Memory and rejuvenation effect on the cluster-glass phase of 1-D spin-chain compound $\text{Ca}_3\text{Co}_{2-x}\text{Bi}_x\text{O}_6$

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Abstract. We studied the structural, static, and dynamic properties of $\text{Ca}_3\text{Co}_{2-x}\text{Bi}_x\text{O}_6$ ($x = 0$ and 0.2) by means of powder X-ray diffraction and magnetization measurements. We reveal the rejuvenation phenomena in magnetic relaxation under cyclic temperature change and quenching below $T_{c2}$. The reproduced step in the memory curve confirms the striking feature of rejuvenation effect in these samples. The observed memory and rejuvenation effects are discussed in the framework of hierarchical model of glassy phase.

1. Introduction
Study of aging, memory, and rejuvenation effects in a glassy system has attracted enormous attraction in the last few decades [1]. The glassy feature in a system is highly frustration related which arises due to competing magnetic interaction. $\text{Ca}_3\text{Co}_2\text{O}_6$ is one of the geometrically frustrated compounds which belongs to the family of Quasi 1-D spin-chain compound of structure $\text{A}_3\text{BB’O}_6$ [2]. It crystallizes in the $\text{K}_4\text{CdCl}_6$ (rhombohedral) type structure with space group $R\overline{3}c$. The crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ consists of an infinite number of chains of alternating face-sharing $\text{Co}_6\text{O}_{18}$ octahedral ($\text{Co}1$) and $\text{Co}_6\text{O}_{18}$ trigonal prisms ($\text{Co}2$), which are running along the c-axis. It possesses an Ising-like character with spin parallel to the chains, while the intra-chain and inter-chain coupling are ferromagnetic and antiferromagnetic, respectively, which give rise to geometric frustration and unusual magnetic behavior [3, 4].

The interest in relaxation phenomena revived by the effect of temperature changes, which revealed non-trivial memory and rejuvenation effects in the magnetic system [5, 6]. In this work, we carried out a comprehensive study of the structural and magnetic properties of $\text{Ca}_3\text{Co}_{2-x}\text{Bi}_x\text{O}_6$. The magnetic memory and rejuvenation effects in the system has been demonstrated by the magnetic relaxation measurements.

2. Experimental Details
Polycrystalline samples of $\text{Ca}_3\text{Co}_{2-x}\text{Bi}_x\text{O}_6$ ($x = 0$ and 0.2) were prepared by standard solid-state reaction method. Powder X-ray diffraction measurements were performed on all the samples at room temperature using a Rigaku X-ray diffractometer (XRD) (TTRAX III) with Cu-Kα ($\lambda = 1.5406\ \text{Å}$) radiation from scattering angle ($2\theta$) $10°$ to $80°$. The magnetization data were taken using a vibrating sample magnetometer (VSM) probe installed in a quantum design physical property measurement system (PPMS).
3. Results
X-ray diffraction pattern of Ca$_3$Co$_{2-x}$Bi$_x$O$_6$ ($x = 0$ and 0.2) samples were taken at room temperature. Rietveld refinement was carried out by considering that the substituted Bi atom replaces the Co from the 6$a$ site. Fig. 1 presents the graphical output of the Rietveld refinement performed to the XRD pattern of $x = 0$ and 0.2 samples. All the diffraction peaks were indexed within the rhombohedral structure that belongs to the space group $R\bar{3}c$. The lattice parameters $a$ and $c$ obtained from the refinement increases for $x = 0.2$ sample. It is consistent with the fact that the Bi$^{3+}$ (1.24 Å) ion has a larger ionic radius compared to Co$^{3+}$ (0.61 Å) ion. The structure visualization and bond-length analysis have been done using VESTA software. The intra-chain bond-length (Co1-Co2) increases from 2.596 Å for the parent compound to 2.598 Å for $x = 0.2$ sample. In the same way, the inter-chain bond-length (Co2-Co2) increases from 5.520 Å for the parent compound to 5.523 Å for $x = 0.2$ sample. According to these results, we could expect an interplay of reduced dimensionality and bond randomness effect introduced by Bi-substitution, due to which the exchange interaction between magnetic ions may get modified.

![Figure 1: Rietveld refined XRD pattern of Ca$_3$Co$_{2-x}$Bi$_x$O$_6$ ($x = 0$ and 0.2) samples.](image1)

