Revised model for thermopower and site inversion in \( \text{Co}_3\text{O}_4 \) spinel

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A revised model for thermopower and site inversion in \(\text{Co}_3\text{O}_4\) spinel

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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 \(\text{Co}_3\text{O}_4\) 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 (\(\sim100\%\)) 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 \(\text{Co}^{3+}\) 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, the technique has seen widespread use. In the spinel-type oxides \((A)^{\text{tet}}[B]^{\text{oct}}\text{O}_4\), where \((A)^{\text{tet}}\) and \([B]^{\text{oct}}\) 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 (\(\text{Fe}_3\text{O}_4\) and \(\text{Co}_3\text{O}_4\)), for instance, are amongst 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, \(\text{Co}_3\text{O}_4\) possesses a normal spinel-type structure \((\text{Co})^{2+}[\text{Co}]^{3+}\text{O}_4\) with \(\text{Co}^{2+}\) \((S=3/2)\) cations on the tetrahedral \((A)^{\text{tet}}\) sites, and low-spin (LS) \(\text{Co}^{3+}\) \((S=0)\) cations on octahedral \([B]^{\text{oct}}\) sites. On the other hand, \(\text{Fe}_3\text{O}_4\), is an inverse spinel \((\text{Fe})^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]^{\text{oct}}\text{O}_4\) with \(\text{Fe}^{3+}\) cations on the tetrahedral \((A)^{\text{tet}}\) sites, and and \(\text{Fe}^{2+}/\text{Fe}^{3+}\) cations on octahedral \([B]^{\text{oct}}\) 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 formula

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

where \(k_B\) is Boltzmann’s constant, \(e\) is the elementary positive charge, \(\beta\) is the Heikes degeneracy term and \(\chi\) is the fraction of cations in higher oxidation state on the
conducting sites (i.e., \([M^{3+}\text{oct}]\) 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 \(\chi\) from the Heikes formula.

This original method of using thermopower to determine the cation distribution in \(\text{Fe}_3\text{O}_4\), proposed in a seminal paper by Wu and Mason in 1981, 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. How ever, some subsequent reports were unable to explain the experimental results using these assumptions. In fact, instead of calculating the Heikes degeneracy term \(\beta\) outright, 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. For a proper fit to the data of one report, \(\beta\) would have to change from \(\beta = 1\) at low carrier concentrations to \(\beta = 2\) at high concentrations.

Twenty years later, Koshikae and coworkers 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:

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

where \(g_{(2+)}\) and \(g_{(3+)}\) are the electronic degeneracy terms for the electron donors (\(\text{Co}^{2+}\)) and electron acceptors (\(\text{Co}^{3+}\)), and \(\chi_{(3+)}\) is the fraction of electronic acceptors. 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. Nevertheless, it has been found that Koshikae and coworkers’ modified expression success fully describes the thermopower of a variety of other oxide compounds, including derivatives of sodium cobaltate \(\text{Ca}_3\text{Co}_4\text{O}_9\), cobalt perovskites \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\), layered molybdenum oxides \((\text{Bi}_{1-x}\text{Pb}_x)\text{Sr}_2\text{Rh}_1\text{O}_6\), manganese perovskites \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) and double perovskites \(\text{Ca}(\text{Mn}_{3-x}\text{Cu}_x)\text{MnO}_3\), iron based structures \(\text{SrFeO}_2\), \(\text{REBa}_2\text{Co}_3\text{O}_{7+x}\) \((\text{RE} = \text{Gd, Nd})\), as well as \(\text{LiMn}_2\text{O}_4\) spinel.

Despite the success of Koshikae 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, mixed spinels. To address these issues, we have investigated the temperature dependence of the thermopower of \(\text{Co}_3\text{O}_4\). To do so, we have calculated the cation distributions at different temperatures by applying different variations of the original model 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.

II. EXPERIMENTAL DETAILS

Cylindrical pellets were fabricated from nanometer-sized \(\text{Co}_3\text{O}_4\) 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 \(\text{Co}_3\text{O}_4\) and \(\text{CoO}\) 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 \(\text{Co}_3\text{O}_4\) or slowly cooled at 1 K/min to obtain phase-pure \(\text{Co}_3\text{O}_4\). Intermediate cooling rates resulted in mixtures of \(\text{CoO}\) and \(\text{Co}_3\text{O}_4\) 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, \(\sigma\), 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 \(\Delta T = 20\) K, 30 K and 40 K using thermocouple probes \(\sim 3\) mm apart. Measurements were made as the samples were heated and then cooled at \(\sim 10\) 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 (Figure 1) reveal three characteristic conductivity regimes with an activation energy of \(0.35 \pm 0.08\) eV (418 K to 540 K), \(0.15 \pm 0.05\) eV (540 K to 890 K) and \(2.28 \pm 0.06\) eV (890 K to 1188 K). These are...
FIG. 1. An Arrhenius plot of electrical conductivity for Co₃O₄ measured in air shows three characteristic regions, each with a different activation energy. Above 1188 K, Co₃O₄ decomposes to CoO, a band conductor. 

