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# Hall effect measurements on thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ : On how to determine the charge carrier concentration in strongly correlated misfit cobaltites

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The Hall coefficient  $R_H$  and electrical conductivity of misfit calcium cobalt oxide  $(\text{Ca}_2\text{CoO}_{3-\delta})_q(\text{CoO}_2)$  (CCO) were measured at room temperature for different oxygen vacancy concentrations  $\delta$ . Based on these and numerous previous results, it is shown that the charge carrier concentrations  $n$  obtained by the classical formula  $R_H = 1/ne$  are between  $3$  and  $6 \times 10^{20} \text{ cm}^{-3}$  and thereby much lower than those derived by other experimental techniques and fail to explain the observed electric properties of CCO. We show that the experimental results are well described using an earlier proposed  $t$ - $J$ -model for strongly correlated electrons on a triangular lattice. The hopping parameter  $t$  for CCO was found to be  $\approx -20 \text{ K}$  and the charge carrier concentration of fully oxidized CCO to be  $5.7 \times 10^{21} \text{ cm}^{-3}$  (0.41 hole type carriers per formula unit), in agreement with other experimental techniques. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921861>]

## I. INTRODUCTION

Today, a significant part of the energy from many industrial processes is lost as waste heat. Therefore, the upconversion of heat into usable, less entropic forms of energy could be a promising way of increasing the efficiency of these processes. Generators based on thermoelectric materials offer an elegant and reliable way to re-use part of the waste heat, as, for example, generated in cars.

Recently, several classes of oxide materials have been investigated for their thermoelectric application potential, because of their high chemical stability, abundance, and low toxicity in comparison with their non-oxide competitors (e.g., Refs. 1 and 2). In particular, several misfit cobaltites are found to be among the most promising and studied p-type candidates.

The common building block of these materials is a layer of edge-sharing  $\text{CoO}_6$ -octahedra, stacked along the  $\vec{c}$  direction, separated by layers of different compositions of a rock salt symmetry (see Ref. 3 for a recent review). The mismatch of the  $b$ -axis lattice parameter of the rock salt (RSL) and the  $\text{CoO}_2$ -layer (COL) leads to an incommensurate misfit modulation along that axis. The chemical composition of misfit cobaltites can be generally written as  $(\text{RSL})_q(\text{CoO}_2)$ , where  $q$  is the misfit parameter defined as  $q = b_{\text{COL}}/b_{\text{RSL}}$  and RSL stands for the chemical composition of the rock salt layer. Charge transport is considered to be due to mobile hole charge carriers inside the COL, while the RSL acts as a charge reservoir regulating the hole concentration by preserving the overall charge neutrality. Thus, the concentration of charge carriers in the COL of misfit cobaltites is determined by the charge transfer between the two electrostatically charged subsystems. The hole concentration  $h$  per formula unit can be expressed as

$$h = 1 - q \cdot A, \quad (1)$$

where  $A$  is the electrostatic charge of the RSL per formula unit.  $h$  can thus be changed via a variation of the misfit parameter  $q$ , or a variation of the charge  $A$ . For example, the latter can be achieved by substitution of an element with different valency or the formation of effectively positively charged oxygen vacancies.

