Origin of coexisting large Seebeck coefficient and metallic conductivity in the electron doped SrTiO$_3$ and KTaO$_3$

Hidetomo Usui, Shinsuke Shibata$^1$, and Kazuhiko Kuroki

Department of Applied Physics and Chemistry, The University of Electro-Communication, Chofu, Tokyo 182-8585, Japan

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We study the origin of the large Seebeck coefficient despite the metallic conductivity in the La-doped SrTiO$_3$ and Ba-doped KTaO$_3$. We calculate the band structure of SrTiO$_3$ and KTaO$_3$, from which the Seebeck coefficient is obtained using the Boltzmann’s equation. We conclude that the multiplicity of the $t_{2g}$ bands in these materials is one major origin of the good thermoelectric property in that when compared at a fixed total number of doped electrons, the Seebeck coefficient and thus the power factor are larger in multiple band systems than in single band ones because the number of doped electron bands per band is smaller in the former. We also find that the second nearest neighbor hopping integral, which generally has negative values in these materials and works destructively against the Seebeck effect, is nearly similar between KTaO$_3$ and SrTiO$_3$ despite the larger band width in the former. This can be another factor favorable for thermopower in the Ba-doped KTaO$_3$.

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I. INTRODUCTION

The discovery of the large Seebeck coefficient in Na$_x$CoO$_2$[2] and the findings in cobaltates/cobaltites[3–7] and rhodates[8, 9] that followed have brought up an interesting possibility of finding good thermoelectric materials that have relatively high (metallic) conductivity. These cobaltates and rhodates are materials where holes are doped into the $d^0$ configuration, namely the electron configuration where the $t_{2g}$ bands are fully filled. On the other hand, there is another class of $t_{2g}$ transition metal oxides where relatively good thermoelectric properties are obtained, namely the electron doped materials such as SrTiO$_3$. When Sr is partially replaced by La in SrTiO$_3$, electrons are doped in the originally $d^0$ configuration. This material exhibits large Seebeck coefficient despite showing metallic conductivity, and the power factor, i.e., the Seebeck coefficient squared times the conductivity, is comparable to that of Bi$_2$Te$_3$. Quite recently, good thermoelectric properties have also been observed in Ba-doped KTaO$_3$. This is another $t_{2g}$ oxide, where electrons are doped into the originally $d^0$ configuration, but is a 5$d$ system as compared to the 3$d$ in SrTiO$_3$. Here again, relatively large Seebeck coefficient is observed despite the metallic conductivity.

Theoretically, there have been several approaches that explain the large Seebeck coefficient in oxides. From the first principles band calculation studies, it has been pointed out that the narrowness of the band structure in Na$_x$CoO$_2$ and related rhodates is an important factor[12, 13]. We have proposed that besides the width of the band, the shape of the band, which we call the “pudding-mold” type band, is important for the coexistence of the large Seebeck coefficient and the high conductivity in Na$_x$CoO$_2$[14] and related rhodates[15, 16]. On the other hand, Koshibae et al. derived a formula for the Seebeck coefficient in the $T$(temperature) $\rightarrow$ $\infty$ limit, and pointed out that the orbital degeneracy originates large entropy, leading to the large Seebeck coefficient[17, 18].

In the present study, we propose that yet another mechanism, where the band multiplicity plays an important role, is at work in the electron doped $t_{2g}$ materials. Namely, when there are multiple (nearly) equivalent bands at the Fermi level, and the number of doped electrons per band is fixed, the Seebeck coefficient is essentially the same regardless of the number of bands, while the conductivity increases with the multiplicity of the bands thus resulting in an enhanced power factor. In other words, when the total number of doped electrons itself is fixed, the Seebeck coefficient and thus the power factor is larger for multiple band systems because the Fermi energy stays low. We also examine the effect of the band shape, and show that the second nearest neighbor hopping integral, which generally has negative values in these materials and work destructively against the Seebeck effect, is nearly similar between KTaO$_3$ and SrTiO$_3$ despite the larger band width in the former. This can be another factor favorable for good thermoelectric properties in the Ba-doped KTaO$_3$.

