Thermopower in transition-metal perovskites

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High-temperature thermopower is an entropy that a carrier carries. Owing to spin and orbital degrees of freedom, a transition metal perovskite exhibits large thermopower at high temperatures. In this paper, we revisit the high-temperature thermopower in the perovskites to shed light on the degrees of freedom. Thus, we theoretically derive an expression of thermopower in one-dimensional octahedral-MX₆-clusters chain using linear-response theory and electronic structure calculation of the chain based on the tight-binding approximation. The derived expression of the thermopower is consistent with the extended Heikes formula and well reproduced experimental data of several perovskite oxides at high temperatures. In this expression, a degeneracy of many electron states in octahedral ligand field (which is characterized by multiplet term) appears instead of the spin and orbital degeneracies. Complementarity in between our expression and the extended Heikes formula is discussed.

I. INTRODUCTION

Transition-metal (M) oxides are one of fascinating many-body systems, which exhibits Mott insulating state [1], spin-state crossover [2], peculiar magnetism accompanied by orbital ordering [3], high-temperature superconductivity [4], huge magnetoresistance [5], large thermopower [6], exotic superconductivity [6, 7], multiferroicity [8], spin-orbit related Mott insulating state [11], spin frustration (possibly spin liquid) [12], and other relativistic effects such as Weyl semi-insulating state [11], spin-state crossover [2], peculiarity of thermoelectric voltage (V) as $V_T \equiv -d \ln 2$, and can be applied for thermoelectric energy conversion [17]. Thermopower at high-temperature limit in the quantum many-body systems is interpreted as entropy that a carrier carries in a regime of linear response theory with the Hubbard model [18, 19]. Chaikin and Beni generalized Heikes formula [18] to explain thermopower of interacting Fermi systems with spin, and explained thermopower of strongly correlated p-electron system (one-dimensional organic conductor) with spin entropy term $-\frac{3}{2} \ln 2$ [19]. Further, Dourmec extended the formula to apply for a system containing a mixed valent cation $M^{n+}/M^{(n+1)+}$ using spin multiplicity $(2S_n + 1)$ [20]. Marsh and Parr-Pratt again extended the formula to take into account the orbital degeneracy, and qualitatively explained thermopower of LaCrO₃ [21], LaMnO₃ [22] and their related perovskite systems. Koshibae et al. also explained the large thermopower of NaCo₂O₄ using the spin and orbital degrees of freedom and proposed application of their theory to Co perovskite oxides [23]. In their theories, such degrees of freedom are introduced by counting a number of cases in many electrons configuration in $e_g$ and $t_{2g}$ orbitals, and they seem to work well. To further consider the degrees of freedom, we derive a similar formula constructed from many electron states in MX₆ cluster with octahedral ligand (X: ligand element) field without a use of one-band Hubbard model.

In this paper, we construct thermopower of one-dimensional MX₆-clusters chain model targeting the 3d-transition-metal perovskite oxides with $t_{\perp} \gg 1$. In a derived expression of the thermopower, we find that a degeneracy of many-electron states in the MX₆-cluster is included instead of the degeneracies of spin and orbital. We will discuss the relation between spin and orbital degrees of freedom and the degeneracy of the many-electron states. We further apply our formula to experimental data of several 3d-transition-metal perovskite oxides. Lastly, effects of spin-orbit interaction and Jahn-Teller distortion on the thermopower and further possible application of our theory will be discussed in the section of III. G.
clusters-chain model. See Fig. 2). Third, we derive an
coulomb interaction (electron structure of periodically aligned
approximation (molecular-orbital theory) for the construc-
tion of the electronic structure of periodically aligned
one-dimensional MX₆-clusters-chain system (hereafter,
clusters-chain model. See Fig. 2. Third, we derive an
expression of thermopower at high-temperature limit for
the clusters-chain model, in a regime of linear-response
theory. Last, we discuss complementarity in between the
extended Heikes formula and our expression.

II. METHODS

In this section, first, we briefly review the crystal (ligand)
field theory. We see many d-electron states in octa-
htedral ligand field, term symbol, and how to count
degeneracy of the states that is represented by the
term symbol. Second, we explain the tight-binding ap-
proximation (molecular-orbital theory) for the construct-
ion of the electronic structure of periodically aligned
one-dimensional MX₆-clusters-chain system (hereafter,
clusters-chain model. See Fig. 2). Third, we derive an
expression of thermopower at high-temperature limit for
the clusters-chain model, in a regime of linear-response
theory. Last, we discuss complementarity in between the
extended Heikes formula and our expression.

A. Crystal field theory (CFT)

To calculate physical properties of solids, we generally
need to treat its electronic structure correctly taking
into account periodicity of the crystal. However, if on-site
coulomb interaction (U) is much larger than inter-atomic
transfer integral (t), we may discuss the physical proper-
ties of the crystal based on the atomic electronic states.
Effects from other atoms can be treated as crystal field or
ligand field which includes hybridization with p-orbitals
of the ligands.

