Field-induced Commensurate-Incommensurate phase transition in a Dzyaloshinskii-Moriya spiral antiferromagnet.

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We report an observation of a commensurate-incommensurate phase transition in a Dzyaloshinskii-Moriya spiral magnet Ba$_2$CuGe$_2$O$_7$. The transition is induced by applying a magnetic field in the plane of spin rotation. In this experiment we have direct control over the strength of the commensurate potential, while the preferred incommensurate period of the spin system remains unchanged. Experimental results for the period of the soliton lattice and bulk magnetization as a function of external magnetic field are in quantitative agreement with theory.

Studies of Commensurate-Incommensurate (CI) phase transitions have a long history, dating back to pioneering works of Frenkel and Kontorova [1] and Frank and van der Merwe [2]. Since then CI transitions were discovered and studied in a number of such seemingly unrelated systems as noble gas monolayers adsorbed on graphite surface [3,4], charge density wave materials [5,6], and rare-earth magnets [7] (For comprehensive reviews see for example Ref. [8]). As a rule, CI transitions result from a competition between two distinct terms in the Hamiltonian that have different “built-in” spatial periodicities and are often referred to as potential and elastic energy, respectively. The potential energy by definition favors a structure commensurate with the crystal lattice. The elastic term is intrinsic to the system where the transition occurs, and has a different “natural” built-in period. In many known realizations of CI, such as adsorbed gas monolayers, it is the period set by the elastic term that can be varied in an experiment to drive the transition, whereas both the strength and the period of the potential remain constant. In other systems, such as rare-earth magnets, both the elastic term (exchange coupling between spins) and the potential (magnetic anisotropy) can be changed, but only indirectly, by varying the temperature.

From the very start it was clear that in its purest form a CI transition may be driven by the change of the strength of the potential alone, with the two “built-in” periods remaining constant. An elegant experimental realization of this type of CI was first proposed by Dzyaloshinskii [9], who considered an incommensurate spiral magnetic structure in a magnetic field applied in the plane of rotation of spins. In this model incommensurability is intrinsic to the spin system and results from spin-spin interactions. The role of the potential is played solely by an external magnetic field $H$, that favors a commensurate spin-flop state. In a real magnetic material with this type of CI transition an experimentalist would have a convenient handle on the strength of the potential term, adjusting it by simply changing the magnetic field. Such systems are not easy to find. In most spiral magnets, e.g., cubic MnSi [10] and FeGe [11], even a small field is sufficient to realign the spin plane perpendicular to the field direction. While RbMnBr$_3$ [12] may actually be one material where this does not occur, to our knowledge, the most crucial quantities, namely the incommensurability parameter $\zeta$ and magnetization $M$, have not been measured as a function of the external field in any “clean” realization of Dzyaloshinskii’s model to date. In the present paper we report the first direct experimental observation of a Dzyaloshinskii-type field-induced CI transition in Ba$_2$CuGe$_2$O$_7$, also presenting experimental data for $\zeta(H)$ and $M(H)$. On the theoretical side we go beyond a qualitative analysis of the critical properties (close to the phase transition), as was previously done by Dzyaloshinskii. Dealing with this particular system, we construct an exactly solvable model and derive exact results that are in quantitative agreement with experiment throughout the entire phase diagram.

The structural and magnetic properties of Ba$_2$CuGe$_2$O$_7$ are discussed in detail in Ref. [13]. In the layered tetragonal crystal structure the magnetic Cu$^{2+}$ sites form a square lattice with nearest-neighbor (nn) distances of 6 Å along the (1,1,0) and (1,-1,0) directions, respectively. The low-temperature ($T_N = 3.26$ K) magnetic phase is a weak distortion of the Néel spin arrangement, with all spins confined to the (1, −1, 0) plane and the staggered magnetization slowly rotating upon translation along the (1,1,0) direction. The propagation vector is $(1 + \zeta, \zeta, 0)$, where
\( \zeta = 0.027 \). Only the nearest-neighbor in-plane antiferromagnetic exchange constant is significant and is equal to \( J_{ab} = 0.48 \) meV. The coupling between adjacent Cu-planes is ferromagnetic, with \( |J_c|/|J_{ab}| \approx 1/37 \). We have previously suggested that the incommensurate structure is a result of Dzyaloshinskii-Moriya (DM) antisyymmetric exchange interactions. The corresponding term in the Hamiltonian can be written as \( \mathbf{D}(\mathbf{S}_1 \times \mathbf{S}_2) \), where \( \times \) denotes the vector product and \( \mathbf{D} \) is a vector associated with the oriented bond between the two interacting spins.