II. FORMULATION

A. Boltzmann’s equation approach

We first briefly summarize the Boltzmann’s equation approach adopted in the present study[13, 19]. In this approach, the Seebeck coefficient is given as

$$S = \frac{1}{eT}k_0^{-1}k_1$$

(1)
where $e(< 0)$ is the electron charge, $T$ is the temperature, tensors $K_0$ and $K_1$ are given by

$$K_n = \sum_{\vec{k}} \tau(\vec{k}) \hat{v}(\vec{k}) \left[ -\frac{\partial f(\varepsilon)}{\partial \varepsilon}(\vec{k}) \right] (\varepsilon(\vec{k}) - \mu)^n. \quad (2)$$

Here, $\varepsilon(\vec{k})$ is the band dispersion, $\hat{v}(\vec{k}) = \nabla_{\vec{k}} \varepsilon(\vec{k})$ is the group velocity, $\tau(\vec{k})$ is the quasiparticle lifetime, $f(\varepsilon)$ is the Fermi distribution function, and $\mu$ is the chemical potential. Hereafter, we simply refer to $(K_n)_{xx}$ as $K_n$, and $S_{xx} = (1/eT)(K_1/K_0)$ (for diagonal $K_0$) as $S$. Using $K_0$, conductivity can be given as $\sigma_{xx} = e^2K_0 \equiv \sigma = 1/\rho$. As an input of the band structure in this calculation, we use the first principles calculation as described below. $\tau(\vec{k})$ will be taken as an (undetermined) constant in the present study, so that it cancels out in the Seebeck coefficient, while the conductivity and thus the power factor has to be normalized by a certain reference.

### B. Band Calculation

SrTiO$_3$ and KTaO$_3$ have cubic perovskite structures. We use the experimentally determined lattice constants in the band calculation, which are $a = 3.90528 \text{Å}$ for SrTiO$_3$ \cite{20} and $a = 3.9883 \text{Å}$ for KTaO$_3$ \cite{21}. For SrTiO$_3$, we have obtained the band structure using the Quantum-ESPRESSO package \cite{22}. In order to obtain a tight binding model on which we can perform various analysis, we construct the maximally localized Wannier functions (MLWFs) \cite{23} for the outer energy window 0 eV < $\epsilon_k$ − $E_F$ < 5 eV and for the inner windows 0 eV < $\epsilon_k$ − $E_F$ < 4 eV, where $\epsilon_k$ is the eigenenergy of the Bloch states and $E_F$ is the Fermi energy. These MLWFs, centered at Ti sites in the unit cell, have three orbital symmetries (orbital 1: $d_{xy}$, 2: $d_{yz}$, 3: $d_{zx}$). With these effective hoppings and on-site energies, the tight-binding Hamiltonian is obtained, and finally the Seebeck coefficient is calculated using eq. $(1)$. For KTaO$_3$, we have obtained the band structure using the WIEN2K package \cite{24}. The Seebeck coefficient is calculated using the BoltzTraP code \cite{25}.

### III. CALCULATION RESULTS OF THE SEEBECK COEFFICIENT

In this section, we present the band calculation results and the calculation results of the Seebeck coefficient. The calculated band structures of SrTiO$_3$ and KTaO$_3$ are shown in Fig. 1. In both materials, there are three $t_{2g}$ bands right above the Fermi level, and for SrTiO$_3$, the band structure of the three band tight binding model is superposed to the original first principles band. The band structure of the two materials look similar, but the band width is wider for KTaO$_3$ due to the widely spread nature of the 5$d$ orbitals.

![Fig. 1: The band structure of (a) SrTiO$_3$ and (b) KTaO$_3$.](image)

![Fig. 2: The calculated Seebeck coefficient for (a) SrTiO$_3$ and (b) KTaO$_3$ plotted as functions of temperature for various doping rate $x$.](image)
The calculated Seebeck coefficient for the two materials is shown in Fig.2 against the temperature at $x = 0.05$ and $x = 0.1$ for SrTiO$_3$, and $x = 0.009$ for KTaO$_3$. We have chosen these $x$ to make comparison with the experiments\cite{10, 11}. Here we take a rigid band approach, and assume that the hole concentration $n_h$ is equal to the La (SrTiO$_3$) and Ba (KTaO$_3$) content.

For SrTiO$_3$. The Seebeck coefficient at 300K is $S(x = 0.05) = -87\mu V/K$ and $S(x = 0.1) = -58\mu V/K$. Experimentally, the Seebeck coefficient at 300K is $S(x = 0.05) = -147\mu V/K$ and $S(x = 0.1) = -88.7\mu V/K$\cite{10}. Thus the calculation result is somewhat reduced from the experimental result. The reason for this is probably due to the reduction of the band width due to the strong correlation effect of the 3d orbitals. In fact, it has been known from the comparison between band calculations and the angle resolved photoemission studies that the band width of the 3d electron materials is generally reduced by a factor of about two, and in fact taking this effect into account reproduces the experimental results of Na$_x$CoO$_2$ well\cite{14}. If we calculate the Seebeck coefficient at 300K by reducing the band width by 50% from the bare LDA result, we get $S(x = 0.05) = -149\mu V/K$ and $S(x = 0.1) = -103\mu V/K$ (Fig.2(a)), which are in fact fairly close to the experimental values.

