Revised model for thermopower and site inversion in Co_3O_4 spinel

Taylor D. Sparks*
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

Aleksander Gurlo
Institute for Material Science and Technologies, Technische Universität Berlin, D-10587 Berlin, Germany

Michael W. Gaultois
Leverhulme Research Centre for Functional Materials Design, The Materials Innovation Factory, Department of Chemistry, University of Liverpool, 51 Oxford Street, Liverpool, L7 3NY, United Kingdom

David R. Clarke
School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

(Received 16 May 2018; revised manuscript received 9 July 2018; published 30 July 2018)

In recent years, the fundamental understanding of thermopower in strongly correlated systems as it relates to spin and orbital degeneracy has advanced, but the consequences for determining cation distribution have not been considered. In this work we compare measurements of the electrical conductivity and thermopower in Co_3O_4 spinel with different models for the thermopower based on different assumptions of the cation distributions. Using thermopower measurements we calculate the *in situ* cation distribution according to three different models: case (i) the original Heikes equation, case (ii) Koshibae and co-workers' modified Heikes equation, and case (iii) a new model, using the modified Heikes equation but with contributions from both octahedral and tetrahedral sites. We find that only the modified Heikes equation that includes contributions from both octahedral and tetrahedral sites satisfies the constraints of stoichiometry in the spinel structure. The findings suggest either complete (∼100%) inversion of the spinel structure if no change in spin state, or a combination of a minimum 40% inversion with a change in spin state of the octahedral Co^{3+} cation.

DOI: 10.1103/PhysRevB.98.024108

I. INTRODUCTION

The Seebeck coefficient is one of the principal parameters used to characterize thermoelectric materials, and is often referred to as the thermopower Q. Because it is an intrinsic material property deeply linked to the electronic structure, it has been used to provide information about the coordination and oxidation state of metal cations in small polaron conductors. Since Wu and Mason originally demonstrated thermopower could be used to determine the cation distribution in spinels [1], the technique has seen widespread use. In the spinel-type oxides $(A)^{\mathrm{tet}}[B]_2^{\mathrm{oct}}O_4$, where $(A)^{\mathrm{tet}}$ and $[B]_2^{\mathrm{oct}}$ refer to the tetrahedral and octahedral sites, respectively, different cations can occupy the A and B sites. The site occupancy is determined by factors such as crystal field stabilization energy, as well as the size and charge of the cations. As a consequence, the distribution of cations over tetrahedral and octahedral sites determines a variety of physical and chemical properties of spinel-type materials. The iron (II, III) and cobalt (II, III) oxides (Fe_3O_4 and Co_3O_4), for instance, are among the most studied group of the 2–3 spinel-type oxides. Despite similar compositions and elements, they form completely different structures in terms of cation distribution. In an ideal case, Co_3O_4 possesses a normal spinel-type structure $(Co)^{2+}[Co]_2^{3+}O_4$ with Co^{2+} ($S = 3/2$) cations on the tetrahedral $(A)^{\mathrm{tet}}$ sites, and low-spin (LS) Co^{3+} ($S = 0$) cations on octahedral $[B]^{\mathrm{oct}}$ sites. On the other hand, Fe_3O_4 is an inverse spinel $(Fe)^{3+}[Fe^{2+}Fe^{3+}]^{\mathrm{oct}}O_4$ with Fe^{3+} cations on the tetrahedral $(A)^{\mathrm{tet}}$ sites, and Fe^{2+}/Fe^{3+} cations on octahedral $[B]^{\mathrm{oct}}$ sites. In practice, however, the cation distribution over the tetrahedral and octahedral sites strongly depends on the specimen history, including synthesis conditions, calcination/annealing temperature, and heating and cooling rates. In addition, the degree of cation intermixing between the tetrahedral and octahedral sites increases with temperature, making the correlation between the oxide structure and properties, particularly thermopower, highly dependent on the processing conditions. The basic principle underlying the use of thermopower measurements to determine the cation distribution in spinels is that, for small-polaron conductors, the thermopower depends on the fraction of conducting sites. This is quantified by the Heikes formula [2]

$$Q = \frac{k_B}{e} \ln\left(\beta \frac{\chi}{1-\chi}\right), \tag{1}$$

where k_B is Boltzmann's constant, e is the elementary positive charge, β is the Heikes degeneracy term, and χ is the fraction of cations in higher oxidation state on the conducting sites (i.e., $[M^{3+}]^{\mathrm{oct}}$ in the 2–3 spinels). If multiple ions are present on a

*sparks@eng.utah.edu

site and one acts as a carrier dopant, then the concentration of this ion is simply χ from the Heikes formula.

This original method of using thermopower to determine the cation distribution in Fe_3O_4, proposed in a seminal paper by Wu and Mason in 1981 [1], made two important assumptions. First, the thermopower and electrical conductivity of the spinel oxides originate solely from the ions occupying the octahedral B site. Second, the orbital degeneracy term is unity due to a Jahn-Teller distortion and the subsequent formation of a Kramers doublet, which leaves only a spin degeneracy term [3]. However, some subsequent reports were unable to explain the experimental results using these assumptions [3–5]. In fact, instead of calculating the Heikes degeneracy term β outright, it has commonly been used as a fitting parameter, ranging between $\beta = 1$ and $\beta = 2$. Noninteger values have been justified by ignoring the vibrational entropy term associated with ions surrounding the polaron site [3]. For a proper fit to the data of one report, β would have to change from $\beta = 1$ at low carrier concentrations to $\beta = 2$ at high concentrations [5].