Fig. 2 depicts the temperature dependence of magnetization for Ca$_3$Co$_{2-x}$Bi$_x$O$_6$ ($x = 0$ and 0.2) samples measured under zero-field cooled (ZFC) and field cooled (FC) conditions in an applied magnetic field of 1000 Oe. For the parent compound, the magnetization starts rising below 25 K, and the ZFC-FC curves bifurcate at temperature 16 K. Below this temperature, the ZFC curves attain a maximum, while the FC magnetization increases monotonously with decreasing temperature. The divergence between M(T) ZFC-FC curves followed by a cusp in the ZFC curve are usually characteristics of glassy behavior. Similar to the parent compound, the magnetization for $x = 0.2$ sample starts rising below 22 K. The curve changes its behavior for low-temperature, i.e., the sharp peak in the ZFC curves for $x = 0$ sample broadens for $x = 0.2$ sample and shifts towards higher temperature. In the earlier study for the parent compound, the sudden increase in the magnetization below 25 K ($T_{c1}$) is a transition from paramagnetic to partially disordered antiferromagnetic state [3], and the cusp at 9.1 K ($T_{c2}$) has a place on spin-cluster-glass [3]. The transition temperature $T_{c1}$ and $T_{c2}$ were determined from $dM/dT$.
$vs. \ T$ plot. It is found that with Bi-substitution, the $T_{c1}$ decreases from 25 K for the parent compound to 22 K for $x = 0.2$ sample. On the other hand, the $T_{c2}$ increases from 9.1 K for the parent compound to 11.2 K for $x = 0.2$ sample, which indicates the increment in glassy feature due to Bi-substitution. We speculate that the modification in the relative strength of intra-chain and inter-chain interactions is the origin of the feature due to the random occupation of the $6a$ site by Bi atoms. Furthermore, the susceptibility data in the high-temperature region obey the Curie-Weiss law $\chi_{\text{mol}} = \frac{C_{\text{mol}}}{T - \theta}$, where $C_{\text{mol}}$ is molar curie constant, and $\theta$ is Curie temperature. As expected from the non-magnetic ion substitution, the $\mu_{\text{eff}}$ decreases from 5.6 $\mu_B$ for the parent compound to 5.03 $\mu_B$ for $x = 0.2$ sample. On the other hand, the $\theta$ remains fixed (31 K) for both samples.

In order to demonstrate the memory in the system, the samples were cooled down from room temperature to 6 K in an applied field of 100 Oe, and the magnetization was recorded. The cooling process was interrupted at $T = 6$ K, and the magnetic field was switched off for 5400 sec. In this duration, the samples were allowed to relax. The same magnetic field (100 Oe) was re-applied immediately after the relaxation, and the cooling was resumed. The obtained magnetization curve is designated as interrupted field cooled cooling (IFCC) curve, and it produces a step-like feature at 6 K (Fig. 3). After reaching 2 K, the samples were heated under the same field without interruption, and $M(T)$ was recorded up to 30 K, which is designated as memory curve (Fig. 3). FC curve in the same field (FCW) without any interruption was measured for reference (Fig. 3). Interestingly, the obtained memory curve at interrupting point ($T = 6$ K) attempts to follow the path traced during IFCC process, which is a clear signature of the magnetic memory in the system.

To understand the memory effect in details, we perform the magnetic relaxation measurement $M(t)$ under decreasing temperature cycle. In this protocol, the samples were cooled down from room temperature to 6 K in a field of 100 Oe. At 6 K, the $M(t)$ was recorded for 5400 sec after switching off the field. To generate the memory curve, we have repeatedly followed a two-step process after finishing the relaxation. In this process, the samples were cooled down to 2 K from 6 K in zero field, and $M(t)$ was measured for $t_m$ ($t_m$=900 sec for $x = 0$ sample and 450 sec for $x = 0.2$ sample) followed by warming of samples back to 6 K in zero field and re-recording the $M(t)$ for $t_m$. Fig. 4 shows the memory curves generated by following the decreasing temperature
cycle protocol. It is observed that the state of the samples before cooling is recovered when the sample is cycled back to the initial temperature (6 K). This is a straightforward demonstration of the rejuvenation of magnetic relaxation and memory effect in a cluster-glass system, where the sample remembers its previous state even after experiencing a large change in magnetization. The 6 K relaxation curve under the same field (100 Oe) was measured for reference (Fig. 4).

The observed memory and rejuvenation effect in this system can be discussed in the framework of hierarchical model of glassy phase [7]. In the hierarchical model, the glassy phase is a multi-valleyed free energy landscape at temperatures below $T_{c2}$. These free energy valleys are metastable states which split into new sub valleys on decreasing the temperature and get merged on increasing the temperature. Fig. 5 shows the schematic representation of free-energy landscape at $T = 2$ and 6 K under decreasing temperature cycle. For the decreasing temperature cycle ($T - \Delta T$), each metastable state splits into a set of sub valleys while cooling the samples to 2 K from 6 K. In the present case, the $\Delta T = 4$ K is large enough that the energy barrier separating the metastable states become too high, and the system cannot overcome these barriers during the time $t_m$. Thus, the relaxation occurs only within the sub valleys of each set. As the temperature is restored to 6 K, the sub valleys and barriers merge back to the original free-energy landscape, and the relaxation at 6 K is not disturbed by the intermediate relaxations at 2 K.

**Conclusion**

We prepared polycrystalline samples of $\text{Ca}_3\text{Co}_{2-x}\text{Bi}_x\text{O}_6$ ($x = 0$ and 0.2) by standard solid-state reaction method. Magnetic properties were found to be sensitive to Bi-substitution, due to which the $T_{c1}$ decreases while, the $T_{c2}$ increases for $x = 0.2$ sample. Our study throws fresh light on the memory and rejuvenation effects in this system. A detailed analysis via relaxation measurements demonstrates the evolution of the system through a number of metastable states and memory effects. It is to be mentioned that a comprehensive study which involves dc magnetization and magnetic relaxation measurements for intermediate Bi-composition will strengthen the current observations.

**References**

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