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Magnetic Anisotropy in a spin 1/2 Quasi-One-Dimensional Antiferromagnetic Copper(II) Complex $\text{CuCl}_2(\text{pdz})$ with a Staggered g -tensor

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We report an unusual magnetic anisotropy in $S = 1/2$ 1D antiferromagnetic (AF) compound $\text{CuCl}_2(\text{pdz})$ (pdz = pyridazine). Magnetic susceptibility for $H // a^*$ and $H // c$ showed characteristic behavior in $S = 1/2$ 1D Heisenberg AF system, whereas that for $H // b$ exhibit a $1/T$ contribution. The origin of such the anomalous anisotropy in the magnetic susceptibility is explained by the staggered g -tensor of this compound.

Introduction

In recent years there have been extensive studies on the physical properties of one-dimensional (1D) electron systems because of their particular characteristic properties, e.g. quantum effects and nonlinear phenomena, etc. In the field of molecule-based magnetism, many attractive magnetic properties have been reported, such as spin-Peierls transition,¹⁻³ Haldane gap,⁴⁻⁵ and slow relaxation of magnetization in several ferro- or ferri-magnetic chain compounds.⁶⁻⁸

To date, numerous theoretical and experimental studies have been made on spin 1/2 1D antiferromagnetic (AF) Heisenberg compounds.⁹⁻¹¹ Many of these are concerned with Cu(II) chain compounds,¹²⁻¹⁴ where their magnetic behavior can be well described by the spin 1/2 isotropic Heisenberg model (Bonner-Fisher model). Recently, several Cu(II) chain compounds have shown to show an anisotropic behavior, which shows $1/T$ contribution when magnetic field is applied along to a specific direction.¹⁵ This behavior is not consistent with the uniform Heisenberg chain model. Recently, Oshikawa and Affleck theoretically proposed that staggered local g tensor of neighboring magnetic ions or the Dzyaloshinsky-Moriya (DM) interaction can cause the anisotropic magnetic susceptibility, and also gives rise to a magnetic field-induced spin gap.¹⁸ Although such an unusual behavior has been attracting attention as one of the novel quantum phenomena, the number of compounds, showing field-induced spin gap is few^{16,17} because most of such compounds are measured with polycrystalline sample, and in most cases, such a behavior is explained by paramagnetic impurities which are caused by chain ends or lattice defects. In this study, we studied an magnetic anisotropy of a spin 1/2 Quasi-1D compound $\text{CuCl}_2(\text{pdz})$ (pdz = pyridazine) with a large single crystals, in which staggered g -tensor is structurally expected.

Experimental

Polycrystalline sample of $\text{CuCl}_2(\text{pdz})$ was synthesized according to the literature.¹⁹ A large single crystal suitable for magnetic measurements using a single crystal with a size of $6 \times 0.7 \times 0.4 \text{ mm}^3$ (2.83 mg) was obtained by slow evaporation of concentrated hydrochloric acid solution of the $\text{CuCl}_2(\text{pdz})$. Although crystal structure of $\text{CuCl}_2(\text{pdz})$ was already reported,²⁰ an X-ray single-crystal structure analysis was performed to determine the orientations of the chains in relation to the crystal faces using a Rigaku AFC-7R diffractometer. The magnetic susceptibility measurements were performed using a Quantum Design MPMS-5 SQUID between 2 - 300 K. A single crystal of $\text{CuCl}_2(\text{pdz})$ was mounted on the cut Teflon® rod (2 mm \square) with an Apiezon® greases.

ESR spectra were measured with the Bruker EMX spectrometer equipped with a gas-flow type cryostat Oxford ESR 900.