Here, we briefly review the crystal field theory (CFT).
CFT describes a breaking of a degeneracy of electron
orbital states (d or f orbital states) of atom (or ion) due
to a static electric field produced by a surrounding charge
distribution. Suppose d-electrons of the atom (or the ion)
are surrounded by 6 negative charges (−Ze, Z: positive
integer, e: charge unit) at \( R_k = (a, 0, 0), (0, a, 0), (0, 0, a), (−a, 0, 0), (0, −a, 0), \) and (0, 0, −a). Then, the
Hamiltonian \( (H_n) \) of the \( n \) d-electrons \( (n: \) a number of
d-electrons) is described as

\[
H_n = \left( \sum_{i=1}^{n} \frac{p_i^2}{2m_e} + v_{core}(r_i) + v_{CF}(r_i) \right) + \sum_{j>i=1}^{n} \frac{e^2}{r_{ij}},
\]

where \( m_e, p_i, r_i = |r_i|, \) and \( r_{ij} = |r_i - r_j| \) represent
electron mass, momentum of \( i \)-th electron, distance in
between a position of \( i \)-th electron and the origin, and
relative distance in between \( r_i \) and \( r_j \). \( v_{core}(r_i) \) is a
potential of atom and valence electrons (central force
field approximation), \( v_{CF}(r_i) \) is a crystal field, \( v_{CF}(r_i) = \sum_{k=1}^{6} \frac{Z_k e^2}{r_{ik}}, \)
and the last term represents electron inter-
action between d electrons. When \( n = 1 \), the fourth
term vanishes which results in well known \( d_{x^2−y^2} \) (we
denote this as \( \phi_a \) or \( v \)), \( d_{x^2−y^2} \) (\( \phi_u \) or \( u \)), \( d_{xy} \) (\( \phi_c \) or \( \zeta \)), \( d_{yz} \) (\( \phi_c \) or \( \xi \)), and \( d_{xz} \) (\( \phi_p \) or \( \eta \)) wave functions
are obtained. Note that these wavefunctions are real func-
tions. For \( v_{core}(r_i) = −\frac{Ze^2}{r^2} \), energy gap in between \( e_g \) and
t₂g orbitals is evaluated as \( 10Dq \), where \( D = \frac{352}{243} \) and
\( q = \frac{3}{4} \langle r^4 \rangle \text{ (average of } r^4, \langle r^4 \rangle = \int R_{nd}^2 r^2 dr, \text{ } R_{nd}
\)
is radial wavefunction of \( nd \) states.\[24\]. Parameters \( Z \)
a and \( a \) can tune the energy gap. In this sense, \( Z \) and \( a \)
can express material’s characteristics. Thus, under
octahedral coordination, 5-fold d orbitals split into 3-fold t₂g
and 2-fold e_g orbitals.

