Ab-initio calculation of conductivity and thermopower in Nd$_x$Co$_4$Sb$_{12}$ compounds

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Abstract

In this article we present a calculation of the conductivity and thermopower for Nd$_x$Co$_4$Sb$_{12}$ compounds. The velocities are calculated using a spectral collocation method. The kinetic coefficients are obtained according to Boltzmann transport theory in the constant relaxation time approximation.

Introduction

Cobalt Antimony skutteridtes are currently investigated as potential materials for thermoelectric applications. However their thermal conductivity is too high to achieve a high figure of merit. Insertion of rattling atoms inside the large voids characteristic of the skutterudite structure can reduce the thermal conductivity without to much perturbation of the electronic structure to preserve the good power factor. Rare earth elements are naturally good candidate for doping due to their small effective radii. In the following we will consider Nd doped skutterudite and we calculate their conductivity and thermopower according to Boltzmann transport theory. In the first part we describe the method we use to calculate the thermopower and the conductivity. In part II we present the results.

I-Theory

When electric field and temperature gradient are applied on a sample, electric and heat current density, j and j_Q, are created. Then if we make a linear response approximation they can be related by the kinetic coefficient L_{ij}.

$$j = L_{11}\vec{E} + L_{12}\left(-\frac{\nabla T}{T}\right)$$
$$j_Q = L_{21}\vec{E} + L_{22}\left(-\frac{\nabla T}{T}\right)$$

To calculate these coefficients from the band structure, we must define a microscopic model for the system response to the applied field. In this paper the model we choose is the one of Boltzman transport theory. This means that we consider the Boltzmann equation:

$$\frac{\partial f}{\partial t} + v\cdot\nabla_r f + F\cdot\nabla_p f = -\sum_i C[f]$$

Once we make a constant relaxation time approximation,

$$C_i = \frac{f - f_0}{\tau_i}$$

this equation is easily solved and we find the well known expression for the kinetic coefficients:

$$L_{11}^{\alpha\beta} = \frac{e^2}{8\pi^3}\int Dk\left\{\tau\frac{\partial f_0}{\partial\mu}v_\alpha v_\beta\right\}$$

$$L_{12}^{\alpha\beta} = -\frac{e}{8\pi^3}\int Dk\left\{\tau\frac{\partial f_0}{\partial\mu}v_\alpha v_\beta(E_k-\mu)\right\}$$

$$L_{22}^{\alpha\beta} = \frac{1}{8\pi^3}\int Dk\left\{\tau\frac{\partial f_0}{\partial\mu}v_\alpha v_\beta(E_k-\mu)^2\right\}$$

Now, following Mahan [4], these coefficients can be rearranged and express as functional of the transport function $\sigma(E)$.

$$\sigma_{\alpha\beta}(E) = \frac{e^2\tau}{(2\pi)^3}\int_{E_k=E}\frac{dS}{|\nabla E_k|}v_\alpha v_\beta$$

$$L_{11} = \int dE\left\{\frac{\partial f_0}{\partial\mu}\sigma(E)\right\} \tag{1}$$

$$L_{12} = L_{21} = -\frac{1}{e}\int dE\left\{\frac{\partial f_0}{\partial\mu}(E-\mu)\sigma(E)\right\} \tag{2}$$

$$L_{22} = \frac{1}{e^2}\int dE\left\{\frac{\partial f_0}{\partial\mu}(E-\mu)^2\sigma(E)\right\} \tag{3}$$
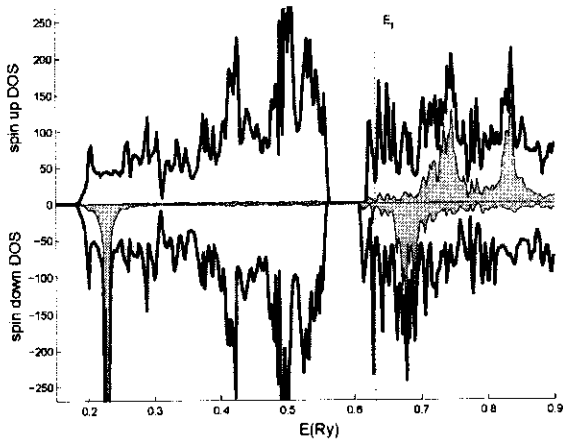
We should therefore calculate the transport function. It depends on squared velocities, which are then integrated over surface of constant energy. These integrations are performed using the tetrahedron method. This is the standard method used for integration over the Brillouin zone. It is fast and

accurate since it reduces the noise encountered in simple summation over sampling points in the Brillouin zone.