Results and Discussion

Fig. 1 shows a perspective view of the crystal structure of $\text{CuCl}_2(\text{pdz})$. Although the crystal structure of $\text{CuCl}_2(\text{pdz})$ was previously reported by Fetzer *et al.*,²⁰ in the present study, we reanalyzed the crystal structure in order to relate the crystal outline to the crystallographic axes. Relation between crystal outline and crystallographic axes are shown in Figs. 1c and 1d. This complex forms 1D chains along the c axis and each copper ion is coordinated by two nitrogen atoms and two chloride ions, forming square planar coordination geometry. The Cu-N and Cu-Cl bonds are 2.040 and 2.298 Å, respectively. Blue and red arrows in Fig. 1 show one of the principal axes (normal to the square plane) of the crystal field. Although all copper ions are

crystallographically equivalent, the local principal axis of the crystal field of each copper ion is tilted to each other.

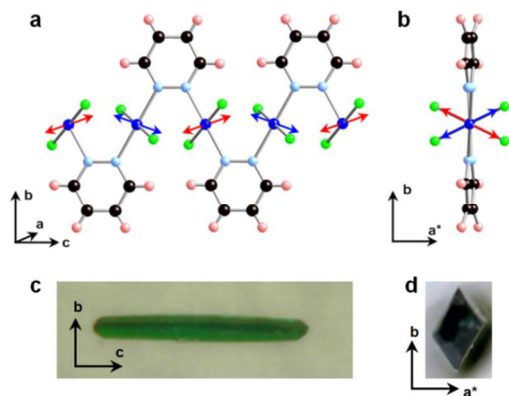


Fig. 1 Perspective views of a chain of $\text{CuCl}_2(\text{pdz})$ onto the a) bc and b) a^*b plane. Blue and red arrows show two principal axes of the crystal field. c) and d) is photographs of $\text{CuCl}_2(\text{pdz})$ taken from a directions same with those of a) and b), respectively.

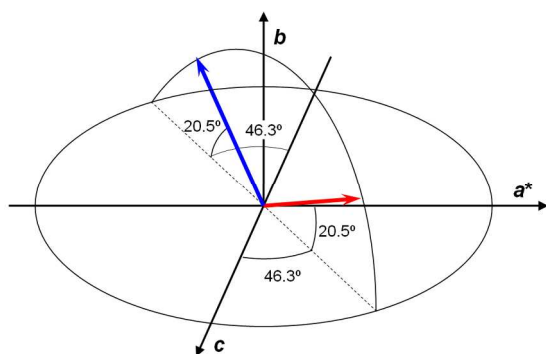


Fig. 2 A schematic geometrical view of the principal axes as shown in Fig. 1. The relation of the principal axes with respect to the crystallographic axes.

A schematic geometrical view of the principal axes of each $\text{Cu}(\text{II})$ ion is shown in Fig. 2. Blue and red arrows represent principal axes as shown in Fig. 1. Directions of blue and red arrows are tilted by 20.5° from the a^*c plane. The projected arrows onto a^*c plane are tilted by 46.3° from the bc plane.

In order to clarify the local g -tensor, we measured the orientation dependence of the ESR spectra (Fig. 3) at room temperature. The raw ESR spectra were shown in the ESI. We obtained $g_{a^*} = 2.161$, $g_b = 2.069$, $g_c = 2.160$. By assuming that the obtained g -values are the average of two magnetically inequivalent local g -tensors owing to the fast magnetic exchange, we can deconvolute the local g -value of each of the magnetically inequivalent two sublattices (blue and red lines in Fig. 3). The resulting diagonal elements of the g -tensor are $g_x = 2.04$, $g_y = 2.08$ and $g_z = 2.26$, where x , y and z directions are parallel to the N-Cu-N , Cl-Cu-Cl , and normal to the square plane directions, respectively. Detail of the analysis is given in the Electronic Supplementary Information (ESI). When considering the anisotropy of the g -value on the $\text{Cu}(\text{II})$ ions, the g -tensors are staggered for a pair of nearest neighbor copper ions. Therefore, for a general magnetic field direction, these ions become magnetically inequivalent.