When \( n > 1 \), electron correlation should be taken into
account. Tanabe and Sugano have constructed solutions
for \( n \) d-electrons \( (1 ≤ n ≤ 9) \) in the crystal field (strong
crystal field limit) \[25\][26]. As a result, the many-electron
state is found to be expressed as a linear combination
of Slater determinants including \( \phi_a(u), \phi_u(v), \phi_c(\zeta), \phi_c(\xi), \phi_p(\eta), \) \( \phi_p(\gamma) \) (spin up), \( \phi_a(u), \phi_u(v), \phi_c(\zeta), \phi_c(\xi), \phi_p(\eta), \phi_p(\gamma) \) (spin down). Write the many-electron state as
\( \Phi_s(t_{2g}^n e_{g}^{2S+1} \Gamma M_s \gamma), \) where \( p \) and \( q \) \( (n = p + q) \) repre-
sent a number of electrons at t₂g orbitals \( (\zeta, \xi, \eta, \zeta) \) and
e orbitals \( (u, v), \) \( 2S+1 \) represents multiplet term, \( M_s \)
is an eigenvalue of total spin angular momentum \( (S_z) \),
and \( \gamma \) represents ground function of irreducible repres-
entation \( \Gamma \) (e.g., \( \Gamma = T_{2g}, \gamma = \xi, \eta, \zeta \)). As an example,
we briefly treat \( n = 2 \). A number of cases for \( (t_{2g})^2 \)
configuration is 15 \( = \left( \begin{array}{c} 5 \end{array} \right) \). Thus, we can provide 15
Slater determinant as \( |\xi\eta|, |\xi\eta|, \cdots, |\xi\xi| \). Then, using
a linear combination \( \Phi_s \) of these 15 Slater determi-
nants, \( \langle \Phi_s | \Phi_s \rangle \Phi_s \) can be diagonalized, then we obtain
\( \Phi_s = \Phi_s(t_{2g}^{2} e_{g}^{2S+1} \Gamma M_s \gamma). \) This solution is further charac-
terized by multiplet term which represents symmetry of
the many-electron states under octahedral ligand field.
For example, \( \Phi_s(t_{2g}^{2} e_{g}^{2S+1} \Gamma M_s \gamma), \) \( \gamma = |\xi\eta|, |\eta\zeta|, \) and \( |\zeta\zeta| \). \( \Phi_s(t_{2g}^{2} e_{g}^{2S+1} \Gamma M_s \gamma), \) \( \gamma = |\xi\eta|, |\eta\zeta|, \) and
\( |\zeta\zeta| \). These 9 functions are energetically degenerate. A
degeneracy of the multiplet term \( 2S+1 \) is a product of
spin multiplicity \( (2S + 1) \) and \( \Gamma_0, \) \( \Gamma_0 \) is a dimensional
number of irreducible representation \( (1 \text{ for } \Gamma \text{ for } A(B), \Gamma \text{ for } E, \text{ and } \)3 for \( T \). Thus, a degeneracy of \( 3^2 \text{ for } T \) is expressed as
\( 3 \times 3 = 9. \)
Next, let’s see briefly multiplet theory of atom. Many-electron state of a free ion is expressed using term symbol \(2S+1L\), where \(L\) is total orbital angular momentum \((L = S, P, D, F, G, \cdots\) corresponds to 0, 1, 2, 3, 4, \(
\cdots\), respectively). A degeneracy of the many-electron state is expressed as \((2S + 1)(2L + 1)\). For example, \(d^5\) has 252-fold degeneracies \((-10C_5)\), however, under spherical coulomb potential, it splits and the ground term becomes to \(6S\). Thus, the degeneracy decreases from 252 to 6. Under weak crystal field, this ground states remain alive and expressed as \(6A_1g\). As shown above, for strong crystal field limit, we see how to construct many-electron states by Tanabe and Sugano. By connecting weak-crystal field limit \([27]\), Tanabe and Sugano constructed Tanabe-Sugano diagram \([27]\). Each states in the diagrams are labelled by term symbols, which shows symmetry of the many-electron states under ligand field and its degeneracies of each states. Thus, Tanabe-Sugano diagram gives information on the degeneracies of d electrons wavefunctions in octahedral ligand field. The number of the degeneracy can be read from the term symbol. Table I lists ground multiplet term and degeneracy \((\Gamma)\) that the multiplet term represents for \(0 \leq n \leq 10\). Note that the intermediate spin states are excited states in Tanabe-Sugano diagram. In our theory, the degeneracy of the ground multiplet term plays an important role. Ligand field theory succeeded in explaining several physical properties such as thermochanical properties (hydration enthalpies) and geometric distortions (Jahn-Teller distortion and spinel structures), various spectroscopies of transition metal coordination complexes, in particular optical spectra (colors), magnetic properties (spin-orbit-coupling related magnetism) and so on \([24, 27]\).

**B. Electronic structure of one-dimensional \(N\)-clusters chain model**

As a next step, let’s construct one-dimensional \(N\)-clusters chain model. \((N : \text{a number of clusters})\) We assume tight binding approximation of the clusters. The Hamiltonian of the clusters chain model is described as

\[
H_N = \sum_{l=1}^{N} H_{n,l} + \sum_{l \neq m} V_{l,m},
\]

where \(H_{n,l}\) represent the Hamiltonian of the \(l\)-th cluster (equivalent to Eq. (1)), \(n_l\) represents a number of d electrons at \(l\)-th cluster, and inter-cluster interaction in between \(l\)-th and \(m\)-th clusters is introduced as \(V_{l,m}\) (see Fig. 2). The many-electron wave function of the \(N\)-clusters chain is constructed by a linear combination of one of the degenerated wave functions of the \(l\)-th cluster \(\Phi_{n,l}(t_{l}^{e}e^{j}; 2S+1 \Gamma M_s \gamma)\) as

\[
\Psi_N = \sum_{l=1}^{N} c_l \Phi_{n,l}(t_{l}^{e}e^{j}; 2S+1 \Gamma M_s \gamma),
\]

where \(c_l\) is normalized constant. Since both \(H_N\) and \(\Psi_N\) are real function, the matrix elements are expressed as real symmetric matrix,

\[
\langle \Psi_N | H_N | \Psi_N \rangle = \sum_{l} \left( \begin{array}{c} \vdots \\ E_{l-1} \\ \vdots \\ t_{l-1,l} \\ E_l \\ t_{l,l+1} \ldots t_{l,m} \\ \vdots \\ E_{l+1} \\ \vdots \\ c_m \\ \vdots \end{array} \right) \left( \begin{array}{c} \vdots \\ c_l \\ \vdots \\ t_{l,m,l} \\ \vdots \end{array} \right)
\]

