Magnetic properties of GdBaCo$_2$O$_{5.5-\delta}$ single crystals

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Abstract. The layered perovskite compounds REBaCo$_2$O$_{5.5-\delta}$ (RE = Rare Earth) display interesting magnetic properties arising from the variable spin states of the Co ions. There is a competition between the antiferromagnetic and ferromagnetic ordering in these materials. These compounds also allow a wide variation of oxygen stoichiometry to tune the magnetic properties. Single crystals of GdBaCo$_2$O$_{5.5-\delta}$ have been grown by the floating-zone technique in air. The as-grown crystal displays a twinned structure. Oriented crystals isolated from the as-grown boule were annealed in a flow of oxygen to vary the oxygen stoichiometry. Magnetization measurements have been carried out on both as-grown and annealed crystals. Results of the specific heat of GdBaCo$_2$O$_{5.56}$ crystals as well as the magnetic properties studied as a function of applied pressures (0 to 8 kbar) are presented.

1. Introduction

Rare earth cobalt oxides of the type REBaCo$_2$O$_{5.5-\delta}$ (RE = Rare Earth) exhibit many interesting phenomena such as giant magnetoresistance, metal-insulator transitions, charge and orbital ordering and metamagnetic transitions [1, 2]. REBaCo$_2$O$_{5.5-\delta}$ compounds possess a layered crystal structure with layers of [CoO$_2$]-[BaO]- [CoO$_2$]-[REO$_{0.5-\delta}$] stacked along the ‘c’ axis. These compounds are particularly interesting because the oxygen content can be easily varied by controlled annealing, and this in turn leads to the observation of a variety of ground states. The oxygen content controls the nominal valence state of the Co ions, which is altered during the annealing process, from a value of 2.5+ to 3.5+; the ‘parent’ state is obtained for a Co valence of 3+, obtained for an oxygen content of $\delta = 0$. A rich phase diagram is seen for compounds on either side of this ‘parent’ composition [1]. GdBaCo$_2$O$_{5.5-\delta}$ has been the most well studied of all the rare earths because of the ease with which high quality crystals can be obtained with a wide range of oxygen stoichiometries and due to Gd$^{3+}$ being a 4f ion with zero orbital moment.

Over the entire ‘doping’ range in GdBaCo$_2$O$_{5.5-\delta}$, on either side of the insulating $\delta = 0$ compound, the magnetic behaviour of the compound is dictated by a competition between the ferromagnetic (FM) and antiferromagnetic (AFM) interactions. These interactions are susceptible to external stimuli such as magnetic field, temperature and doping levels, which bring about FM to AFM transitions. Experiments on single crystals reveal that the magnetic properties are highly anisotropic in these materials [1].

In this paper, we present the investigation of the magnetic properties of GdBaCo$_2$O$_{5.5-\delta}$ single crystals with varying oxygen stoichiometry. Results of the heat capacity and the pressure dependence of magnetic properties of one of the oxygen rich crystals GdBaCo$_2$O$_{5.56}$ are also presented.

2. Experimental details
A high-quality single crystal of GdBaCo$_2$O$_{5.5-\delta}$ was grown in flowing air by the floating-zone technique using a four-mirror optical image furnace. A growth rate of 0.5 mm/h was used to obtain the best crystals. Oriented parallelepiped samples with the edges along the \textit{a}, \textit{b} and \textit{c} axes were cut out from the as-grown boule for the magnetic measurements. X-ray Laue diffraction showed that the as-grown GdBaCo$_2$O$_{5.5-\delta}$ crystal displays a twinned structure in which the \textit{a} and \textit{b} axes are intermixed. Several pieces of the as-grown crystal were annealed at different temperatures to obtain crystals of varying oxygen content. The oxygen content of both the as-grown and annealed crystals were determined using a standard thermogravimetric analysis (TGA) method (Mettler Toledo TG/DSC). For the TGA measurements, samples of about 50 mg were heated at the rate of 2 °C per minute from room temperature to 1000 °C in 3% H$_2$–97% Ar at a pressure of 1 atm. The magnetization measurements were carried out in a Quantum Design SQUID Magnetometer. An easyLab Mcell 10 high pressure cell was used to perform magnetic measurements under hydrostatic pressure of up to 8 kbar. The magnetic field was applied both along the \textit{c}-axis and \textit{ab}-plane of the crystal for the measurements. The heat capacity measurements were performed in a Quantum Design Physical Property Measurement System (PPMS).

