NMR study on the quasi-one dimensional antiferromagnet BaCo$_2$Si$_2$O$_7$

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Abstract. NMR study has been performed on the quasi-one dimensional antiferromagnet BaCo$_2$Si$_2$O$_7$, in which three inequivalent CoO$_4$ tetrahedra, slightly tilted from one another, are linked at vertices to form a chain along the easy-axis $c$. In its magnetically ordered state at 3.6 K, $^{59}$Co-NMR spectra were measured in the field region up to 12 T. From the observed three distinct sets of quadrupolar-split peak groups, three different hyperfine fields at Co sites were determined. They are slightly tilted from $c$-axis and are all different both in magnitude and direction, which is in agreement with the non-collinear magnetic structure.

1. Introduction

The relation between magnetic and crystal structure is a fundamental problem in magnetism. The chiral spin structure found recently in the B20 lattice such as MnSi demonstrates its importance[1,2], but on the contrary the simple collinear two-sublattice spin structure was found in CuSiO$_3$ with the spiral crystal structure[3,4]. The key parameter to determine the effect of the lattice is the Dzyaloshinsky-Moriya (DM) interaction, which tends to cant antiferromagnetic spins to form a non-collinear spin structure, which attracts much interest recently, because it is expected to cause a charge anomaly, and hence the multiferroics[5-7]. The title compound BaCo$_2$Si$_2$O$_7$ is a quasi-one dimensional antiferromagnet with $T_N = 21$ K, consisting of vertex-sharing three inequivalent CoO$_4$ tetrahedra, which are tilted from one another (Fig. 1) and are connected to form a chain along the $c$-axis[8]. So far, an intensive study by macroscopic measurements on the compound has revealed that it shows an easy-axis type anisotropy along the $c$-axis including an enhancement in the paramagnetic susceptibility along the $c$-axis and a weak ferromagnetic magnetization in the ordered state below $T_N$ at nearly zero field [8,9]. Though the latter seems to be quite consistent with the anisotropy, the $d^7$ configuration of Co atom in the tetrahedral environment leads usually to the isotropic spin state rather than the Ising-type one. The spin structure of the system is not reported until now. So, in order to investigate microscopically the spin state in this compound, we have performed NMR study in its ordered state. From the analysis of $^{59}$Co-spectra in the wide range of applied field 0-12 T, successful extraction of the hyperfine field at each inequivalent Co site will be demonstrated.

2. Experimental

The single crystalline sample was prepared by floating zone method [9]. The sample quality, as well as the macroscopic behavior was investigated by X-ray diffraction, specific heat, magnetic susceptibility[9]. The crystal structure of the compound belongs to the monoclinic space group of $C2/c$ [8]. For the angle $\beta = 90.299^\circ$ is close to $90^\circ$, the shape of unit cell can be considered as a cuboid.
For $^{59}$Co-NMR measurements, spectra were obtained by recording the spin-echo amplitude against the magnetic field ($\vec{H} \parallel c$), which was slowly ramped between 0 and 12 T. The resonance frequency was kept constant while ramping the field, and was changed between 44 and 110 MHz with a step of 1 MHz[10,11]. As the $^{59}$Co nucleus ($I = 7/2$) possesses the electric quadrupole moment, the quadrupolar splitting sensitively reflects the local environment, specifically the electric field gradient (EFG) tensor[12]. For the help for later discussion, we state here in detail the local structure around the Co atom. There are three crystallographically-in equivalent Co sites 1, 2 and 3. The shape of CuO$_4$ tetrahedra for each site is slightly different from one another, and also, each tetrahedron is slightly tilted from one another. As shown in Fig. 1, the site 3 includes the two tetrahedra, which are connected with the inversion symmetry, denoted as 3 and 3’. The line-ups of these Co sites along the two inequivalent chains $\alpha$ and $\beta$ in the unit cell are 3-1-3’-2-3 and 3’-2-3-1-3’, respectively. The EFG tensor for each Co site is calculated by the point charge model (PCM) approximation[13] and shown in Table 1. Reflecting the tilting of each tetrahedron, all the Co sites have different eigenvalues and principal axes. These tensors determines the quadrupolar split in each spectrum as described later. Note that each two corresponding Co sites in the chain $\alpha$ and $\beta$ have the identical EFG tensor. This means that the NMR signal from the corresponding two chains must be degenerated as long as the hyperfine field is the same.