where \(E_l\) is one cluster energy \(\langle \Phi_{n,l}(t_{l}^{e}e^{j}; 2S+1 \Gamma M_s \gamma)|H_{n,l}|\Phi_{n,l}(t_{l}^{e}e^{j}; 2S+1 \Gamma M_s \gamma)\rangle\), \(t_{l,m}\) is inter-cluster interaction energy \(\langle \Phi_{n,l}(t_{l}^{e}e^{j}; 2S+1 \Gamma M_s \gamma)|V_{l,m}|\Phi_{n,m}(t_{m}^{e}e^{j}; 2S+1 \Gamma M_s \gamma)\rangle\), \(t_{l,m}=t_{m,l}\) is trivial as \(V_{l,m}\) is two-body coulomb interaction. Thus, using a proper orthogonal matrix, this matrix can be exactly diagonalized, then eigenvalues and eigenstates of the \(N\)-clusters chain are exactly determined.

Now, let’s apply this general discussion to \(M^{3+/4+}\) mixed-valent system. We set \(E_0 = E_3\) or \(E_4\), where they are energy of a cluster with \(M^{3+}\) or \(M^{4+}\). A number of \(M^{4+}\) clusters is \(M\), and a number of \(M^{3+}\) clusters is \(N - M\). Under this condition, we take into account the nearest neighbor inter-cluster interaction, namely \(t_{l-1,l} \neq 0, t_{l,l+1} \neq 0\), and \(t_{l,m} = 0\) \((m \neq l - 1 \text{ or } l + 1)\). Total energy \(E(d^n)\) of the \(MX_6\) cluster with \(d^n\) is \(E(d^n) = E_0 + nE_0 + \frac{n(n-1)}{2}U\), where \(E_0\) is total energy of \(d^n\) cluster, \(E_0\) is one-electron energy, and \(U\) is average of coulomb and exchange energies in between two electrons. Thus, \(E(d^n) - E(d^{n-1})\) becomes \(E_0 + U(n-1)\). Then, the \(E_3 - E_4\) value can be regarded as Hubbard \(U\). Thus, this approximaion is regarded as Hubbard-like model. Then, the narrow band-like feature with the width of \(W \sim t_{l-1,l}, t_{l,l+1}\) will be formed around \(E_3\) and \(E_4\). Using small inter-cluster interaction, thus, \(U/W \gg 1\) can be realized.

Here, we briefly discuss \(t_{l-1,l}\) and \(t_{l,l+1}\) from microscopic orbital point of view. The values of the hopping integrals in between s, p, and d orbitals for \((l', m', n')\) direction were already calculated as Slater-Koster parameter in Table I of Ref. \([28]\). According to Slater and Koster, the hopping integral in the high-symmetric one-dimensional model \([\text{two centers are connected along the directions of } (1, 0, 0), (0, 1, 0), (0, 0, 1)]\) automatically becomes zero for several orbital cases. Thus, to avoid the zero hopping integral, tilted zigzag chain structure as seen in GdFeO\(_3\)-type structure is effective. Then, all the hopping in between d orbitals become possible, which means that electron can move from one edge to another edge through the crystal with energy, although the value
of the hopping integral depends on the orbital. Then, if one uses a condition of $W \ll k_B T \ll U$ (highly flat-band situation) where $k_B$ and $T$ represent Boltzmann constant and temperature, all the hopping can almost equally occur with use of the help of the thermal energy much larger than the band width. Thus, local degeneracy in the MX$_6$ octahedron can be kept even if such a flat band structure is constructed by the cluster chain. Since the orthorhombic GaFeO$_3$-type perovskite has three inequivalent directions $(a, b, c)$, explicitly speaking, hopping integral along the one axis is slightly different from the ones along the other axes. However, the condition of $W \ll k_B T \ll U$ can make the same local degeneracy along these axes. There are other structures composed of MX$_6$ octahedra. For example, edge-shared MX$_6$ octahedra can make a MX$_2$ layer with triangular lattice. For this case, $t_{2g}^{-1}$ hopping would be preferable compared with $e_g^{-1}g$ hopping. However, if such a material satisfies the condition of $W \ll k_B T \ll U$, we can also use the local degeneracy to apply our theory to such a material.

C. Thermopower of the one-dimensional $N$-clusters chain model

Since the electronic structure of the $N$-clusters chain is exactly determined, now we can define energy flux $(J_q)$ and current flux $(J)$. Then, we can discuss thermopower. The expression of the thermopower is expressed as,

$$S = -\frac{k_B}{e} \left[ \frac{1}{k_B T} \left( \frac{J_q}{J} \right)_{\nabla T=0} - \frac{\mu}{k_B T} \right],$$

where $\mu$ represents chemical potential $[22]$. When a material can be well described as band picture (mean-field approximation), the Boltzmann equation regime works well. Based on the band calculation and the Boltzmann equation, Singh reproduced a large thermopower ($\sim 110 \mu$V/K) of NaCo$_2$O$_4$ at 300 K $[29]$. Even if band picture does not work well (ex. correlated hopping conduction), by carefully taken into account interactions in a Hamiltonian, Kubo-Luttinger formalism $[30, 31]$ works well. Recently, Matsuura et al. explained large thermopower of ($\sim 20$ mV/K) at around 10 K taking into account electron-phonon interaction $[32]$. Thermopower of strongly correlated electron system including 3d transition metal perovskite oxide has been quali-

