Study on the origin of large thermopower in hole doped LaRhO$_3$ based on ab-initio downfolding

Hidetomo Usui$^1$, Kazuhiko Kuroki$^1$ and Ryotaro Arita$^2$

$^1$Department of Applied Physics and Chemistry, The University of Electro-Communication, Chofu, Tokyo 182-8585, Japan
$^2$Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8656, Japan
E-mail: h_usui@vivace.e-one.uec.ac.jp

Abstract. We study the origin of the large thermopower and its peculiar hole concentration in the Ni-doped LaRhO$_3$. We calculate the band structure and construct the maximally localized Wannier functions, from which a tightbinding Hamiltonian is obtained. The Seebeck coefficient is calculated within the Boltzmann’s equation approach using this effective Hamiltonian. We find that the Seebeck coefficient remains nearly constant within a large hole concentration range, which is consistent with the experimental observation. The origin of this peculiar doping concentration is discussed.

1. Introduction

The discovery of large thermopower in Na$_x$CoO$_2$[1] and the findings in cobaltates/cobaltites[5, 6, 7, 8, 9] and rhodates[10, 11] that followed have brought up an interesting possibility of finding good thermoelectric materials that have relatively low resistivity. We have recently proposed that the “pudding-mold” type band is the origin for the coexistence of the large thermopower and the low resistivity in this material [2]. Let us first summarize our idea. Using the Boltzmann’s equation, the thermopower 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

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

(2)

Here, $\varepsilon(k)$ is the band dispersion, $v(k) = \nabla_k \varepsilon(k)$ is the group velocity, $\tau(k)$ 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 $\sigma_{xx} = e^2K_0 \equiv \sigma = 1/\rho$. Roughly speaking for a constant $\tau$, $K_0 \sim \Sigma' (v_A^2 + v_B^2)$, $K_1 \sim (k_BT)\Sigma'' (v_B^2 - v_A^2)$ (apart from a constant factor) stand, where $\Sigma'$ is a summation over the states in the range of $|\varepsilon(k) - \mu| < k_BT$, and $v_A$ and $v_B$ are typical velocities for the states above and below $\mu$, respectively. If we consider a band that has a somewhat flat portion at the top (or the bottom), which sharply bends into a highly dispersive portion below...
(above). We will refer to this band structure as the “pudding mold” type. For this type of band with \( \mu \) sitting near the bending point, \( v_A^2 \gg v_B^2 \) holds for high enough temperature, so that the cancellation in \( K_1 \) is less effective, resulting in \( |K_1| \propto (k_B T)^\gamma v_A^2 \) and \( K_2 \propto \Sigma v_A^2 \), and thus large \( |S| \sim O(k_B/|e|) \sim O(100)\mu V/K). Moreover, the large \( v_A \) and the large FS results in a large \( K_0 \propto \sigma \) as well, being able to give a large power factor \( S^2/\rho \), which is important for device applications.

In the present study, we focus on a possibly related rhodate LaRhO\(_3\)[3] with Ni doping, in which large thermopower has been observed. In this material, the Seebeck coefficient at 300K steeply decreases up to the Ni content of \( x = 0.05 \), but then stays around 100\( \mu \)V/K up to about \( x = 0.3 \). On the other hand, the conductivity monotonically grows, resulting in a monotonically increasing power factor (see Figs.2,3).

2. Method

LaRhO\(_3\) has an orthorhombic structure, which is distorted to some extent from the ideal cubic perovskite structure. The experimentally determined lattice constants are \( a = 5.5242(12) \), \( b = 5.7005(12) \), and \( c = 7.8968(17) \)Å, and the internal coordinates are La(0.5140(1), 0.4430(1), 1/4), Rh(1/2,0,0), O(1)(0.4082(11), 0.0204(10), 1/4), O(2)(0.8030(7), 0.2022(7), 0.0475(6)), and spacegroup is Pbnm[12]. For comparison, we also calculate the band structure for the ideal cubic perovskite structure, where the lattice constant is taken as \( a = 3.940 \)Å.[15]

We have obtained the band structure with the Quantum-ESPRESSO package[13]. We then construct the maximally localized Wannier functions (MLWFs)[14] for the energy window \( -1.75eV < \epsilon_k - E_F < -0.64eV \) for the ideal structure of LaRhO\(_3\), \( -1.8eV < \epsilon_k - E_F < -0.5eV \) for the distorted structure of LaRhO\(_3\), where \( \epsilon_k \) is the eigenenergy of the Bloch states and \( E_F \) the Fermi energy. These MLWFs, centered at Rh 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).

