpose, because it can be made to cover a very wide range of pressure by changing the

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culet diameter of the diamond anvils and is easy to install in a cryostat for low temperature experiments [1, 2]. In view of the extremely small amount of sample confined in the pressure cell, however, there are technical difficulties in using a DAC to make sensitive magnetic measurements. As a result of a very poor filling factor of the detection coil located outside the pressure cell, the background signal generally changes substantially with both temperature and pressure as compared to the change in the sample signal. Magnetic measurements in a DAC are, therefore, restricted mainly to detection of a superconducting transition temperature or the Curie temperature at which a large and sudden change in the magnetic susceptibility occurs. There has been much effort to increase the sensitivity and accuracy for detecting sample signals buried under the enormous background [3–8]. The ratio of the sample signal to the background signal strongly depends on the detection method as well as the materials used in the DAC. A superconducting quantum interference device (SQUID) vibrating coil magnetometer (VCM) is one of the solutions for improving the sensitivity [4]. The detection coil, made of a superconducting wire, is vibrated at the position that is the maximum point of the gradient of the magnetic flux threading the detection coil, a few tenths of a millimetre apart from the gasket. Since the contributions of the background signals decrease rapidly with distance l from their sources according to an l^{-4} power law, this method has an advantage over the conventional one using stationary coils, provided that detecting coils are located outside the pressure cell. Using this method, we have performed magnetic measurements for several samples including antiferromagnets [9, 10], ferromagnets [11, 12] and superconductors [13, 14], which provided in return a test for the technical improvements of the measurement system—such as expanding the temperature range of measurements, reducing the noise level and decreasing the background signal at low temperatures [15–17]. The composite bimetallic gasket was developed to expand the pressure range up to 30 GPa for the magnetic measurements with a low magnetic background comparable to that of the BeCu gasket that is generally used as a non-magnetic gasket but supports only about 10 GPa [17]. The development was triggered by the investigation of the magnetic behaviour of Cs_2CuF_4 under high pressure, and due to the composite gasket use we have observed a pressure-induced magnetic phase transition in Cs_2CuF_4. In this paper we will report the experimental results of the magnetic susceptibility measurements for Cs_2CuF_4 at pressures up to 26 GPa, as a successful example of sensitive magnetic measurements at such very high pressures.

Cs_2CuF_4 is a member of the group of isomorphous compounds A_2CuF_4 (A = K, Rb, Cs), which are two-dimensional ferromagnets with Curie temperatures T_Cs of 6.25, 6.05 and 4.55 K, respectively. They have the same spin structures at ambient pressure, and the spins in the ordered states lie in the basal plane [18, 19]. Among these compounds, K_2CuF_4 is known as a typical example of a two-dimensional Heisenberg ferromagnet. The relationship between the magnetism and the crystal structure was investigated in detail for K_2CuF_4 and, as a result, the origin of the ferromagnetic interaction between the neighbouring Cu^{2+} ions is the alternating ordering of the 3d hole orbitals, $d_{x^2-z^2}$ and $d_{y^2-z^2}$, resulting from the antiferrodistortive (AFD) arrangement of Jahn–Teller distorted CuF_6 octahedra in the basal plane [20–22]. In 1996 we observed for the first time a pressure-induced magnetic phase transition in K_2CuF_4 at a pressure of about 10 GPa: T_C starts to decrease rapidly around 7 GPa, and the ferromagnetic behaviour disappears at pressures higher than 10 GPa [11]. The idea of the experiment was that reducing the volume of the unit cell using pressure would cause a change in the arrangement of the AFD to another type of arrangement, such as a ferrodistortive (FD) one, in which the elongated axes of the distorted octahedra align parallel, as seen in the alignment of CuO_6 octahedra in the two-dimensional antiferromagnet La_2CuO_4 [23], and if so, the change of the orbital arrangement could be detected through magnetic measurements as a change in the magnetism which depends on the configuration of the hole orbitals. Subsequently, structural studies such

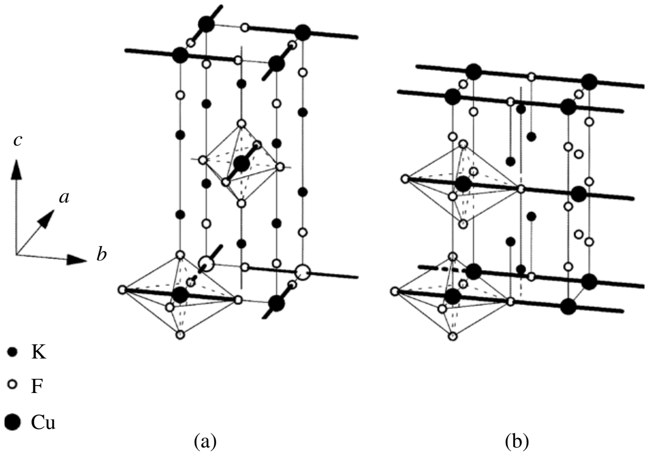


Figure 1. Schematic drawing of the crystal structures of K_2CuF_4 (a) in the low pressure phase and (b) in the high pressure phase. The bold lines show the longest axes of the CuF_6 octahedra.