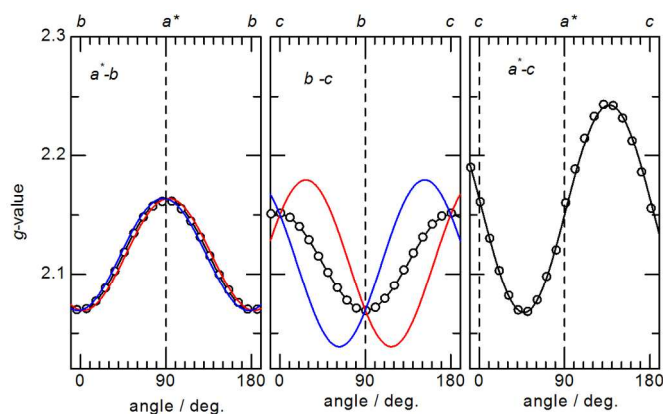


Fig. 3 Orientation dependence of the g -values (circles) for $\text{CuCl}_2(\text{pdz})$ obtained by the ESR spectra at room temperature. Blue and red lines show the fitted local g -values of the two magnetically inequivalent sublattices as shown in Fig. 2.

Fig. 4 shows magnetic susceptibilities of $\text{CuCl}_2(\text{pdz})$ for the magnetic field (10 kOe) (a) $H \parallel a^*$, (b) $H \parallel c$, and (c) $H \parallel b$. The data for $H \parallel a^*$ and $H \parallel c$ showed characteristic behavior of the spin $1/2$ 1D Heisenberg AF system. These susceptibilities can be fitted by a Bonner-Fisher curve,²¹ and we obtained the best fit values of $J/k_B = -54.4$ K and $g = 2.20$ for $H \parallel a^*$, where the Hamiltonian is defined as $H = -2J\sum S_i S_{i+1}$. The AF superexchange interaction is considered to operate between neighboring copper ions through the σ bond, which consists of the dx^2-y^2 orbital of a copper ion and the sp^2 orbital of pyridazine ligand. In many reported cases, the magnetic susceptibility of 1D-AF systems has a $1/T$ contribution at low temperatures due to the presence of small amounts of paramagnetic impurities, which arise from chain defects. In the present sample, however, no $1/T$ behavior was observed down to 5 K, suggesting that this crystal is high quality. For $H \parallel b$, the susceptibility exhibits a minimum at 5 K, suggesting that the magnetic order occurs at *ca.* 5 K due to the a weak inter-chain interaction through the π - π stacking of pyridazine molecules.

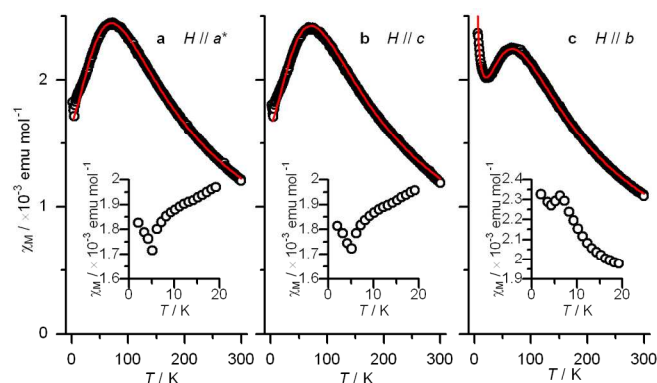


Fig. 4 Magnetic susceptibility of $\text{CuCl}_2(\text{pdz})$ for a) $H \parallel a^*$, b) $H \parallel c$, and c) $H \parallel b$ in 10 kOe. Red lines show the best fits to the Bonner-Fisher theory for a) and b), and by the sum of Bonner-Fisher and Curie components for c). Insets show the magnification of the low temperature regions.

When $H \parallel b$, the susceptibility could not be reproduced by the Bonner-Fisher curve alone and was finally fitted to the sum of a Bonner-Fisher and a Curie (C/T) contributions. Such behavior has been usually observed in systems that contain paramagnetic impurities. In this complex, however, no $1/T$ behavior was observed for $H \parallel a^*$ and $H \parallel c$. Thus, the observed $1/T$ behavior is not from magnetic impurity but from intrinsic origin. This unusual behavior observed in the present complex can be explained as follow.