In this paper, we study the misfit calcium cobaltite (CCO), with a nominal composition  $(\text{Ca}_2\text{CoO}_{3-\delta})_q(\text{CoO}_2)$  ( $q \approx 0.62$ ), often also denoted as  $\text{Ca}_3\text{Co}_4\text{O}_9$ .<sup>4–8</sup> CCO is one of the most promising and studied oxide materials for thermoelectric energy harvesting, but also applications as electrode material in fuel cells,<sup>9,10</sup> hydrogen evolution catalyst,<sup>11</sup> or as a transparent conducting oxide<sup>12</sup> have been proposed recently. Despite the vital research activity on CCO, such a fundamental property as the charge carrier concentration is still unclear: The reported carrier concentration  $n$  of ceramic samples obtained by measurement of the Hall factor  $R_H$  via the classical relation  $R_H = 1/ne$  ranges from  $3$  to  $6 \times 10^{20} \text{ cm}^{-3}$  (e.g., Refs. 13–21). These concentrations translate — employing typical relative densities of the sample around 90% and a theoretical density of  $4.68 \text{ g cm}^{-3}$  (Ref. 4) — to a molar charge carrier concentration of  $\approx 0.02$ – $0.04$  per formula unit CCO. However, these values are significantly lower than carrier concentrations obtained by other techniques (e.g., X-ray absorption spectroscopy (XAS),<sup>22</sup> electron energy loss spectroscopy (EELS),<sup>23</sup> density functional theory (DFT),<sup>24,25</sup> and thermopower renormalization<sup>26</sup>) ranging from  $0.3$  to  $0.6$  per formula unit. Further, the obtained concentrations from Hall effect measurements also fail to explain the limited effect of doping on the transport parameters, as shown in the following.<sup>27</sup>

Only few studies report on acceptor doping on the Ca site. For example, if we consider  $(\text{Ca}_{2-x}\text{M}_x\text{CoO}_3)_q(\text{CoO}_2)$  with an acceptor doping level of  $x = 0.1$ , the molar hole-type

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charge carrier concentration increases nominally by  $q \times x = 0.062$ , that is by more than the concentration as obtained from classical Hall effect measurements for nominally undoped CCO ( $\leq 0.04$ ). Expressing the conductivity,  $\sigma$ , simply as the product of charge carrier concentration and mobility, and assuming the mobility to be approximately constant upon doping, a more than twofold increase of the conductivity is expected. However, the reported increase of  $\sigma$  is much less than that: e.g.,  $\approx 30\%$  for  $M = \text{Na}$  and  $x = 0.2$  (Ref. 28) or  $\approx 10\%$  for  $M = \text{K}$  and  $x = 0.2$ .<sup>29</sup> On the other hand, such doping behavior could be understood assuming a significantly higher hole concentration for nominally undoped CCO, e.g., 0.4 per formula unit. Then, acceptor doping by  $x = 0.2$  on the Ca site is expected to increase the nominal charge carrier concentration by  $\approx 25\%$  from 0.4 to 0.52 per formula unit, in qualitative agreement with the experimental observation.

A similar argument is valid for the case of donor doping on the Ca site, which has been more widely studied: Electron doping by more than the hole concentration of nominally undoped CCO should lead to a p-n-transition manifesting in a negative Seebeck coefficient for the doped sample. However, the reported results only show a relatively small increase of the (positive) Seebeck coefficient, as expected for minor changes of the carrier concentration.<sup>19,30–33</sup> Finally, we note that also the frequently used Heikes formula to describe the high temperature limit of the Seebeck coefficient yields a molar hole concentration around 0.5 to describe the experimentally observed Seebeck coefficient of  $\approx 150 \mu\text{V K}^{-1}$  (assuming both  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  in a low spin configuration).<sup>34</sup>

In summary, all available experimental and theoretical evidences (XAS, EELS, DFT, thermopower renormalization, doping studies, and Heikes formula) points towards that CCO cannot be treated as a simple semiconductor or metal at room temperature and below. In particular, there is a significant underestimation of the charge carrier concentration in CCO by the classical interpretation of Hall effect measurements.

In this paper, we systematically vary the charge carrier concentration of a single sample and study the resulting changes in the electrical conductivity and Hall coefficient at room temperature. In many oxides, the oxygen stoichiometry can be varied in a significant range by the formation of oxygen vacancies or interstitials without decomposition, depending on the surrounding atmosphere and temperature. An oxygen vacancy carries an effectively positive charge and therefore acts as a donor species of two electrons to the system.

For CCO, it has been shown previously that the RSL can accommodate oxygen vacancies up to  $\delta \leq 0.15$ , while preserving its overall structure.<sup>7,8,35,36</sup> In contrast, the COL is stable towards oxygen nonstoichiometry.<sup>8,37</sup> By the controlled formation of oxygen vacancies, it is therefore possible to vary the carrier concentration in CCO via Eq. (1) in a significant range. To analyse our results, we employ a model developed for strongly correlated carriers on a triangular lattice. By precisely controlling the oxygen vacancy concentration, we can extract the relevant parameters of the

suggested model and provide a consistent description of the charge carrier concentration in CCO.