Twenty years later, Koshibae and co-workers [6] proposed a modified form of the Heikes formula to describe the thermopower of strongly correlated oxides in order to account for both spin and orbital degeneracy in addition to the electronic degeneracy ratio between conducting ions:

$$Q = \frac{-k_B}{e} \ln\left(\frac{g_{(2+)}}{g_{(3+)}}\frac{\chi_{(3+)}}{1-\chi_{(3+)}}\right), \tag{2}$$

where $g_{(2+)}$ and $g_{(3+)}$ are the electronic degeneracy terms for the electron donors (Co^{2+}) and electron acceptors (Co^{3+}), and $\chi_{(3+)}$ is the fraction of electron acceptors [2]. The electronic degeneracy g is the product of spin and orbital degeneracies (i.e., $g = g_{spin} g_{orbital}$). As with the Heikes equation, Eq. (2) strictly holds only at high temperatures and for small polaron conductors [2]. Nevertheless, it has been found that Koshibae and co-workers' modified expression successfully describes the thermopower of a variety of other oxide compounds, including derivatives of sodium cobaltate $Ca_3Co_4O_9$ [7], cobalt perovskites $La_{1-x}Sr_xCoO_3$ [8], layered rhodium oxides $(Bi_{1-x}Pb_x)_{1.8}Sr_2Rh_{1.6}O_y$ [9], manganese perovskites $Pr_{0.5}Ca_{0.5}MnO_3$ and double perovskites $Ca(Mn_{3-x}Cu_x)Mn_4O_{12}$ [10], iron based structures $SrFeO_x$ [11], $RBaCo_2O_{5+x}$ (R = Gd, Nd) [12], as well as $LiMn_2O_4$ spinel [13].

Despite the success of Koshibae and co-workers' modified Heikes formula there remain two outstanding issues regarding thermopower measurements of cation distribution in spinels: (i) incorporating the ratio of spin and orbital degeneracy terms for each ion, and (ii) accounting for the thermopower contributions from ions on both A and B sites in the spinel structure, for example, in mixed spinels. To address these issues, we have investigated the temperature dependence of the thermopower of Co_3O_4. To do so, we have calculated the cation distributions at different temperatures by applying different variations of the original model [1] in order to examine the role of tetrahedral versus octahedral site contributions, electronic degeneracy terms, and possible change in spin states. The results of these calculations are compared with cation distributions calculated from equilibrium free energy thermodynamic arguments by Chen and co-workers which included magnetic contributions [14]. Co_3O_4 is well suited for this investigation because numerous experimental observations [15–22] suggest a high-temperature structural transformation between 600 and 1000 K but there is no consensus as to whether this involves inversion, a change in spin state, or a combination of both. Since the tools for probing magnetic structure are not possible at these high temperatures, instead we utilize *in situ* thermopower measurements.

II. EXPERIMENTAL DETAILS

Cylindrical pellets were fabricated from nanometer-sized Co_3O_4 powder (99.9 wt. %, 50 nm particles, Sigma Aldrich). The powders were first cold pressed with a 6 ton load in a 1/2 in. die and then sintered in air. Pure phase, dense samples of Co_3O_4 and CoO were obtained by firing the samples from room temperature up to 1148 K over 2 h and holding for 6 h, ramping to 1373 K over 1 h and holding for 6 h, ramping back to 1148 K over 2 h and holding for 2 h. From this point, samples were quenched in air to obtain phase-pure CoO, or slowly cooled at 1 K/min to obtain phase-pure Co_3O_4. Intermediate cooling rates resulted in mixtures of CoO and Co_3O_4 phases. Rectangular sections approximately $(8 \times 2 \times 1)$ mm^3 in dimension were cut from the cylindrical pellets for thermoelectric measurements.

The thermopower Q and electrical conductivity σ were measured up to 1200 K using an ZEM-3 instrument (ULVAC-RIKO Inc., Japan) in both air and He environments. Samples approximately $(8 \times 2 \times 1)$ mm^3 in dimension were cut from sintered pellets and polished to have orthogonal faces before being heated. All measurements were made with a temperature difference of $\Delta T = 20$, 30, and 40 K using thermocouple probes ~3 mm apart. Measurements were made as the samples were heated and then cooled at ~10 K temperature intervals, decreasing in temperature until the electrical resistivity was too large for measurement.

III. RESULTS AND DISCUSSION

Electrical conductivity measurements as a function of temperature (Fig. 1) reveal three characteristic conductivity regimes with an activation energy of 0.35 ± 0.08 eV (418 to 540 K), 0.15 ± 0.05 eV (540 to 890 K), and 2.28 ± 0.06 eV (890 to 1188 K). These are attributed to the ionization, extrinsic, and intrinsic conduction regimes, respectively, and agree with the reported hopping energy value 0.17 eV and optical absorption transition of 2.14 eV ($O^{2-} \rightarrow Co^{2+}$) [23]. The temperature ranges corresponding to different conduction mechanisms coincide with high-temperature anomalies from previous *in situ* measurements [15–18,20,22] as well as thermopower reported in this work. The measurements of the conductivity in the CoO phase give an activation energy of 0.47 ± 0.02 eV.