TABLE I. Number of d electrons ($d_{\text{e}}$), electronic configuration, spin state, ground multiplet term ($^{2S+1}l$), and degeneracy of $^{2S+1}l$ ($\Gamma$). The ground terms were referred from Ref$[22]$. * : these intermediate states are excited states in Tanabe-Sugano diagram.

| $d^m$ | electronic configuration | spin state | ground multiplet term ($^{2S+1}l$) | degeneracy of $^{2S+1}l$ ($\Gamma$) |
|--------|--------------------------|------------|---------------------------------|---------------------------------|
| $d^0$  | ($t_{2g}^{-2}$)($e_g^{-2}$) | -          | 1$^1A_{1g}$                     | 1                               |
| $d^1$  | ($t_{2g}^{-1}$)($e_g^{-2}$) | -          | 2$^2T_{2g}$                     | 6                               |
| $d^2$  | ($t_{2g}^{-2}$)($e_g^{-3}$) | -          | 3$^3T_{1g}$                     | 9                               |
| $d^3$  | ($t_{2g}^{-3}$)($e_g^{-4}$) | -          | 4$^4A_{2g}$                     | 4                               |
| $d^4$  | ($t_{2g}^{-4}$)($e_g^{-5}$) | high spin  | 5$^5E_g$                        | 10                              |
|        | ($t_{2g}^{-5}$)($e_g^{-4}$) | low spin   | 3$^3T_{1g}$                     | 9                               |
| $d^5$  | ($t_{2g}^{-5}$)($e_g^{-6}$) | high spin  | 6$^6A_{1g}$                     | 6                               |
|        | ($t_{2g}^{-6}$)($e_g^{-5}$) | * intermediate spin | $^4T_{2g}$ | 12                              |
| $d^6$  | ($t_{2g}^{-6}$)($e_g^{-7}$) | high spin  | $^5T_{2g}$                       | 15                              |
|        | ($t_{2g}^{-7}$)($e_g^{-6}$) | * intermediate spin | $^3T_{1g}$ | 9                               |
| $d^7$  | ($t_{2g}^{-7}$)($e_g^{-8}$) | high spin  | $^4T_{1g}$                       | 12                              |
|        | ($t_{2g}^{-8}$)($e_g^{-7}$) | low spin   | $^4T_{2g}$                       | 6                               |
| $d^8$  | ($t_{2g}^{-8}$)($e_g^{-9}$) | -          | $^3A_{2g}$                       | 3                               |
| $d^9$  | ($t_{2g}^{-9}$)($e_g^{-10}$) | -          | $^2E_g$                          | 4                               |
| $d^{10}$ | ($t_{2g}^{-10}$)($e_g^{-11}$) | -        | $^1A_{1g}$                       | 1                               |

FIG. 2. (Color online) Schematic figure of periodically aligned one-dimensional N-clusters chain. The broken arrow represents inter-cluster interaction in between $l$-th and $m$-th clusters ($V_{l,m}$).

$$\Delta$$
tatively explained based on single-band Hubbard model \[21\] \[23\]. And introduced degeneracies of spin and orbital plays an important role. To further consider the degrees of freedom, we evaluate the thermopower of the one-dimensional N-clusters chain.

First, we consider the term \( \frac{1}{k_BT} \) \( \left( \frac{\partial}{\partial T} \right) \) \( \frac{W}{k_BT} \) is an averaged energy that a carrier carries. For our model, against an external field \( \text{such as electric field} \ E \) or temperature gradient \( \nabla T \) as perturbation, most of the initial states excites within the band width \( W \). So that we may evaluate \( \frac{1}{k_BT} \) \( \left( \frac{\partial}{\partial T} \right) \) \( \frac{W}{k_BT} \) as \( \sim \frac{W}{k_BT} \). Thus, for \( W \ll k_BT \ll U \), at the limit of \( T \to \infty \),

\[
\lim_{T \to \infty} S = \frac{\mu}{eT} = -\frac{1}{e} \left( \frac{\partial s}{\partial N_e} \right)_{E,V},
\]

where, \( s \), \( N_e \), \( E \), and \( V \) represents entropy, electron number, energy and volume in the N-clusters chain, respectively. We call this high-temperature limit value. According to the Marsh, Parris, and Koshibae \[21–23\], an external field \( \text{such as electric field} \ E \) or temperature gradient \( \nabla T \) as perturbation, most of the initial states excites within the band width \( W \). So that we may evaluate \( \frac{1}{k_BT} \) \( \left( \frac{\partial}{\partial T} \right) \) \( \frac{W}{k_BT} \) as \( \sim \frac{W}{k_BT} \). Thus, for \( W \ll k_BT \ll U \), at the limit of \( T \to \infty \),

\[
\lim_{T \to \infty} S = \frac{\mu}{eT} = -\frac{1}{e} \left( \frac{\partial s}{\partial N_e} \right)_{E,V},
\]

By substituting Eq. 8 to Eq. 9 and using Stirling’s approximation,

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

is obtained as a final formula where \( x \) is defined as \( \frac{W}{k_BT} \).

