Effect of oxygen ordering on the structural and magnetic properties of the layered perovskites PrBaCo$_2$O$_{5+\delta}$

# Effect of oxygen ordering on the structural and magnetic properties of the layered perovskites $PrBaCo_2O_{5+\delta}$

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## Abstract

The influence of oxygen ordering on the structural and magnetic properties of the layered Co-based perovskites $PrBaCo_2O_{5+\delta}$ ($0.16 < \delta < 0.80$) was investigated by means of both x-ray diffraction and bulk magnetic measurements. For this purpose, two series of samples were prepared, following different routes: in the first group, annealing was followed by slow cooling at a rate of $6\,°C\,h^{-1}$; in the second group, the samples were rapidly quenched into liquid metal gallium from different annealing temperatures. Clear correlations between the thermal treatment and the degree of oxygen ordering could be established. Furthermore, we found that only the slowly cooled ($\delta \in [0.44\text{–}0.5]$) samples show clear signs of long-range oxygen ordering. The magnetic properties confirm the extreme sensitivity of the $\delta \sim 0.5$ region to the sample preparation method: while for $\delta < 0.35$ an antiferromagnetic state is found independently of the cooling rate, compounds with oxygen stoichiometry close to $\delta \sim 0.5$ display magnetization curves which depend strongly upon the synthesis history. For $\delta \in [0.35\text{–}0.7]$, the temperature and field dependences of the magnetization measurements point toward the appearance of a cluster glass, in which oxygen-rich and oxygen-poor clusters coexist. The long-range ferromagnetic order, observed for larger oxygen contents ($\delta > 0.7$), could thus be arising from the percolation of oxygen-rich ferromagnetic clusters.

(Some figures in this article are in colour only in the electronic version)

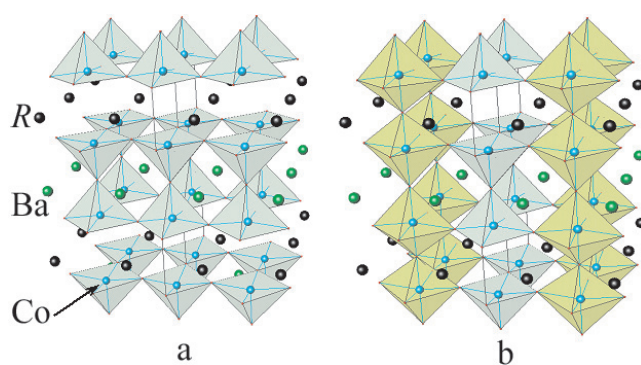[4] Author to whom any correspondence should be addressed.

**Figure 1.** Schematic crystal structure of (a) $RBaCo_2O_{5.0}$ and (b) $RBaCo_2O_{5.5}$.

## 1. Introduction

The effect of oxygen ordering on the electronic, magnetic and structural properties of various kinds of perovskites has been the subject of numerous studies in the past few years. It was for example shown that, in cuprate high-temperature superconductors, the degree of ordering of the excess oxygen, necessary to control the doping level, strongly correlates with the superconducting properties. We will focus here on the cobalt oxides with an oxygen-deficient perovskite-related 112-type structure $RBaCo_2O_{5+\delta}$ (R = rare earth). These materials have recently attracted renewed attention due to their extraordinary magnetic and transport properties, in particular after the discovery of giant negative magnetoresistance with resistivity ratios of $\sim$30% in the compounds with R = Er, Gd and $\delta$ = 0.4 [1–8]. So far, most investigations have concentrated on two particular compositions for which an ordering of the oxygen vacancies possibly exists, namely $\delta$ = 0 and 0.5. In $RBaCo_2O_5$ ($\delta$ = 0) the pyramidal positions are occupied by both $Co^{2+}$ and $Co^{3+}$ ions, which are present in the same amount (see figure 1). In contrast, in $RBaCo_2O_{5.5}$ ($\delta$ = 0.5) only $Co^{3+}$ ions are present, which coexist in *ideally alternating* octahedral $CoO_6$ and pyramidal $CoO_5$ environments. Neutron diffraction measurements indicate that $RBaCo_2O_5$ ($\delta$ = 0) compounds are antiferromagnets (AFM) with $T_N \sim 340$ K (R = Tb, Dy, Ho) [7], $\sim$350 K (R = Y) [8], $\sim$380 K (R = Nd) [9]. For several of them (R = Tb, Dy, Ho, Y) charge ordering was also reported [5–7]. Materials with $\delta$ = 0.5 exhibit essentially a more complicated electronic and magnetic behaviour. A metal–insulator transition takes place in the temperature range $300 < T_{MI} < 340$ K (depending on R), which seems to be related to a spin state transition of the $Co^{3+}$ ions [1–4, 10–14]. At least two magnetic anomalies have been observed upon decreasing temperature: (i) from a paramagnetic state (PM) to a state where spontaneous magnetization is observed, followed by a (ii) AFM ordering [3, 4, 8, 12, 13]. Both the nature of these transitions and the spin state of the cobalt ions are still under discussion [14].