The Seebeck coefficient of Co_3O_4 as a function of temperature (measured in air and helium) is shown in Fig. 2 together with that of CoO (measured in helium only). A key feature of the graph is that the spinel Co_3O_4 samples measured in air and helium both have a maximum in thermopower of ~600 μV/K around 850 K. Above this temperature, the thermopower decreases almost linearly with increasing temperature until it

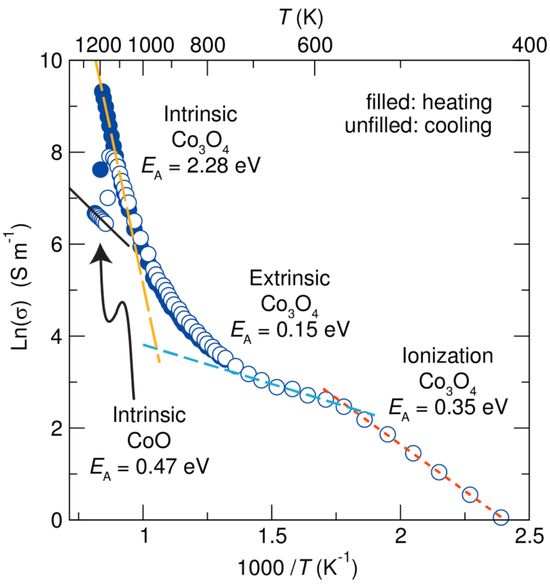

FIG. 1. An Arrhenius plot of electrical conductivity for Co_3O_4 measured in air shows three characteristic regions, each with a different activation energy. Above 1188 K, Co_3O_4 decomposes to CoO, a band conductor.

abruptly increases with a slope of ~250 $\mu V/K^2$ in air and ~400 $\mu V/K^2$ in helium. The region of approximately linear decrease correlates to changes in the spinel structure, such as inversion, discussed in the next section. The discontinuity in thermopower (1188 K in air and 1150 K in He) is attributed to the decomposition of the spinel Co_3O_4 to rock-salt CoO, which has been previously observed by both high-temperature XRD and Raman spectroscopy [22].

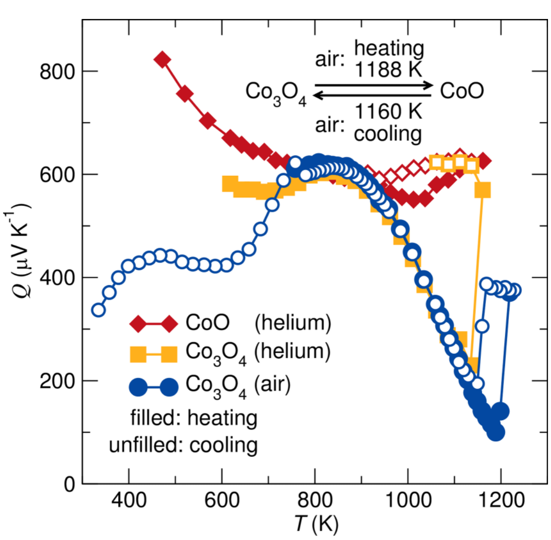

FIG. 2. Co_3O_4 has a maximum thermopower of ~600 $\mu V/K$ near 850 K before the thermopower decreases linearly with temperature until transformation to CoO. This decrease in thermopower with increasing temperature is attributed to inversion of the spinel structure. In the range 900 to 1100 K the CoO sample likely begins to transform to Co_3O_4 during the thermopower measurement before returning to the CoO phase at high temperatures.

In Co_3O_4 with normal spinel-type structure, positive thermopower at low temperature suggests hole hopping conduction dominates. However, at high temperatures there is a decrease in thermopower coincident with the intrinsic conduction regime. It is possible that the reduction in thermopower is due to these intrinsic carriers where electrons have higher mobilities [20].

Previous work has shown Co_3O_4 decomposes to CoO in air at a temperature above 1100 K, with no phase transformation prior to decomposition [22,24,25]. Consequently, the anomalous electrical conductivity and thermopower behavior of Co_3O_4 at lower temperatures, from 600 to 1000 K, must be due to changes in the Co_3O_4 spinel structure itself rather than as a result of a phase transformation to CoO.

Some of the possible combinations of ionic species and spin states available on tetrahedral and octahedral sites are summarized for the inversion and spin unpairing processes in Fig. 3. Owing to the complexity of the possible combinations, several possible charge transfer processes (i.e., hopping) need to be considered in the calculation of cation distributions from the thermopower measurements. These will be discussed in the following sections; first considering only inversion, and then the possibility of inversion and spin unpairing.

A. Cation distribution from thermopower measurements: Effect of inversion

We aim to explain the behavior of the Co_3O_4 thermopower at elevated temperatures through the distribution of Co^{2+}/Co^{3+} cations in different spin states over the tetrahedral and octahedral sites in Co_3O_4. Initially we ignore possible spin state transition and argue through thermopower measurements made on the Co_3O_4 sample measured in air (Fig. 4) that Co_3O_4 changes from a normal spinel below 850 K to a disordered spinel $[Co_O^{3+}] = 0.64$ (complete disorder would be $[Co_O^{3+}] = 2/3 \approx 0.67$), at the highest temperature before the onset of the spinel to rock-salt transformation. The results from these calculations will be compared to the predicted cation distribution given by the minimization of the equilibrium free energy in Co_3O_4 based on a thermodynamic assessment of the Co-O system [14].