as x-ray diffraction and Raman scattering ones revealed that a structural phase transition occurs at the corresponding pressure with a change in the arrangement of the CuF_6 octahedra in the basal plane as well as the stacking of the basal plane along the *c*-axis [24, 25]. In the high pressure phase they are arranged in the FD order with their elongated axes along the *b*-axis, suggesting an antiferromagnetic interaction between the neighbouring Cu^{2+} ions. Figure 1 shows a schematic drawing of the crystal structures in the low pressure and the high pressure phases of K_2CuF_4.

After the discovery of the pressure-induced magnetic phase transition in K_2CuF_4, we proceeded with experiments on Rb_2CuF_4 and Cs_2CuF_4 to investigate the effects of the replacement of K^+ by larger cations, Rb^+ and Cs^+, on the pressure-induced phase transition. For Rb_2CuF_4 a pressure-induced magnetic phase transition was observed at about 10 GPa, the same as the critical pressure of K_2CuF_4 [26]. Using the x-ray diffraction method at room temperature we confirmed that the crystal structure after the transition is the same as that of the high pressure phase of K_2CuF_4. It was found that the relative values of the lattice parameter *a* are nearly the same at the transition pressure for K_2CuF_4 and Rb_2CuF_4. The above result suggests that the response of the basal plane of the CuF_6 octahedra to compression is essential for the structural transitions in these two compounds.

Manaka *et al* carried out high pressure neutron scattering experiments on Cs_2CuF_4 and K_2CuF_4, and found unexpectedly that only the interlayer exchange interaction of Cs_2CuF_4 changes from ferromagnetic to antiferromagnetic at a certain pressure below 2.2 GPa [27]. The intralayer exchange interaction of Cs_2CuF_4 and both the interlayer and intralayer exchange interactions of K_2CuF_4 remain unchanged at pressures of 2.2 and 2.7 GPa, respectively. As will be shown subsequently in this paper, the magnetic measurement of Cs_2CuF_4 revealed that the magnetic transition temperature increases gradually with pressure even at pressures above 10 GPa, a quite different behaviour from that for the other two compounds.

2. Experimental details

The magnetic susceptibility measurements in a DAC were carried out by using the SQUID VCM. A commercial hardened BeCu alloy (C1720-HT NGK Insulators, Ltd) was used to make

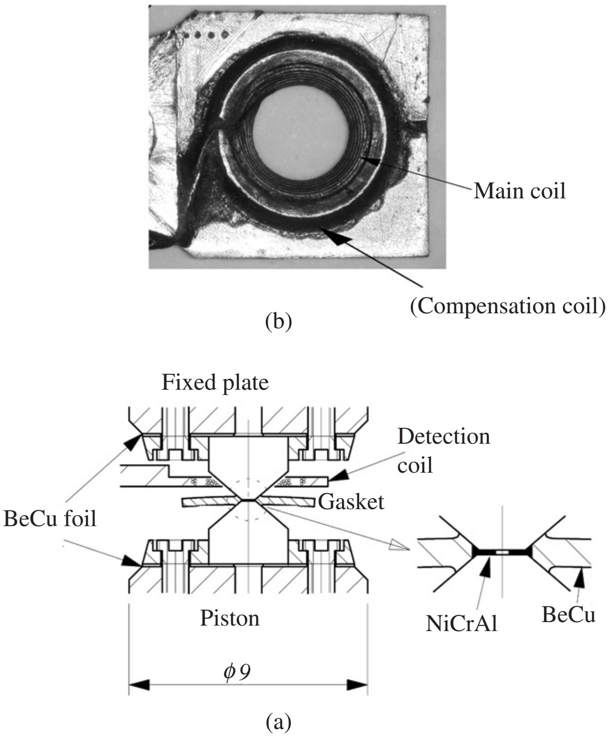
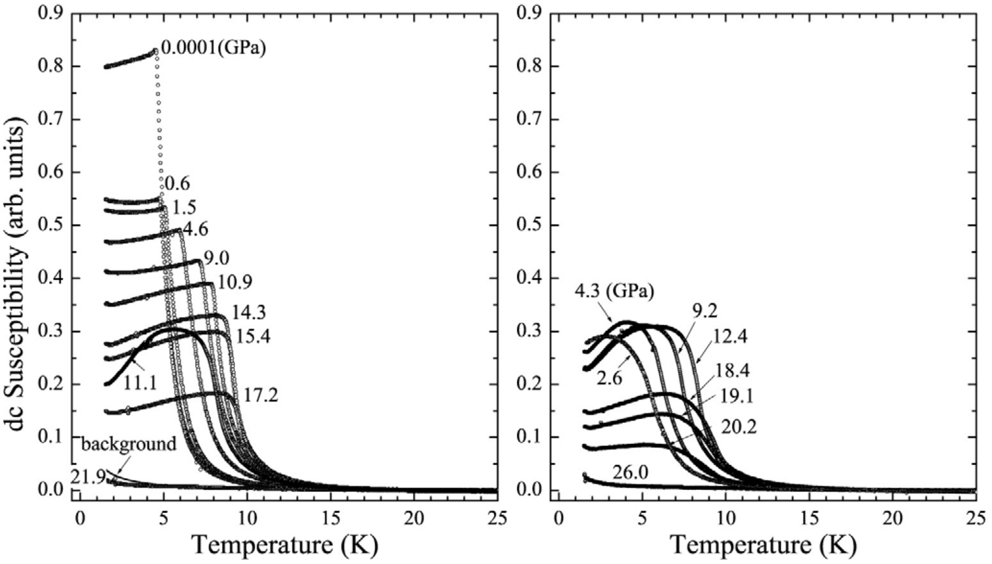


