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Phys. Rev. B **98**, 024108 — Published 30 July 2018

DOI: [10.1103/PhysRevB.98.024108](https://doi.org/10.1103/PhysRevB.98.024108)

A revised model for thermopower and site inversion in Co_3O_4 spinel

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(Dated: July 9, 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 coworkers' 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 ($\sim 100\%$) 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.

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 $(A)^{tet}[B]_2^{oct}\text{O}_4$, where $(A)^{tet}$ and $[B]_2^{oct}$ 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 amongst the most studied group of the 2-3 spinel-type oxides. Despite similar compositions and 30 elements, they form completely different structures in 31 terms of cation distribution. In an ideal case, Co_3O_4 32

possesses a normal spinel-type structure $(\text{Co})^{2+}[\text{Co}]_2^{3+}\text{O}_4$ with Co^{2+} ($S=3/2$) cations on the tetrahedral $(A)^{tet}$ sites, and low-spin (LS) Co^{3+} ($S=0$) cations on octahedral $[B]^{oct}$ sites. On the other hand, Fe_3O_4 , is an inverse spinel $(\text{Fe})^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]^{oct}\text{O}_4$ with Fe^{3+} cations on the tetrahedral $(A)^{tet}$ sites, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations on octahedral $[B]^{oct}$ 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 inter-mixing 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 formula²

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

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.*, $[M^{3+}]^{oct}$ in the 2-3 spinels). If multiple ions are present on a 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 originates 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 $\beta = 2$. Non-integer 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 coworkers⁶ 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:

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

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.*, $g = g_{\text{spin}}g_{\text{orbital}}$). As with the Heikes equation, Equation 2 strictly holds only at high temperatures and for small polaron conductors.² Nevertheless, it has been found that Koshibae and coworkers' modified expression successfully describes the thermopower of a variety of other oxide compounds, including derivatives of sodium cobaltate $\text{Ca}_3\text{Co}_4\text{O}_9$,⁷ cobalt perovskites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$,^{8,122} layered rhodium oxides $(\text{Bi}_{1-x}\text{Pb}_x)_{1.8}\text{Sr}_2\text{Rh}_{1.6}\text{O}_y$,^{9,123} manganese perovskites $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and double perovskites $\text{Ca}(\text{Mn}_{3-x}\text{Cu}_x)\text{Mn}_4\text{O}_{12}$,¹⁰ iron based structures SrFeO_x ,¹¹ $RE\text{BaCo}_2\text{O}_{5+x}$ ($RE = \text{Gd}, \text{Nd}$)^{12,126} as well as LiMn_2O_4 spinel.¹³

Despite the success of Koshibae and coworkers' 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 model¹ 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 coworkers which included magnetic contributions.¹⁴ Co_3O_4 is well suited for this investigation because numerous experimental observations¹⁵⁻²² suggest a high-temperature structural transformation between 600 K 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 temperature, 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 inch 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 hours and holding for 6 hours, ramping to 1373 K over 1 hour and holding for 6 hours, ramping back to 1148 K over 2 hours and holding for 2 hours. 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 $(8 \times 2 \times 1) \text{ mm}^3$ 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 $(8 \times 2 \times 1) \text{ mm}^3$ 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 $\Delta T = 20 \text{ K}$, 30 K and 40 K using thermocouple probes $\sim 3 \text{ mm}$ apart. Measurements were made as the samples were heated and then cooled at $\sim 10 \text{ K}$ 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 (Figure 1) reveal three characteristic conductivity regimes with an activation energy of $0.35 \pm 0.08 \text{ eV}$ (418 K to 540 K), $0.15 \pm 0.05 \text{ eV}$ (540 K to 890 K) and $2.28 \pm 0.06 \text{ eV}$ (890 K to 1188 K). These are