In discussing the relationship between thermopower measurements and the cation distribution, we consider three cases of increasing sophistication:

(i) A cation distribution as proposed by Wu and Mason [1], in which only hopping between the ions on the B sites occurs and $\beta = 2$.

(ii) Again, B site contributions only but including Koshibae and co-workers' treatment [6], with both orbital and spin degeneracy ratios for Co^{2+} and Co^{3+}.

(iii) Presented in this work, contributions to the thermopower from ions on both A and B sites calculated using Koshibae and co-workers' expression.

Case (i). According to Wu and Mason's model, the thermopower for small-polaron octahedral hopping mechanism Q_{OO} is given by

$$Q_{OO} = \frac{k_B}{e} \ln\left(\beta \frac{\chi}{1-\chi}\right), \tag{3}$$

where χ is the fraction $[Co_O^{3+}]$. Combining the spin degeneracy $g_{spin} = 2S + 1$, and orbital degeneracy $g_{orbital} = 3$, the

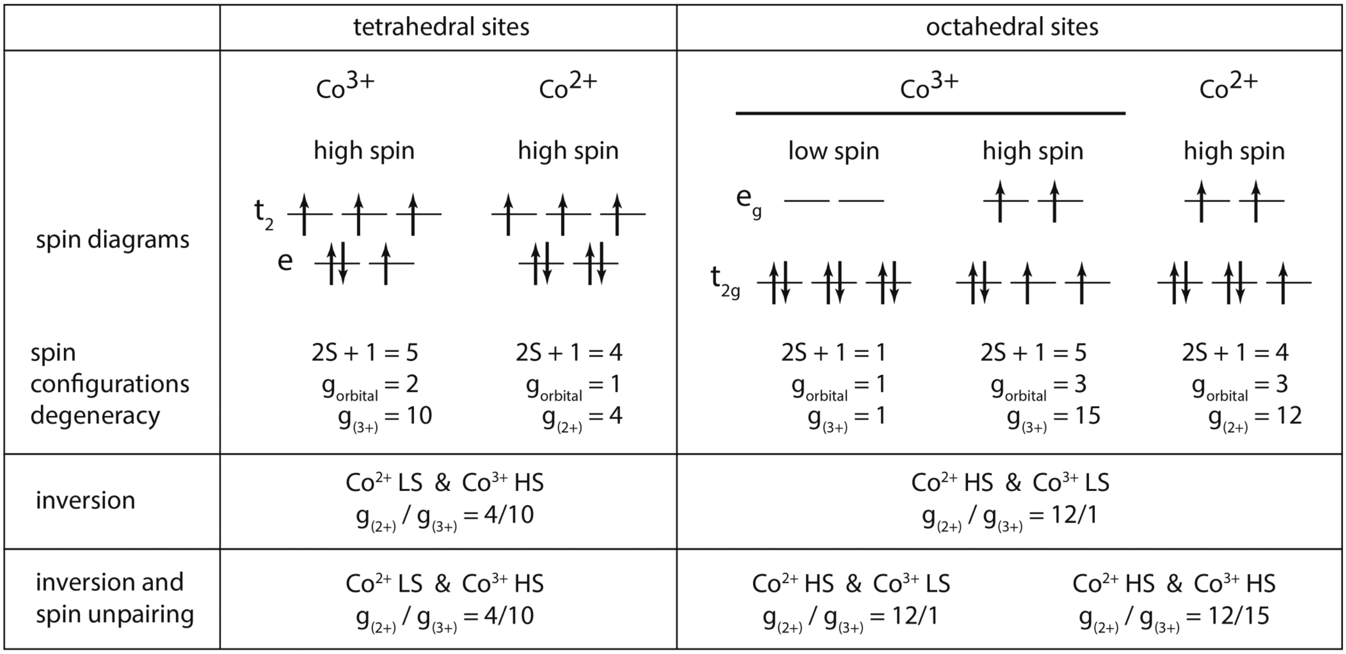

FIG. 3. Possible occupation of tetrahedral and octahedral sites in spinel-type Co_3O_4 at elevated temperatures due to the inversion and spin unpairing processes and the corresponding electronic degeneracies ($g = g_{\text{spin}} g_{\text{orbital}}$). Spin degeneracy is $g_{\text{spin}} = 2S + 1$, where S is the spin. Total orbital degeneracy is calculated as a product of orbital degeneracies for each orbital type (t_{2g}, e_g, ...): $\prod \frac{(n_{\text{orbital}})!}{(n_{\text{orbital}} - n_e)! n_e!}$, where n_{orbital} is the number of orbitals of one type and n_e denotes the number of unpaired electrons on this specific orbital type.

electronic degeneracy term of this octahedral Co^{2+} electron donor should have the value of $\beta = 12$ (see Fig. 3: $g_{(2+)} = 12$). However, as will be explained in discussing case (ii), a value of $\beta = 12$ produces inconsistent results for the cation distribution. If we treat β as a fitting parameter, as some previous authors have done, and select its value arbitrarily to be $\beta = 2$, then there is closer agreement to Chen and co-workers' calculations as shown in Fig. 4 [14]. Assigning $\beta = 2$ appears to have no physical basis unless octahedral Co^{2+} ions are low spin with a Jahn-Teller distortion, but we observe no evidence to support either of these possibilities. It is also appropriate to mention that the distribution determined by Chen and co-workers using free energy arguments assumes equilibrium conditions, and our samples may not have been able to reach perfect equilibrium at every temperature for thermopower measurements. Therefore, the onset of inversion as determined by thermopower measurement is not observed at such an early temperature as predicted by Chen and co-workers [14].

