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First-principles study on the origin of large thermopower in hole-doped LaRhO₃ and CuRhO₂

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Abstract

Based on first-principles calculations, we study the origin of the large thermopower in Ni-doped LaRhO₃ and Mg-doped CuRhO₂. We calculate the band structure and construct the maximally localized Wannier functions from which a tight binding Hamiltonian is obtained. The Seebeck coefficient is calculated within the Boltzmann's equation approach using this effective Hamiltonian. For LaRhO₃, we find that the Seebeck coefficient remains nearly constant within a large hole concentration range, which is consistent with the experimental observation. For CuRhO₂, the overall temperature dependence of the calculated Seebeck coefficient is in excellent agreement with the experiment. The origin of the large thermopower is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of large thermopower in Na_xCoO₂ [1] and the findings in cobaltates/cobaltites [4–8] and rhodates [9, 10] 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 low resistivity in this material [2]. Let us first summarize our idea. Using Boltzmann's equation, the thermopower is given as

$$\mathbf{S} = \frac{1}{eT} \mathbf{K}_0^{-1} \mathbf{K}_1 \quad (1)$$

where e (<0) is the electron charge, T is the temperature, and tensors \mathbf{K}_0 and \mathbf{K}_1 are given by

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

Here, $\varepsilon(\mathbf{k})$ is the band dispersion, $v(\mathbf{k}) = \nabla_{\mathbf{k}} \varepsilon(\mathbf{k})$ is the group velocity, $\tau(\mathbf{k})$ is the quasiparticle lifetime, $f(\varepsilon)$ is the Fermi distribution function and μ is the chemical potential. Hereafter, we simply refer to $(\mathbf{K}_n)_{xx}$ as K_n , and $S_{xx} = (1/eT)(K_1/K_0)$ (for diagonal \mathbf{K}_0) as S . Using K_0 , conductivity can be given

as $\sigma_{xx} = e^2 K_0 \equiv \sigma = 1/\rho$. Roughly speaking for a constant τ , $K_0 \sim \Sigma'(v_A^2 + v_B^2)$, $K_1 \sim (k_B T) \Sigma'(v_B^2 - v_A^2)$ (apart from a constant factor) stand, where Σ' is a summation over the states in the range of $|\varepsilon(\mathbf{k}) - \mu| < \sim k_B T$, and v_A and v_B are typical velocities for the states above and below μ , respectively. 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 μ 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 $|K_1| \sim (k_B T) \Sigma' v_A^2$ and $K_0 \sim \Sigma' v_A^2$, and thus large $|S| \sim O(k_B/|e|) \sim O(100) \mu\text{V K}^{-1}$. Moreover, the large v_A and the large FS result in a large $K_0 \propto \sigma$ as well, being able to give a large power factor S^2/ρ , which is important for device applications.

In the present study, we focus on a possibly related rhodate LaRhO₃ [3] with Ni doping and CuRhO₂ [15, 16] with Mg doping, in which large thermopower has been observed. In Ni-doped LaRhO₃, the Seebeck coefficient at 300 K steeply decreases up to the Ni content of $x = 0.05$, but then stays around $100 \mu\text{V K}^{-1}$ up to about $x = 0.3$. On the other hand, the conductivity monotonically grows, resulting in a monotonically increasing power factor (see figure 2). For CuRhO₂, the two existing experiments give different

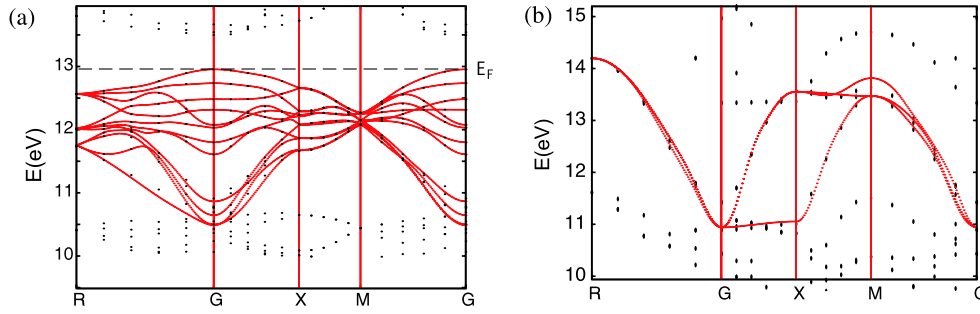


Figure 1. The band structure of the distorted (a) and the ideal (b) structure. The tight binding mode (solid lines) together with the LDA band calculation results (dotted) are shown.