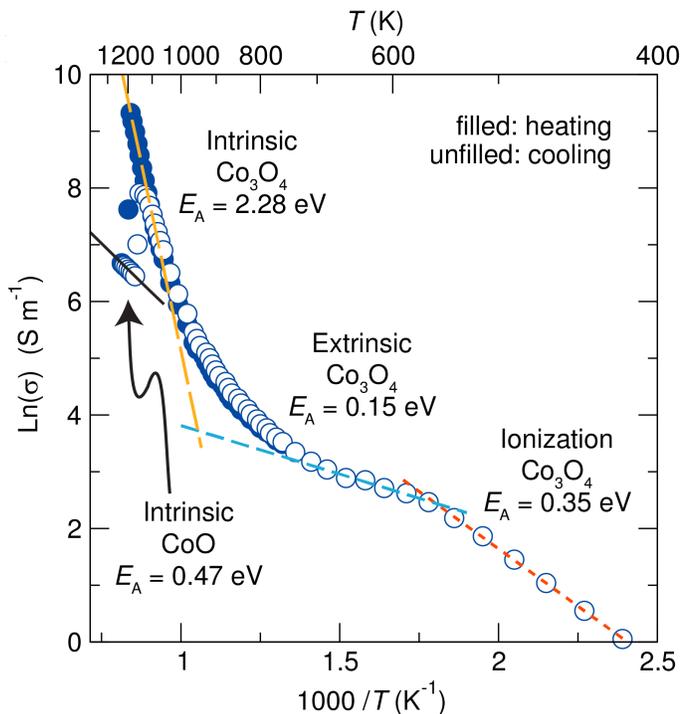


FIG. 1. An Arrhenius plot of electrical conductivity for Co_3O_4 measured in air shows three characteristic regions, each with a different activation energy. Above 1188 K, Co_3O_4 decomposes to CoO , a band conductor.

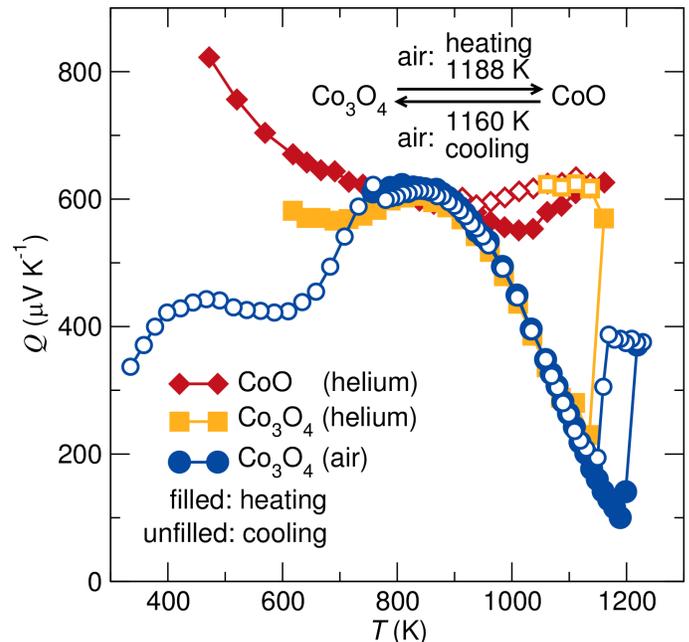


FIG. 2. Co_3O_4 has a maximum thermopower of $\sim 600 \mu\text{V}/\text{K}$ near 850 K before the thermopower decreases linearly with temperature until transformation to CoO . This decrease in thermopower with increasing temperature is attributed to inversion of the spinel structure. In the range 900 K 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.

134 attributed to the ionization, extrinsic, and intrinsic con-
 135 duction regimes, respectively, and agree with the re-
 136 ported hopping energy value 0.17 eV and optical absorp-
 137 tion transition of 2.14 eV ($\text{O}^{2-} \rightarrow \text{Co}^{2+}$).²³ The tempera-
 138 ture ranges corresponding to different conduction mech-
 139 anisms coincide with high-temperature anomalies from
 140 previous *in situ* measurements^{15–18,20,22} as well as ther-
 141 mopower reported in this work. The measurements of the
 142 conductivity in the CoO phase give an activation energy¹⁶⁷
 143 of 0.47 ± 0.02 eV.

144 The Seebeck coefficient of Co_3O_4 as a function of
 145 temperature (measured in air and helium) is shown in
 146 Figure 2 together with that of CoO (measured in heli-
 147 um only). A key feature of the graph is that the
 148 spinel Co_3O_4 samples measured in air and helium both
 149 have a maximum in thermopower of $\sim 600 \mu\text{V}/\text{K}$ around
 150 850 K. Above this temperature, the thermopower de-
 151 creases almost linearly with increasing temperature un-
 152 til it abruptly increases with a slope of $\sim 250 \mu\text{V}/\text{K}^2$ in
 153 air and $\sim 400 \mu\text{V}/\text{K}^2$ in helium. The region of approxi-
 154 mately linear decrease correlates to changes in the spinel
 155 structure, such as inversion, discussed in the next sec-
 156 tion. The discontinuity in thermopower (1188 K in air,
 157 and 1150 K in He) is attributed to the decomposition
 158 of the spinel Co_3O_4 to rock-salt CoO , which has been
 159 previously observed by both high-temperature XRD and
 160 Raman spectroscopy.²²