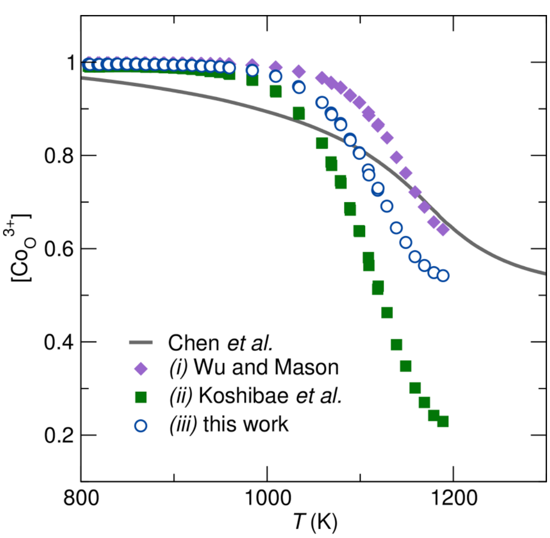

FIG. 4. Fractional occupancy of Co^{3+} ions on the octahedral sublattice in Co_3O_4 as a function of temperature calculated from the experimental thermopower measurements of Co_3O_4 in air according to case (i) (squares), case (ii) (circles), and case (iii) (diamonds) described in detail in the text. The solid line is the distribution calculated thermodynamically from free energies according to the procedure given by Chen and co-workers [14]. Good agreement with Chen and co-workers' prediction was found for case (iii), proposed in this work, with no variable parameters. Case (i) also had good agreement, but only when an unphysical value of $\beta = 2$ was used.

Case (ii). Following Koshibae and co-workers' treatment [6], the spin and orbital degeneracy of both octahedral Co^{2+} and Co^{3+} ions are needed to calculate the thermopower. The Co^{2+} ion electronic degeneracy is $g_{(2+)} = 12$, the same as in case (i). The Co^{3+} d^6 electrons are low spin and fully occupy the t_{2g} orbital so the electronic degeneracy is $g_{(3+)} = 1$ and $g_{(2+)}/g_{(3+)} = 12/1$. This distribution result is not self-consistent though because it requires more Co^{2+} ions on the octahedral site than are initially present in the formula unit; the $[Co_O^{3+}]$ fraction cannot be less than 1/2 without introducing oxygen vacancies (see Fig. 5). However, thermal analysis and redox titration in our previous publication suggests a nearly stoichiometric composition with minimal oxygen vacancies is a good approximation for Co_3O_4 [22]. Furthermore, the Seebeck coefficient and electrical conductivity in Co_3O_4 do not depend on oxygen partial pressure as one might expect with a nonstoichiometric spinel.

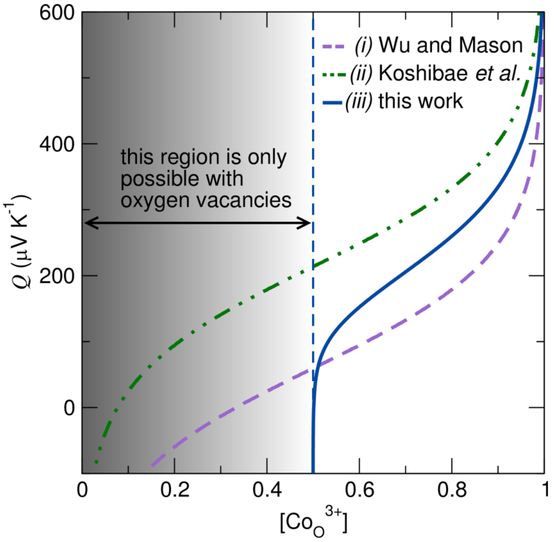

FIG. 5. Thermopower plotted against fractional occupancy of Co^{3+} ions on the octahedral sublattice according to cases (i), (ii), and (iii) described in detail in the text. The vertical dotted line represents the minimum possible value for Co_3O_4. As thermopower decreases due to inversion, both cases (i) and (ii) approach the limit of $[Co_O^{3+}] = 0$, in violation of stoichiometry in the spinel structure. Meanwhile, case (iii) remains consistent with stoichiometry requirements.

At the highest temperature measured, before decomposition to the rock-salt CoO occurs, the fraction of $[Co_O^{3+}]$ determined by both cases (i) and (ii) were close to or less than 1/2 and the decomposition from Co_3O_4 to CoO likely occurs before inversion in Co_3O_4 is complete. The decomposition is sensitive to changes in oxygen partial pressure, as demonstrated by Mocala and co-workers [21], who found the decomposition of Co_3O_4 in air [$p(O_2) = 0.21$ bar] occurs at 1180 K, and increases to 1240 K at $p(O_2) = 1$ bar. Under higher pressures of $p(O_2) = 20$ bar, the transformation is predicted to take place at 1350 K [21]. Because thermopower values decreased linearly with increasing temperature until the abrupt transformation to rock-salt CoO, the thermopower will likely continue to decrease if larger oxygen partial pressures are used to suppress the transformation. In this scenario both cases (i) and (ii), based on the thermopower contribution from the B site only using Wu and Mason as well as Koshibae and co-workers' models, respectively, would no longer be self-consistent. This is because they would require less $[Co_O^{3+}]$ on the B site than allowed by spinel stoichiometry (Fig. 5).