Due to the wide accessible range of oxygen nonstoichiometry and a strong tendency of the oxygen ions and vacancies to order in 112-type cobaltites [3, 8], one can expect a dependence of structural, transport and magnetic properties not only upon the oxygen content itself, but also upon the synthesis history. The extra oxygen ions ($\delta > 0$), which are known to fill $RO_\delta$ layers, can create complex crystal structures with mixed octahedral and pyramidal cobalt environments. Indeed, as a function of $\delta$, several kinds of superstructures have been reported along with various possible models of oxygen ordering [3, 8, 15]. The influence of the oxygen inhomogeneity on the magnetic properties of $RBaCo_2O_{5+\delta}$ was pointed out

**Table 1.** Annealing temperatures (see the text), lattice parameters, pseudocubic cell volume $V$ and orthorhombic distortions $O_S = (a - b)/(a + b)$ of the RQ (upper part) and SC (lower part) PrBaCo$_2$O$_{5+\delta}$ compounds.

| $\delta$ | $T_{an}$ (K) | Supercell | $a$ (Å) | $b$ (Å) | $c/2$ (Å) | $V$ (Å$^3$) | $O_S \times 10^3$ |
|---|---|---|---|---|---|---|---|
| 0.23(1) | 1188 | $a_p \times a_p \times 2a_p$ | 3.9401(2) | 3.9331(2) | 3.7999(3) | 58.886 | 0.88 |
| 0.28(1) | 1093 | $a_p \times a_p \times 2a_p$ | 3.9374(2) | 3.9296(2) | 3.8035(3) | 58.849 | 0.99 |
| 0.35(1) | 993 | $a_p \times a_p \times 2a_p$ | 3.9414(2) | 3.9163(2) | 3.8082(3) | 58.782 | 3.19 |
| 0.48(1) | 723 | $a_p \times a_p \times 2a_p$ | 3.9288(2) | 3.9044(2) | 3.8079(3) | 58.412 | 3.11 |
| 0.54(1) | 623 | $a_p \times a_p \times 2a_p$ | 3.9266(2) | 3.9024(2) | 3.8103(3) | 58.386 | 3.08 |
| 0.56(1) | 573 | $a_p \times a_p \times 2a_p$ | 3.9166(2) | 3.9025(2) | 3.8146(3) | 58.304 | 1.81 |
| 0.59(1) | 523 | $a_p \times a_p \times 2a_p$ | 3.9090(2) | 3.9037(2) | 3.8147(3) | 58.210 | 0.68 |
| 0.71(1) | 293 | $a_p \times a_p \times 2a_p$ | 3.9009(2) | 3.8994(2) | 3.8172(3) | 58.064 | 0.20 |
| 0.17(1) | | $a_p \times a_p \times 2a_p$ | 3.9486(2) | 3.9455(2) | 3.7953(3) | 59.137 | 0.38 |
| 0.28(1) | | $a_p \times a_p \times 2a_p$ | 3.9438(2) | 3.9340(2) | 3.8032(3) | 59.007 | 1.25 |
| 0.44(1) | | $a_p \times 2a_p \times 2a_p$ | 3.9432(2) | 3.9080(2) | 3.8039(3) | 58.617 | 4.48 |
| 0.46(1) | | $a_p \times 2a_p \times 2a_p$ | 3.9418(2) | 3.9083(2) | 3.8027(3) | 58.584 | 4.26 |
| 0.50(1) | | $a_p \times 2a_p \times 2a_p$ | 3.9389(2) | 3.9059(2) | 3.8041(3) | 58.526 | 4.21 |
| 0.60(1) | | $a_p \times a_p \times 2a_p$ | 3.9215(2) | 3.9018(2) | 3.8145(3) | 58.365 | 2.52 |
| 0.79(1) | | $a_p \times a_p \times 2a_p$ | 3.8960(2) | 3.8913(2) | 3.8238(3) | 57.970 | 0.60 |