161 In Co_3O_4 with normal spinel-type structure, positive¹⁸⁵

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 re-
 duction 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 trans-
 formation prior to decomposition.^{22,24,25} Consequently,
 the anomalous electrical conductivity and thermopower
 behavior of Co_3O_4 at lower temperatures, from 600 K
 to 1000 K, must be due to changes in the Co_3O_4 spinel
 structure itself rather than as a result of a phase trans-
 formation 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 pro-
 cesses in (Figure 3). Owing to the complexity of the pos-
 sible combinations, several possible charge transfer pro-
 cesses (*i.e.*, hopping) need to be considered in the cal-
 culation 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.

| | tetrahedral sites | | octahedral sites | | |
|------------------------------|---|---|--|--|---|
| | Co ³⁺ | Co ²⁺ | Co ³⁺ | | Co ²⁺ |
| | high spin | high spin | low spin | high spin | high spin |
| spin diagrams | t_2 \uparrow \uparrow \uparrow e $\uparrow\downarrow$ \uparrow | \uparrow \uparrow \uparrow $\uparrow\downarrow$ $\uparrow\downarrow$ | e_g — — t_{2g} $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ | \uparrow \uparrow $\uparrow\downarrow$ \uparrow \uparrow | \uparrow \uparrow $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow |
| spin configurations | $2S + 1 = 5$ | $2S + 1 = 4$ | $2S + 1 = 1$ | $2S + 1 = 5$ | $2S + 1 = 4$ |
| orbital degeneracy | $g_{\text{orbital}} = 2$ $g_{(3+)} = 10$ | $g_{\text{orbital}} = 1$ $g_{(2+)} = 4$ | $g_{\text{orbital}} = 1$ $g_{(3+)} = 1$ | $g_{\text{orbital}} = 3$ $g_{(3+)} = 15$ | $g_{\text{orbital}} = 3$ $g_{(2+)} = 12$ |
| inversion | Co ²⁺ LS & Co ³⁺ HS $g_{(2+)} / g_{(3+)} = 4/10$ | | Co ²⁺ HS & Co ³⁺ LS $g_{(2+)} / g_{(3+)} = 12/1$ | | |
| inversion and spin unpairing | Co ²⁺ LS & Co ³⁺ HS $g_{(2+)} / g_{(3+)} = 4/10$ | | Co ²⁺ HS & Co ³⁺ LS $g_{(2+)} / g_{(3+)} = 12/1$ | Co ²⁺ HS & Co ³⁺ HS $g_{(2+)} / g_{(3+)} = 12/15$ | |

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.

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 $\text{Co}^{2+}/\text{Co}^{3+}$ 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 Co_3O_4 sample measured in air (Figure 4) that Co_3O_4 changes from a normal spinel below 850 K to a disordered spinel, $[\text{Co}_O^{3+}] = 0.64$, (complete disorder would be $[\text{Co}_O^{3+}] = 2/3 \approx 0.67$) 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 coworkers' 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 coworkers' expression.

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

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

where χ is the fraction $[\text{Co}_O^{3+}]$. Combining the spin degeneracy, $g_{\text{spin}} = 2S + 1$, and orbital degeneracy, $g_{\text{orbital}} = 3$, the electronic degeneracy term of this octahedral Co^{2+} electron donor should have the value of $\beta = 12$ (see Figure 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 coworkers' calculations as shown in Figure 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 coworkers using free energy arguments assumes equilibrium conditions, and our samples may not have been able to reach perfect equilibrium at every temperature

