Step-like magnetization in a spin-chain system: Ca$_3$Co$_2$O$_6$

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(Dated: June 29, 2021)

Due to a ferromagnetic in-chain coupling between Co$^{3+}$ ions at trigonal sites, chains Ca$_3$Co$_2$O$_6$ are considered as large rigid spin moments. The antiferromagnetic Ising model on the triangular lattice is applied to describe an interchain ordering. An evolution of metastable states in a sweeping magnetic field is investigated by the single-flip technique. At the first approximation two steps in the magnetization curve and a plateau at 1/3 of the saturation magnetization are found. Four steps in magnetization are determined in high-order approximations in agreement with experimental results.

PACS numbers: 75.25.+z, 75.30.Kz, 75.50.Ee

Among other spin-chain compounds, Ca$_3$Co$_2$O$_6$ has drawn recently considerable attention to their complex magnetic behavior [1, 2, 3, 4, 5, 6]. The most intriguing feature observed in Ca$_3$Co$_2$O$_6$ is a step-like shape of the magnetization curve [2, 6]. The number of the steps in the curve depends strongly on a sweep rate of the external magnetic field and temperature [2, 5]. Two steps become apparent in the temperature range from 12 K to 24 K [5]. The first step takes place at the zero magnetic field. Then the magnetic moment remains constant at 24 K [5]. The first step takes place at the zero magnetic field. At least four equidistant steps are clearly visible below 10 K at a very low sweep rate. They are accompanied by a sizeable hysteresis. Similar phenomena were observed in other spin-chain compounds, e.g. Ca$_3$CoRhO$_6$ [2, 6].

The structure of Ca$_3$Co$_2$O$_6$ consists of Co$_2$O$_6$ chains running along the c axis. The Ca ions are situated between them. The chains are made up of alternating, face-sharing CoO$_6$ trigonal prisms and CoO$_6$ octahedra. The crystalline electric field splits the energy level of Co$^{3+}$ ions into the high-spin ($S = 2$) and low-spin ($S = 0$) states. The Co$^{3+}$ ions situated in the trigonal environment (CoI) are in the high-spin state and the octahedral Co sites (CoII) occurs in the low-spin state. In the last case the energy difference between the low-spin and high-spin states is very small and a tiny fraction of CoII sites is reported to be in the high-spin state. The crystalline electric field leads also to a very strong Ising-like anisotropy at the CoI sites. The chains form triangular lattice in the ab plane that is perpendicular to the chains. An in-chain exchange interaction between magnetic Co ions through the octahedra with non-magnetic Co ions is ferromagnetic (FM). It causes the in-chain FM ordering of Co ions at about 40 K. The interchain interaction is antiferromagnetic (AFM) and much weaker than the in-chain one. A partial AFM order of chains appears at 24 K. A weak feature concerned most probably with a transition in a new interchain order was also observed at around 12 K. This scenario of magnetic interactions in Ca$_3$Co$_2$O$_6$ is consistent with results of x-ray photoemission spectroscopy [3], neutron scattering [4], magnetization and specific heat measurements [1, 2, 3, 4, 5, 10], nuclear magnetic resonance [11], and theoretical calculations of indirect interactions between CoI sites [12].

The model presented in Ref. [2] deals with an in-chain structure of Ca$_3$Co$_2$O$_6$ and magnetization dynamics explained in terms of the quantum tunnelling. In this Letter, we develop a new model for a description of the step-like magnetization in Ca$_3$Co$_2$O$_6$ at low temperatures, shifting the stress on the interchain magnetic order. The strong FM in-chain coupling makes it possible to consider a Ca$_3$Co$_6$ chain as a large rigid spin formed by CoI ions. There are only two projections of the chain spin onto the c axis due to the strong Ising-like anisotropy. Including the AFM coupling between the nearest-neighbor chain spins we arrive to the Ising Hamiltonian on the triangular lattice

$$H = J \sum_{<ij>} \sigma_i^z \sigma_j^z - B \sum_i \sigma_i^z$$

where \(\sigma_i^z = \pm 1\) is the c-axis projection of the \(i\)-th chain spin, \(J > 0\) is the parameter of the AFM interchain coupling, \(B\) is the magnetic field, \(<ij>\) denotes the summation over all the nearest-neighbor pairs on the triangular lattice.