Case (iii). In this third case, we consider the thermopower contributions from both A and B sites in the spinels using Koshibae and co-workers's thermopower expression. An earlier analysis by Dieckmann also considered octahedral, tetrahedral, and octahedral-tetrahedral small-polaron hopping in magnetite, but using Heikes' original thermopower expression with Wu *et al*'s $\beta = 2$ [26]. In light of Koshibae and co-workers' modified thermopower expression, the role of tetrahedral sites in Co_3O_4 conduction should be reinvestigated.

As described in case (i), inversion creates electron donors on the octahedral site. Interestingly, as suggested by Koumoto and Yanagida [20], it is also possible that inversion simultaneously hole dopes the tetrahedral site. Tetrahedral Co^{2+} ions are high spin with three unpaired electrons in the t_2 triplet, but tetrahedral Co^{3+} ions have only two unpaired electrons in the t_2 triplet. The contribution to thermopower from multiple, parallel conduction mechanisms, octahedral and tetrahedral hopping, is calculated according to a weighted fraction of the electrical conductivity of each mechanism as follows:

$$Q_{\text{total}} = \frac{\sigma_{OO} Q_{OO} + \sigma_{TT} Q_{TT}}{\sigma_{\text{total}}}, \quad (4)$$

where σ_{OO}, σ_{TT}, Q_{OO}, and Q_{TT} are the contributions to electrical conductivity and thermopower from octahedral and tetrahedral hopping, respectively [27].

To proceed we need to evaluate the electrical conductivity on each sublattice. Let us take the Fe_3O_4(magnetite) case. The results of Mössbauer spectroscopy of Fe_3O_4 at low temperatures have been attributed to electron hopping along the octahedral sublattice [28]. A subsequent detailed analysis by Dieckmann and co-workers separated octahedral sublattice hopping contributions to electrical conductivity from other mechanisms and found that octahedral hopping dominated conduction, but significant tetrahedral or octahedral-tetrahedral conduction exists at high temperatures [26]. We attempted a similar analysis for Co_3O_4, but it is not straightforward because Co_3O_4 is a large band-gap semiconductor, unlike Fe_3O_4, which is a half-metal. Consequently, the onset of thermally activated carriers in Co_3O_4 masks the contribution of tetrahedral and octahedral-tetrahedral hopping mechanisms at high temperatures. Furthermore, analysis at higher temperatures is not possible because of the decomposition of Co_3O_4 to CoO.

Nevertheless, consider, for the sake of qualitative argument, that at high temperatures significant conduction occurs in Co_3O_4 by the hole-doped tetrahedral sublattice in addition to the electron doped octahedral sublattice. If we assume that conduction is proportional to the site fraction such that 1/3 of the conduction occurs via tetrahedral conduction and 2/3 via octahedral conduction, then we can use Eq. (4) to express the total thermopower as

$$Q_{\text{total}} = \tfrac{2}{3} Q_{OO} + \tfrac{1}{3} Q_{TT}. \quad (5)$$

The thermopower due to conduction on the octahedral sites would be the same as in case (ii) and the thermopower due to the tetrahedral sites would depend on the electronic degeneracies of high spin Co^{2+} and Co^{3+} in tetrahedral coordination, 4 and 10, respectively. Because the carriers are now holes, instead of electrons, the sign is also changed to give

$$Q_{TT} = \frac{-k_B}{q} \ln\left(\frac{4}{10}\frac{\chi}{1-\chi}\right), \quad (6)$$

with χ now being $[Co_T^{3+}]$.

Calculating the cation distribution for case (iii) leads to two conclusions. The first is agreement with Chen and co-workers' predictions as well as case (i), which relied on an arbitrary β parameter. The second is that, even if the thermopower were to continue to decrease with temperature, as we predict it will for samples measured in high oxygen pressures, the inversion would remain self-consistent because $[Co_O^{3+}]$ would approach the high-temperature limit of $[Co_O^{3+}] = 0.5$, in agreement with Chen and co-workers' prediction of the site occupancies. To illustrate this important point, consider Fig. 5 where we have plotted thermopower against $[\mathrm{Co}_O^{3+}]$ based on each of the three cases considered here. The lowest value for thermopower measured in air on our samples was 109 μV/K and the lowest permissible thermopower values according to Koshibae and co-workers' and Wu and Mason's models are 215 and 60 μV/K, respectively. In contrast to both of these we see that in our model the $[\mathrm{Co}_O^{3+}]$ fraction approaches the physically sensible limit of $[\mathrm{Co}_O^{3+}] = 0.5$ even for very low thermopower values.

B. Cation distribution from the thermopower measurements: Effect of spin unpairing and inversion

Some authors have attributed the high temperature structural anomaly in Co_3O_4 to a spin unpairing. Therefore, for completeness, we discuss here the role a change in spin state could play in determining the thermopower of Co_3O_4. A key feature of Koshibae and co-workers' model is that it successfully accounts for the change in spin state from low-spin (LS) to HS of Co^{4+} ions in $NaCo_2O_4$ with increasing temperature [6]. There has been extensive debate regarding the spin state of octahedral Co^{3+} in Co_3O_4 at high temperatures. Chen and co-workers summarize that measurements as diverse as lattice parameter [15–17], electromotive force of oxygen potential [16,19], and heat capacity all indicate a high temperature anomaly at 1120 K, just before Co_3O_4 transforms to CoO [21]. Many authors believe that a second-order transition from LS → HS in Co^{3+} ions takes place at this temperature. However, the effect this would have on cation distribution is still debated. Kale, for example, suggests an inverse spinel [16], Liu and Prewitt favor a disordered spinel [17], and Mocala and co-workers suggest a normal spinel with only 5% to 10% disorder [21].