### 3. Results and Discussion

Figure 2 shows field-swept NMR spectra measured with different resonance frequencies $\omega_0 = 43.83 - 113.83$ MHz. One can immediately find major three peak groups A, B and C, which are all quadrupolar split. The mass center for each group was extracted and plotted in Fig. 3, which shows the relation between $\omega_0$ and the field, where the signal is observed. There are the two branches of $\omega_0$, the one, which increases monotonically with increasing $H_0$, and the other, which decreases with increasing $H_0$ and takes a minimum and increases again, forming a parabola-like shape. There is no jump in data points up to 12 T, indicating that there is no spin-flip transitions in this field region. Carefully looking parabolas, one finds that it is slightly asymmetric, that is, the gradient at high field side is a little bit larger than that in low field.

We analyze this field-dependence of $\omega_0$ with a quite simple idea in the following. In general, NMR signal is observed when the total field $[\vec{H}_{\mu} + \vec{H}_{0}]$ matches $\omega_0/\gamma$, where $\gamma = 10.03$ (MHz/T) is the nuclear gyromagnetic ratio of $^{59}$Co nucleus, $\vec{H}_{0} = (0,0,H_0)$, the applied field, and $\vec{H}_{\mu}$, the hyperfine field at Co site produced by $\vec{\mu}$, the ordered moment of Co 3d-spins. If we assume the collinear and two-sub-lattice spin structure along the $c$-axis, that is, $\vec{H}_{\mu} = (0,0,\pm H_{\mu})$, then $\omega_0$ should trace the oblique rectangle shape shown by dashed lines in Fig. 3, which apparently does not accord with the observed $\omega_0$. In order to refine the model to reproduce the data, we take into account the two simple assumptions. One is that $\vec{H}_{\mu}$ may be slightly tilted from the $c$-axis as

![Fig 1. Schematic crystal structure of BaCo$_2$Si$_2$O$_7.$](image)

| Co | The largest eigenvalue of EFG tensor and its principal axis |
|----|----------------------------------------------------------|
| 1  | 0.0463 (+0.8815, 0, -0.4721) |
| 2  | 0.2132 (+0.9946, 0, -0.1039) |
| 3  | 0.1600 (+0.7682, ±0.457, +0.4483) |

Table 1. The largest eigenvalue (in the unit of esu/Å$^2$) and its principal axis of EFG, calculated by PCM for each Co site.
This effect \( H_\mu \), \( \alpha \). 10^5 - he data points \( \theta \) \( \cos T \). 5 \( H_\mu \), \( \alpha \). sin \( \phi \), \( \pm H_\mu \cos \theta \), where \( \phi \) and \( \theta \) are polar coordinates, and the plus and minus signs correspond to moments in two-sublattice, that is, the positive sign is taken for the one with the hyperfine field oriented along the applied field, and the negative sign, in the opposite direction. Another assumption is that with increasing \( H_0 \), \( \theta \) may change from its zero-field value \( \theta_0 \) as \( \theta = \theta_0 + aH_0 \) (\( \theta_0 + aH_0 \)), where \( a \) is a small proportional constant, for the sublattice with the hyperfine field oriented along the applied field (the opposite direction), respectively. This effect reflects the fact that with increasing field along the \( c \)-axis, the ordered moments change their direction slightly.