3. Results and Discussion

The calculated band structure for the distorted structure is shown in Fig.1 along with that for the ideal structure. The tightbinding model Hamiltonian for the distorted structure consists of 12 bands (4 Rh per unit cell), while the model for the ideal structure contains three \( t_{2g} \) bands. The calculated Seebeck coefficient at 300K is shown in Fig.2 as a function of hole concentration together with the experimental result.[3] Here we assume that the hole concentration \( n_h \) is equal to the Ni content. It can be seen that the Seebeck coefficient steeply decreases with doping with \( n_h < 0.05 \), but stays nearly constant for \( n_h > 0.1 \) for the distorted structure in particular. As a result the (normalized) power factor monotonically grows with doping, which is at least in qualitative agreement with the experimental observation.

Now, in order to understand this peculiar hole concentration dependence of the Seebeck coefficient, we now turn to the density of states (DOS). The comparison of the DOS between the two structures is shown in Fig.3. The DOS at the band top is larger for the ideal case since the three bands are degenerate. Thus, for low doping, \( E_F \) stays closer to the band top for the ideal structure, resulting in a larger Seebeck coefficient. This is a typical example where the multiplicity of the bands lead to an enhanced thermopower, i.e., the larger the number of bands, the closer the \( E_F \) to the band top. In the case of the distorted structure, as the hole concentration increases, \( E_F \) lowers and hits the portion of the band with a large DOS (Fig.3left). Therefore, \( E_F \) hardly moves with doping, resulting in a slow decrease of the Seebeck coefficient. A large DOS region lies in a lower energy regime in the ideal structure, and therefore the Seebeck coefficient continues to decrease with doping (up to a larger doping concentration). The large Seebeck coefficient of about 80\( \mu \)V/K in the distorted structure can be considered as due to the flatness of the top of the bands (around the \( \Gamma \) point), i.e., the pudding mold type band.
4. Conclusion
To conclude, we have calculated the band structure of LaRhO$_3$ for the distorted perovskite structure as well as for the ideal cubic perovskite structure. A tightbinding model is obtained via maximally localized Wannier orbitals, and the Seebeck coefficient is calculated using the model. The Seebeck coefficient barely decreases for the hole concentration of $n_h > 0.1$ in agreement with the experiment, which we attribute to the peculiar uprise of the DOS near the band top. The large value of the Seebeck coefficient of about 80 $\mu$V/K can be considered as due to the flatness of the top of the bands i.e., the pudding mold type band.

We acknowledge I. Terasaki and S. Shibasaki for valuable discussions. This work is in part supported from the Grants-in-Aid, MEXT, Japan.

![Figure 1.](image)

**Figure 1.** The band structure of the distorted (a) and the ideal (b) structure the tightbinding mode (solid lines) together with the LDA band calculation results (dotted) are shown.

References
[1] I. Terasaki *et al.*, Phys. Rev. B 56, R12686 (1997)
[2] K. Kuroki and R. Arita, J.Phys.Soc.Jpn. 76, 083707 (2007)
[3] S. Shibasaki *et al.*, cond-mat/07121626.
[4] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997)
[5] S. Li *et al.*, J. Mater. Chem. 9 (1999) 1659
[6] K. Fujita *et al.*, Jpn. J. Appl. Phys. 40 (2001) 4644
[7] S. Hébert *et al.*, Phys. Rev. B 64 (2001) 172101
[8] Y. Miyazaki *et al.*, J. Phys. Soc. Jpn. 71 (2002) 491
[9] M. Lee *et al.*, Nat. Mater. 5 (2006) 537
[10] S. Okada and I. Terasaki, Jpn. J. Appl. Phys. 44 (2005) 1834
[11] Y. Okamoto *et al.*, J. Phys. Soc. Jpn. 75 (2006) 023704
[12] Réne B. Macquart *et al.*, Crystal Growth and Design 6(6) (2006) 1361-1365
[13] S. Baroni *et al.*, http://www.pwscf.org/.
[14] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997); I. Souza *et al.*, Phys. Rev. B 65, 035109 (2002). The Wannier functions are generated by the code developed by A. A. Mostofi *et al.* (http://www.wannier.org/)
[15] F. S. Galasso, Structure and Properties of Inorganic Solids (Pergamon, New York, 1970)
Figure 2. (a) Seebeck coefficient for the distorted (green) and the ideal (blue) structure. The red line is the experimental result. [3] (b) Power factor of the distorted structure normalized at $n_h = 0$. The red line is the experiment.

Figure 3. DOS of distorted (green) and ideal (blue) structures. The right panel is a blow up of the left.