### D. Comparison with the extended Heikes formula

The extended Heikes formula expresses thermopower in d electron system \[20\] \[23\]. The total number of configurations for \( t \ll k_BT \ll U \) will be written as

\[
g = g_3^{N_A - M} g_4^M \frac{N_A!}{M! (N_A - M)!},
\]

where \( N_A \) is a system size, \( M \) is the number of \( M^4+ \) ions. \( g_3 \) and \( g_4 \) are defined as number of electronic configurations of \( M^3+ \) and \( M^4+ \) ions (spin and orbital degrees of freedom). Substituting Eq. 11 for Eq. 9 then, the thermopower is obtained as

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

where \( x \) is a ratio of \( M^4+ \) ion to the system size \( N_A \) \( (x = \frac{M^4+}{N_A}) \) \[21\] \[23\]. Eqs. 11 and 12 are almost identical to Eqs. 8 and 10.

Now let us compare \( g_i \) with \( \Gamma_i \) \( (i = 3,4) \). According to Marsh, Parris, and Koshibae \textit{et al.}, \[21\] \[23\], a number of \( n \) d-electrons configurations in \( e_g \) and \( t_{2g} \) orbitals with use of spin multiplicity \( (2S + 1) \) and orbital degeneracy is calculated using a number of cases. When \( t_{2g} \) or \( e_g \) orbital is partially occupied, direct product of totally symmetric representation and irreducible representation becomes \( 1 \Gamma_4 \times 2S^+1 \Gamma = 2S^+1 \Gamma \). So that degeneracy of orbital can be dimension of \( \Gamma \) \( (\Gamma = A \lor B \to 1, E \to 2, T \to 3) \). Thus, degeneracy of the ground multiplet term becomes equal to degeneracies of spin and orbital. However, if both \( e_g \) and \( t_{2g} \) orbitals are partially occupied (e.g. excited state such as intermediate spin state of \( \text{Co}^{3+} \)), product of representations becomes \( E_g \times T_{2g} = T_{1g} + T_{2g} \) in \( O_h \) symmetry. Then, the number of the configuration differs from the degeneracies of spin and orbital [e.g. \( t_{2g}^2 e_g^1 \left( S = \frac{3}{2} \right) \rightarrow \) spin multiplicity is 4, orbital degeneracy is 3 for \( t_{2g} \), 2 for \( e_g \), thus degeneracies of spin and orbital becomes 24 \[23\].] because coulomb interaction split 24 states into 12 + 12 states depending on the symmetry of the many electron states. However, if these states are regarded as degenerated due to some ignored interaction in the crystal field approximation \[23\], \( g_i \) becomes identical to \( \Gamma_i \) for \( 0 \leq n \leq 10 \).
Next, we see a difference of the derivations. Marsh and Parris calculated chemical potential with use of “grand canonical ensemble” [21][22]. Koshiba et al., calculated the chemical potential with use of “micro canonical ensemble” [23]. Since different ensembles lead the same expression, the extended Heikes formula is validly constructed based on thermodynamics and quantum statistical mechanics. Our formula is consistent with their results as shown above. We derived our expression of $S$ by considering micro canonical ensemble of exact many electron states at total energy $E$. Since the extended Heikes formula and our formula are almost identical, these formulae are complementary.

Thanks to the comparison shown above, now we recognize an important feature. When thermopower of the metallic perovskite with magnetic interaction is discussed, the Heikes formula has an advantage to guess the degeneracy of the many electron states. Since it is highly difficult to exactly know the eigenstates and the eigenvalues of correlated metallic states ($U \ll k_B T$), our method is not applicable. Thus, thermopower in correlated metallic state even seems to be reproduced by the spin and orbital degeneracies. $S$ at high temperature limit is entropy that a carrier carries. So that the experimental data at high temperatures generally gives an important information about the entangled entropy. The extended Heikes formula is also applicable for even frustrated state with triangular lattice.

III. COMPARISON WITH EXPERIMENTS AND DISCUSSION

As shown in the introduction, a condition, $W \ll k_B T \ll U$ is realizing in 3d-transition-metal perovskite with low $\tau$ (small $W$) [14]. At $V_{ijm} \sim 0$ ($W \ll k_B T$), many of the system exhibit paramagnetic insulating state. Thus, 3d transition metal perovskite with insulating (semiconducting) conductivity due to hopping conduction and para magnetism will exhibit almost saturated thermopower at high temperatures. We investigate $x$ dependence of thermopower at high temperatures from previous works in which the material satisfies this condition. Now, let’s compare experimental data with our expression. (Note that the proper data are not found after $d^7$ in the literature.)