By adjusting those three constants \( \theta_0 \), \( a \) and \( H_\mu \), observed field dependence of \( \omega_0 \)'s for the three Co sites is well reproduced as shown by solid curves in Fig. 3. Especially, note that the field dependence for the signal from each sublattice was successfully reproduced; the data points below (above) 100 MHz corresponds to the moments with the \( c \)-component of the hyperfine field, \(-H_\mu \cos \theta \) \((+H_\mu \cos \theta)\). Obtained parameters are shown in Table 2. Considering the relative amplitude of signal, one can safely assign the group B to the Co site 3, which has twice a fraction of the other two. Thus, the group A and C are assigned either 1 or 2.

The assumption of tilted hyperfine field model can be justified by following three observations. First, the value of \( H_\mu \approx 10 \) T for all three Co sites is reasonable for divalent transition metals. Next, the model well explains the fact that signal disappears at the parabola’s bottom, where the total field becomes parallel with \( h_1 \), the oscillating field for the NMR measurement. The third point is that the quadupolar splitting width is found to be field dependent. For the quadupolar splitting width is proportional to \( 1 - 3 \cos^2 \Theta \), where \( \Theta \) is the angle between the total field \( \vec{H}_\mu - \vec{H}_0 \) and the principal axis of EFG, shown in Table 1, one can see that the width should change with the applied-field only when \( \vec{H}_\mu \) is tilted from \( \vec{H}_0 \), hence from the \( c \)-axis. Thus, we can conclude here that the hyperfine field at each Co site is non-collinear, which suggests the non-collinear spin structure.

Next, we proceed and discuss a possible arrangement of ordered moments. If one accepts the criterion to minimize the antiferromagnetic

| Co   | \( H_\mu \)(T) | \( \theta_0 \)(deg) | \( a \)(deg/T) |
|------|---------------|----------------|-------------|
| 1 or 2 | 10.3(1)       | 36(2)          | 0.45(3)     |
| 2 or 1 | 10.2(1)       | 15(2)          | 0.40(3)     |
| 3    | 10.4(1)       | 22(2)          | 0.50(3)     |

Table 2. The size, direction and coefficient for field dependence of the hyperfine field for each Co site.

Fig. 2. Field-swept spectra of \(^{63}\)Co-NMR measured with various frequencies \( \omega_0 \). Each spectrum is drawn shifted in proportion to \( \omega_0 \). The small sharp peaks are spurious signal of \(^1\)H, \(^{19}\)F and \(^{63,65}\)Cu coming from the probe.

Fig. 3 Signal positions of three Co sites for various NMR frequencies \( \omega_0 \). The dashed line shows the collinear model, and the solid curves, non-collinear one. The fitted parameters are shown in Table 2.
exchange energy, the spin structure in each chain should be like, 3(+)-1(−)-3′(+)-2(−)-3(+), or 3(−)-1(+)-3′(−)-2(+)-3(−), where signs denote that of the c-component in hyperfine field, and hence the sublattice. These two possible patterns may form a domain structure, which can easily be inverted by applying a low field. Within each domain, there is an imbalance in the net c-component of $\hat{H}_\mu$; this may explain the finite weakferromagnetic moment along the c-axis. However, one should note here that the ordered moment $\vec{\mu}$ is not necessarily parallel with the hyperfine field; the two are connected with the hyperfine coupling tensor. The tensor may have an appreciable anisotropy reflecting the shape of 3$d$ orbitals. In order to determine the moment direction $\vec{\mu}$ completely, the knowledge of hyperfine coupling tensor is indispensable, and for its determination by so-called $K-\chi$ plot method, the NMR measurement in the paramagnetic state is now in progress. Finally, we note here that the azimuth $\phi$’s, which are remained to be undetermined, is expected to be obtained by investigating the applied-field dependence of quadrupolar splitting with a higher precision, which is also in progress.

Summary

$^{59}$Co-NMR study has been performed on the quasi one dimensional antiferromagnet BaCo$_2$Si$_2$O$_7$ in its ordered state. The hyperfine field at each four inequivalent Co sites was determined to be approximately 10 T, and tilted appreciably from the c-axis, which is in agreement with the non-collinear-type spin structure.

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