A change in spin state alters the spin and orbital degeneracy and would, therefore, affect the thermopower analysis of cases (ii) and (iii) in Eq. (2). For example, the octahedral Co^{3+} electronic degeneracy term increases from $g = 1$ to $g = 15$ with a LS → HS transition. The cation distribution calculated according to cases (ii) and (iii) assuming different spin states for octahedral cobalt cations is shown in Fig. 6. We note that when a Co^{3+} LS → HS transition is assumed, a self-consistent cation distribution is obtained for case (ii). For case (iii) a self-consistent cation distribution is found regardless of the spin state of Co^{3+}, but the scenario closest to Chen and co-workers' prediction is that if both cations remain low spin. Figure 6 also shows that neither case (ii) nor case (iii) can account for the thermopower produced by a spin state transition alone; both cases show that a minimum of ~10% inversion must be present. Mocala and co-workers showed the anomaly in heat capacity, reportedly due to Co^{3+} LS → HS, begins at 1000 K and continues until decomposition. Figure 2 shows that thermopower decreases at an almost continuous rate from 900 K until transformation to CoO with no abrupt change that could be attributed to a high temperature change in spin state. For these reasons, we cannot conclude definitively that a change in spin state occurs; it remains possible that the thermopower results solely from complete (100%) inversion of the Co_3O_4 structure, or by a combination of a minimum of 40% inversion and a change in spin state.

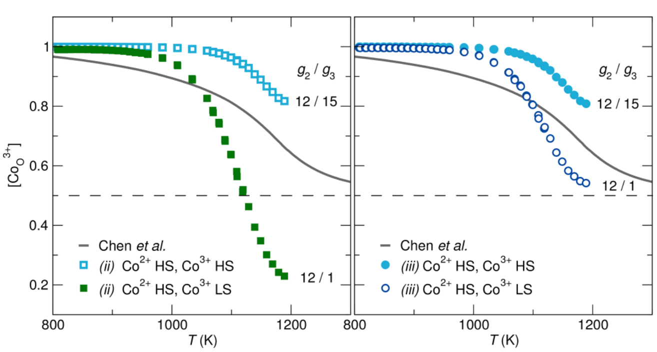

FIG. 6. Fractional occupancy of Co^{3+} ions on the octahedral site in Co_3O_4 as a function of temperature accounting for different octahedral Co^{3+} spin states in case (ii) (left) and case (iii) (right) The solid line is the distribution calculated from free energies according to the procedure given by Chen *et al.* [14]. The dashed horizontal line represents the minimum Co^{3+} octahedral occupancy based on stoichiometry.

IV. CONCLUSION

The electrical and thermoelectric properties of Co_3O_4 are reported from room temperature up to 1200 K. The thermopower reaches a maximum value (~600 μV/K) around 850 K and above this temperature it decreases almost linearly with temperature to 109 μV/K at 1188 K, at which point the structure transforms to CoO rock-salt. The transformation temperature decreased slightly (~40 K) when measured in helium, rather than air. The thermopower correlates to inversion of the Co_3O_4 structure, but the cation distribution cannot be explained in a quantifiable and consistent way unless a change in spin state is considered using with Koshibae and co-workers' modified thermopower expression, case (ii). When thermopower contributions from both electron-doped octahedral sites as well as hole-doped tetrahedral sites are included, taking into account both spin and orbital degeneracy as well as the ratio of these electronic degeneracies, case (iii), a self-consistent cation distribution, is observed with or without a change in spin state. This case agrees well with Chen and co-workers' thermodynamic cation distribution calculated from free energies. While the anomalous high-temperature structure of Co_3O_4 has often been attributed to a change in spin state of the Co^{3+} ions, the thermopower observed in the current work suggests that this high-temperature structure could involve either complete inversion alone or a combination of a minimum of 40% inversion and a change in spin state. Further investigation of the high-temperature structure of Co_3O_4 relying on magnetic moment refinement, bond length analysis, Raman and x-ray photoelectron spectroscopy, chemical titration, and thermogravimetric analysis could potentially shed further light on the role of inversion vs a change in spin state and are the subject of a future contribution [22].

ACKNOWLEDGMENTS

M.W.G. thanks the Leverhulme Trust for funding this research via the Leverhulme Research Centre for Functional Materials Design. A.G. thanks the Alexander von Humboldt Foundation for support through a Feodor Lynen Fellowship for Experienced Researchers, hosted by D.R.C. at Harvard University. T.D.S. acknowledges funding and support from NSF CAREER Award 1651668.

[1] C. C. Wu and T. O. Mason, Thermopower measurement of cation distribution in magnetite, J. Am. Ceram. Soc. **64**, 520 (1981).

[2] R. R. Heikes and R. W. Ure, *Thermoelectricity: Science and Engineering* (Interscience, New York, 1961).