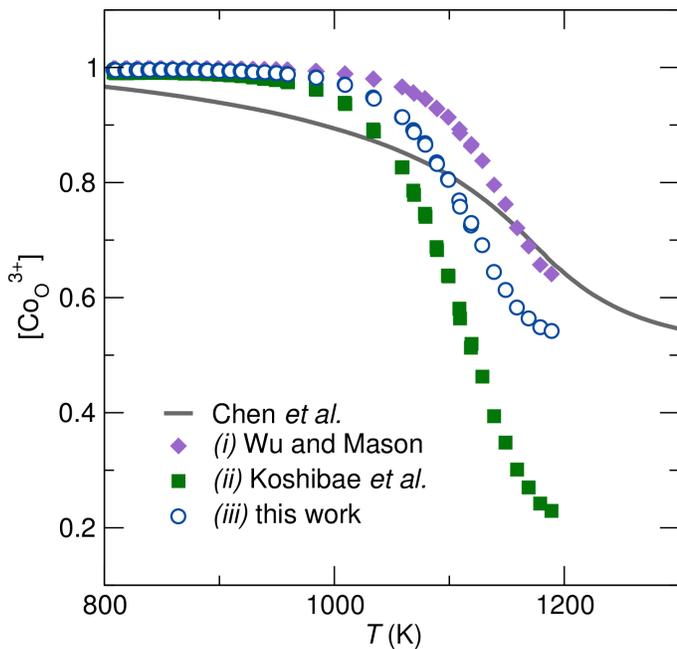


FIG. 4. Fractional occupancy of Co^{3+} ions on the octahedral sublattice in Co_3O_4 as a function of temperature calculated from the experimental thermopower measurements of Co_3O_4 in air according to *case (i)* (squares), *case (ii)* (circles) and *case (iii)* (diamonds) described in detail in the text. The solid line is the distribution calculated thermodynamically from free energies according to the procedure given by Chen and coworkers¹⁴ Good agreement with Chen and coworkers' 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.

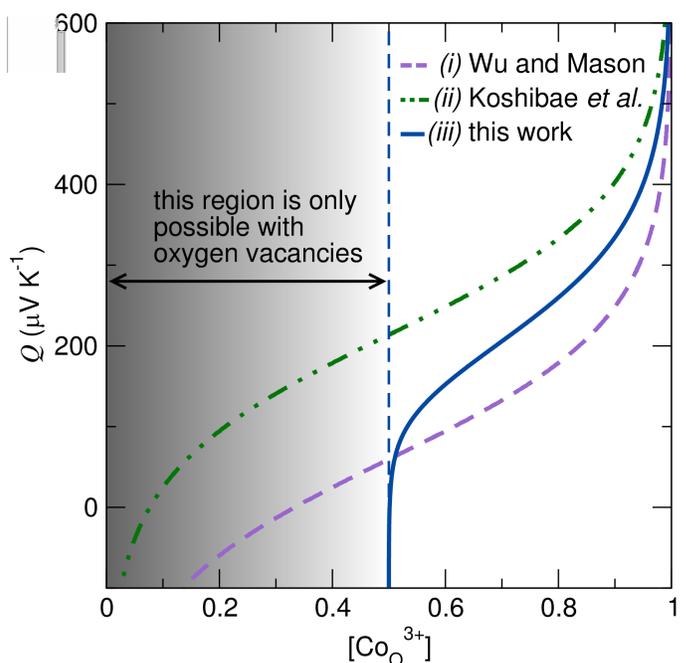


FIG. 5. Thermopower plotted against fractional occupancy of Co^{3+} ions on the octahedral sub-lattice according to *cases (i)*, *(ii)* and *(iii)* described in detail in the text. The vertical dotted line represents the minimum possible value for in Co_3O_4 . As thermopower decreases due to inversion, both *cases (i)* and *(ii)* approach the limit of $[\text{Co}_3\text{O}^{3+}] = 0$, in violation of stoichiometry in the spinel structure. Meanwhile, *case (iii)* remains consistent with stoichiometry requirements.

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 coworkers.¹⁴

Case (ii). Following Koshibae and coworkers' 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 $[\text{Co}_3\text{O}^{3+}]$ fraction cannot be less than $1/2$ without introducing oxygen vacancies (see Figure 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 non-stoichiometric spinel.

At the highest temperature measured, before decomposition to the rock-salt CoO occurs, the fraction of

$[\text{Co}_3\text{O}^{3+}]$ determined by both *case (i)* and *case (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 coworkers,²¹ who found the decomposition of Co_3O_4 in air ($p(\text{O}_2) = 0.21$ bar) occurs at 1180 K, and increases to 1240 K at $p(\text{O}_2) = 1$ bar. Under higher pressures of $p(\text{O}_2) = 20$ 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 *case (i)* and *case (ii)*, based on the thermopower contribution from the B site only using Wu and Mason as well as Koshibae and coworkers' models, respectively, would no longer be self-consistent. This is because they would require less $[\text{Co}_3\text{O}^{3+}]$ on the B site than allowed by spinel stoichiometry (Figure 5).