as well [16, 17]. Since very little is known about the precise relationship existing between the methods of preparation and the observed physical properties of cobalt oxides, we have undertaken systematic x-ray diffraction and bulk magnetic measurements on two series of PrBaCo$_2$O$_{5+\delta}$ samples, prepared by two alternative annealing routes: either slowly cooled (SC), or rapidly quenched (RQ) from various temperatures.

## 2. Experiment

An initial ceramic material was synthesized by conventional solid state reaction, starting with the high-purity oxides Pr$_6$O$_{11}$, Co$_3$O$_4$ and barium carbonate BaCO$_3$. The powders were mixed, pressed into pellets and heated in air several times, the temperature being increased in steps from 800 to 1140 °C. The samples were then oxidized at 2 bar of pure oxygen by heating up to 800 °C for 24 h. The as-synthesized compound had an oxygen stoichiometry of $\delta = 0.79(1)$ as determined from iodometric titration analysis. The powder was then separated into two batches, which were processed in two different ways:

SC: the oxygen content of each compound of the first series was individually reduced by annealing (850 °C, 10 h) in an evacuated quartz ampoule filled with the appropriate amount of metallic copper getter and then cooled very slowly at a rate of 6 °C h$^{-1}$.

RQ: different oxygen contents for the samples of the second series were obtained by annealing in a helium flow at different temperatures (see table 1) in a vertical tube furnace for ten hours. The samples were then dropped into liquid metal gallium, to achieve rapid quenching.

We used both iodometric titration and gas volumetric analysis to measure the oxygen content, since it is crucial to know the exact content of oxygen in the samples. Therefore we elucidate the details of the two above-mentioned methods. The principle of iodometric titration is the following: by dissolving the PrBaCo$_2$O$_{5+\delta}$ sample in dilute hydrochloric acid containing potassium iodide, a reduction–oxidation reaction takes place. Whereas Co$^{4+}$ and Co$^{3+}$ cations are reduced to Co$^{2+}$, iodine is oxidized and liberated in the solution. Thus,

the oxygen content can be calculated from the amount of iodine obtained, which is in turn determined by titration with sodium thiosulfate. In gas volumetric analysis the sample is dissolved in a dilute nitric acid. During dissolution $Co^{4+}$ and $Co^{3+}$ cations are reduced to $Co^{2+}$ and a stoichiometric amount of gaseous oxygen is evolved. The amount of this oxygen (a volume at known temperature and pressure) can be measured and an average oxidation state of the Co cations and therefore the oxygen content can be calculated. For each analysis, three to five parallel experiments were carried out. We have obtained good agreement within $\pm 0.02$ in $\delta$ for both iodometric titration and gas volumetric analysis. Determination accuracy of $\pm 0.01$ in $\delta$ can be reached in both methods. More details about the peculiarities of oxygen determination in layered cobalt perovskites are published elsewhere [18].

The phase purity control and the structure determination were carried out using x-ray powder diffraction (Cu K$\alpha$ radiation). Room temperature patterns were collected by scanning the angular range $5° \leqslant 2\Theta \leqslant 100°$ in steps of $0.02°$. The analysis was done with the program Fullprof [19] and the lattice parameters were determined with silicon as a standard. The temperature dependent DC magnetization measurements were carried out in both field-cooled (FC) and zero-field-cooled (ZFC) modes, using a Quantum Design PPMS. A magnetic field $H = 0.1$ T was applied in the temperature range $T = 2$–$350$ K. For several selected samples the field dependent DC magnetization was measured as well.