[3] C. Gleitzer, J. Nowotny, and M. Rekas, Surface and bulk electrical properties of the hematite phase Fe_2O_3, Appl. Phys. A **53**, 310 (1991).

[4] J. B. Goodenough, Seebeck coefficients in vanadium spinels, Mater. Res. Bull. **5**, 621 (1970).

[5] H. L. Tuller and A. S. Nowick, Small polaron electron transport in reduced CeO_2 single crystals, J. Phys. Chem. Solids **38**, 859 (1977).

[6] W. Koshibae, K. Tsutsui, and S. Maekawa, Thermopower in cobalt oxides, Phys. Rev. B **62**, 6869 (2000).

[7] Y.-H. Lin, C.-W. Nan, Y. Liu, J. Li, T. Mizokawa, and Z. Shen, High-temperature electrical transport and thermoelectric power of partially substituted $Ca_3Co_4O_9$-based ceramics, J. Am. Ceram. Soc. **90**, 132 (2007).

[8] J. Androulakis, P. Migiakis, and J. Giapintzakis, $La_{0.95}Sr_{0.05}CoO_3$: An efficient room-temperature thermoelectric oxide, Appl. Phys. Lett. **84**, 1099 (2004).

[9] S. Okada and I. Terasaki, Physical properties of Bi-based rhodium oxides with RhO_2 hexagonal layers, Jpn. J. Appl. Phys. **44**, 1834 (2005).

[10] W. Kobayashi, I. Terasaki, M. Mikami, R. Funahashi, T. Nomura, and T. Katsufuji, Universal charge transport of the Mn oxides in the high temperature limit, J. Appl. Phys. **95**, 6825 (2004).

[11] G. V. M. Williams, E. K. Hemery, and D. McCann, Magnetic and transport properties of $SrFeO_x$, Phys. Rev. B **79**, 024412 (2009).

[12] A. A. Taskin, A. N. Lavrov, and Y. Ando, Origin of the large thermoelectric power in oxygen-variable $RBaCo_2O_{5+x}$ (R = Gd, Nd), Phys. Rev. B **73**, 121101 (2006).

[13] T. D. Sparks, A. Gurlo, and D. R. Clarke, Enhanced *n*-type thermopower in distortion-free $LiMn_2O_4$, J. Mater. Chem. **22**, 4631 (2012).

[14] M. Chen, B. Hallstedt, and L. J. Gauckler, Thermodynamic assessment of the Co-O system, J. Phase Equilib. **24**, 212 (2003).

[15] B. Touzelin, Study of the oxides of cobalt and nickel by high temperature x-ray diffraction in controlled atmosphere, Rev. Int. Hautes. Temp. Refract. **15**, 33 (1978).

[16] G. M. Kale, S. S. Pandit, and K. T. Jacob, Thermodynamics of cobalt (II, III) oxide (Co_3O_4): Evidence of phase transition, Trans. Jpn. Inst. Met. **29**, 125 (1988).

[17] X. Liu and C. T. Prewitt, High-temperature x-ray diffraction study of Co_3O_4: Transition from normal to disordered spinel, Phys. Chem. Miner. **17**, 168 (1990).

[18] V. M. Brabers and A. D. D. Broemme, Low-spin–high-spin transition in the Co_3O_4 spinel, J. Magn. Magn. Mater. **104–107**, 405 (1992).

[19] H. S. C. O'Neill, Thermodynamics of Co_3O_4: A possible electron spin unpairing transition in Co^{3+}, Phys. Chem. Miner. **12**, 149 (1985).

[20] K. Koumoto and H. Yanagida, Electrical conduction in pure and Li substituted Co_3O_4, J. Am. Ceram. Soc. **64**, 156 (1981).

[21] K. Mocala, A. Navrotsky, and D. M. Sherman, High-temperature heat capacity of Co_3O_4 spinel: Thermally induced spin unpairing transition, Phys. Chem. Miner. **19**, 88 (1992).

[22] T. D. Sparks, A. Gurlo, M. W. Gaultois, G. Cherkashinin, L. Laversenne, and D. R. Clarke, The high-temperature structure of Co_3O_4: Insight from *in situ* and *ex situ* measurements, Phys. Rev. B (to be published).

[23] P. H. T. Ngamou and N. Bahlawane, Influence of the arrangement of the octahedrally coordinated trivalent cobalt cations on the electrical charge transport and surface reactivity, Chem. Mater. **22**, 4158 (2010).

[24] A. Navrotsky, C. Ma, K. Lilova, and N. Birkner, Nanophase transition metal oxides show large thermodynamically driven shifts in oxidation-reduction equilibria, Science **330**, 199 (2010).

[25] I.-H. Jung, S. A. Decterov, A. D. Pelton, H.-M. Kim, and Y.-B. Kang, Thermodynamic evaluation and modeling of the Fe-Co-O system, Acta Mater. **52**, 507 (2004).

[26] R. Dieckmann, C. A. Witt, and T. O. Mason, Defects and cation diffusion in magnetite (V): Electrical conduction, cation distribution and point defects in $Fe_{3-\delta}O_4$, Berichte Bunsengesell. Phys. Chem. **87**, 495 (1983).

[27] A. F. Joffe, J. Auth, and E. Gilde, *Physik der Halbleiter* (Akademie, Berlin, 1958).

[28] W. Kündig and R. Steven Hargrove, Electron hopping in magnetite, Solid State Commun. **7**, 223 (1969).