Figure 2. (a) Cross-sectional drawing of the area around the diamond anvils and (b) photograph of the detection coil. The inside of the main coil (20 turns) that has no bobbin was cone shaped. The compensation coil (10 turns), covered with Stycast No 2850FT, was located around the main coil, forming a concentric gradiometer.

the DAC. It was of clamp type and had no alignment mechanisms for the anvils which were fixed mechanically to pistons through small BeCu rings. An unaged BeCu foil, 0.1 mm in thickness, was placed between the anvil and the piston as a cushion. For sensitive measurements at pressures that a BeCu gasket hardly supports, we used a newly developed composite bimetallic gasket, which was designed so that the load was supported mainly by the inner NiCrAl washer which was slightly larger than the culet of the anvil [17]. The BeCu girdle, 5 mm in diameter and 0.4 mm in thickness, prevents the NiCrAl from fracturing. This composite gasket yields a temperature dependence of the background signal at low temperatures not very different from that with the BeCu gasket, while it has nearly the same mechanical strength as a NiCrAl alloy. A pair of anvils with culet diameters of 600 and 650 μm was used, and a hole 235 μm in diameter was drilled at the centre of the gasket. Figure 2 shows the enlarged view around the diamond anvils with the detection coil.

A 4:1 methanol–ethanol mixture that was dehydrated using a molecular sieve was used as a pressure transmitting medium. The pressure was determined by the shift of the superconducting transition temperature of lead located in the gasket hole [28]. A magnetic field of 3 Oe was applied along the a-axis, which is the easy axis of the magnetic moment at ambient pressure, and the signal due to the magnetization induced by the magnetic field was detected as a function of temperature with increasing temperature. Single crystals of Cs_2CuF_4 were grown by the Bridgman method from a melt of a mixture of Cs and CuF_2 with the molar ratio of 2:1 in a platinum crucible. We found that the crystals thus obtained were extremely hygroscopic.



(a) (b)

Figure 3. Temperature dependence of the dc magnetic susceptibility of Cs_2CuF_4 in the temperature range from 1.5 to 25 K at various pressures up to 26 GPa, the sequences being (a) 0.0001 (GPa), 0.6, 1.5, 4.6, 9.0, 10.9, 14.3, 15.4, 17.2, 21.9 and 11.1; and (b) 4.3, 9.2, 12.4, 18.4, 19.1, 20.2, 26.0 and 2.6.

Samples were cut out of the single crystal to produce a flat plate shape perpendicular to the a-axis and fitted into the gasket hole of the DAC. The operation was performed in an atmosphere of dry nitrogen flowing in a glove bag to prevent damage of the crystal by moisture from the air.

3. Results and discussion

Figure 3 shows the temperature dependence of the dc magnetic susceptibility $\chi = M/H$ of Cs_2CuF_4 in the temperature range from 1.5 to 25 K at several pressures up to 26 GPa. The sample was 140 μm × 120 μm with a thickness less than 27 μm, as approximated by comparison to the final gasket thickness. It underwent successively two pressure excursions, the first to 21.9 GPa and the second to 26.0 GPa, the sequence being 0.0001 (GPa), 0.6, 1.5, 4.6, 9.0, 10.9, 14.3, 15.4, 17.2, 21.9, 11.1, 4.3, 9.2, 12.4, 18.4, 19.1, 20.2, 26.0 and 2.6. The $\chi(T)$ curves in the second half of the sequence, starting from 4.3 GPa, are shown in figure 3(b) for clarity. The curve that was obtained with no sample at the beginning of the pressure sequence was used as a background signal, shown in figure 3(a), and was subtracted together with the contribution of the lead manometer from all the observed signals to obtain $\chi(T)$.

