Origin of the high Seebeck coefficient of the misfit \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{[CoO}_2]\) cobaltate from site specific valency and spin state determinations

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Layered misfit cobaltate \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{[CoO}_2]\), which emerged as an important thermoelectric material [A. C. Masset et al. Phys. Rev. B, 62, 166 (2000)], has been explored extensively in last decade for the exact mechanism behind its high Seebeck coefficient. Its complex crystal and electronic structures have inhibited consensus among such investigations. This situation has arisen mainly due to difficulties in accurate identification of the chemical state, spin-state and site-symmetries in its two subsystems (rocksalt \([\text{Ca}_2\text{CoO}_3]\) and triangular \([\text{CoO}_2]\)). By employing resonant photoemission spectroscopy (RPES) and X-ray absorption spectroscopy (XAS) along with charge transfer multiplet (CTM) simulations (at the Co ions) we have successfully identified the site symmetries, valencies and spin-states of the Co in both the layers. Our site symmetry observations explain the experimental value of high Seebeck coefficient and also confirm that the carriers hop within the rocksalt layer which is in contrast to earlier reports where hopping within triangular \(\text{CoO}_2\) layer has been held responsible for large Seebeck coefficient.

The materials that can convert heat into electricity are often called as thermoelectric materials. A good thermoelectric material should possess low thermal conductivity (\(\kappa\)), high Seebeck coefficient (\(S\)) and high electrical conductivity (\(\sigma\)) to provide maximum value of figure of merit (\(S^2/\kappa\)). The cobalt-based layered structure family \((\text{Na}_x\text{CoO}_2, \text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9 \text{ and } \text{Ca}_3\text{Co}_4\text{O}_9)\) fulfilling the above mentioned requirements has become popular. The later one also has high \(S\) value and its chemical stability of the thermoelectric materials at high temperatures is also a common issue from the application point of view and this restricts the use of Na.

Earlier, the \(\text{Ca}_3\text{Co}_4\text{O}_9\) (CCO) emerged as a new candidate for thermoelectricity from misfit cobaltate family with stability up to high temperatures\(^5\). Its crystal structure comprises two incommensurately modulated subsystems sharing the same \(a\) and \(c\) but different \(b\) lattice parameters (see supplementary for details). The chemical structure of CCO (precise chemical formula \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{[CoO}_2]\)) is similar to that of \(\text{Na}_2\text{CoO}_2\) and can be compared with its \(x=2/3\) composition. In CCO, the layer \(\text{CoO}_2\) is presumed to be conducting and the rocksalt layer \(\text{Ca}_2\text{CoO}_3\) insulating, as is suggestive from studies on other iso-structural compounds\(^6,7\). Mixed valency of \(\text{Co}^{3+}\) and \(\text{Co}^{4+}\) is reported by x-ray photoemission and absorption spectroscopy\(^6,7\). And the Heikes formula was employed to calculate \(S\) values which was first used by Koshibae\(^4\) for explaining the \(S\) value, in high temperature, for mixed valent cobaltates. However, the origin of large \(S\) in this compound is controversial and has been proposed in different ways. By electron energy loss spectroscopy (EELS) measurement it was shown that to maintain charge neutrality holes from the rocksalt layers transfer into \(\text{CoO}_2\) layer and increases the concentration of mobile holes in it which enables high \(S\) [Ref. 8]. Also using 2p-3d resonant photoemission spectroscopy (RPES) it is reported\(^9\) that the Co 3d and O 2p hybridized states are spread from \(E_F\) up to 8 eV and \(S\) has been calculated using Boltzmann metallic conduction with extended band, not by Heikes formula. Moreover, theoretically, application of Heikes formula is reported in rocksalt\(^10\) as well as in \(\text{CoO}_2\) layer, both\(^11,12\) and these controversies continue because of the lack of experimental evidence.