Case (iii). In this third case, we consider the thermopower contributions from both A and B sites in the spinels using Koshibae and coworkers's thermopower expression. An earlier analysis by Dieckmann also considered octahedral, tetrahedral and octahedral-tetrahedral small-polaron hopping in magnetite, but us-

ing Heikes' original thermopower expression with Wu et al's $\beta = 2$.²⁶ In light of Koshibae and coworkers' 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 3 unpaired electrons in the t_2 triplet, but tetrahedral Co^{3+} ions have only 2 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.

To proceed we need to evaluate the electrical conductivity on each sub-lattice. Let us take 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 sub-lattice. A subsequent detailed analysis by Dieckmann and coworkers separated octahedral sub-lattice 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 sub-lattice in addition to the electron doped octahedral sub-lattice. 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 Equation 4 to express the total thermopower as

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

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 $[\text{Co}_T^{3+}]$.

Calculating the cation distribution for *case(iii)* leads to two conclusions. The first is agreement with Chen and coworkers' 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 $[\text{Co}_O^{3+}]$ would approach the high-temperature limit of $[\text{Co}_O^{3+}] = 0.5$, in agreement with Chen and coworkers' prediction of the site occupancies. To illustrate this important point, consider Figure 5 where we have plotted thermopower against $[\text{Co}_O^{3+}]$ based on each of the three cases considered here. The lowest value for thermopower measured in air on our samples was $109 \mu\text{V}/\text{K}$ and the lowest permissible thermopower values according to Koshibae and coworkers' and Wu and Mason's models are $215 \mu\text{V}/\text{K}$ and $60 \mu\text{V}/\text{K}$, respectively. In contrast to both of these we see that in our model the $[\text{Co}_O^{3+}]$ fraction approaches the physically sensible limit of $[\text{Co}_O^{3+}] = 0.5$ 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 coworkers' 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 coworkers 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 \rightarrow 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 coworkers 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 *case(ii)* and *case(iii)* in Equation 2. For example, the octahedral Co^{3+} electronic degeneracy term increases from $g = 1$ to $g = 15$ with a LS \rightarrow HS transition. The cation distribution calculated according to *case(ii)* and