The velocities are calculated using a spectral collocation method. Since the method is less common, although well known in applied mathematics, we shall briefly outline the main ideas. The velocities are the derivatives of the energies bands,

$$v_k^n = \frac{1}{\hbar} grad \, E_n(k)$$

To performed such a differentiation numerically, we can define an interpolating function of the energies bands $E_n(k)$ since they are only known on a discreet set of points in the Brillouin zone (we call $e_n(k)$ the discreet function). Then, we calculate the velocities as the derivatives of the interpolative function. In the case of spectral collocation we choose the interpolating function to be the Inverse Discreet Fourier Transform (IDFT), evaluated at a general position k, of the function $ê_n(k)$ (where ^ denote the discret Fourier Transform). It is well known that the DFT of the function $e_n(k)$ is related to the Fourier transform of the function $E_n(k)$ by the Poisson summation formula which simply express that both are close (on a bounded interval defined by the discretization length) when the transform for $E_n(k)$ is rapidly decaying. Now we can take advantage of this properties since the energies band are regular functions (they are analytic except at degeneracy points). Their Fourier transforms are therefore rapidly decaying and then close to the DFT of $e_n(k)$. Now since Fourier transformations are isometric this is also true for the inverse transforms which are nothing but $E_n(k)$ itself and the interpolating function if k is extended to the whole Brillouin zone.
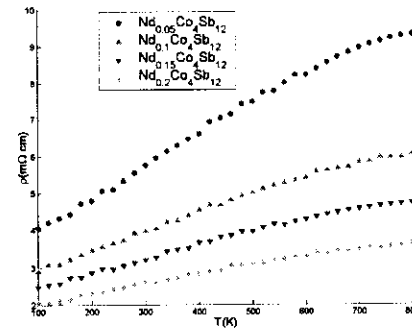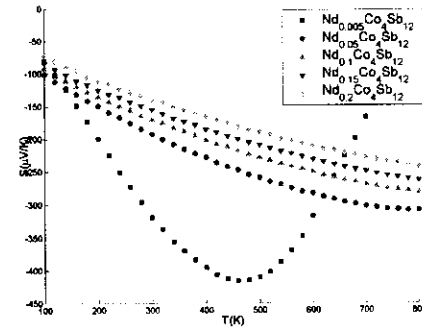
and the Hall coefficient. The details of this implementation will be reported in a subsequent paper [1]. In the next section we will present the result for Nd doped Cobalt Antimony skutterudites.

II-Results

When Cobalt Antimony skutterudites are doped with Nd atoms, these atoms occupy the voids at positions (2a) and then partly fill the host lattice. Nd is a rare earth element and therefore its valence electron are localized and do not hybridize strongly with the host material. We performed an LDA+U calculation on the filled skutterudite $NdCo_4Sb_{12}$ to make these considerations more precise (Fig .1). We see that Nd is in a 3+ state and the 4f states form very narrow bands that are located around 0.4 Ry below the conduction band for the spin down states. Empty f states are more than 0.1 Ry above the gap.

Figure 2 Calculated conductivity and Seebeck coefficient.