The strong dependence of the magnetization curve shape on the magnetic field sweep rate and temperature shows that the state of the system of the chain spins in the magnetic field is far from equilibrium. At the low sweep rate the system is rather in a metastable state than in the ground state. It is convenient to formulate necessary conditions of the metastability of the system in the following form

$$\sigma_i^z h_i \leq 0$$

where

$$h_i = J \sum_{j(i)} \sigma_j^z - B$$

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is the effective field for the $i$-th chain, $j(i)$ denotes summation over the nearest-neighbors of the $i$-th chain. We have used the unstrict inequality in Eq. (2) keeping in mind a strong degeneracy of partially ordered AFM arrangements on the triangular lattice. A transition from one metastable state to another occurs through exited states. We obtain $\sigma_z^i h_i > 0$ at least for one chain in a exited state by definition. Let $\Delta E_i = 2\sigma_z^i h_i > 0$ be the excitation energy per CoI site of the $i$-th chain. It follows from this that the probability of an exited chain at energy of such an arrangement equals the ground state of alternating rows of spin-up and spin-down chains. The formation curve starting with an initial state that consisted of samples. Earlier to nonequilibrium dynamics of the AFM Ising system using the single-flip technique that was applied to numerical Monte Carlo simulations, we improved the approximation used above including tripod configurations. Since the chains placed in the centers of hexagons have an arbitrary projections of chain spins onto $c$ axis. The entropy density of the first approximation equals $S_1 = (1/3)\ln 2 \approx 0.231$. An arbitrary small external magnetic field lifts degeneracy of chain spins in the centers of hexagons orienting them along the magnetic field ($\sigma_z^i = 1$). We consider that the spin-up chains (the black circles) are directed parallel to the magnetic field. The grey circles become black in Fig. 1. This causes a step at $B = 0$ with the height of $1/3$ where the full magnetization is taken as unity. Then, one third of the spin chains remain spin-down or antiparallel to the field. Since they are surrounded by 6 spin-up chains (the black circles) are directed parallel to the magnetic field $B_C = 6J$ where a transition to the fully-polarized FM state takes place. The magnetization curve for the first approximation is shown in Fig. 2. It should be noticed that this curve is in an excellent agreement with the experimental data at the intermediate temperatures.

We can improve the approximation used above including tripod configurations. Since the chains placed in the centers of hexagons have an arbitrary projections of the spin onto $c$ axis, it occurs that three of them neighboring with the same chain of the honeycomb sublattice are in the same state. Then the configuration shown in Fig. 3 can appear. The chain spin in the center of the tripod belongs to the honeycomb sublattice but, nevertheless, it can have an arbitrary $c$ projection of the chain spin. These states increase the entropy density up to $S = (5/12) \ln 2 \approx 0.289$ and involve various types of configurations: isolated tripods and connected tripods. It is convenient to consider them separately. After straightforward calculations we obtain the probability...

\[ S = \frac{2}{\pi} \int_0^\pi \ln(2 \cos \omega) d\omega \approx 0.3383, \]

where $\omega$ is the effective field for the $i$-th chain, $j(i)$ denotes summation over the nearest-neighbors of the $i$-th chain. We have used the unstrict inequality in Eq. (2) keeping in mind a strong degeneracy of partially ordered AFM arrangements on the triangular lattice. A transition from one metastable state to another occurs through exited states. We obtain $\sigma_z^i h_i > 0$ at least for one chain in a exited state by definition. Let $\Delta E_i = 2\sigma_z^i h_i > 0$ be the excitation energy per CoI site of the $i$-th chain. It follows from this that the probability of an exited chain at energy of such an arrangement equals the ground state of alternating rows of spin-up and spin-down chains. The formation curve starting with an initial state that consisted of samples. Earlier to nonequilibrium dynamics of the AFM Ising system using the single-flip technique that was applied to numerical Monte Carlo simulations, we improved the approximation used above including tripod configurations. Since the chains placed in the centers of hexagons have an arbitrary projections of chain spins onto $c$ axis. The entropy density of the first approximation equals $S_1 = (1/3)\ln 2 \approx 0.231$. An arbitrary small external magnetic field lifts degeneracy of chain spins in the centers of hexagons orienting them along the magnetic field ($\sigma_z^i = 1$). We consider that the spin-up chains (the black circles) are directed parallel to the magnetic field. The grey circles become black in Fig. 1. This causes a step at $B = 0$ with the height of $1/3$ where the full magnetization is taken as unity. Then, one third of the spin chains remain spin-down or antiparallel to the field. Since they are surrounded by 6 spin-up chains (the black circles) are directed parallel to the magnetic field $B_C = 6J$ where a transition to the fully-polarized FM state takes place. The magnetization curve for the first approximation is shown in Fig. 2. It should be noticed that this curve is in an excellent agreement with the experimental data at the intermediate temperatures.