3. Results and discussion

Oxygen stoichiometry:

Previous work [1, 2] has shown that the oxygen content of GdBaCo$_2$O$_{5.5-\delta}$ crystals can be controlled by annealing at various temperatures and oxygen partial pressures. Two different annealing conditions were used in this study to produce crystals with different oxygen contents, following the methods described in [1]. Oriented pieces of the as-grown crystals were annealed in a flow of oxygen at a pressure of 1 bar (i) at 300 °C for 1 hour and (ii) at 400 °C for 70 hours. The oxygen contents of the crystals determined by the TGA method were 5.29 (for the as-grown crystal), 5.38 (for the crystal annealed in 1 bar oxygen at 300 °C for 1 hour), and 5.56 (for the crystal annealed in 1 bar oxygen at 400 °C for 70 hours). Weight losses in the TGA measurement were accurate to 0.1 \mu g and therefore the exact oxygen excess/deficiency \textquoteleft\textquoteleft\delta\textquoteright could be estimated to an accuracy better than 0.005.

![Figure 1](image1.png)  
**Figure 1** Magnetization of (a) GdBaCo$_2$O$_{5.29}$, (b) GdBaCo$_2$O$_{5.38}$, and (c) GdBaCo$_2$O$_{5.56}$ as a function of temperature in a field of 1 kOe with \textit{H} // \textit{ab}-plane and \textit{c}-axis.

![Figure 2](image2.png)  
**Figure 2** Heat capacity $C_p$ as a function of temperature of a GdBaCo$_2$O$_{5.56}$ crystal.
Magnetic measurements:

The measured magnetization as a function of temperature for the three different crystals with varying oxygen stoichiometry is shown in Figure 1. The striking feature in all the results is the marked anisotropy of the magnetization. In this study, due to the twinned nature of the crystals, the magnetic measurements have been performed parallel and perpendicular to the ‘ab’ plane of the crystal. The low temperature increase seen in the magnetization is due to the paramagnetic contribution to the signal from the Gd$^{3+}$ ions. It is seen that as the oxygen content in this compound is increased, an increase in the magnetization is observed around 250 K. For the as-grown crystal, GdBaCo$_2$O$_{5.29}$, the magnetization observed for $H // ab$ shows a very small anomaly at $T_c$ 272 K, whilst the ‘c’ axis magnetization is featureless. For the oxygen rich compound, GdBaCo$_2$O$_{5.56}$, for $H // ab$-plane, $M$-$T$ curve increases rapidly around 280 K reaching a maximum at 262 K. Subsequently, the magnetization drops abruptly, levelling off around 220 K. These results are similar to what are seen by Taskin et al [1, 2] for similar compositions (oxygen contents of 5.485 to 5.525), where the rapid increase of magnetization has been interpreted as the onset of ferromagnetic ordering and the subsequent sudden drop is a FM $\rightarrow$ AFM transition. These transitions are seen only for $H // ab$. This is the plane containing the CoO$_2$ layers, and the Co spins are confined to this layer. In contrast, the magnetization for $H // c$-axis in GdBaCo$_2$O$_{5.56}$ is much smaller and featureless, with only a small bump around 273 K, which may be attributed to a small misalignment of the crystal. For the crystal with the intermediate oxygen stoichiometry, GdBaCo$_2$O$_{5.38}$, we see that the magnetization observed is slightly larger than for GdBaCo$_2$O$_{5.29}$ and the transition observed is similar to that seen for GdBaCo$_2$O$_{5.56}$. It therefore appears that the ferromagnetic component grows in magnitude as the oxygen content is increased, while the onset of FM order is seen at the same temperature in the three different crystals studied here. Our results appear to follow the same trend as those observed by Taskin et al. [1, 2], for crystals with oxygen stoichiometries in the same range.