Note that the Co valency estimation from approximate chemical formula \((\text{Ca}_2\text{Co}_4\text{O}_9)\) gives Co in +3 oxidation state, while in the misfit form the chemical formula contains \(\text{CoO}_2\) and \(\text{Ca}_2\text{Co}_3\) which individually supposedly contains Co ions in +4 and +2 states, respectively. However, on comparing its actual chemical formula \([\text{Ca}_2\text{CoO}_3]_{0.62}\text{[CoO}_2]\) with equivalent \(\text{Na}_2/3\text{CoO}_2\), one gets clue that the cobalt in \(\text{CoO}_2\) layers has +3.34 oxidation state and +3.05 in rocksalt layer. This suggests that the holes should transfer from the \(\text{CoO}_2\) to rocksalt layer but the scenario reported\(^8\) is contrary to this. Unfortunately, no direct tool exist that can estimate the correct valency in these two subsystems. Literature also contains controversies regarding the spin-states of the \(\text{Co}^{3+}\) and the \(\text{Co}^{4+}\) ions also and that which layer is conducting layer, rocksalt or triangular?

In this report we address the above issues and unravel the observation of different valency and spin states in the
rock salt and the CoO$_2$ layers by utilizing the symmetry as a distinction tool for two subsystems. The results are unique and provide the evidence of presence of D$_{3d}$ and D$_{4h}$ symmetries, both. Cobalt ions in mixed spin states (high spin state + low spin state) and +3/+4 valency are found to play role in the rocksalt layer for high Seebeck coefficient. We also confirm that DOS of triangular layer is adjacent to E$_F$ and contains Co in +3 only. Based on our results of chemical states and spins states in both these layers we have employed the Heikes formula in the rocksalt and calculated value of S is in excellent agreement with the experimental value.

Polycrystalline CCO has been synthesized using solid state route using post calcination method. X-ray diffraction has been performed at P09, DESY, Germany with 0.539 Å wavelength using image plate detector (Perkin Elmer XRD1621 detector having 40 × 40 cm$^2$ active area with 2048 × 2048 pixels). Single phase synthesis is confirmed by Rietveld refinement using monoclinic superspace group C2/m(080)000, where b=1.612 is the structural modulation vector (see supplementary Fig. S1 & S2). Magnetic susceptibility and resistivity as a function of temperature have been done to confirm the quality of the sample (see Fig. S3 (a & b)). X-ray photoemission spectroscopy (XPS) has been carried out using Omicron energy analyzer (EA-125) with Al Kα (1486.6 eV) x-ray source. Valence band spectra (VBS) with the incident photon energies in the range of 4468 eV were recorded at BL-02 of Indus-1 synchrotron, RRCAT, India. The experimental resolution in this photon energy range was estimated to be ~0.30 eV. The XAS experiments were performed at BL-01 of Indus-2 synchrotron, RRCAT, India. In the XAS experiments energy resolution at the Co L$_{3,2}$ edges was ~0.3 eV.

Fig. 1 (a) shows the Rietveld refined XRD pattern of CCO. Inset shows the supercell (a,13b, c) comprising both subsystems (see Fig. S1 & S2 and related text). It shows the cobalt environments in triangular CoO$_2$ layer and rocksalt layer. Fitted Co 2p and O 1s core XPS are displayed in Fig. 1 (b & c). XPS fitting reveals the +3 (∼68%) and +4 (∼32%) oxidation states of the cobalt ion in CCO. Therefore, average cobalt valency is found to be +3.22. The O 1s XPS shows lattice oxygen deficiency which may act as an electron doping at the cobalt sites in the rocksalt layer i.e. [Ca$_2$CoO$_{3−s}$]$_{0.62}$[CoO$_2$]. The mixed valency can not tell about which layer contains how much proportion of an oxidation state (+3 or +4) and also not about the spin-states.