## 3. Results and discussion

### 3.1. Structure

For both sets of samples with low oxygen content ($\delta < 0.3$) the Rietveld analysis reveals an orthorhombic *Pmmm* space group, with lattice parameters $a \sim b \sim a_p$ and $c \sim 2a_p$. Here $a_p$ refers to the cell parameter of the ideal cubic perovskite. The orthorhombic distortion in the $a$–$b$ plane is rather small (see figure 2 and table 1), which is in agreement with structural studies performed on $RBaCo_2O_5$ ($\delta = 0$) R = (Eu, Gd) [3], (Tb, Dy, Ho) [7], Y [5, 8], and Nd [9]. The lattice parameter $c$ grows with $\delta$, while $a$ and $b$ decrease. Increasing the oxygen content $\delta \in [0.35$–$0.7]$ results in a fast growing orthorhombic distortion, which reaches its maximum value near $\delta \sim 0.5$ and almost vanishes again for $\delta > 0.7$. The strength of the orthorhombic distortion is found to depend on the synthesis history in the following way: the values of the lattice parameters $b$ and $c$ nearly coincide for the two sets of samples, while the parameter $a$ of the SC materials is systematically larger than that of the RQ series. In addition, the dependence of the $c$ parameter upon the oxygen content reveals a kink anomaly around $\delta \sim 0.5$ for both series. As seen in the inset of figure 2(a), the volume of the pseudocubic unit cell contracts almost linearly with increasing oxygen content over the whole measured $\delta$ range at an average rate of 0.3% per $\delta = 0.1$.

In order to explain the values of the $a/b$ anisotropy close to $\delta = 0.5$, *observed for all samples, independently of the thermal treatment*, it was proposed that the oxygen vacancies order within the $PrO_\delta$ layers, resulting in an alternation of oxygen-rich and oxygen-deficient $a$–$c$ layers, and consequently in a doubling of the unit cell along the $b$ direction [3]. After close examination of our x-ray data, we found that the diffraction patterns of the SC samples in the $\delta \in [0.44$–$0.50]$ range exhibit a weak, yet sharp resolution-limited Bragg peak ((011) for the $a_p \times 2a_p \times 2a_p$ supercell), in contrast to the diffraction patterns of the RQ samples, where only traces of size-broadened Bragg reflections were detected (see the inset of figure 2(b)). The pronounced (011) Bragg peak confirms the proposed long-range oxygen ordering in the *slowly cooled* samples with $\delta \in [0.44$–$0.50]$, while the existence of a broad (011) reflection indicates a decreasing of the average size of the oxygen ordered regions for the
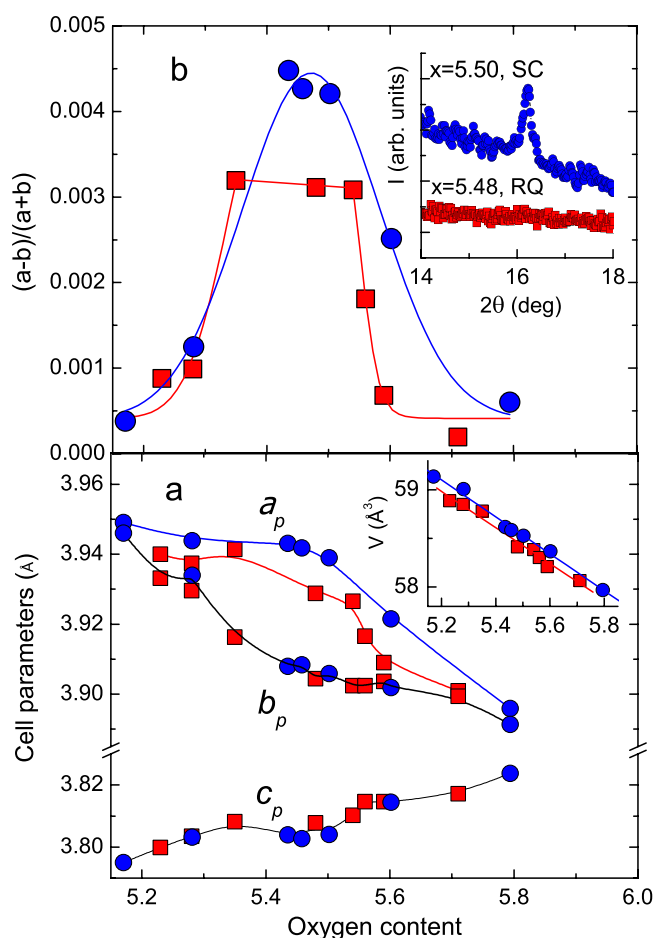
**Figure 2.** Lattice parameters (a) and orthorhombic distortions (b) of PrBaCo$_2$O$_{5+\delta}$ as a function of oxygen content for both the SC (bullets) and RQ (squares) compounds. The lines are guides to the eyes. The inset shows the volume of the pseudocubic unit cell (a) and typical x-ray diffraction patterns (b) of RQ and SQ samples around $2\Theta = 16.2°$. A weak (011) reflection in the SQ data can be observed, thus confirming the ordering of oxygen ions (see text).