When considering the anisotropy of the g -tensor and AF interactions between the nearest neighbor sites, the expected easy axis of each sublattice is shown by blue and red solid arrows, as illustrated in Fig. 2. Under the condition of $H \parallel a^*c$ plane, the vector sum of the blue and red arrows in Fig. 2 should be perpendicular to the applied field, which leads to the cancellation of the net magnetization along the direction of the field. For $H \parallel b$ axis, on the other hand, the vector sum is parallel to the applied field ($\parallel b$). Thus, the net magnetization along the chain survives. This can be the reason for the unusual magnetic anisotropy in the present system. Such an anisotropic Curie (C/T) contribution has been reported in several compounds showing field-induced gap. Thus, the present compound can also be a candidate material for field-induced gap system.

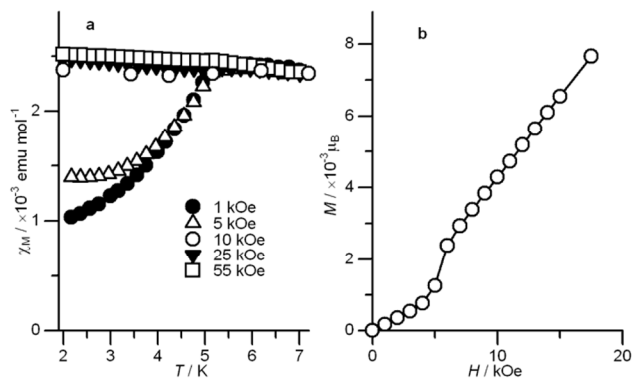


Fig. 5 a) Temperature dependence of magnetic susceptibilities measured at several magnetic fields ($H \parallel b$) and b) a magnetization curve at 2.0 K ($H \parallel b$) in $\text{CuCl}_2(\text{pdz})$

Fig. 5a shows the temperature and magnetic field dependence of the magnetic susceptibility at low temperature region ($H \parallel b$). Under a condition of $H \leq 5 \text{ kOe}$, the susceptibility was rapidly decreased with decreasing temperature. This result can be recognized as the antiferromagnetic magnetic ordering of this sample. On the other hand, no decrease of the susceptibility was observed under $H \geq 10 \text{ kOe}$. In order to investigate this behavior in detail, the magnetization (M - H) process measurement was carried out. The result is shown in Fig. 5b. A sudden increase of magnetization was observed between 5 and 6 kOe. This behavior suggests that some spin-flop transition occurs. A plausible mechanism of spin-flop transition is shown in Fig. 6. By considering the anisotropy of the g -tensor, intra- and inter-chain antiferromagnetic interactions, spin axes under

zero field are illustrated as Fig. 6a. When external field is applied parallel to b axis, the magnetization energy overcomes the inter-chain exchange energy above a critical field (H_c), resulting in a spin-flop transition at the field ($H_c \sim 5$ or 6 kOe). Spin arrangements above the critical field are illustrated as Fig. 6b.

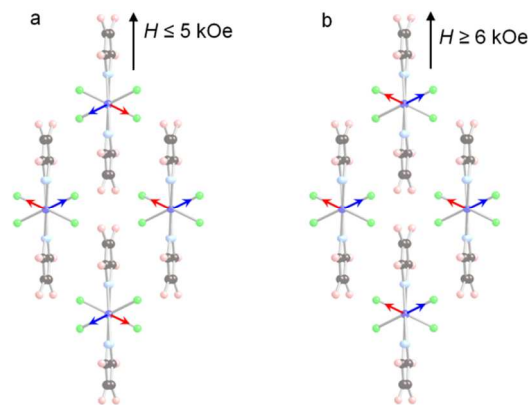


Fig. 6 Plausible spin directions for the antiferromagnetic ordered state under the external magnetic field a) below 5 kOe and b) above 6 kOe. Blue and red arrows indicate the spin directions of the magnetically inequivalent sublattices.