## II. EXPERIMENTAL

A polycrystalline disk-shaped sample of CCO with thickness  $d = 1.4 \text{ mm}$  was fabricated as described elsewhere.<sup>36</sup> Four Au electrodes were painted on the sample (Metalor M-0034 ink) and fired at  $850^\circ\text{C}$  in air to ensure good ohmic contacts (see inset in Fig. 1). The electric properties were measured on a single sample to exclude sample-specific effects of the microstructure or relative density as the cause for the observed changes. For all electrical measurements, we used an Agilent 34970A multichannel voltmeter and an Agilent E3642A current source. The oxygen vacancy concentration was varied by annealing the sample at high temperatures and in a controlled oxygen partial pressure  $p\text{O}_2$ , while monitoring the weight change due to in- and out-diffusion of oxygen ions using a CI Electronics MK2 microbalance. When equilibrium was reached, the sample was quenched to room temperature, effectively freezing the oxygen content (see Ref. 36 for experimental details). This method only allows the determination of changes in the oxygen stoichiometry relative to an *a priori* unknown reference state. The values for  $\delta$  given in this manuscript are calculated using  $\delta_0 = 0$  at low temperatures and high oxygen partial pressure as a reference, as suggested by, e.g., Refs. 31 and 35. All values would be set off by a constant  $\delta_0$ , when assuming an oxygen deficient reference state, as obtained by Morita *et al.*<sup>38</sup> This has, however, no influence on our discussion or the extracted parameters, as seen in Results and Discussion. The in-plane conductivity is measured by the van der Pauw technique. Room temperature measurements of  $R_H$  were performed using a permanent magnet with  $B = 1.02 \text{ T}$ . The Hall resistance  $U_{wy}/I_{xz}$  was obtained by a linear fit of six  $I$ - $U$  measurements with current steps of  $200 \text{ mA}$ . All measurements were performed in both current

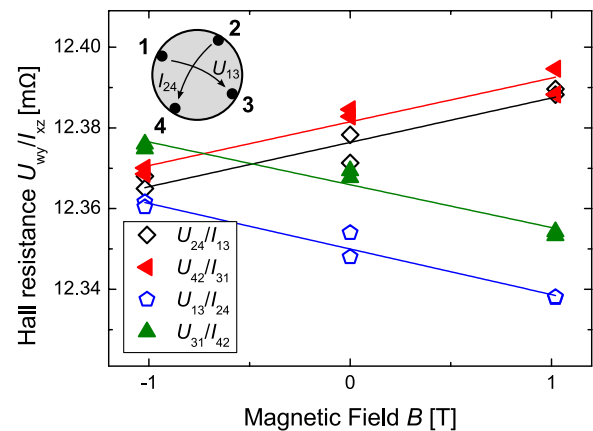


FIG. 1. An example of measured values of the Hall resistance  $U_{wy}/I_{xz}$  against the magnetic field  $B$  for one particular oxygen vacancy concentration of the sample. Each Hall resistance has been measured twice. From these measurements, the Hall factor is determined via Eq. (2). Different current directions and electrode pairs (visualized by different colors and symbols) were used to eliminate thermoelectric effects and increase statistical significance. Inset: Sample sketch with the four Au electrodes and exemplary current/voltage directions.