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We include this type of configurations in the second approximation for the initial state. The entropy density of the second approximation is $S_2 \approx 0.259$. Applying the external magnetic field we again obtain a step at the zero magnetic field but the chain spins in the centers of hexagons sharing joint corners with the tripod center remain in the spin-down state because they are surrounded by 4 spin-up and 2 spin-down nearest-neighbors. The height of the step ($\Delta M(B/J)$) can be expressed through probability of the isolated-tripod configuration as $\Delta M(0) = (1/3) - 2P_2$. The spin chains in the centers of the tripod hexagons flip at the new critical magnetic field $B_C = 2J$. While the magnetic fields increases further, the curve occurs at the 1/3-plateau and coincides with the curve obtained in the first approximation (see Fig. 2).

The third approximation is to include configurations with isolated pairs of connected tripods. These configurations change the heights of the steps but give no new features in the magnetization curve. The probability of the pair of isolated tripod is $P_3 \approx 0.010$. The entropy density increases up to $S_3 \approx 0.273$.

An isolated configuration of three tripods connected as a star is taken into account in the framework of the fourth approximation (see Fig. 4). The probability of this configuration is $P_4 \approx 0.0035$ and the entropy density in the fourth approximation is $S_4 \approx 0.280$. The key feature of this configuration is that there are chain spins that are surrounded by 5 spin-up and one spin-down nearest-neighbors. These chain spins remain stable up to the new critical magnetic field $B_C = 4J$. To calculate the step of in the magnetization curve we have to calculate a number of various sequences of spin flips. The final value of the step is $\Delta M(4) \approx 0.008$ that is significantly smaller then $\Delta M(2) \approx 0.12$.

There is a variety of more complex configurations then the tripod. However, it should be mentioned that further approximations should change the heights of the steps but they can not cause new features in the magnetization curve. As it follows from Eq. (2) there exist only four critical magnetic fields related to the four configurations of the nearest-neighbors shown in Fig. 2.

The magnetization curve obtained in the fourth approximation reproduces the key features of the experimental data at the very low sweep rate, namely, the four
equidistant steps in the magnetization curve. In contrast with our results, the third step in the experimental curve is much larger than the second one. This quantitative discrepancy can be eliminated in higher order approximations that can be investigated both analytically, by the technique used in the present Letter, or numerically, applying Monte Carlo simulation. Approximations of higher orders are of importance for quantitative calculations of the magnetization curve because the calculation convergence for the magnetic moment is slower than that for the configuration probability.

Few questions on the magnetization of Ca$_3$Co$_2$O$_6$ are still unclear. There were observed weak smeared features in the experimental curve at high magnetic fields above the last step. They can stem from the small fraction of CoII sites that are the high-spin state, because they increase the chain spin and cause higher critical fields. The sizeable hysteresis also draws attention in the experimental curve. It depends drastically on the temperature and the magnetic field sweep rate. It should be mentioned that while the magnetic field sweeps down and crosses the highest critical field $B_C = 6J$ the chain spins flip down at random and the system occurs in a new state that is different from that at the sweeping-up process.

In conclusion, we have developed a new model for the step-like magnetization of Ca$_3$Co$_2$O$_6$, spin-chain compound. It can be applied also to other spin-chain compounds with the triangular lattice of chains, e.g. Ca$_3$CoRhO$_6$. Due to the in-chain FM coupling between Co$^{3+}$ ions at trigonal sites, Co$_2$O$_6$ chains are considered at low temperatures as a large rigid spins with the strong Ising-like anisotropy. The AFM Ising model on the triangular lattice is applied to the system of rigid FM-ordered chains. The crucial point of the model is the supposition that the system is out of equilibrium, because the dependence of the magnetic moment on the magnetic field in the ground state of the AFM Ising model on the triangular lattice is smooth with the exception of the step at the zero magnetic field. For the honeycomb AFM structure two steps were found in the theoretical magnetization curve in excellent agreement with experimental data at the intermediate temperatures. At higher approximations four equidistant steps were determined in accordance with experimental curves at the low temperatures and very low magnetic field sweep rate. The results obtained in the present Letter and the model of Ref. can be regarded as two limiting cases. The first deals with the nonequilibrium interchain ordering assuming the chain spins to be rigid. An in-chain fragmentation and the quantum tunnelling of the magnetic moment of the fragments are investigated in the second case totally neglecting the interchain ordering.

I am grateful to C. Demangeat and M. Drillon for fruitful discussions and hospitality during my stay at Institut de Physique et Chimie des Matériaux de Strasbourg en Unité mixte de recherche.

This study was partially supported by the INTAS grant (03-51-4778) "Hierarchy of scales in magnetic nanostructures".

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