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 (O²⁻ → Co²⁺). The temperature ranges corresponding to different conduction mechanisms coincide with high-temperature anomalies from previous in situ measurements 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 Co₃O₄ as a function of temperature (measured in air and helium) is shown in Figure 2 together with that of CoO (measured in helium only). A key feature of the graph is that the spinel Co₃O₄ samples measured in air and helium both have a maximum in thermopower of ~600 μV/K near 850 K. Above this temperature, the thermopower decreases almost linearly with increasing temperature until it abruptly increases with a slope of ~250 μV/K² in air and ~400 μV/K² 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, 1150 K in He) is attributed to the decomposition of the spinel Co₃O₄ to rock-salt CoO, which has been previously observed by both high-temperature XRD and Raman spectroscopy.

In Co₃O₄ 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.

Previous work has shown Co₃O₄ decomposes to CoO in air at a temperature above 1100 K, with no phase transformation prior to decomposition. Consequently, the anomalous electrical conductivity and thermopower behavior of Co₃O₄ at lower temperatures, from 600 K to 1000 K, must be due to changes in the Co₃O₄ 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 (Figure 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.
FIG. 3. Possible occupation of tetrahedral and octahedral sites in spinel-type \( \text{Co}_3\text{O}_4 \) 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 \( t^2_g, e_g, \ldots \): \( \prod \frac{(n_{\text{orbital}})!}{(n_{\text{orbital}} - n_e)!n_e!} \), where \( n_{\text{orbital}} \) is the number of orbitals of one type and \( n_e \) denotes the number of unpaired electrons on this specific orbital type.

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A. Cation distribution from thermopower measurements: effect of inversion

We aim to explain the behavior of the \( \text{Co}_3\text{O}_4 \) 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 \( \text{Co}_3\text{O}_4 \). Initially we ignore possible spin state transition and argue through thermopower measurements made on \( \text{Co}_3\text{O}_4 \) samples measured in air (Figure 4) that \( \text{Co}_3\text{O}_4 \) changes from a normal spinel below 850 K to a disordered spinel, \( [\text{Co}^{3+}_3\text{O}_4]=0.64 \), (complete disorder would be \( [\text{Co}^{3+}_3\text{O}_4]=2/3 \approx 0.67 \)) 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 \( \text{Co}_3\text{O}_4 \) 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 Koashi and coworkers’ treatment,\(^6 \) with both orbital and spin degeneracy ratios for \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \),

(iii): presented in this work, contributions to the thermopower from ions on both A and B sites calculated using Koashi 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

\[
Q_{OO} = \frac{k_B}{e} \ln \left( \frac{\beta}{1 - \chi} \right)
\]

where \( \chi \) is the fraction \([\text{Co}^{3+}_3\text{O}_4] \). Combining the spin degeneracy, \( g_{\text{spin}} = 2S + 1 \), and orbital degeneracy, \( g_{\text{orbital}} = 3 \), the electronic degeneracy term of this octahedral \( \text{Co}^{2+} \) 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 \( \beta \) 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 \( \text{Co}^{2+} \) 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.
electronic degeneracy is low spin and fully occupy the \( g^{2+} \) orbital so the \( g^{2+} \) to \( g^{3+} \) distribution result is not self-consistent though because it requires more \( g^{2+} \) ions on the octahedral site than are initially present in the formula unit; the \( [\text{Co}^{3+}_O] \) fraction cannot be less than 1/2 without introducing oxygen vacancies (see Figure 5). However, thermal analysis and redox titration in our previous publication suggest a nearly stoichiometric composition with minimal oxygen vacancies is a good approximation for \( \text{Co}_3\text{O}_4 \). Further more, the Seebeck coefficient and electrical conductivity in \( \text{Co}_3\text{O}_4 \) 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 \( [\text{Co}^{3+}_O] \) determined by both \textit{case (i)} and \textit{case (ii)} were close to or less than 1/2 and the decomposition from \( \text{Co}_3\text{O}_4 \) to CoO likely occurs before inversion in \( \text{Co}_3\text{O}_4 \) is complete. The decomposition is sensitive to changes in oxygen partial pressure, as demonstrated by Mocala and coworkers, who found the decomposition of \( \text{Co}_3\text{O}_4 \) in air \( (p(O_2) = 0.21 \text{ bar}) \) occurs at 1180 K, and increases to 1240 K at \( p(O_2) = 1 \text{ bar} \). Under higher pressures of \( p(O_2) = 20 \text{ bar} \), the transformation is predicted to take place at 1350 K. 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 \textit{case (i)} and \textit{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 \( [\text{Co}^{3+}_O] \) on the \( B \) site than allowed by spinel stoichiometry (Figure 5).