directions to avoid the influence of thermoelectric effects, and with an interval of 60 s to minimize any temperature effect due to Joule heating. The Hall resistance as a function of the magnetic field, taken for a certain oxygen vacancy concentration as an example, is shown in Fig. 1. All measurements were taken in random order and repeated twice to check for consistency and reproducibility. Each Hall resistance can be measured with a high accuracy (the linear fit of a  $U(I)$ -measurement typically has  $1 - R^2 \approx 10^{-7}$ ), but small variations are observed, when repeating the measurement under nominally identical conditions. This variation could be, for example, due to small changes of the room and/or sample temperature, and we identify its magnitude with the measurement accuracy. We could not detect any dependency of the van der Pauw resistivity on the magnetic field, in agreement with data reported by Masset *et al.*<sup>4</sup> Therefore, the  $B$ -field dependency of the Hall resistance shown in Fig. 1 can be solely attributed to the Hall effect. The Hall factor  $R_H$  is determined from the slope of the Hall resistances vs. the magnetic field  $B$  and averaged over the four different electrode combinations shown in Fig. 1

$$\frac{U_{wy}}{I_{xz}} = R_H \cdot \frac{B}{d}. \quad (2)$$

The oxygen nonstoichiometry  $\delta$  was varied in random order to demonstrate the reversibility of oxygen reduction and oxidation.

### III. RESULTS AND DISCUSSION

The in-plane conductivity  $\sigma$  and the Hall coefficient  $R_H$  of CCO as a function of  $\delta$  are shown in Fig. 2. It is seen that  $\sigma$  decreases with increasing  $\delta$ , indicating the decrease of charge carriers (holes) when oxygen vacancies are formed (Fig. 2(a)). The Hall coefficient  $R_H$  is positive, in agreement with holes being the majority charge carrier in CCO.  $R_H$  increases with increasing  $\delta$ , from  $11 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$  for  $\delta \approx 0.02$  to  $16 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$  for  $\delta \approx 0.14$  (Fig. 2(b)). Using the classical relation  $R_H = 1/ne$ , these values correspond to a charge carrier concentration  $n$  of  $5.7 \times 10^{20}$  (0.047 per formula unit) and  $3.9 \times 10^{20} \text{ cm}^{-3}$  (0.032 per formula unit), respectively. These values are in agreement with carrier concentrations for CCO derived from Hall effect measurements reported by others,<sup>13–21,39</sup> but in disagreement with estimates for the charge carrier concentration made from other techniques, as explained in the introduction. In general, the transport properties of CCO are highly anisotropic caused by its layered crystal structure, with relatively high conductivity within the COL (along the  $ab$ -direction) and low conductivity across (along  $c$ ). This anisotropy is also present for a polycrystalline specimen due to a pronounced grain alignment during pressing and sintering. For example, Kenfaui *et al.* reported an anisotropy  $\sigma_{ab}/\sigma_c$  of  $\approx 80$  for a polycrystalline CCO sample, densified at a pressure of 30 MPa.<sup>40</sup> The results for in-plane measurements on CCO ceramics are thus dominated by the contribution of the COL, explaining the similar experimental values for  $R_H$  for samples with identical composition, but prepared using different fabrication methods and thus different degrees of grain