*rapidly quenched* samples. Therefore, the present x-ray results show that anomalies in the orthorhombic distortion parameter $O_S = (a - b)/(a + b)$ alone are not sufficient for us to infer long-range oxygen ordering in the PrO$_\delta$ layers.

### 3.2. Magnetic properties

We now turn to the analysis of the magnetic properties of these materials. According to our magnetic measurements, all compounds with $\delta < 0.3$ exhibit a PM $\leftrightarrow$ AFM transition around room temperature. The relevant transition temperatures are given in table 2. Similarly to the structural aspect discussed above, the synthesis history of the compounds with low $\delta$ seems to have little influence on their magnetic properties. In contrast, the magnetic properties of the compounds with $0.35 < \delta < 0.7$ depend strongly on the oxygen nonstoichiometry as well as on the synthesis history (see figures 3(b), (c), (f), (g)). The FC magnetization curves show
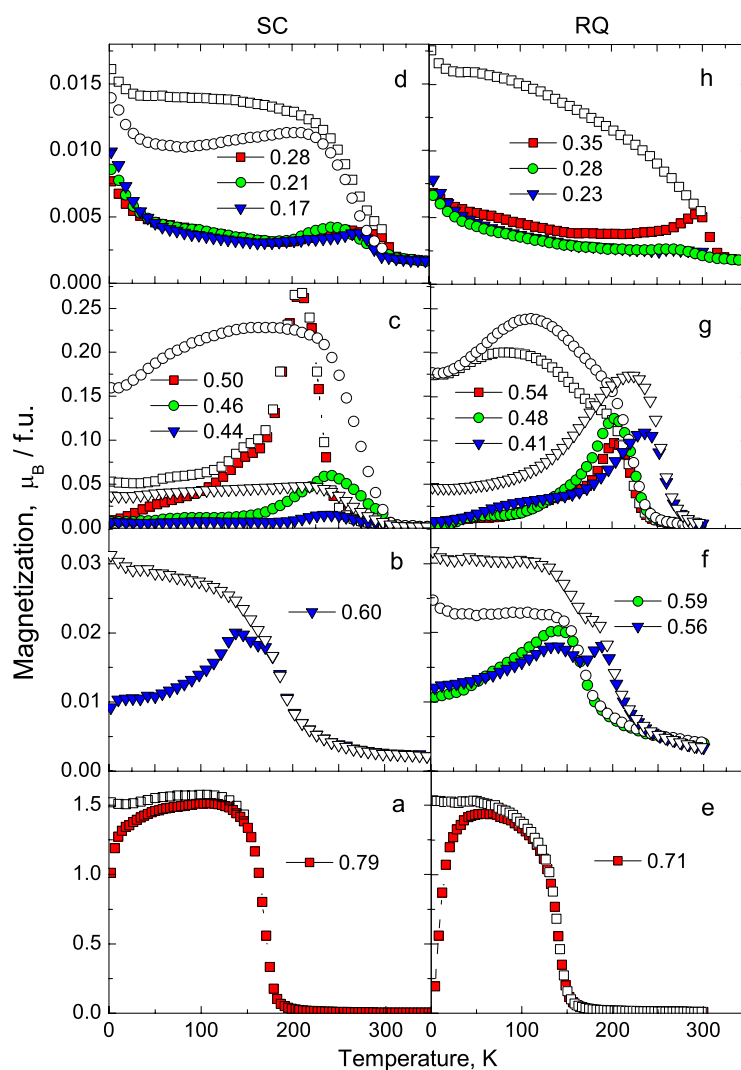
**Figure 3.** Magnetization of the SC ((a)–(d)) and RQ ((e)–(h)) series of $PrBaCo_2O_{5+\delta}$. Filled and open marks denote ZFC and FC magnetization measured in $H = 0.1$ T, respectively. Note the different orders of magnitude of the magnetization for the different panels.