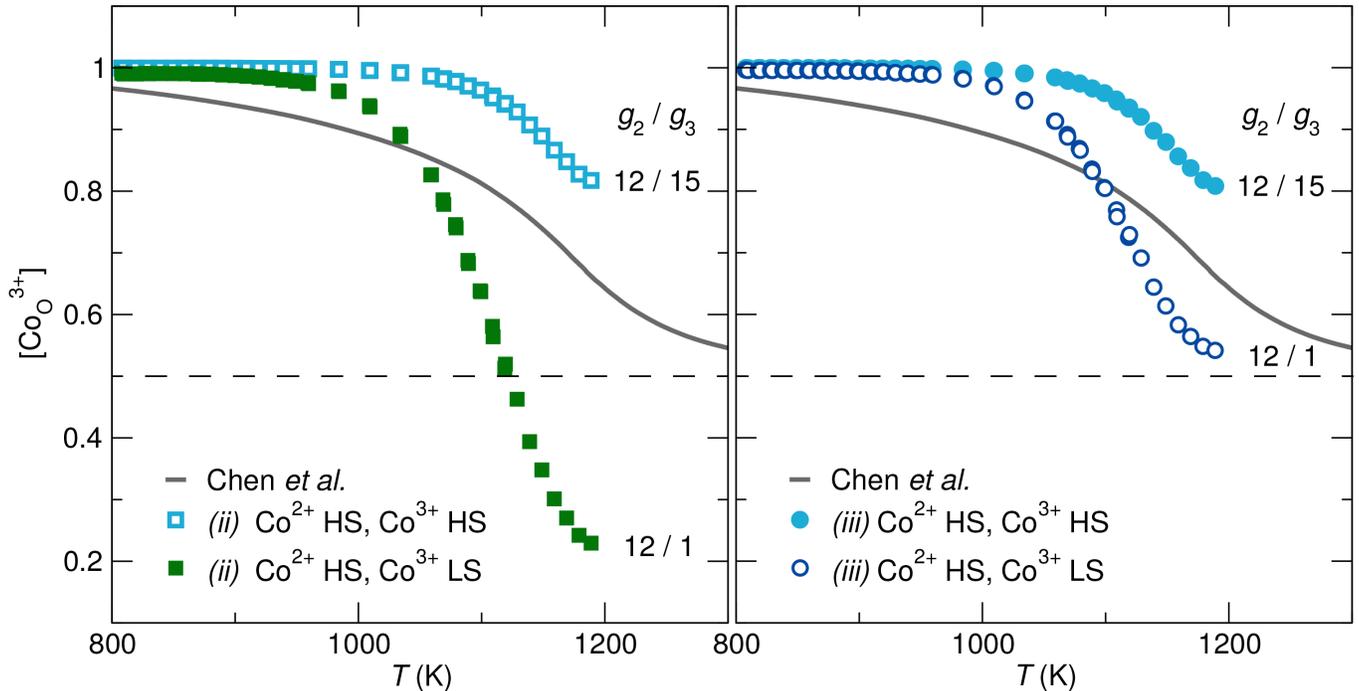


FIG. 6. Fractional occupancy of Co^{3+} ions on the octahedral site in Co_3O_4 as a function of temperature accounting for different octahedral Co^{3+} spin states in *case (ii)* (left) and *case (iii)* (right). The solid line is the distribution calculated from free energies according to the procedure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

359 *(iii)* assuming different spin-states for octahedral cobalt³⁵⁸
 360 cations is shown in Figure 6. We note that when a Co^{3+} ³⁵⁶
 361 LS \rightarrow HS transition is assumed, a self-consistent cation³⁵⁷
 362 distribution is obtained for *case (ii)*. For *case (iii)* a self-³⁵⁸
 363 consistent cation distribution is found regardless of the³⁵⁹
 364 spin state of Co^{3+} , but the scenario closest to Chen and³⁶⁰
 365 coworkers' prediction is that if both cations remain low³⁶¹
 366 spin. Figure 6 also shows that neither *case (ii)* nor *case*³⁶²
 367 *(iii)* can account for the thermopower produced by a spin³⁶³
 368 state transition alone; both cases show that a minimum³⁶⁴
 369 of $\sim 10\%$ inversion must be present. Mocala and cowork-³⁶⁵
 370 ers showed the anomaly in heat capacity, reportedly due³⁶⁶
 371 to Co^{3+} LS \rightarrow HS, begins at 1000 K and continues un-³⁶⁷
 372 til decomposition. Figure 2 shows that thermopower de-³⁶⁸
 373 creases at an almost continuous rate from 900 K until³⁶⁹
 374 transformation to CoO with no abrupt change that could³⁷⁰
 375 be attributed to a high temperature change in spin state.³⁷¹
 376 For these reasons, we cannot conclude definitively that a³⁷²
 377 change in spin state occurs; it remains possible that the³⁷³
 378 thermopower results solely from complete (100%) inver-³⁷⁴
 379 sion of the Co_3O_4 structure, or by a combination of a³⁷⁵
 380 minimum of 40% inversion and a change in spin state.³⁷⁶

381 IV. CONCLUSION

382 The electrical and thermoelectric properties of Co_3O_4 ³⁸¹
 383 are reported from room-temperature up to 1200 K. The³⁸²
 384 thermopower reaches a maximum value ($\sim 600 \mu\text{V}/\text{K}$)³⁸³

around 850 K and above this temperature it decreases al-
 most linearly with temperature to $109 \mu\text{V}/\text{K}$ 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 struc-
 ture, 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 coworkers'
 modified thermopower expression, *case (ii)*. When ther-
 mopower contributions from both electron-doped octa-
 hedral sites as well as hole-doped tetrahedral sites are
 included, taking into account both spin and orbital de-
 generacy as well as the ratio of these electronic degenera-
 cies, *case (iii)*, a self-consistent cation distribution is ob-
 served with or without a change in spin state. This case
 agrees well with Chen and coworkers' 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
 suggest that this high-temperature structure could in-
 volve 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 spec-
 troscopy, chemical titration, and thermogravimetric anal-
 ysis could potentially shed further light on the role of in-

414 version vs a change in spin state and are the subject of⁴¹⁶
 415 a future contribution.²²

ACKNOWLEDGMENTS

417 MWG thanks the Leverhulme Trust for funding this
 418 research via the Leverhulme Research Centre for Func-
 419 tional Materials Design. AG thanks the Alexander von
 420 Humboldt Foundation for support through a Feodor Ly-
 421 nen Fellowship for Experienced Researchers, hosted by
 422 DRC at Harvard University.

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