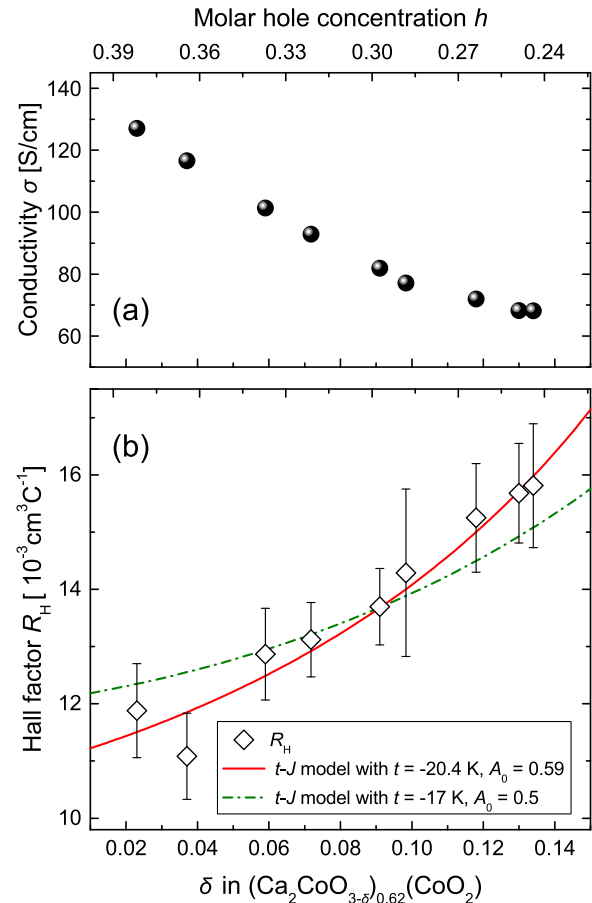


FIG. 2. (a) The conductivity  $\sigma$  of  $(\text{Ca}_2\text{CoO}_{3-\delta})_{0.62}(\text{CoO}_2)$  with varying oxygen vacancy concentration  $\delta$ .  $\sigma$  decreases with increasing  $\delta$ , indicating a depletion of hole type carriers. (b) The Hall coefficient  $R_H$  as a function of  $\delta$ .  $R_H$  increases with  $\delta$ . Error bars indicate the weighted average statistical error of the linear regression in Fig. 1. Dashed and solid lines are calculated using Eq. (5) and different parameters  $A_0$  and  $t$  as explained in the text. The hole concentration for the top x-axis was calculated using Eq. (5) and  $A_0 = 0.59$ .

alignment. In any case, as our data are obtained for a single polycrystalline sample, the observed variation of  $R_H$  with  $\delta$  cannot be explained by microstructural effects, but only by a variation of the charge carrier concentration.

Previously, Eng *et al.* have noticed the relevance of strong electronic correlations to understand the Hall coefficient in CCO.<sup>39</sup> They reported a Hall coefficient of  $12.5 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$  at room temperature for an epitaxial thin film sample — similar to our results for  $\delta \approx 0$  — combined with a strong temperature dependency of  $R_H$ , which cannot be explained within the simple Drude picture. In order to obtain a meaningful estimate for the charge carrier concentration via the classical relation  $R_H = 1/ne$ , Eng *et al.* extrapolated their low temperature ( $T < 100 \text{ K}$ ) data, where the influence of electronic correlations on the Hall coefficient is negligible,<sup>41,42</sup> to high temperatures. They obtained an estimate for the ordinary Hall coefficient of  $R_H = 2.6 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1}$ , corresponding to a hole concentration of 0.36 per formula unit.

We will in the following discuss our room temperature data using a model capturing the strongly correlated character of charge carriers found in CCO and with special

attention to the topology of the misfit family. Charge transport in CCO is expected to occur within the  $\text{CoO}_2$ -layers. In these layers, cobalt ions form a triangular lattice, which has been studied theoretically using a  $t$ - $J$ -model based on the Hubbard model. In particular, it was pointed out that the Hall-coefficient  $R_H$  in systems based on a triangular lattice does *not* yield the charge carrier concentration as in regular conductors, but that it can be described as<sup>43,44</sup>

$$R_H = -\frac{V k_B T}{4e t} \frac{1+x}{x(1-x)}, \quad (3)$$

where  $V$  is the volume of a unit cell containing one cobalt ion inside the  $\text{CoO}_2$ -layer ( $\approx 7.3 \times 10^{-23} \text{ cm}^3$  for  $\text{CCO}^4$ ),  $x$  is the molar electron concentration away from half filling, and  $t$  is the hopping parameter scaling the kinetic term of the studied Hamiltonian. For simplicity, we will in the following refer to  $t$  as a temperature, rather than an energy unit. In the case of CCO,  $x$  can be identified with the concentration of  $\text{Co}^{3+}$  in the  $\text{CoO}_2$ -layer, which is related to the hole concentration  $h$  via  $h = 1 - x$ . By creating oxygen vacancies, the electrostatic charge of the RSL increases, which is compensated by an increase of  $x$  (cf. Eq. (1)). Accordingly, we can express  $x$  for an oxygen deficient sample as