In literature, previous reports have shown the Co$^{3+}$ and Co$^{4+}$ in low-spin states (LSS)$_{6,11}$. GGA calculations resulted Co$^{3+}$ in high-spin state (HSS) and Co$^{4+}$ in intermediate state (ISS). To investigate spin-states we performed the XAS measurements. This spectroscopy is able to probe the spin-states which appear in the multiplet feature(s) changes as the orbital occupation changes as well as symmetry of crystal field. Note that the orbital occupation depends upon the local symmetry around the metal ion. Usually, symmetry of octahedra depends on the type of the connectivity. For example, corner shared octahedra generally accepts high symmetry ($O_h$ or D$_{4h}$) while the edge shared low symmetry (D$_{3d}$). In the case of $O_h$ symmetry the resulting cubic crystal field splits the metal d orbitals into $e_g$ and $t_{2g}$ orbitals which further splits into $a_{1g}$, $b_{1g}$ and $e_g^*$, $b_{2g}$, in lower symmetry like D$_{4h}$ (tetragonal crystal field). For the D$_{3d}$ symmetry (trigonal crystal field) case octahedra is compressed along the (111)-direction, and degeneracy in $e_g$ orbitals exists but $t_{2g}$ splits into $a_{1g}$ and $e_g^*$. It is known that Co environment in CoO$_2$ layer is in the D$_{3d}$ symmetry and the rocksalt layers possess octahedra with distorted $O_h$ symmetry. Therefore, for the calculation of XAS patterns using the charge transfer multiplet simulation (CTM), we have considered the symmetry in the rocksalt as D$_{4h}$. Here we used the hopping parameters as $T_{eg}=2$ eV & $T_{t_{2g}}=1$ eV and to include the hybridization between states we reduced the atomic multiplet to 80% (i.e. Slater integrals $F_{dd}=F_{pd}=G_{pd}=0.8$). Distortion parameters $D_x$ & $D_y$ (for D$_{4h}$) and $D_x$ & $D_y$ (for D$_{3d}$) have been calculated from $\Delta_{eg}$ & $\Delta_{t_{2g}}$ using relations reported elsewhere. Other parameters in the simulation are adopted from literature and tabulated in Table S1. Fig. 2 (a) shows simulated XAS patterns for Co$^{3+}$ and Co$^{4+}$ in LSS and HSS in D$_{4h}$ as well as D$_{3d}$ crystal field symmetry. Fig. 2 (b) shows the experimentally observed XAS spectra and a simulated XAS spectra which is an
TABLE I. Concentration of Co ions with different spin states and valencies in D\(_{4h}\) and D\(_{3d}\) symmetry.

| Ion | D\(_{4h}\) | D\(_{3d}\) |
|-----|-----------|-----------|
| Co\(^{3+}\) HSS | 20% | 0 |
| Co\(^{3+}\) LSS | 14% | 34% |
| Co\(^{4+}\) HSS | 0 | 0 |
| Co\(^{4+}\) LSS | 32% | 0 |

iterative mixing of patterns shown in (a). Combination of Co\(^{3+}\)/Co\(^{4+}\) valencies and their spin-states under D\(_{4h}\) and D\(_{3d}\) symmetries which resulted the best fit (Fig. 2 (b)) are tabulated in Table I. Note that this combination is obtained under the constraints that fraction of Co\(^{3+}\) and Co\(^{4+}\) are 68% and 32%, respectively, as observed from XPS.

FIG. 2. (a) Simulated XAS spectra of Co\(^{3+}\) and Co\(^{4+}\) ions in HS and LS under D\(_{4h}\) and D\(_{3d}\) crystal fields. (b) Experimental and simulated XAS spectra of CCO. (c) Schematic of the crystal field effects in O\(_h\) and D\(_{3d}\) symmetries on degeneracy of d orbitals.

Fig. 3 show the RPES results, the valence band (VB) spectroscopy in the 3p-3d resonance region (44-68 eV). In this energy interval there may be two favorable excitations, first direct photoemission and second super Coster-Kronig (SCK) decay, which are given as 3p\(^6\)3d\(^n\) + h\(\nu\) \(\rightarrow\) 3p\(^6\)3d\(^{n-1}\) + e\(^-\) and 3p\(^6\)3d\(^n\) + h\(\nu\) \(\rightarrow\) [3p\(^5\)3d\(^{n+1}\)]\(^*\) \(\rightarrow\) 3p\(^6\)3d\(^{n-1}\) + e\(^-\), respectively, and the interference between these two give rise to resonance\(^2\) in the intensity of 3d dominated bands in the valence band. Using the results of reported\(^9\) 2p-3d RPES, we fitted the valence band spectra using four peaks as \(t_{2g}\) anti-bonding (AB), O 2p non-bonding (NB), \(t_{2g}\) bonding (B) and \(e_g\) bonding (B). These assignments are made up of by assuming the O\(_h\) crystal field. Inadequate fitting (Fig. 3 (a)) reveals the failure of this model. The constant intensity plots (CIS) show resonance and anti-resonance features. Although these resonance and anti-resonance are poor, yet give hints of 3d dominance. Moreover, the contour plot (see Fig. 3 (b)) clearly shows the two resonances at \(~52.5\) eV (feature A) and \(~58\) eV (feature B). These resonances have not been observed before and are indispensable to symmetry related information.