A. $d^0/d^1$ system

$d^0/d^1$ system corresponds to $Ti^{4+}/Ti^{3+}$ system. SrTiO$_3$ is a band insulator, and with La doping (electron doping), $Sr_{1-x}La_xTiO_3$ ($0.0 \leq x \leq 0.1$) exhibits paramagnetic metallic states. Thermopower of the system exhibits negatively large value, which is highly expected as a n-type thermoelectric material [33]. With $La^{3+} \rightarrow Pr^{3+}$, $Pr_{1-x}Sr_xTiO_3$ exhibits insulating state possibly due to narrower $W$ than that of $La_{1-x}Sr_xTiO_3$.

Figure 3 shows $x$ dependence of thermopower in $Pr_{1-x}Sr_xTiO_3$ ($0.7 \leq x \leq 0.98$) at 1200 K [34]. With $\Gamma_3 = 6$ and $\Gamma_4 = 1$, Eq. 11 is drawn as a broken line. The $x$ dependence of the thermopower is referred from the Fig. 5 in Ref. [31]. They still gradually increase even at 1200 K due to rather large $W$ of this system. However, the thermopower data seem to saturate at higher temperatures. So that we plot these data in Fig. 3(a) with the theoretical curve.

B. $d^1/d^2$ system

The filling controlled Mott transition system $La_{1-x}Sr_xVO_3$ [37] is a typical $d^1/d^2$ system ($V^{4+}$/3$^+$ system). According to the schematic metal-insulator diagram in Fig. 65 of Ref. [14], this system has rather large $W$. So that thermopower of this system does not indicate its saturation (they exhibit strong $T$-dependence) even at high temperatures (1250 K). Thus, our expression can not treat this result. Combining the extended Heikes formula and dynamical mean field theory (DMFT) calculation on the single-band Hubbard model, M. Uchida et al., indicate that the thermopower merge a value expected by the Heikes formula for $U \ll k_B T$ limit at high temperatures.

![Graph showing thermopower data and theoretical curves for $Pr_{1-x}Sr_xTiO_3$ and $La_{1-x}Sr_xVO_3$ systems.]

**FIG. 3. (Color online) $x$ dependence of thermopower in (a) $d_0/d_1$-system $Pr_{1-x}Sr_xTiO_3$ at 1200 K [34], (b) $d_3/d_4$-systems $La_{1-x}Sr_xCrO_3$ at 1400 K [35] and $Pr_{1-x}CaCrO_3$ at 300 K [36], (c) $d_4/d_5$-system $La_{1-x}Sr_xFeO_3$ at 1573 K [37], and (d) $d_3/d_0$-system $La_{1-x}Ca_2CO_3O_7$ at 300 K [38]. In each figure of (a)-(d), Eq. 11 is drawn as a broken line. Numbers of $\Gamma_3$ and $\Gamma_4$ are displayed in the each figure.**
C. \(d^2/d^3\) system

La\(\text{1-xSr}_x\text{CrO}_3\) is a typical \(d^2/d^3\) system (Cr\(^{4+}\)/Cr\(^{3+}\) system) which exhibits insulating \(T\) dependence, and its thermopower almost saturates above 1000 K \[33\]. Pr\(_{1-x}\text{Ca}_x\text{CrO}_3\) \[34\] has a narrower \(\Delta\) than that of La\(_{1-x}\text{Sr}_x\text{CrO}_3\). The thermopower of this system almost saturate above 250 K. And paramagnetic insulating state is realized above 250 K. Pal et al., has shown that the \(x\) dependence of the thermopower is qualitatively explained by the extended Heikes formula. Marsh and Parris repro-
dependence of the thermopower is qualitatively explained by the extended Heikes formula. Marsh and Parris repro-
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D. \(d^3/d^4\) system

La\(_{1-x}\text{Sr}_x\text{MnO}_3\) \[22\], and La\(_{1-x}\text{Ca}_x\text{MnO}_3\) \[22\] are the typical model materials of \(d^3/d^4\) system (Mn\(^{3+}\)/Mn\(^{4+}\) system). From extensive research of these systems, a rich phase diagram is obtained. Charge ordering, ferromagnetism due to strong magnetic coupling, Jahn-Teller instability and phase separation cause the rich phases. Marsh and Parris explained the \(x\) dependence of the thermopower of these systems using their theory \[22\]. It seems to us that in particular, \(\Gamma_0 = 1\) (\(\Gamma_0\) : spin degeneracy) due to long-range magnetic coupling and \(\Delta_{JT} \ll k_BT\), \(U \ll k_BT\) cause weak \(x\) dependence of the thermopower below \(x \approx 0.2\). Palstra et al., also reported \(x\) dependence of the thermopower for La\(_{1-x}\text{Ca}_x\text{MnO}_3\), and found almost \(x\) independent values at 475 K \[40\]. Kobayashi et al., reported \(x\) dependence of the thermopower of CaMn\(_{3-x}\)Cu\(_x\)Mn\(_3\)O\(_{12}\) with narrower M-O-M bond angle (= 142\(^\circ\)), and found almost \(x\) independent values at 1373 K \[41\]. They exhibit insulating \(T\) dependence of electrical conductivity possibly due to narrow band width \(W\). However, Jahn-Teller instability and short- and long-range magnetic interaction seems to cause the small almost \(x\) independent thermopower.