$$x = A_0 + 2 \cdot q(\delta) \cdot \delta, \quad (4)$$

where  $A_0$  is the  $\text{Co}_{\text{COL}}^{3+}$  concentration for a sample of CCO oxidised carefully at low temperatures and high  $p\text{O}_2$ ,  $q \approx 0.62$  is the misfit parameter, and the factor 2 reflects the effectively double positive charge of an oxygen vacancy. In the following, we neglect the variation of the misfit parameter  $q$  with  $\delta$ , as we expect it to be weak and its influence on  $x$  to be only minor as compared to the effect of oxygen vacancies. Combining Eqs. (3) and (4), we get

$$R_H(\delta) = -\frac{V k_B T}{4e t} \frac{1 + A_0 + 2q\delta}{(A_0 + 2q\delta)(1 - A_0 - 2q\delta)}. \quad (5)$$

A numeric fit of the experimental data with respect to Eq. (5) describes the experimental  $R_H$  well and yields  $A_0 = 0.59 \pm 0.02$  and  $t = -20.4 \pm 0.9 \text{ K}$ . The negative sign of  $t$  confirms the hole-type character of charge carriers in CCO, and the magnitude of  $t$  is in the same range as values reported by Hébert *et al.* for other types of misfit cobaltites.<sup>3</sup> We note that  $R_H(x)$  from Eq. (5) is quite sensitive to both  $A_0$  and  $t$ , effectively allowing to discriminate between different values discussed in the literature. For example, for  $A_0 = 0.5$  as suggested by DFT<sup>24</sup> and EELS<sup>23</sup> studies of CCO, the best fit is obtained for  $t = -17 \text{ K}$  and describes the experimental data significantly worse (Fig. 2(b)). We further note that Eq. (3) implies a linear increase of  $R_H$  with increasing temperature, with a slope depending on  $x$  and  $t$ . Indeed, Eng *et al.* reported an almost linear increase of  $R_H(T)$  for  $T \geq 100 \text{ K}$ . The observed slope of  $\approx 0.031 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1} \text{ K}^{-1}$  agrees well with the one calculated from Eq. (3) (with  $x = A_0 = 0.59$  and  $t = -20.4 \text{ K}$ ) of  $0.036 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1} \text{ K}^{-1}$ .

The corresponding hole concentration  $h = 1 - x$  of the presently studied samples using the  $t$ - $J$ -model is between 0.4 ( $5.7 \times 10^{21} \text{ cm}^{-3}$ ) for  $\delta = 0.02$  and 0.24 ( $3.4 \times 10^{21} \text{ cm}^{-3}$ )

for  $\delta = 0.14$ , roughly an order of magnitude larger than the values obtained by the analysis using the classical formula  $R_H = 1/ne$ .

In the limit of low concentrations of charge carriers, the influence of strong correlations is expected to disappear. However, the Hall coefficient presented here does not show any sign of relaxation to its conventional, uncorrelated value, even for the lowest carrier concentration ( $h \approx 0.25$ ) realised in this study. This observation is consistent with results for  $R_H$  of other misfit cobaltites, showing a similar  $T$ -dependency for hole concentrations as low as  $h = 0.1$ .<sup>3,45</sup>

The values extracted from the  $t$ - $J$ -model are in agreement with estimates derived from other experimental techniques. Further, the limited effect of doping on the electric properties can — based on these significantly higher charge carrier concentrations for nominally undoped CCO — now be qualitatively understood without any further and unlikely assumptions regarding a distinct sensitivity of the carrier mobility on different doping species.

In particular does a hole concentration of 0.41 for fully oxidized CCO agree well with a model presented in Ref. 36. There, we could describe the oxygen nonstoichiometry and electrical transport of CCO using a hole concentration of 0.38 based on the formal charge neutrality of  $(\text{Ca}_2^+ \text{Co}^{3+} \text{O}_3)_{0.62} (\text{Co}^{3.38+} \text{O}_2)$ . Here, the 3+ valence state of Co within the RSL has been somewhat debated: While some structural studies report on a mixed valent  $\text{Co}^{2+/3+}$  state within the RSL,<sup>4,46</sup> more direct, spectroscopic and magnetic methods have not found any sign of  $\text{Co}^{2+}$  in CCO at room temperature,<sup>22,23,47</sup> in agreement with the results presented here.