We propose that the valence band be defined by combination of D\(_{4h}\) and D\(_{3d}\) crystal field as is observed from the XAS. But separation of these (D\(_{4h}\) and D\(_{3d}\)) in RPES is not feasible due to the resolution limitations. However, in order to include D\(_{3d}\) symmetry the total number of participating orbitals must increase, as shown in Fig. 4 (a). We have assigned six features as \(a_{1g}\) AB, \(e_{\pi}^g\) AB, O 2p NB, \(e_{\pi}^g\) B, \(a_{1g}\) B and \(e_g\) B to define the VB. In this model the CIS plots (Fig. 4 (c)) clearly show two resonances (corresponding to feature A & B) energies in 3d bands.

In the earlier reported model for the CoO\(_2\) layer with O\(_h\) symmetry the \(t_{2g}\)AB band is near \(E_F\). However, in the present modified scheme of bands the main contribution near \(E_F\) is from the \(a_{1g}\) AB band as shown in the CIS plot. Its resonance for photon energy \(~52.5\) eV confirms that the feature A which corresponds to the triangular CoO\(_2\) layer has dominant Co 3d character. Our observation is in agreement with the \(ab\)\(^{-}\)\(initio\) theory results\(^11\) that the CoO\(_2\) layer contribute DOS near Fermi
(S \propto \frac{1}{T}) which is also not the case\textsuperscript{25}. Aforementioned counterintuitive scenarios motivated researchers to use Heikes formula for understanding the origin of high Seebeck coefficient at higher temperatures.

In literature many controversies exist regarding the band positioning of particular layers and S evaluation via Heikes formula. Asahi \textit{et al.}\textsuperscript{10} using first principal GGA showed that CoO\textsubscript{2} states lie in the gap while the rocksalt contribute at the $E_F$. They calculated S in the rocksalt layer which was 41 $\mu$V/K. Including correlation (DFT+U), Rebola \textit{et al.}\textsuperscript{11} found that CoO\textsubscript{2} is actually contributing at the $E_F$ and rocksalt forms gap and they calculated S in CoO\textsubscript{2} layer to be 227 $\mu$V/K. Soret \textit{et al.}\textsuperscript{12} using cluster quantum chemical methods with correlation, supported the results of Rebola but estimated S as 125 $\mu$V/K in the CoO\textsubscript{2} layer using non degenerate character of $a_{1g}$ orbitals. Our results related to electronic structures are consistent with these recent theoretical results but observation of the mixed valency in rocksalt layer motivates us to utilize the Heikes formula in rocksalt layer.

According to the Heikes formula, in high temperature limit, the thermopower can be written as\textsuperscript{26} $S = \frac{-k_B}{e} \ln \left( \frac{g_3 x}{g_4 (1-x)} \right)$, where $k_B$ is the Boltzmann constant and $e$ is the charge, negative sign is because of electron’s negative charge, $N$ represents number of electrons and $g$ represents total number of configurations. Chaikin \textit{et al.}\textsuperscript{26} have reported that spin degeneracy also plays an important role in determining the correct value of S. After him Koshih\textit{a}\textsuperscript{4} introduced the factor $g_3/g_4$, ratio of the degeneracy for different valencies (+3 and +4), to further improve the approximation to the S value. The modified formula is given by Eq. (1)

\[
S = \frac{-k_B}{e} \ln \left( \frac{g_3 x}{g_4 (1-x)} \right)
\]  

where $x$ represents the fraction of holes in the system. Koshih\textit{a}\textsuperscript{4} \textit{et al.} calculated the values of $g_3/g_4$ with different combinations of Co\textsuperscript{3+} and Co\textsuperscript{4+} [Ref. 4]. Utilizing the above mentioned arguments and using the hole concentration as $x = 0.32$ and fraction of Co\textsuperscript{3+} in HSS and LSS in rocksalt layer (see Table. I), we have calculated the Seebeck coefficient as, $S = \frac{-k_B}{e} \ln \left( \frac{(0.2) \times (g_{3,HSS})}{g_{4,LSS}} \frac{x}{1-x} + \frac{(0.14) \times (g_{3,LSS})}{g_{4,LSS}} \frac{x}{1-x} \right)$ which results S = 120.98 $\mu$V/K. This value of S is in excellent agreement and closest to the experimental value\textsuperscript{25,27} and validates our findings.