As for KTaO$_3$, the calculation of the Seebeck coefficient at $x = 0.009$ gives $S(300K) = -160\mu V/K$. This is roughly in agreement with the experimental result which is about $-200\mu V/K$\cite{11}. A reason why the bare LDA band structure gives good agreement with the experiments is because KTaO$_3$ is a 3$d$ system, where the electron correlation effects are expected to be small compared to 3$d$ systems like SrTiO$_3$. In fact, for a number of rhodates, i.e. 4$d$ systems, the Seebeck coefficient calculated from the bare LDA band structure gives fairly good agreement with the experiments\cite{12, 13, 14}.

### IV. EFFECT OF THE BAND MULTIPlicity

Having found that the experimentally observed Seebeck coefficient is roughly reproduced within the first principles band calculation + the Boltzmann’s equation approach (with some additional consideration of band narrowing), we now explain why the Seebeck coefficient is large in these materials despite the relatively large conductivity. In other words, we seek for the origin of the large power factor $S^2\sigma$.

In the three orbital model, the Seebeck coefficient $S_{xx}$ is given as

$$S_{xx} = \frac{1}{eT} \frac{K_{1}^{dxy} + K_{1}^{dyz} + K_{1}^{dzx}}{K_{0}^{dxy} + K_{0}^{dyz} + K_{0}^{dzx}},$$

(3)

where $K_{n}^{dij}$ stands for $K_n$ of the $d_{ij}$ ($i,j = x,y,z$) orbital. From eq. (2), the group velocity $v_{dij}$ is the important factor in $K_n$. $v_{dxy}$ is equal to $v_{dzx}$ because $d(\varepsilon_{xy})/dx$ is equal to $d(\varepsilon_{zx})/dx$, so that $K_n^{dxy} = K_n^{dzx}$.

Also, $K_n^{dyz} \sim 0$ because $v_{dyz}$ is very small. So the Seebeck coefficient is

$$S_{xx} \sim \frac{1}{eT} \frac{2K_{1}^{dxy}}{2K_{0}^{dxy} + K_{0}^{dyz} + K_{0}^{dzx}} = \frac{1}{eT} \frac{K_{1}^{dxy}}{K_{0}^{dxy}} = S_{xx}^d.$$

(4)

Namely, the total Seebeck coefficient is equal to the Seebeck coefficient of the $d_{xy}$ single orbital system. On the other hand, the conductivity is

$$\sigma = e^2 (K_0^{dxy} + K_0^{dyz} + K_0^{dzx}) \sim 2e^2 K_0^{dxy} = 2\sigma_{dxy}. \quad (5)$$

Therefore the power factor is

$$P_{xx} = \sigma S_{xx}^d \sim 2\sigma_{dxy}^2 (S_{xx}^d)^2 = 2P_{dxy}.$$

The left hand side here is the power factor of the three orbital system, while $P_{dxy}$ in the right hand side is that of the $d_{xy}$ single orbital system. Thus the multiplicity of the orbitals is advantageous for large power factor. Note that the comparison here between the three orbital and the single orbital systems is given for the same number of electrons per band. If we present this relation between the three and one orbital systems using the doping concentration $x$, it should be given as $S_{xx}(3x) = S_{xx}^d(x)$ and $P_{xx}(3x) = 2P_{dxy}(x)$.

In Fig.3 we show the actual calculation result of the Seebeck coefficient and the power factor (normalized at $x = 0.13$ of the single orbital model) of the $t_{2g}$ three orbital model of SrTiO$_3$ and a single orbital model where only the $d_{xy}$ orbital is considered. It can be seen that the above relation is indeed satisfied. It is also worth noting that the doping dependence of the power factor is in striking agreement with the experimental observation (Fig.3 in ref.\cite{10}). From this figure, we can see that for a fixed doping concentration, both the Seebeck coefficient and the power factor is larger for multiorbital systems than in single orbital ones. This can intuitively be understood from Fig.3(c), namely, the Fermi level tends to stay lower for systems with multiple bands for a fixed number of doped electrons, and lower Fermi level results in a large Seebeck coefficient, while the large number of electrons (due to the multiplicity of the bands) enhances the conductivity\cite{16}. The present result suggests that the band multiplicity is at least one of the main reasons why the Seebeck coefficient is large despite the metallic conductivity. The orbital degeneracy has been considered as a factor to obtain good thermoelectric properties in the context of entropy\cite{17, 18}, but we stress here that the present mechanism provides another way where the band multiplicity can play an important role\cite{10}.