In order to estimate the field induced gap energy directly, the heat measurement in a magnetic field was carried out. Temperature dependence of heat capacities with the applied field $H = 0, 10, 30, 50$ and 70 kOe and $H \parallel b$ are shown in Fig. 7. A cusp was observed at ca. 5 K, which is attributable to the magnetic ordering of $\text{CuCl}_2(\text{pdz})$ at all measured magnetic fields. Heat capacity was slightly decreased with increasing magnetic field just above the critical temperature. Although this might be caused by the field induced gap, any quantitative discussion cannot be done because of the large cusp due to the magnetic ordering.

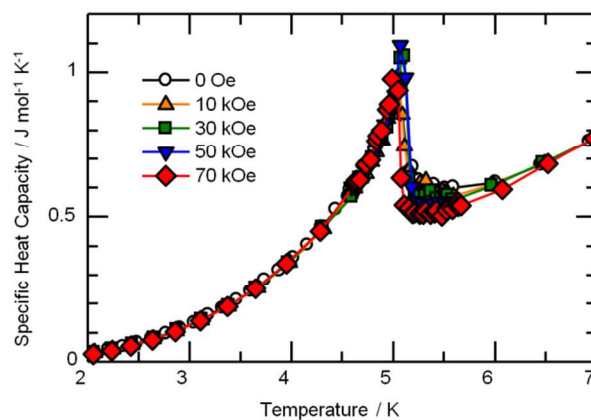


Fig. 7 Temperature dependence of heat capacities with the applied field $H = 0, 10, 30, 50$ and 70 kOe ($H \parallel b$).

Conclusions

In summary, we observed an unusual magnetic anisotropy in the spin 1/2 1D antiferromagnetic compound $\text{CuCl}_2(\text{pdz})$. Magnetic susceptibility shows almost no $1/T$ behavior in low temperature range at the condition of $H \parallel a^*$ and c , whereas $1/T$

behavior is observed below 20 K at $H // b$. This behavior can be accounted for by a staggered local crystal field of this compound. This compound is a candidate for a field-induced gap system.

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Notes and references

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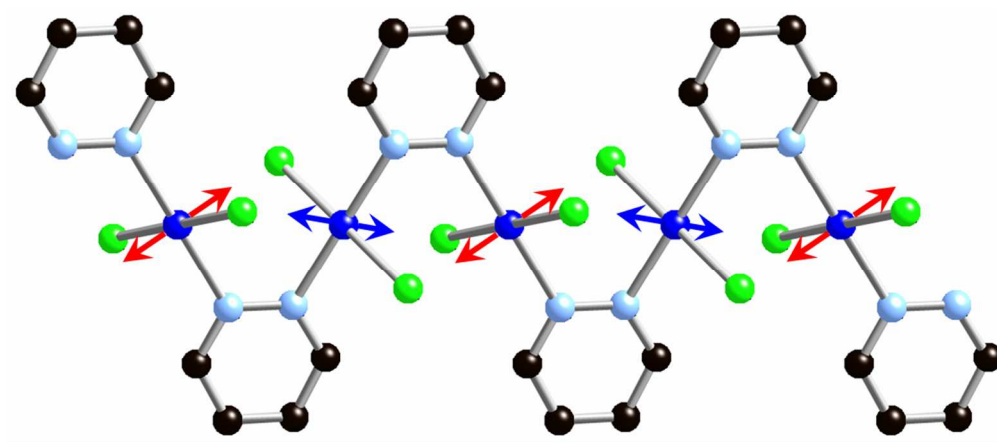
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† Electronic Supplementary Information (ESI) available: ESR spectra, detailed procedure of g-value analysis, magnetic susceptibility of polycrystalline sample and magnetization curve along a^* and c axes at 2.0 K. See DOI: 10.1039/b000000x/

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Graphical abstract