In conclusion, we have identified the symmetries around the Co ions in both the subsystems, triangular and rocksalt, and quantified the spin-states and valencies in each subsystem. RPES results strengthen our two sites existence in different environments by showing two resonances from each subsystem. Calculated value of S, using the Heikes formula by including the obtained spin degeneracy, ∼ 120.98 $\mu$V/K is in excellent agreement with the experiments. Our results confirm that the rocksalt layer
is main contributor to the high Seebeck coefficient value of this compound. Our experiments and results not only solve the pending and debated issue of origin of temperature independent high Seebeck coefficient of this complex misfit $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ cobaltate also pave a way for spectroscopic solutions to complex compounds with non-degenerate sites and valencies.

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Supplementary: Origin of the high Seebeck coefficient of the misfit $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ cobaltate from site specific valency and spin state determinations

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I. STRUCTURAL DETAILS OF THE LAYERED MISFIT [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] OBTAINED FROM SYNCHROTRON X-RAY DIFFRACTION RESULTS:

FIG. S1. (Left panel) Schematic of Ca$_2$CoO$_3$ unit cell with lattice parameters $a = 4.83$ Å, $b_1 = 4.55$ Å and $c = 10.85$ Å. (Right panel) Schematic of CoO$_2$ unit cell with lattice parameters $a$, $b_2 = 2.82$ Å and $c$. Both of these subsystems of [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] share the same $a$ and $c$ but different $b$. This structure is known as modulated structure because one of the unit cell can be assumed as modulated on the other, for example Ca$_2$CoO$_3$ is modulated on CoO$_2$ with modulation vector $b = b_1/b_2 = 1.6134$ or CoO$_2$ is modulated on Ca$_2$CoO$_3$ with $b = b_2/b_1 = 0.6197$. (Wycoff positions are adopted from Ref. S1)
In order to refine the structure in a single unit cell we have employed the supercell approach by approximating the modulation vector to commensurate value i.e. $b = b_1/b_2 = 1.6134 \approx 13/8$. (Upper panel) Schematic of supercell of the CoO$_2$ subsystem (a, 13$b_2$, c) and (Lower panel) schematic of supercell of the Ca$_2$CoO$_3$ subsystem (a, 8$b_1$, c).
II. MAGNETIC AND ELECTRICAL CHARACTERIZATION RESULTS OF THE SAMPLE USED FOR SPECTROSCOPIC INVESTIGATIONS WHICH ARE PRESENTED IN THE PAPER:

FIG. S3. (a) Susceptibility (M/H) and inverse susceptibility (H/M), measured under 10 kOe applied field, vs temperature. Inset shows the 7T field cooled MH loop at 5 K. The susceptibility exactly matches with the values reported by Sugiyama et al. Ref. [S2], and highlights the quality and reproducibility of the sample. (b) Resistivity vs temperature of the sample showing the behavior similar to reported elsewhere [S3].
III. PARAMETERS UTILIZED IN THE CHARGE TRANSFER MULTIPLET SIMULATIONS

TABLE S 1. Crystal field parameters used in the simulation of the XAS.

| Symmetry | $U_{dd}$ (eV) | $U_{pd}$ (eV) | 10Dq (eV) | $\Delta_C$ (eV) | $\Delta_{eg}$ (eV) | $\Delta_{t_{2g}}$ (eV) |
|----------|---------------|---------------|----------|----------------|-------------------|------------------------|
| $D_{4h}$  |               |               |          |                |                   |                        |
| Co$^{3+}$ HSS | 5             | 6             | 1.2      | 4.5            | 0.7               | 0                      |
| Co$^{4+}$ HSS | 5             | 6             | 2.0      | -3.5           | 0.7               | 0                      |
| Co$^{3+}$ LSS | 5             | 6             | 1.9      | 4.5            | 0.7               | 0                      |
| Co$^{4+}$ LSS | 5             | 6             | 2.4      | -3.5           | 0.7               | 0                      |
| $D_{3d}$  |               |               |          |                |                   |                        |
| Co$^{3+}$ HSS | 5             | 6             | 1.2      | 4.5            | 0                 | 0.26                   |
| Co$^{4+}$ HSS | 5             | 6             | 2.0      | -3.5           | 0                 | 0.26                   |
| Co$^{3+}$ LSS | 5             | 6             | 1.9      | 4.5            | 0                 | 0.26                   |
| Co$^{4+}$ LSS | 5             | 6             | 2.4      | -3.5           | 0                 | 0.26                   |

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