### V. EFFECT OF THE BAND SHAPE

In the present materials, the density of states per band is not so large around the Fermi level. This can roughly be understood in terms of the tight binding model. Namely, the tight binding model on a square
lattice has electron hole symmetry when only the nearest neighbor hopping \( t_1 \) is considered. The introduction of the second nearest neighbor hopping \( t_2 \) breaks this electron-hole symmetry, and for \( t_{2g} \) systems, this hopping integral usually has a negative sign when writing down the Hamiltonian in the form \( H = \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j \). When \( t_2 \) is negative, the density of states tends to be large in the upper half of the band and small in the lower half. In this sense, the effect of the so-called “pudding mold type” band [13], where a flat portion of the band has to be present near the Fermi level, is not relevant to the present electron doped materials. This can in fact be seen as follows. Since we have found that \( S_{xx} \simeq S_{xx}^{\text{var}} \) (assuming same electron number per band) in the preceding section, we concentrate here on the \( d_{xy} \) single orbital model of SrTiO\(_3\). In this model, the nearest and second nearest neighbor hoppings of the MLWF tight-binding Hamiltonian are \( t_1 = -0.28 \text{eV} \) and \( t_2 = -0.078 \text{eV} \). To see how \( t_2 \) affects the Seebeck coefficient, we vary \( t_2 \) while fixing \( t_1 = -0.28 \text{eV} \), and calculate the Seebeck coefficient at 300K as shown Fig. 3(a). It is found that the smaller \(|t_2|\) is, the larger the Seebeck coefficient. This is because the lower part of the band (where the Fermi level exists) becomes less dispersive as \(|t_2|\) is decreased when \( t_2 \) is negative. This can be seen in the calculation of the density of states (DOS) given in Fig. 3(b), namely, the DOS at the band bottom for \( t_2 = 0 \text{eV} \) is about twice larger than for \( t_2 = -0.13 \text{eV} \). Thus the negative value of \( t_2 \) (i.e., the band shape) in SrTiO\(_3\) is not favorable for thermopower, and the good thermoelectric properties seem to come mainly from the multiplicity of the bands.

We have also evaluated \( t_1 \) and \( t_2 \) for KTaO\(_3\) from the obtained band structure as listed in table 1 together with some related materials. Although \( t_1 \) is much larger compared to that in SrTiO\(_3\) as expected from the 5d nature, \( t_2 \) is not much changed, and the ratio \(|t_2/t_1|\) is the smallest among the materials considered here. In fact, \(|t_2/t_1|\) is also small in Zr and Nb compounds, namely 4d systems with small number of electrons. So it seems that the ratio \(|t_2/t_1|\) tends to be small for large principle quantum number. This trend can be considered as another factor working favorable for the thermopower in KTaO\(_3\) despite the wide band width.

| Material      | \( t_1 \) (eV) | \( t_2 \) (eV) | \(|t_2/t_1|\) |
|---------------|----------------|----------------|---------------|
| PbTiO\(_3\)   | -0.23          | -0.073         | 0.31          |
| BaTiO\(_3\)   | -0.25          | -0.066         | 0.26          |
| SrTiO\(_3\)   | -0.28          | -0.078         | 0.28          |
| BaZrO\(_3\)   | -0.40          | -0.081         | 0.20          |
| NaNbO\(_3\)   | -0.45          | -0.091         | 0.20          |
| KTaO\(_3\)    | -0.52          | -0.094         | 0.18          |
| BaMnO\(_3\)   | -0.17          | -0.067         | 0.41          |

### VI. CONCLUSION

To conclude, we have studied the origin of the large Seebeck coefficient in SrTiO\(_3\) and KTaO\(_3\). In SrTiO\(_3\), from the first principles band calculation results, a tight-binding model is obtained via the maximally localized Wannier orbitals, and the Seebeck coefficient is calculated using the tight-binding model. In KTaO\(_3\), from
FIG. 4: (a) The Seebeck coefficient of the single orbital model for $x = 0.017$, $t_1 = -0.28$eV and $T = 300$K plotted as functions of $t_2$. (b) The density of states at $t_1 = -0.28$eV, $t_2 = 0$eV (solid red) and $t_2 = -0.13$eV (dashed green).

In both materials, the large Seebeck coefficient despite the relatively large conductivity is largely due to the multiplicity of the bands, i.e., essentially the same value of the Seebeck coefficient is obtained for the same number of electrons per band, so that when the total number of doped electrons itself is the same, the Seebeck coefficient and thus the power factor are larger for multiple band systems. Also, we have examined the effect of the band shape. Although the negative $t_2$ value is not favorable for the electron doped thermoelectric materials, 4d and 5d systems such as KTaO$_3$ tend to have similar $t_2$ values as in 3d systems despite the wide band width, and this can be another factor that is advantageous for good thermoelectric properties.

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[∗] present address: Department of Physics, Tohoku University, Sendai, 980-8578, Japan
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