\textbf{Case (iii).} In this third case, we consider the thermopower contributions from both \( A \) and \( B \) sites in the spinels using Koshibae and coworkers’ 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 $\text{Co}_3\text{O}_4$ 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 in inversion simultaneously hole dopes the tetrahedral site.21 Tetrahedral Co$^{2+}$ ions are high spin with 3 unpaired electrons in the $t_2$ triplet, but high spin 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

$$Q_{\text{total}} = \frac{Q_{OO} \sigma_{OO} + Q_{TT} \sigma_{TT}}{\sigma_{\text{total}}}$$

where $Q_{OO}$, $Q_{TT}$, $\sigma_{OO}$, and $\sigma_{TT}$, 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 sub-lattice. Let us take Fe$_3$O$_4$ (magnetite)28 case. The results of Mössbauer spectroscopy of Fe$_3$O$_4$ at low temperatures have been attributed to electron hopping along the octahedral sub-lattice.29 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$_3$O$_4$, but it is not straightforward because Co$_3$O$_4$ is a half-metal, unlike Fe$_3$O$_4$, which is a half-metal. Consequently, the onset of thermally activated carriers in Co$_3$O$_4$ 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$_3$O$_4$ to CoO.

Nevertheless, consider, for the sake of qualitative argument, that at high temperatures significant conduction occurs in Co$_3$O$_4$ 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

$$Q_{\text{total}} = \frac{2}{3} Q_{OO} + \frac{1}{3} Q_{TT}$$

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 expression is also changed to give

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

with $\chi$ now being [Co$^{3+}$].

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 $\beta$ 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$^{3+}$] would approach the high-temperature limit of [Co$^{3+}$] = 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 [Co$^{3+}$] based on each of the three cases considered here. The lowest value for thermopower measured in air on our samples was 109 $\mu$V/K and the lowest permissible thermopower values according to Koshibae and coworkers’ and Wu and Mason’s models are 215 $\mu$V/K and 60 $\mu$V/K, respectively. In contrast to both of these we see that in our model the [Co$^{3+}$] fraction approaches the physically sensible limit of [Co$^{3+}$] = 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$_3$O$_4$ 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$_3$O$_4$. 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$^{3+}$ ions in Na$_2$Co$_2$O$_4$ with increasing temperature.6 There has been extensive debate regarding the spin-state of octahedral Co$^{3+}$ in Co$_3$O$_4$ at high temperatures. Chen and coworkers summarize that measurements as diverse as lattice parameter,15-17 electromagnetic force of oxygen potential,16,19 and heat capacity all indicate a high temperature anomaly at 1120 K, just before Co$_3$O$_4$ 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 Mocella 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 (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\(_3\)O\(_4\) 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. (iii) assuming different spin-states for octahedral cobalt\(^{3+}\) cations is shown in Figure 6. We note that when a Co\(^{3+}\)\(_{\text{LS}}\) → 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 coworkers’ 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 \(\sim 10\%\) inversion must be present. Mocala and coworkers showed the anomaly in heat capacity, reportedly due to Co\(^{3+}\)\(_{\text{LS}}\) → 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\(_3\)O\(_4\) structure, or by a combination of minimum of 40\% inversion and a change in spin state.

### IV. CONCLUSION

The electrical and thermoelectric properties of Co\(_3\)O\(_4\) are reported from room-temperature up to 1200 K. The thermopower reaches a maximum value (\(\sim 600 \mu\text{V/K}\)) around 850 K and above this temperature it decreases almost linearly with temperature to 109 \(\mu\text{V/K}\) at 1188 K, at which point the structure transforms to CoO rock-salt. The transformation temperature decreased slightly (\(\sim 40\text{ K}\)) when measured in helium, rather than air. The thermopower correlates to inversion of the Co\(_3\)O\(_4\) 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 coworkers’ 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 coworkers’ thermodynamic cation distribution calculated from free energies. While the anomalous high-temperature structure of Co\(_3\)O\(_4\) 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 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\(_3\)O\(_4\) 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 in-
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