



Effects of Ho-ion substitution on the magnetic properties of the $\text{Ca}_3\text{Co}_2\text{O}_6$ frustrated spin-chain compound

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ABSTRACT

Ho^{3+} -ion doped spin-chain compounds $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ ($x = 0, 0.05, 0.1, 0.15$) were prepared by a conventional solid-state reaction method. Rietveld refinement of the X-ray diffraction patterns at room temperature confirmed the rhombohedral structure with the $R\bar{3}c$ space group. The results reveal that the solid solubility of the Ho element in $\text{Ca}_3\text{Co}_2\text{O}_6$ is in the range of $x = 0.1$ – 0.15 . Magnetic measurement suggests that with the increased Ho content: (1) the ferromagnetic transition temperature T_c and spin freezing temperature T_f decrease obviously; (2) the ferrimagnetic configuration becomes less stable; (3) the dynamic characteristics become slower; and (4) the antiferromagnetic (AFM) interaction enhances gradually. Based on these phenomena, the mechanism was discussed in detail. The magnetic correlation length is broken at a low Ho^{3+} -ion level, and the Ho^{3+} -ion pair formation along the chain with a high level of doping was interpreted.

1. Introduction

Materials exhibiting geometrical frustration are always fascinating due to their potential applications and complex magnetic interactions [1]. In some triangular-lattice antiferromagnets, complete long-range antiferromagnetic (AFM) order cannot be formed, and some spectacular physical phenomena can be observed due to the incompatibility of the lattice geometry and the local interactions [2].

Among these materials, $\text{Ca}_3\text{Co}_2\text{O}_6$ and its numerous isostructural phases have attracted much attention [3]. They crystallize in $K_2\text{CdCl}_6$ (rhombohedral) derived structures ($R\bar{3}c$ space group) with the formula of $A'_3\text{ABO}_6$ [4]. Herein, A' can be occupied either by Ca, Sr, or Ba ions, while the A and B sites can be occupied by a wide variety of cations, including transition metals and rare-earth elements. Face-sharing AO_6 trigonal prisms and BO_6 octahedra arrange along the c-axis alternately, forming quasi-one-dimensional spin chains. In the ab-plane, each chain is surrounded by six equally spaced chains, with the A' cations located between them [5]. For $\text{Ca}_3\text{Co}_2\text{O}_6$, both of the AO_6 trigonal prisms and the BO_6 octahedra sites are occupied by Co cations. However, due to the different crystalline fields, the Co cations have different spin states [high spin state ($S = 2$) at the trigonal prism sites and low spin state ($S = 0$) at the octahedral sites] [6], although Co ions located at both of the two sites are in a trivalent oxidation state. The intrachain

interaction along the c-axis is ferromagnetic (FM) and the interchain interaction in the ab-plane is AFM. The structural characteristics and magnetic interactions give rise to exotic magnetic behavior including (1) partially disordered AFM states below 24 K; (2) well-spaced magnetization steps; and (3) the existence of spin freezing below 10 K [7].

To clarify the microstructural mechanism of the observed magnetic properties, e.g., the magnetization steps, many previous investigations have focused on magnetism [8,9,10,11], structure [12], specific heat [13] and magnetic entropy [14]. Alternatively, as an effective method, substitution of the Co element by other suitable ions has also been adopted [15,16]. Because of the similarities with the experimental phenomenon of single-molecule magnets, quantum tunneling of magnetization (QTM) was proposed as the dominant mechanism behind this multiple step behavior [17]. However, this mechanism has also been challenged [14]. Therefore, significant efforts are being made to understand the magnetic properties. In comparison with some other ions, the Ho^{3+} ion has some advantages as follows: (1) strong uniaxial single-ion anisotropy; (2) large spin value; and (3) smaller ionic radius (0.9 \AA) and hence a higher solid solubility [18]. The doping of Ho^{3+} ions into $\text{Ca}_3\text{Co}_2\text{O}_6$ may have a large influence on its magnetism, and hence may provide us with some useful information for clarifying the micro-mechanism of magnetism.

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2. Experimental procedures

Polycrystalline $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ ($x = 0, 0.05, 0.1, 0.15$) samples were obtained by calcining CaCO_3 , Co_2O_3 , and Ho_2O_3 precursors at 800°C and at 1000°C subsequently. The X-ray diffraction (XRD) patterns were collected using a Philips X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation. Rietveld structural refinement was performed with the General Structure Analysis System (GSAS) program [19]. The magnetization was measured by a superconducting quantum interference device magnetometer. During the measurements of AC susceptibility, an AC driving field of 10 Oe was applied. Before each measurement, the sample was zero-field cooled (ZFC) from a paramagnetic state (70 K) to the desired temperature. Time-dependent magnetization was firstly magnetized with a constant field of 5 T at 5 K. Then the field was switched off and the magnetization was recorded as a function of time subsequently.