E. \(d^4/d^5\) system

La\(_{1-x}\text{Sr}_x\text{FeO}_3\) \[42\] is a typical \(d^4/d^5\) system (Fe\(^{4+}\)/Fe\(^{3+}\) system). La\(_{1-x}\text{Sr}_x\text{FeO}_3\) \((x = 0.1 \text{ and } 0.25)\) exhibit paramagnetic insulating state \[14\]. The thermopower almost saturate for \(x = 0.1\) above 1173 K. We plotted the data at 1573 K with \(\Gamma_3 = 6\) and \(\Gamma_4 = 10\) (for high spin) in Fig. 3(c).

F. \(d^5/d^6\) system

LaCoO\(_3\) is well-known as a spin-state crossover system \[2\]. With Sr doping, the system experiences MIT and shows ferromagnetic metallic state. Co-O-Co bond angle is smaller for A = Ca than that for A = Sr. La\(_{1-x}\text{Sr}_x\text{CoO}_3\) \[43, 44\] is a typical \(d^5/d^6\) system (Co\(^{3+}\)/Co\(^{4+}\) system), and exhibits insulating temperature dependence of resistivity up to \(x = 0.2\) although it’s \(x \approx 0.3\) for La\(_{1-x}\text{Ca}_x\text{CoO}_3\). The thermopower seems to saturate around 300 K. (Note that at higher temperatures this system exhibits temperature induced MIT. Toward the MIT, \(S\) decreases with \(T\).) We replotted the thermopower data at 300 K in La\(_{1-x}\text{Ca}_x\text{CoO}_3\) with \(\Gamma_3 = 9\) and \(\Gamma_4 = 6\) (intermediate state for Co\(^{3+}\), low spin state for Co\(^{4+}\)) in Fig. 3(d).

G. general discussion

As shown above, our formula well reproduces the thermopower of 3d transition metal perovskite oxides with small \(W\) and large \(U\) without both short- and long-range magnetic coupling. Although the extended Heikes formula seems to be applicable even for the correlated metallic state with magnetic interaction at a limit of \(U \ll k_BT\) (for \(V^{4+}/V^{3+}\), and Mn\(^{4+}\)/Mn\(^{3+}\) systems). In general, these conditions give weak \(x\) dependence of the thermopower and rather small \(S\) value due to small spin degree of freedom (~ 1). Thus, entanglement in between other clusters works to decrease the thermopower. Jahn-Teller effect and spin orbit interaction can also be treated within our regime beyond the present evaluation. For example, La\(_{1-x}\text{Ca}_x\text{MnO}_3\) has Jahn-Teller instability. The distortion of the MnO\(_6\) octahedron induces \(5E_g \rightarrow 5A_{1g} + 5B_{1g}\), namely 10-fold degeneracies becomes 5-fold degeneracies with energetically stable state and 5-fold degeneracies with unstable state. This effect is treated as \(\Gamma_3 = 10 \rightarrow 5\) for \(d^4/d^3\) system. As shown here, these effects break the degeneracy of the many electron states at any energy \(E\), which gives smaller \(S\) values than that the present one. Presently, our theory is applied to only the compounds with MX\(_6\) octahedra. However, for example, if one uses local degeneracy of another cluster such as tetrahedron, triangular prism, and so on, one could discuss thermopower of the other structures with those clusters within the condition of \(W \ll k_BT \ll U\), which is beyond the present paper. In addition, we would like to note that our theory can treat \(d^0\) to \(d^{10}\) electrons, which includes other valences of \(M\) ion.

IV. CONCLUSION

In conclusion, we widely investigate thermopower (at high temperatures) of 3d transition metal perovskite oxides comparing the extended Heikes formula. We constructed an expression of the thermopower from many oxides comparing the extended Heikes formula. We con-
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tron states that multiplet term represents at the total energy $E$. Comparison of our expression with the extended Heikes formula, complementarity of these formula be- come clear. Thermopower in correlated metallic state with small $U$ and the magnetic coupling can be treated by the extended Heikes formula. This is highly efficient because without knowing the exact many electron states, we can evaluate thermopower with considering the inner degrees of freedom. Even in transport, we see an importance of crystal symmetry, which regulates a value of thermopower.

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