broad maxima which strongly depend upon the external field, while the ZFC magnetization data demonstrate a more complicated behaviour, typically with broad, weak peaks. As illustrated in figure 3, even a slight deviation of the oxygen content from the ideal composition of $\delta = 0.5$ considerably reduces the magnitude of the signal. Only for the SC sample $PrBaCo_2O_{5.50}$ ($\delta = 0.50$; see figure 3(c)) do we find nearly coinciding ZFC and FC magnetization curves together with the well known successive PM $\leftrightarrow$ FM $\leftrightarrow$ AFM transitions [4, 8]. The magnitude of the spontaneous magnetization for this sample is far above those for any other samples. Despite the fact that the ZFC spontaneous magnetization of both the RQ and SC compounds with $\delta \in [0.35–0.7]$ shows a marked increase at $T_C$, followed by a drop below $T_N$, we do not believe that our samples, except for the slowly cooled $\delta = 0.5$ sample, display simple long-range magnetic ordering. The large difference between ZFC and FC magnetization curves

**Table 2.** Types of order and transition temperatures of the RQ (upper part) and SC (lower part) PrBaCo$_2$O$_{5+\delta}$ compounds.

| $\delta$ | Type of order | Transition temp. (K) |
|---|---|---|
| 0.23(1) | AFM | 290(5) |
| 0.28(1) | AFM | 290(5) |
| 0.35(1) | CG | 305(5) |
| 0.48(1) | CG | 224(5) |
| 0.54(1) | CG | 222(5) |
| 0.56(1) | CG | 198(5) |
| 0.59(1) | CG | 169(5) |
| 0.71(1) | FM | 140(3) |
| 0.17(1) | AFM | 286(5) |
| 0.28(1) | CG | 306(5) |
| 0.44(1) | CG | 300(5) |
| 0.46(1) | CG | 300(5) |
| 0.50(1) | AFM/FM | 190(3)/229(3) |
| 0.60(1) | CG | 186(10) |
| 0.79(1) | FM | 167(3) |

indicates rather the existence of a cluster glass (CG) state as earlier reported for R$_{1-x}$Sr$_x$CoO$_3$ (R = La, Nd) [20–22]. The strong variation of the magnetization with $\delta$ shows that only a fraction of the sample volume is in a FM-ordered state. Since in addition our field dependent magnetization measurements $M(H)$ at different temperatures below $T_{CG}$ show a lack of saturation in external fields up to 9 T (not shown), we conclude that upon oxygen doping the system separates into oxygen-rich clusters (with predominant FM Co$^{3+}$/Co$^{4+}$ states) and an oxygen-poor matrix (with predominant AFM Co$^{2+}$/Co$^{3+}$ states).

PrBaCo$_2$O$_{5+\delta}$ samples in the range $\delta > 0.7$ exhibit qualitatively similar behaviours for the two series, namely an observable PM $\leftrightarrow$ FM transition (see figures 3(a), (e)). The existence of a ferromagnetic state can be explained within the framework of a percolating network of FM clusters, when the concentration of oxygen-rich domains exceeds a critical value[5]. The observed discrepancy between DC magnetization measurements at $H = 1$ T, where FM behaviour was observed, and zero-field neutron powder diffraction measurements, where AFM order was found [23], can be explained within such a percolation model, since the concentration of FM clusters is expected to grow as a function of increasing magnetic field.

## 4. Conclusion

In conclusion, we have shown that the magnetic properties of PrBaCo$_2$O$_{5+\delta}$ depend dramatically on the nature of the oxygen ordering. As a consequence, special attention should be paid to systematically controlling and characterizing the oxygen distribution in layered cobalt perovskites; otherwise erroneous conclusions about the magnetic properties (spin state of Co) could be reached. The correlation between the oxygen content and unit cell parameters obtained in the present work will be useful for estimating the oxygen content $\delta$ and the character of the oxygen ordering in further studies, especially if single-crystal samples become available.

[5] Note: in an independent study, the critical value for the appearance of FM ordering was found to be $\delta > 0.85$ [23], a value larger than the one found in the current work. Clearly, more detailed structural (preferably neutron diffraction as well as synchrotron x-ray) and magnetic relaxation studies are necessary to understand these discrepancies.

## Acknowledgments

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