results. In [16], the Seebeck coefficient is found to be nearly independent of doping, while it decreases with doping in [15].

2. Method

LaRhO₃ 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 [11]. 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 [14]. CuRhO₂ has an delafossite structure whose experimental lattice constants are $a = 5.810910$ and $c = 32.437162$ Å. We have obtained the band structure of these materials with the Quantum-ESPRESSO package [12]. We then construct the maximally localized Wannier functions (MLWFs) [13] for the energy window $-1.75 \text{ eV} < \epsilon_k - E_F < -0.64 \text{ eV}$ for the ideal structure of LaRhO₃, $-1.8 \text{ eV} < \epsilon_k - E_F < 0.5 \text{ eV}$ for the distorted structure of LaRhO₃ and $-10 \text{ eV} < \epsilon_k - E_F < 4 \text{ eV}$ for CuRhO₂, where ϵ_k is the eigenenergy of the Bloch states and E_F is the Fermi energy. With these effective hoppings and on-site energies, the tight binding Hamiltonian is obtained, and finally the Seebeck coefficient is calculated using equation (1). The doping concentration x is assumed to be equal to the hole concentration, and a rigid band is assumed.

3. Results and discussions

We first present results for LaRhO₃. The calculated band structure for the distorted structure of LaRhO₃ is shown in figure 1 along with that for the ideal structure. The tight binding 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 300 K is shown in figure 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.

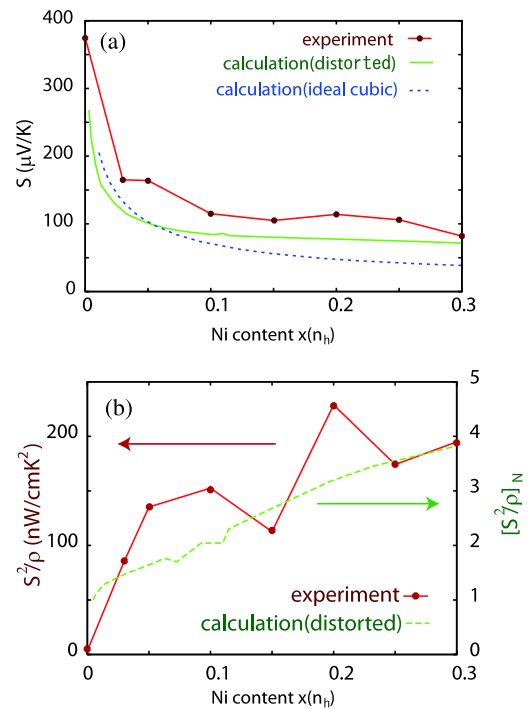


Figure 2. (a) Seebeck coefficient for the distorted (green solid) and the ideal (blue dashed) structure. The red line is the experimental result [3]. (b) Power factor of the distorted structure normalized at $n_h = 0$. The red line is the experimental data [3].