3. Results

The XRD patterns of $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ ($x = 0, 0.05, 0.1, 0.15$) are indexed as a rhombohedral structure and refined with the $R\bar{3}c$ space group (as shown in Fig. 1). The single phase $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ with a structure similar to $\text{Ca}_3\text{Co}_2\text{O}_6$ can be obtained in the case of $x \leq 0.1$. As the x increases to 0.15, a small amount of CaO phase can be detected. To confirm that the Ho ions really occupy the Co site, it is necessary to clarify the origin of the CaO phase. Instead of replacing the Co ions, it can be assumed that the doped Ho ions occupy the Ca^{2+} ions sites. Based on this assumption, the CaO content should be 15% of the $\text{Ca}_3\text{Co}_2\text{O}_6$ when $x = 0.1$. The extremely high CaO content conflicts with the absence of the second phase observed in the $x = 0.1$ sample. Therefore, the CaO phase results from the solid solubility limit of the Ho ions in the $\text{Ca}_3\text{Co}_2\text{O}_6$ compound when $x = 0.15$, reflecting the occupation of the Co sites by the Ho ions indirectly. According to Rietveld structural refinement, the calculated lattice parameters and selected Co1–Co2 bond distance are listed in Table 1. Both the lattice constants c and the Co1–Co2 bond distance increase with x rising from 0 to 0.1. This also suggests that the bigger Ho^{3+} ions have been substituted into

Table 1
Unit-cell dimensions and selected bond distances for $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ ($x = 0, 0.05, 0.1, 0.15$).

x	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	Co1–Co2(\AA)	χ^2
0	9.07908	10.38176	741.115	2.5954	1.405
0.05	9.07296	10.38879	740.617	2.5972	1.299
0.1	9.07307	10.40280	741.634	2.6007	1.304
0.15	9.07584	10.37807	740.322	2.5945	1.377

the Co^{3+} sites in the matrix material $\text{Ca}_3\text{Co}_2\text{O}_6$ successfully. The result is in accordance with the above analysis.

Fig. 2 shows the ZFC and field cooling (FC) curves of the four samples ($x = 0, 0.05, 0.1, 0.15$) measured in a field of 0.1 T. In the case of $x = 0$, the curve presents an upturn below $T_c = 24$ K, and this phenomenon could be attributed to the intrachain FM order. With a further decrease in temperature, one peak appears around $T_f \cong 10$ K for the ZFC curve, suggesting the existence of a spin freezing phenomenon. Below T_f , the ZFC heating curve branches from the FC cooling one. To check the subtle features of the magnetization behaviors, the magnetization of all the four samples was measured again in the 0.01 T field (the subtle features (including impurities) are more easily seen in the lower field). Nevertheless, the ZFC/FC curves measured at a lower field have no differences from the ones measured at the higher field. The separation of the ZFC and FC curves of the $x = 0$ sample between T_f and T_c still exists, implying that the separation is an intrinsic characteristic of the $\text{Ca}_3\text{Co}_2\text{O}_6$ compound and it should be related to the partially disordered AFM state [7]. As the Ho content increases from $x = 0$ to $x = 0.1$, the ferromagnetic transition temperature T_c and spin freezing temperature T_f decrease obviously, accompanied by the broadening of the freezing peak. For the $x = 0.15$ sample, the freezing peak almost disappears and the ZFC and FC curves tend to be superposed. These, together with the dramatic reduction in magnetization, indicates the tremendous influence of Ho doping on the magnetization of $\text{Ca}_3\text{Co}_2\text{O}_6$.

To obtain more information, the inverse magnetic susceptibility (H/M) of the $x = 0$ –0.15 samples were plotted and are presented in Fig. 3(a). All the H/M curves follow the Curie–Weiss law at high

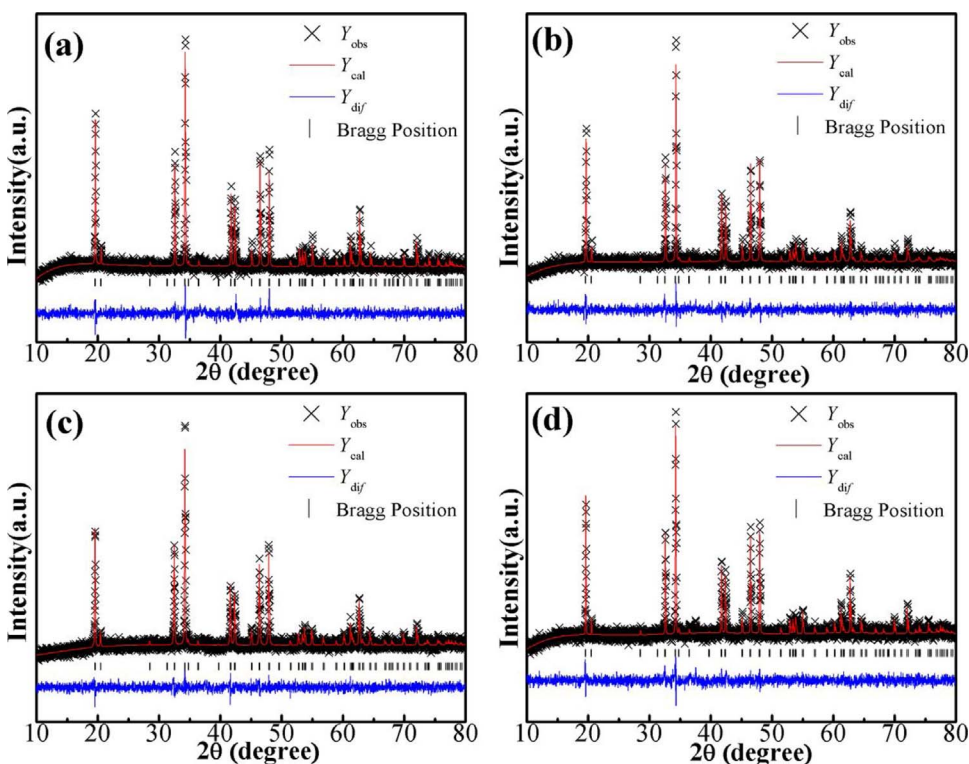


Fig. 1. X-ray diffraction patterns of $\text{Ca}_3\text{Co}_{2-x}\text{Ho}_x\text{O}_6$ with (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$ samples: experimental, calculated, and difference.

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