Combining systematic Hall effect measurements with the precise control of the oxygen vacancy concentration has thus been demonstrated as an approach to extract relevant parameters as the hopping parameter  $t$  and the charge carrier concentration  $x_0$  of strongly correlated oxides. We note that the alternative measurement of the Hall coefficient as a function of temperature does not allow for the individual determination of charge carrier concentration and hopping parameter. To this end, additional information has to be gathered from other experiments, e.g., angle-resolved photoemission spectroscopy (ARPES)<sup>48</sup> or thermopower scaling.<sup>49</sup>

Finally, we want to discuss the influence of oxygen vacancies on the carrier mobility  $\mu$  in CCO.  $\mu$  can be derived by the standard expression

$$\sigma = e \cdot h \cdot V \cdot \mu, \quad (6)$$

with  $V$  being the unit cell volume as defined previously and  $h$  the hole concentration calculated from the experimental  $R_H$  via Eq. (5) (with  $t = -20.4 \text{ K}$  and  $h = 1 - x$ ). The derived charge carrier mobility  $\mu$  does not show a clear dependency on oxygen nonstoichiometry  $\delta$  (or equivalently on the charge carrier concentration) with values around  $\approx 0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Fig. 3). Oxygen vacancies are formed mainly on oxygen sites within the RSL,<sup>8,37</sup> while charge transport is assumed to occur within the COL. Hence, charge carriers within the COL are not scattered efficiently by the oxygen defects, leaving the mobility effectively unchanged upon oxygen vacancy formation, as observed experimentally. This result indicates that the

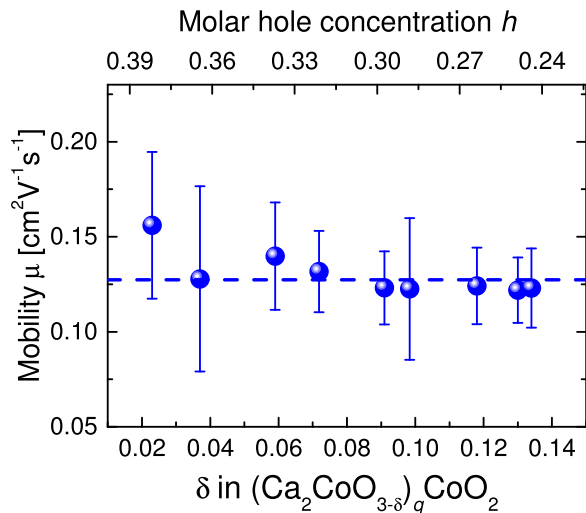


FIG. 3. The carrier mobility calculated via Eqs. (5) and (6) against oxygen nonstoichiometry  $\delta$ . Obtained values range around  $\approx 0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (dashed line) with no clear dependency on  $\delta$ .

carrier mobility within the COL is indeed relatively independent of the interlayer strain between the RSL and COL, which is known to change systematically with the oxygen vacancy concentration.<sup>37</sup> Thereby, our simple discussion of different doping studies is justified.

#### IV. CONCLUSION

In conclusion, we have shown that the classical interpretation of the measured Hall coefficient in  $(\text{Ca}_2\text{CoO}_3)_q(\text{CoO}_2)$  (CCO) — and misfit cobaltites in general — results in misleadingly low values for the charge carrier concentration. Instead, we have analyzed the Hall coefficient in CCO on the basis of a  $t$ - $J$ -model for strongly correlated charge carriers on a triangular lattice. The charge carrier concentration is reversibly varied in a single sample by the precise control of the oxygen content. The Hall coefficient calculated from the  $t$ - $J$ -model is in good agreement with the experimental data, using a molar hole concentration of 0.41 ( $5.7 \times 10^{21} \text{ cm}^{-3}$ ) for fully oxidized CCO and a hopping parameter  $t \approx -20 \text{ K}$ . The suggested model for charge carriers in CCO is thus consistent with all available experimental and theoretical data, thereby providing a deeper and more detailed understanding of CCO and related materials.

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