Spin waves and the origin of commensurate magnetism in Ba$_2$CoGe$_2$O$_7$.

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The square-lattice antiferromagnet Ba$_2$CoGe$_2$O$_7$ is studied by means of neutron diffraction and inelastic scattering. This material is isostructural to the well-known Dzyaloshinskii-Moriya helimagnet Ba$_2$CuGe$_2$O$_7$ but exhibits commensurate long-range Néel order at low temperatures. Measurements of the spin wave dispersion relation reveal strong in-plane anisotropy that is the likely reason for the suppression of helimagnetism.

I. INTRODUCTION

Several years ago the square-lattice helimagnet Ba$_2$CuGe$_2$O$_7$ was recognized as an extremely interesting material for studying Dzyaloshinskii-Moriya (DM) off-diagonal exchange interactions. A great deal of attention was given to the incommensurate nature of the magnetic ground state, a unique field-induced incommensurato-commensurate (IC) transition and the field dependence of the spiral spin structure. Studies of the spin wave spectrum in the incommensurate and commensurate phases led to the first direct observation of a new type of magnetic interactions in insulators, the so-called KSEA term. Additional theoretical studies shed light on the nature of the so-called “intermediate phase”.

A recent study indicated that an IC transition in Ba$_2$CoGe$_2$O$_7$ can be induced not only by applying an external magnetic field, but also by a partial chemical substitution of the spin-carrying Cu$^{2+}$ ions by Co$^{2+}$. For all Co-concentrations $x$ the solid solution Ba$_2$(Co$_x$Cu$_{1-x}$)Ge$_2$O$_7$ orders magnetically at temperatures between $T_N = 3.2$ K ($x = 0$) and $T_N = 6.7$ K ($x = 1$). Magnetization data suggest that the helimagnetic state realized at $x = 0$ gives way to a canted weak-ferromagnetic structure at some critical concentration $x_c$, estimated to be between 0.05 and 0.1. The mechanism of this transition or crossover is poorly understood. One possible explanation was proposed in Ref. 13.

The structure of Ba$_2$(Co$_x$Cu$_{1-x}$)Ge$_2$O$_7$ is tetragonal, the $S = 1/2$ Cu$^{2+}$ or $S = 3/2$ Co$^{2+}$ ions forming a square lattice within the $(a, b)$ crystallographic plane. The dominant interaction is the antiferromagnetic (AF) coupling $J$ between nearest-neighbor (NN) sites along the $(1, 1, 0)$ direction. In the $x = 0$ compound the helimagnetic distortion is caused by the in-plane component $D_{xy}$ of the Dzyaloshinskii vector $D_x$ associated with the same Cu-Cu bonds. This component retains its direction from one bond to the next, and thus favors a spin spiral state. In contrast, the out-of-plane component $D_z$ is sign-alternating and stabilizes a weak-ferromagnetic structure. The $z$-axis component of $D$ was never detected in Ba$_2$CuGe$_2$O$_7$, where it was assumed to be weak. In Ref. 13 it was tentatively suggested that the out-of-plane component is dominant in the Co-based $x = 1$ material, and stabilizes a commensurate magnetic structure. To verify this hypothesis and better understand the underlying physics, a detailed knowledge of magnetic interactions not only in Ba$_2$CuGe$_2$O$_7$ ($x = 0$), but also in Ba$_2$CoGe$_2$O$_7$ ($x = 1$) is required. In the present paper we report the results of neutron diffraction and inelastic neutron scattering measurements on the $x = 1$ material Ba$_2$CoGe$_2$O$_7$.

II. EXPERIMENTAL

To date, the exact crystal structure of Ba$_2$CoGe$_2$O$_7$ has not been determined. However, powder data indicate that the material is very similar to its Cu-based counterpart and is characterized by the $P4_2/m$ crystallographic space group. The lattice parameters for Ba$_2$CoGe$_2$O$_7$ are $a = b = 8.410$ Å and $c = 5.537$ Å, as measured at $T = 10$ K. In each crystallographic unit cell the magnetic Co$^{2+}$ ions are located at $(0, 0, 0)$ and $(0.5, 0.5, 0)$ positions. The NN Co-Co distance is thus along the $(1, 1, 0)$ direction and equal to $a/\sqrt{2} \approx 5.9$ Å. For the present study we utilized two single crystal samples prepared using the floating zone technique. Both
crystals were cylindrical, roughly 5 mm diameter × 50 mm long, with a mosaic spread of about 0.4°.