Figure 1 Spin up and spin down density of state obtained from an LDA+U calculation (U=0.4 Ry and J=0.07 Ry). The blue line shows the total density of states and the green aera shows the 4f contribution

This method has been implemented in the general non-orthogonal case, with the WIEN2k program as a starting point [2], and is used to calculate the thermopower, the conductivity

From these calculation it is clear that the 4f states are far apart the Fermi level . Then for partly filled skutterudites $Nd_xCo_4Sb_{12}$ the electronic structure around the Fermi level

does not change much with doping. Now since the transport properties involves only states around the Fermi level they can be calculated using the electronic structure for undoped skutterudites. In other words we make a rigid band approximation: the chemical potential is shifted inside the conduction (or valence) band to take into account the right number of electron but the changes in the distribution of energies levels is neglected.
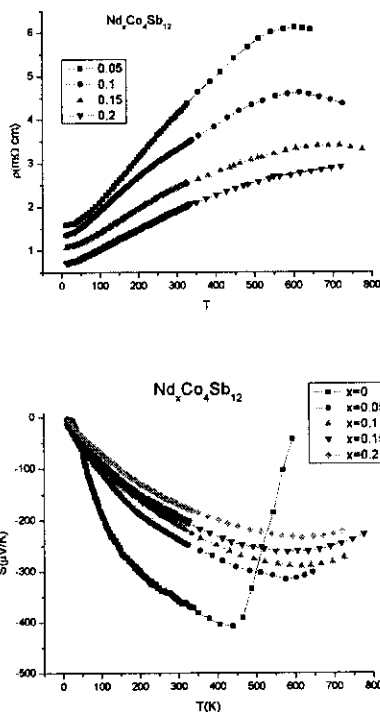
Figure 3   Experimental conductivity and Seebeck coefficient, from ref [3]

So, to calculate the conductivity and thermopower we proceed as follow. First the the electronic structure for CoSb₃ compounds is calculated in a generalized gradient approximation using the WIEN2k program [2]. Next the transport function is calculated using spectral collocation and tetrahedron methods. Finally the kinetic coefficients are calculated according to equations (1-3). Conductivity and thermopower are then easily obtained as $\sigma=L_{11}$ and $S=L_{12}/T\ L_{11}$. The results are shown in Fig. 2. For the electrical conductivity we used $\tau=1.2\ 10^{-14}$ s. For the thermopower τ does not appear, due to compensation between numerator and denominator. Moreover the experimental curves obtained by Kuznetsov et al. are shown in Fig. 3 for comparison. Clearly experimental and theoretical curves are in good agreement in shape and value. For the resistivity this is so as long as the scattering is dominated by impurities. This is of course

consistent with our calculation since we have used a constant relaxation time. In the case of the thermopower theoretical and experimental curves are still in good agreement at low doping concentration. This means the thermopower is less sensible to the detail of the scattering mechanism. Also we should mention that CoSb₃ skutterudites reported as pure sample seems correspond to weakly n-doped compounds, probably because of Ni impurities.

We have not yet discuss the way we choose the concentration of valence electrons. It is neither the theoretical value (3 electron per Nd atom) since in any sample a non negligible amount of secondary phase is present, nor the experimental value directly obtained from Hall measurements using the free electron formula. This amounts to the neglect of the band structure which is far from negligible in skutterudites. Details of the calculation with the effect of the band structure include will be reported in a subsequent paper [1]. For now we only indicate that it leads to consider around 1 valence electron per Nd atom and this value has been used in the calculation of σ and S. The scheme of the calculation is summarized in Fig 4.
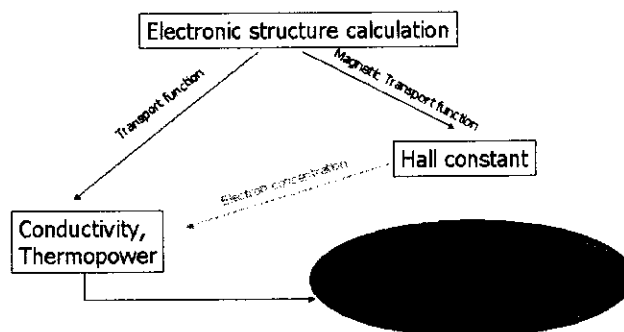
Figure 4   Calculating scheme for the conductivity and the thermopower

Conclusions

We have presented a calculation for the thermopower and the conductivity of Nd$_x$Co₄Sb₁₂ compounds and shown that the electronic structure of undoped Cobalt Antimony skuterudites can be used to calculate the transport function.

References

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