In order to further understand the ground state of the oxygen rich crystals, we measured the specific heat of GdBaCo$_2$O$_{5.56}$ in the temperature range from 2 K to 300 K, and is shown in Figure 2. Two peaks are observed at 257 K and 271 K, which correspond to the AFM $\rightarrow$ FM transition and FM $\rightarrow$ PM transition, respectively. Similar results are reported in TbBaCo$_2$O$_{5.5}$ [3].

![Figure 3](image1.png)  
*Figure 3* Temperature dependence of the $ab$-plane magnetization of GdBaCo$_2$O$_{5.56}$ in different magnetic fields. The inset shows $T_c$ as a function of applied magnetic fields.

![Figure 4](image2.png)  
*Figure 4* Temperature dependence of magnetization of the GdBaCo$_2$O$_{5.56}$ single crystal under various pressures for $H // ab$-plane.
Next, in order to understand the delicate balance of the ferromagnetic and antiferromagnetic interactions in these compounds, we have investigated the effect of an external magnetic field on the magnetic transitions in one of the crystals, GdBaCo$_2$O$_{5.56}$. Figure 3 shows the magnetization of GdBaCo$_2$O$_{5.56}$ as a function of temperature in different external magnetic fields for $H//ab$ plane. As the applied magnetic field is increased, the FM phase becomes more stable and the transition temperature $T_c$ (defined as the minimum in the $dM/dT$ curve) shifts to higher temperatures, from 275 K for $H = 0.1$ kOe to 295 K for $H = 50$ kOe. $T_c$ is shown as a function of applied magnetic field in the inset of Figure 3. The magnetic field also affects the FM to AFM transition, suppressing the sharpness of this transition and shifting this to lower temperatures. The effect of the external field on the competition between the FM and AFM ordering is further seen by the gradual decrease in the drop in magnetization seen at this transition as the external field is increased (Figure 3). It has been reported that at low temperatures and high magnetic fields, there is a transition from AFM to FM state occurring within the ordered spin state and the external field applied is too weak to rotate the spins away from the $ab$ plane, the ‘$a$’ axis in particular [1, 2]. Our results are consistent with this observation.

External pressure can be an effective tool to tune the electronic and magnetic properties of a material. In some $R_{1-x}A_xCoO_3$ cobalt oxides, the pressure-induced temperature shift of $T_c$ is very pronounced [4]. Here we have measured the pressure dependence of the magnetization of a GdBaCo$_2$O$_{5.56}$ single crystal for $H//ab$-plane, as a function of temperature (Figure 4). As can be seen, the magnetic transition is not greatly affected by external pressures of up to 8 kbar used in this study. The shifts in the $T_c$ are not very pronounced even for the maximum pressure applied and it is inferred from this that higher pressures are required if any conclusions are to be drawn about the influence of pressure on the magnetic interactions in this crystal.

4. Summary and Conclusions

We have produced single crystals of GdBaCo$_2$O$_{5.5-\delta}$ with varying oxygen stoichiometry by post annealing the as-grown crystals and carried out a detailed study of the magnetic properties. The effect of magnetic field and pressure on the magnetic properties of the oxygen rich crystal, GdBaCo$_2$O$_{5.56}$, has been investigated. The magnetic fields favour ferromagnetism and destroy the antiferromagnetic state, leading to a shift in $T_c$ to higher temperatures. External pressure of up to 8 kbar does not cause any significant shifts in the magnetic transitions.

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