From the symmetry properties of the lattice we deduce that for a bond between two nn Cu sites along the \((1,1,0)\) direction, the only allowed components of \( \mathbf{D} \) are those along \((1,-1,0)\) and \((0,0,1)\), respectively (Fig. 1). The \((1,-1,0)\)-component does not change sign from one bond to the next, while the \((0,0,1)\) component is sign-alternating. It is the uniform component that is liable for the incommensurate distortion of the Néel structure, and for the rest of the paper we shall ignore the oscillating component, assuming that \( \mathbf{D} \) is in the \((a,b)\) plane. The interaction energy is minimized when all spins are perpendicular to \( \mathbf{D} \). The total exchange energy of the pair of nearest-neighbor spins is given by \( 2J_{ab}\cos \phi + D\sin \phi = \sqrt{4J_{ab}^2 + D^2}\cos(\phi - \alpha) \), where \( \phi \) is the angle between spins, and \( \alpha = \arctan D/2J_{ab} \). The energy is a minimum at \( \phi = \pi + \alpha \). The classical ground state is therefore a spin-spiral, with all spins in the \((1,-1,0)\) plane, and the angle between subsequent spins equal to \( \pi + \alpha \). The angle \( \alpha \) is related to the propagation vector \( \zeta \) by \( \alpha = 2\pi \frac{\zeta}{\sqrt{3}} \approx 10^\circ \). Precisely this spin configuration was found in the initial zero-field neutron diffraction experiments 14,15.

The central experimental result of this paper is the observation of a CI transition in Ba$_2$CuGe$_2$O$_7$, induced by a magnetic field applied along the \((0,0,1)\) direction. Single-crystal magnetization measurements were performed using a conventional DC-squid magnetometer in the temperature range 2–300 K. Experimental \( \chi(H) \equiv \frac{dM}{dT} \) for \( T = 2 \) K are shown in Fig. 3. For \( \mathbf{H} || a \) no anomalies are observed. In contrast, when the field is applied along the \( c \)-axis, a distinct feature is seen around \( H = 2 \) T and indicates the presence of a magnetic phase transition. Neutron diffraction experiments were carried out on the H9 (cold beam) and H4M (thermal beam) 3-axis spectrometers at the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory on a \( \approx 4 \times 4 \times 4 \) mm$^3$ single-crystal sample, in the temperature range 1.3–5 K and magnetic fields up to 6.5 T, applied along the \( c \)-axis of the crystal 13,16. In zero field, at \( T = 2.4 \) K \( < T_N \), elastic scans along the \((1 + \zeta, -\zeta, 0)\) direction show magnetic Bragg reflections centered at an incommensurate position \( \zeta = \pm 0.0273 \) (Ref. 13, Fig. 3b). As the magnetic field increases, the peak moves in closer to the antiferromagnetic zone-center at \((1,0,0)\) [Fig. 3, insert (a)]. At \( H > H_c \approx 2.3 \) T the satellites at \((1 \pm \zeta, \pm \zeta, 0)\) are no longer observed, but are replaced by a single peak at the C-point \((1,0,0)\) [Fig. 3, insert (b)]. The magnetic structure thus becomes commensurate. The experimental field-dependence of the propagation vector \( \zeta \) is shown in the main panel of Fig. 3.

To quantitatively describe the field-dependent behaviour, we follow the approach of Dzyaloshinskii 17. We assume that the vector of local staggered magnetization at point \( \mathbf{r} \) remains in the \((1,0,0)\) plane and forms angle \( \theta(\mathbf{r}) \) with respect to the \( c \)-axis. The free energy per Cu-plane in the continuous limit is then given by:

\[
F = \int \left[ \left( \frac{\rho_s}{2} \left( \frac{\partial \theta(\mathbf{r})}{\partial x} - \frac{\alpha}{\Lambda} \right)^2 + \left( \frac{\partial \mathbf{r}(\mathbf{r})}{\partial y} \right)^2 + \gamma \left( \frac{\partial \theta(\mathbf{r})}{\partial z} \right)^2 \right) - \frac{(\chi_\perp - \chi_\parallel)H^2}{2} \sin^2 \theta(\mathbf{r}) \right] dxdy . \tag{1}
\]