$\chi(T)$ decreases substantially at 0.6 GPa, which may be attributed to the change in the interlayer exchange interaction from ferromagnetic to antiferromagnetic. Because of its magnetic two-dimensionality, the susceptibility curve has a ferromagnetic character after a change in the interlayer exchange interaction, as observed in the high pressure experiments on $(CH_3NH_3)_2CuCl_4$, which is also an ideal two-dimensional ferromagnet [29]. This is different from the case of a magnetic three-dimensional system for which a remarkable change in shape and magnitude is generally expected in the susceptibility curve on such a transition of the magnetic interaction. On further increasing the pressure to about 15 GPa, $\chi(T)$

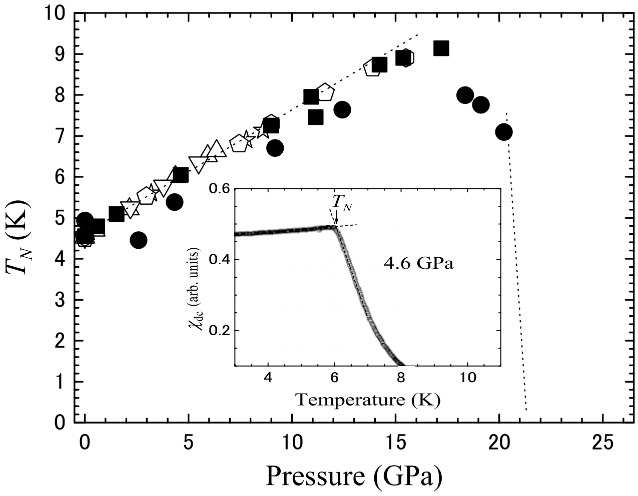


Figure 4. Pressure dependence of the Néel temperature T_N, which was assigned as the intersecting point of two tangential lines drawn on the $\chi(T)$ curves as shown in the inset. Solid squares and solid circles show the results from the $\chi(T)$ curves shown in figures 3(a) and (b), respectively. Other symbols show those from five other experiments with different samples, in which $\chi(T)$ curves were measured in order of increasing pressure.

decreases gradually and decreases so much at 21.9 GPa that the magnetic behaviour due to the ferromagnetic order in the basal plane is no longer detected within the experimental sensitivity of our apparatus. On decreasing the pressure to 11.1 GPa, the intralayer ferromagnetic behaviour recovered. In the second half of the sequence a similar change was observed, and the signal at 26 GPa decreased to the background level as observed at 21.9 GPa. Figure 4 shows the pressure dependence of the Néel temperature T_N, which was assigned as the intersecting point of two tangential lines drawn on the $\chi(T)$ curve as shown in the inset. Solid squares and circles show the results for the first half and the second half of the sequence, respectively. Other symbols show those from five other experiments with different samples, in which $\chi(T)$ curves were measured in order of increasing pressure. The T_N increases linearly with pressure at a rate of 0.3 K GPa^{-1}, reaches a maximum of about 9 K at around 17 GPa and then decreases rapidly to zero. Considering that the T_N values thus assigned have nearly the same pressure dependence for each sequence, the shape change of the $\chi(T)$ curve in the pressure sequence after 21.9 GPa may be attributed as an effect of the residual stress on the formation of the magnetic domain structure near the transition temperature. Similarly, the irreversible decrease in the magnitude of the $\chi(T)$ curve in the first half of the sequence is closely related to the formation of the magnetic domain structure, which is affected by pressure, because an increase in pressure works to create imperfections in the sample, suppressing the motion of the domain wall.

The rapid decrease of T_N above 17 GPa is very similar to the phenomenon of the pressure-induced magnetic transitions observed in K_2CuF_4 and Rb_2CuF_4, strongly suggesting a change in the arrangement of the CuF_6 octahedra from AFD to FD order in the basal plane of Cs_2CuF_4 around 21 GPa, though the critical pressure is more than two times larger than those of K_2CuF_4 and Rb_2CuF_4. Substituting Cs^+ ions at the cation sites seems to affect the nature of the structure of this magnetic system, resulting in an enhancement of the stiffness along the basal plane. A slight change in the cation site from those of K_2CuF_4 and Rb_2CuF_4 could explain such a remarkable change in the pressure characteristic of Cs_2CuF_4. Unfortunately, a precise structural analysis of Cs_2CuF_4 even at ambient pressure has not been performed yet because of its deliquescent nature. We believe that the present work suggests the possibility of a structural difference between Cs_2CuF_4 and the other two compounds. Detailed studies of the crystal structure of Cs_2CuF_4 at ambient pressure as well as at high pressures will be needed for further discussion.

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