The first series of experiments was carried out at the HB1 3-axis spectrometer installed at the High Flux Isotope reactor at Oak Ridge National Laboratory (Setup I). Its main purpose was to determine the spin arrangement in the magnetically ordered state. The sample was mounted with the b axis vertical making (h, 0, l) reflections accessible for measurements. Neutrons with a fixed incident energy of 13.5 meV were used in combination with a pyrolytic graphite (PG) monochromator and analyzer, 30°–40°–20°–120° collimation, and a PG higher-order filter. Sample environment was a closed-cycle refrigerator that allowed measurements at temperatures down to 3.5 K. To isolate the magnetic contribution, integrated intensities were measured in a series of rocking curves at T = 3.5 K < T_{N} and T = 10 K > T_{K}. While using Setup I, it became apparent that the study of magnetic excitations could be much better carried out using of a cold neutron instrument, the relevant energy scale for Ba$_2$CoGe$_2$O$_7$ being about 2 meV. These measurements were therefore performed at the TASP 3-axis spectrometer installed at the SINQ spallation source at Paul Scherrer Institut (Setup II). Neutrons with a fixed final energy of 5.5 meV were used with PG monochromator and analyzer, and a PG filter after the sample. The beam collimation was (guide) – 80°–80°–(open). The sample was mounted with the c axis vertical, making momentum transfers in the (h, k, 0) reciprocal-space plane accessible for measurement. Spin wave dispersion curves were measured along the (h, 0, 0) and (h, h, 0) directions using constant-Q scans in the energy range 0–4 meV. The sample environment was a standard “ILL Orange” He-4 flow cryostat, and most of the data were taken at T = 2 K.

III. RESULTS

A. A model for the spin structure

In the Ba$_2$CuGe$_2$O$_7$ system magnetic ordering gives rise to incommensurate peaks surrounding the integer h, k and l reciprocal-space points. In contrast, in Ba$_2$CoGe$_2$O$_7$ magnetic Bragg scattering was detected below $T_{N}$ = 6.7 K at strictly commensurate positions h, k and l-integer. Due to their location, the magnetic reflections, except those on the (h, 0, 0) and (0, k, 0) reciprocal-space rods, coincide with nuclear ones. Figure 1 shows the measured temperature dependence of the (1, 0, 0) peak intensity (Setup II). The insert shows rocking curves measured above and below the ordering temperature. The appreciable residual intensity seen at T > $T_{N}$ at the (1, 0, 0) forbidden nuclear peak position is due to multiple scattering. 19 non-equivalent magnetic Bragg intensities measured using Setup I were normalized by the resolution volume, which in a 3-axis experiment plays the role of the Lorentz factor. In our case it was calculated using the Cooper-Nathans approximation. The resolution-corrected magnetic intensities $I_{obs}$ are listed in Table I. The observed intensity pattern indicates a planar spin arrangement, with all spins confined to the (a, b) plane, and nearest-neighbor spins aligned antiparallel with each other. The alignment of nearest-neighbor spins along the c direction is “ferromagnetic”. Such a spin structure is identical to the one in the commensurate spin-flop phase of Ba$_2$CuGe$_2$O$_7$ stabilized by an external magnetic field applied along the c axis. As can be seen from Table I where $I_{calc}$ are the calculated magnetic intensities, this simple collinear model reproduces our limited diffraction data for Ba$_2$CoGe$_2$O$_7$ rather well. Due to the possibility of antiferromagnetic domains, the spin orientation within the (a, b) plane could not be determined unambiguously. Neither did we measure the actual magnitude of the ordered moment, since the crystallographic data needed to bring the measured magnetic intensities to an absolute scale is not currently available for Ba$_2$CoGe$_2$O$_7$. It is reasonable to assume that at low temperatures the sublattice magnetization is close to its classical saturation value. Indeed, this is the case in the $S = 1/2$ Cu$^{2+}$-system, where quantum fluctuations may be expected to be even stronger than in the $S = 3/2$ Co$^{2+}$ compound.