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 figure 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 leads 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 (figure 3 left). 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

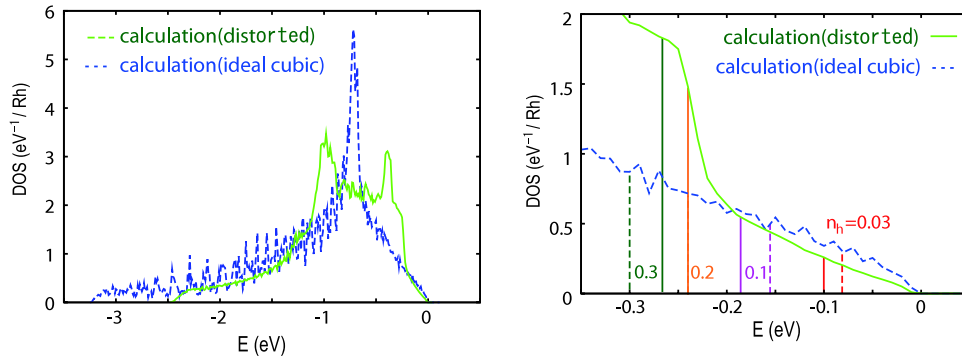


Figure 3. DOS of distorted (green) and ideal (blue) structures. The right panel is a blow-up of the left.

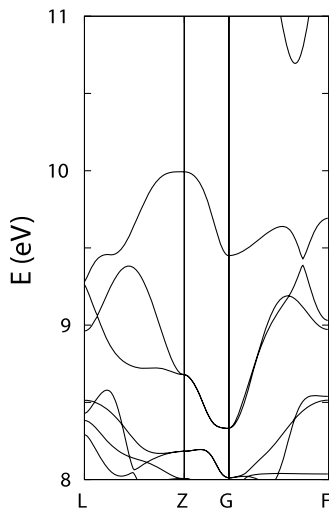


Figure 4. Tight binding band obtained via maximally localized Wannier orbitals.

(up to a larger doping concentration). The large Seebeck coefficient of about $80 \mu\text{V K}^{-1}$ in the distorted structure can be considered as due to the flatness of the top of the bands (around the Γ point), i.e. the pudding mold type band.

We now move on to CuRhO_2 . The calculated band structure is shown in figure 4. Around the Γ point, there is again a pudding mold type band, whose top is very flat. The calculation result of the Seebeck coefficient as a function of temperature is shown in figure 5. We find excellent agreement with the experiment in [15] in a wide temperature range and for the Mg content $x = 0.05$ and 0.1. On the other hand, in [16], the Seebeck coefficient is nearly independent of x . The origin of the discrepancy between this experiment and the present calculation remains as a problem for the future.

4. Conclusion

To conclude, we have studied the origin of the large thermopower in LaRhO_3 and CuRhO_2 . 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 both materials, the large value of the Seebeck coefficient can be considered as due to the flatness of the top of the bands, i.e.

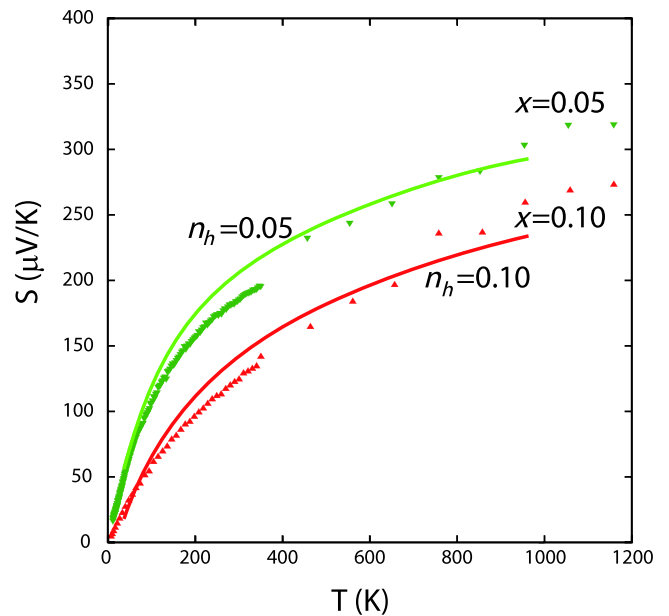


Figure 5. Calculation result of the Seebeck coefficient for CuRhO_2 with the hole concentration of $n_h = 0.05$ and 0.1. The experimental data are from [15].

the pudding mold type band. For LaRhO_3 in particular, 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 increase of T of the DOS near the band top.

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