Here the axes \( x \), \( y \), and \( z \) run along the \((1,1,0)\), \((1,-1,0)\) and \((0,0,1)\) directions, respectively, and \( \mathbf{r} = (x, y, z) \). The first term is the total elastic energy of exchange interactions, and favors a spiral structure of period \( 2\pi \alpha / \Lambda \). In Eq. (1) \( \Lambda \) is the in-plane nn Cu-Cu distance, and \( \rho_s \) is the in-plane spin stiffness, that for classical spins at zero temperature is given by \( \rho_s(0) = \sqrt{J_{ab}^2 + D^2} \). \( \gamma \) is the spin stiffness anisotropy defined by \( \gamma(\Lambda c/\Lambda)^2 = |J_c|/|J_{ab}| \approx 1/37 \) for Ba$_2$CuGe$_2$O$_7$. The second term represents the Zeeman energy. \( \chi_\parallel(T) \) and \( \chi_\perp(T) \) are defined as magnetic susceptibilities with respect to fields that rotate along with the spiral structure and are parallel or perpendicular to the local staggered magnetization, respectively. In the paramagnetic phase \( \chi_\parallel(T) = \chi_\perp(T) \), while at \( T = 0 \) the classical result is \( \chi_\perp(0) = (g\mu_B)^2/(8J_{ab}\Lambda^2) \), and \( \chi_\parallel(0) = 0 \). The equilibrium spin configuration should minimize the free energy (1), and therefore satisfy

\[
\frac{\partial^2 \theta}{\partial x^2} = -\frac{(\chi_\perp - \chi_\parallel)H^2}{\rho_s} \sin \theta \cos \theta = -\frac{1}{2\Gamma^2} \sin 2\theta , \tag{2}
\]

where \( \Gamma = (\rho_s/H^2(\chi_\perp - \chi_\parallel))^{1/2} \).

Expression (2) has the form of the sine-Gordon equation, that is central to describing CI transitions in many systems, and its “soliton lattice” solutions are well-known:

\[
\theta(x) = \arctan (am(x/\beta \Gamma, \beta)) , \tag{3}
\]

where \( am(x, \beta) \) is the Jacobi elliptic function of modulus \( \beta \). Analogues of Eqs. (1) and (2) were derived in Ref. 9. To obtain exact results for \( \zeta(H) \) and \( M(H) \), however, we make one additional crucial step. For each value of \( H \) of all valid solutions, labeled by \( \beta \), one has to choose the one that indeed corresponds to the global minimum of the free energy. This is done by substituting Eq. (3) into Eq. (1) and minimizing the resulting expression with respect to \( \beta \). After some algebra we find that \( F \) is minimized when
One gets:

$$H_c = \frac{\pi \alpha}{2\Lambda} \sqrt{\frac{\rho_s}{\chi_\perp - \chi_\parallel}} \cdot (5)$$

where $E(\beta)$ is the elliptic integral of the second kind. $H_c$ is the critical field at which the CI transition occurs [3]. Indeed, for $H > H_c$, the spin structure is given by the soliton-free solution $\theta(x) \equiv \pi/2$, which corresponds to a commensurate spin-flow phase, as visualized in Fig. 1(a). The staggered magnetization in this case is parallel to the $x$-axis and the spins are slightly tilted in the direction of the field. In the limit $H = 0$ one has $\beta \rightarrow 0$ and $\theta(x) = \frac{\pi}{2n} x$, which corresponds to an unperturbed sinusoidal spin-spiral [Fig. 1(c)]. Most interesting is the case $0 < H < H_c$, where the spin structure may be described as a soliton lattice: regions of the spin-flow phase are interrupted at regular intervals by magnetic domain walls, or solitons [Fig. 1(b)]. In each soliton the direction of staggered magnetization rotates by an angle $\pi$. At $H \rightarrow H_c$, the density of solitons starts to decrease very rapidly, as $1/|\ln(H_c - H)|$. The transition is thus almost first order: as $H \rightarrow H_c$, the two magnetic satellites at $(1 \pm \zeta, \pm \zeta, 0)$ converge to eventually produce a single peak at $(1, 0, 0)$.

The exact expression for $\beta(H)$ [Eq. (3)] enables us to derive parametric equations for the field-dependence of magnetization and incommensurability parameter, and directly compare these predictions to experimental results for Ba$_2$CuGe$_2$O$_7$. Using the formula $M = -\partial F/\partial H$ and the equalities for derivatives of elliptic functions [17] one gets:

$$M = \chi_\parallel H + (\chi_\perp - \chi_\parallel) H_c \frac{1}{\beta^2} \left( 1 - \frac{E(\beta)}{K(\beta)} \right) \cdot (6)$$

The magnetization curve is continuous at the critical field, while $\chi(\parallel) \equiv \frac{\partial M}{\partial H}$ diverges as $H_c$ is approached from below, and is constant and equal to $\chi_\perp$ at $H > H_c$. In zero field $\chi_\perp$ is equal to $(\chi_\parallel + \chi_\perp)/2$. We now use Eq. (3) together with the formula (3) to fit the experimental $\chi(\parallel)$ for Ba$_2$CuGe$_2$O$_7$ measured at $T = 2$ K. With $\chi_\perp = 3.43 \times 10^{-5}$ emu/g, $\chi_\parallel = 0.89 \times 10^{-5}$ emu/g and $H_c = 1.88$ T a very good fit is obtained (Fig. 2 solid line for $H||c$). In the refinement we have included a linear contribution to $\chi(\parallel)$. This term is present in both $\chi_c(\parallel)$ and $\chi_s(\parallel)$ and is a result of non-linear corrections to the local susceptibility, neglected in our treatment.