B. Spin waves

The dispersion of spin wave excitations in Ba$_2$CoGe$_2$O$_7$ was found to be quite different from that in Ba$_2$CuGe$_2$O$_7$. Figure 2 shows typical constant-q
TABLE I: Magnetic Bragg intensities measured in Ba$_2$CoGe$_2$O$_7$ at $T = 3.5$ K in comparison to those calculated for the proposed ($a, b$)-planar collinear antiferromagnetic structure.

| $h$ | $k$ | $l$ | $I_{\text{calc}}$ | $I_{\text{obs}}$ | $\sigma_{\text{obs}}$ | $I_{\text{obs}} - I_{\text{calc}}$ | $\sigma_{\text{obs}}^{-1}$ |
|-----|-----|-----|-------------------|-----------------|----------------|-----------------------------|---------------------|
| -1  | 0   | 0   | 9031             | 8226            | 186            | -4.3                        | 0.0                 |
| -2  | 0   | 0   | 100              | 129             | 84             | 0.8                         | 0.0                 |
| -3  | 0   | 0   | 5577             | 5702            | 84             | 1.5                         | 0.0                 |
| -4  | 0   | 0   | 1405             | 4013            | 0.4            | 0.0                         | 0.0                 |
| -5  | 0   | 0   | 2340             | 3954            | 212            | 7.6                         | 0.0                 |
| 0   | 1   | 0   | -22              | 1323            | -4.3           | 0.0                         | 0.0                 |
| -1  | 1   | 0   | 13294            | 12187           | 230            | -4.8                        | 0.0                 |
| -2  | 1   | 0   | -59              | 223             | -0.3           | 0.0                         | 0.0                 |
| -3  | 1   | 0   | 5880             | 875             | 1260           | -4.0                        | 0.0                 |
| -4  | 1   | 0   | 220              | 301             | 0.7            | 0.0                         | 0.0                 |
| -5  | 1   | 0   | 2260             | 3257            | 1690           | 0.6                         | 0.0                 |
| 0   | 2   | 0   | 21               | 106             | 0.2            | 0.0                         | 0.0                 |
| -2  | 2   | 0   | 70               | 243             | 0.3            | 0.0                         | 0.0                 |
| -3  | 2   | 0   | 5018             | 8775            | 242            | 15.5                        | 0.0                 |
| -4  | 2   | 0   | -150             | 325             | -0.5           | 0.0                         | 0.0                 |
| 0   | 3   | 0   | 689              | 3308            | 0.2            | 0.0                         | 0.0                 |
| -1  | 3   | 0   | 5400             | 5081            | 1897           | -0.2                        | 0.0                 |
| -2  | 3   | 0   | 269              | 123             | 2.2            | 0.0                         | 0.0                 |
| -3  | 3   | 0   | 3134             | 4115            | 6000           | 0.2                         | 0.0                 |

FIG. 2: Typical constant-Q scans measured in Ba$_2$CoGe$_2$O$_7$ at $T = 2$ K. The solid lines are Gaussian fits to the data. Shaded areas represent the background level.

FIG. 3: Dispersion of spin waves along the $(1, 0, 0)$ and $(1, 1, 0)$ reciprocal-space directions measured in Ba$_2$CoGe$_2$O$_7$ at $T = 2$ K (symbols). The solid and dashed lines represent the two spin wave branches in the model defined by Eq. 1 with dispersion relations given by Eq. 2 and parameters chosen to best-fit the data.