As $H \rightarrow H_c$, the soliton density decreases, i.e., the period of the magnetic structure increases with increasing field. In our case expressing $\zeta$ in terms of $\beta$ is rather straightforward and yields:

$$\zeta(H) = \frac{H}{H_c} = \frac{\pi^2}{4\beta} \frac{1}{K(\beta)} \cdot (7)$$

Again, Eq. (3), when combined with Eq. (4), gives a parametric curve for $\zeta(H)$, that can be fit to the experimental data for Ba$_2$CuGe$_2$O$_7$ using $H_c$ as the only adjustable parameter [$\zeta(0) = 0.027$ is measured independently]. The result with $H_c = 2.13$ T is shown in a solid line in Fig. 3. A remarkable agreement is obtained except very close to $H_c$. Discrepancies close to the transition point are to be expected, since the transition is almost first order, the soliton lattice is very soft and easily pinned by any impurities. The same effects prevent us from experimentally observing a true divergence in $\chi(H)$ at the critical field (Fig. 3).

Finally, we can estimate the actual value of the critical field using the previously measured exchange constants and $\zeta(0)$. With $J_{ab} = 0.48$ meV [13] the exchange energy per bond is $J = 2J_{ab}S^2 \approx 0.24$ meV. For $\chi_\parallel$ and $\chi_\perp$ we can use the values for a classical Heisenberg antiferromagnet at $T = 0$. ESR measurements [18] provide us with the gyromagnetic ratios of Cu$^{2+}$: $g_a = 2.044$ and $g_c = 2.474$. Using Eq. (5) and $\chi_\perp = (g_H B)^2/(8J)$ we obtain $H_c = 3.3$ T, that should be compared to the experimental $H_c \approx 2.1$ T. Considering that in these estimates we have completely ignored quantum- and temperature corrections to $\chi$ and $\rho_s$, a 30% consistency is indeed acceptable.

In summary, we have observed a rare type of CI transition that is driven exclusively by the changing strength of the commensurate potential. The latter is directly controlled in an experiment by varying the magnetic field. A transition of this kind was envisioned over three decades ago by Dzyaloshinskii, and now we find that Ba$_2$CuGe$_2$O$_7$ exhibits it in its original form. Now that the underlying physics is rather well understood, Ba$_2$CuGe$_2$O$_7$ can be used as a very neat and simple model system for further studies of spiral magnetism. For example, it would be very interesting to look closer at the magnetic critical behavior. Another promising direction for future work is the study of the effect of an in-plane magnetic field.

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FIG. 1. A schematic view of a Cu-Ge-O layer in Ba$_2$CuGe$_2$O$_7$. The arrows indicate the components of Dzyaloshinskii vector $\vec{D}$, allowed by the symmetry.

FIG. 2. Field dependence of the magnetic susceptibility measured in Ba$_2$CuGe$_2$O$_7$ at $T = 2$ K for the magnetic field applied along the $c$ (circles) and $a$ (crosses) axes of the crystal, respectively. The solid line is a theoretical fit to the data, as described in the text.

FIG. 3. Field dependence of the magnetic propagation vector in Ba$_2$CuGe$_2$O$_7$ measured at $T = 2.4$ K. The solid line is a theoretical fit given by Eqs. (4,7). Insert: Elastic scans across the antiferromagnetic zone center measured in Ba$_2$CuGe$_2$O$_7$ at $T = 2.4K$ for two different values of magnetic field applied along the $(0,0,1)$ direction.

FIG. 4. Spin configurations for the spin-flop phase at $H > H_c$ (a), the soliton lattice at $H = 0.997H_c$ (b) and the circular spin spiral at $H = 0$ (c).
GeO$_4$
\( \chi(10^{-6}\text{ emu/g}) \)

\[ \chi(H(T)) \]

Zheludev et al. Fig. 2
$\text{Ba}_2\text{CuGe}_2\text{O}_7$

$T = 2.4 \text{ K}$

$H_c = 2.13 \text{ T}$

$Q = (1 + \zeta, \zeta, 0)$

(a) $H = 1.9 \text{ T}$

(b) $H = 2.4 \text{ T}$

Zheludev et al Fig. 3
(a) $H/H_c = 1.10$

(b) $H/H_c = 0.9973$

(c) $H = 0$

Zheludev et al. Fig. 4