C. Data analysis

The observed dispersion of spin wave excitations can be understood in the framework of linear spin wave theory.
To construct a model spin Hamiltonian, we assumed that the dominant magnetic interactions in Ba$_2$CoGe$_2$O$_7$ are those between nearest-neighbor spins in the $(a, b)$ plane, as is the case in Ba$_2$CuGe$_2$O$_7$. Given that the $S = 3/2$ Co$^{2+}$ ions are frequently associated with a large magnetic anisotropy, in our model we allowed this coupling to be anisotropic, and also included a single-ion anisotropy term. The resulting model Hamiltonian is written as:

$$\hat{H} = \sum_m \sum_n \left[ J_z S_m^z S_n^z + J_{\perp} S_m^x S_n^x + J_{\parallel} S_m^y S_n^y \right] + A \sum_m \left[ S_m^z \right]^2 + A \sum_n \left[ S_n^z \right]^2. \tag{1}$$

Here $m$ and $n$ label the spins on the two antiferromagnetic square sublattices with origins at $(0, 0, 0)$ and $(0.5, 0.5, 0)$, respectively, and $\sum$ stands for summation over nearest neighbors. Note that the interactions along the $c$ axis are not included in the above expression. They were not measured directly in this work, and are likely to be ferromagnetic, due to the value of the magnetic easy-plane anisotropy in our model. Excellent fits to the data are obtained assuming $S = 3/2$ and using $J = 0.103(1)$ meV and $A = 2.58(3)$. Dispersion curves calculated using these parameters are shown in dashed and solid lines in Fig. 4. Unlike its Cu-based counterpart, Ba$_2$CoGe$_2$O$_7$ is characterized by very strong magnetic easy-plane anisotropy.

IV. DISCUSSION

The strong anisotropy effects in Ba$_2$CoGe$_2$O$_7$ push all spins in the system into the $(a, b)$ crystallographic plane. This effect is similar to that of a magnetic field applied along the $c$ axis that favors an $(a, b)$-planar state in Ba$_2$CuGe$_2$O$_7$. Since the helimagnet-forming uniform component $D_{xy}$ of the Dzyaloshinskii vector is itself in the $(a, b)$ plane, forcing the spins into the $(a, b)$ plane makes the corresponding triple-product in the Hamiltonian $D_{xy}(S_m \times S_n)$ vanish. Only the non-helimagnet-forming sign-alternating $z$-axis component of $D$ remains relevant. As a result, the spin structure may be slightly canted, but is, nevertheless, commensurate.

It is important to stress that effective easy-plane anisotropy was previously detected in Ba$_2$CuGe$_2$O$_7$ as well. However, in this $S = 1/2$ Cu-based system any single-ion term is reduced to a constant and is therefore irrelevant. The only source of anisotropy is a two-ion term, which was shown to be caused by the so-called KSEA interactions. The latter are a very weak effect with an energy scale of $D^2/J \sim 3 \cdot 10^{-2}$. On a square lattice KSEA interactions happen to be just strong enough to distort the helical structure, but not to fully destroy incommensurability. In contrast, as follows from the present study, easy-plane anisotropy in Ba$_2$CoGe$_2$O$_7$ is much stronger, of the order of $J$ itself. The anisotropy is probably due to single-ion effects that are only allowed for $S > 1/2$, and its magnitude is well beyond the critical value needed to destroy the helimagnetic state.

The results discussed above allows us to speculate about the IC transition in Ba$_2$(Co$_x$Cu$_{1-x}$)Ge$_2$O$_7$ that occurs with increasing Co-concentration $x$. Each Co-impurity strongly "pins" the original spiral at the impurity site, firmly conforming the corresponding spin to the $(a, b)$ plane. Helimagnetic correlations are totally destroyed when the characteristic distance between such strong-pinning locations becomes comparable with the period of the unperturbed spiral, which in Ba$_2$CuGe$_2$O$_7$ is roughly 40 nearest-neighbor bonds. This suggests a critical concentration of about $x \approx 2\%$, in reasonable agreement with bulk magnetization data of Ref. 13.

V. CONCLUSION

To summarize, the commensurate nature of the ground state in Ba$_2$CoGe$_2$O$_7$ is primarily due not to a dominant staggered component of the Dzyaloshinskii vector, but to easy-plane anisotropy effects that are orders of magnitude stronger than typical Dzyaloshinskii-Moriya or KSEA interactions. As a result, the destruction of helimagnetism in Ba$_2$(Co$_x$Cu$_{1-x}$)Ge$_2$O$_7$ occurs very rapidly with increasing Co-concentration, as soon as the mean distance between impurities becomes comparable to the period of the spin spiral.
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