Transactions of the Materials Research Society of Japan 29[6] 2763-2766 (2004)

Theory of The Nonparabolic Effects of The Thermoelectric Properties

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Theoretical treatment of the thermoelectricity, based on the Kane's nonparabolic bands model, is developed; Seebeck coefficient, electric conductivity, electronic thermal conductivity are calculated by choosing the skutterudite $CoSb_3$ as an example. The energy dependent relaxation time due to the electron-acoustic phonon interaction is taken into account. It is shown that simple one accepter model yields the reasonable results for the Seebeck coefficient but is insufficient to explain electric conductivity.

Key words: thermoelectric properties, Seebeck coefficient, nonparabolic band, skutterudite

1. INTRODUCTION

Recently, the thermoelectric conversion system is paid much attention as an effective method for recovering the waste heat. The system uses the Seebeck effect in semiconductors as an electric generator [1]. Theoretical work on thermoelectricity has been developed mostly on the basis of the parabolic band model. However, recent many new thermoelectric materials have many atoms in the unit cell and then have the complex electronic structure, which mostly has the nonparabolic nature. $CoSb_3$ type skutterdite material is one of them [2-5].

In a recent work we have discussed the thermoelectric property, assuming the constant (energy-independent) relaxation time and the finite hole concentration in the valance band. It has been shown that at higher temperature both valence band and conduction band contributions to the Seebeck coefficient are important, though the Kane's nonparabolic valance band model describes well the Seebeck coefficient at low temperature [3-5].

It has been also pointed out that Seebeck coefficient is just one of the transport properties; other related properties need to be discussed from the same standing point [5]. However it has been done little so far.

Here in the present work, by using the Kane's nonparabolic band model and taking $CoSb_3$ as an example we will discuss some thermoelectric-related quantities, i.e., Seebeck coefficient, electric conductivity and electronic thermal conductivity in the same point of view.

2. THERMOELECTRIC PROPERTIES IN NONPARABOLIC BANDS

2.1 Nonoparabolic band model

In the Kane's nonparabolic band model the electronic energy E_k with the wave vector k is given by

$$E_k\left(\frac{E_k}{\Delta}-1\right)=\frac{\eta^2k^2}{2m_v}, \tag{1}$$

which, for small k, behaves as a parabolic band

$$E_k=\Delta+\frac{\eta^2k^2}{2m_v} \quad or \quad -\frac{\eta^2k^2}{2m_v}, \tag{2}$$

and, for large k, behaves as a linear band,

$$E_k=\frac{\Delta}{2}\pm\left(\frac{\Delta\eta^2k^2}{m_v}\right)^{1/2}k. \tag{3}$$

Then, density of states is given by

$$N(E_k)=\frac{(2m_v)^{2/3}}{2\pi^2\eta^3}\left|\frac{2E_k}{\Delta}-1\right|\left[E_k\left(\frac{E_k}{\Delta}-1\right)\right]^{1/2}. \tag{4}$$

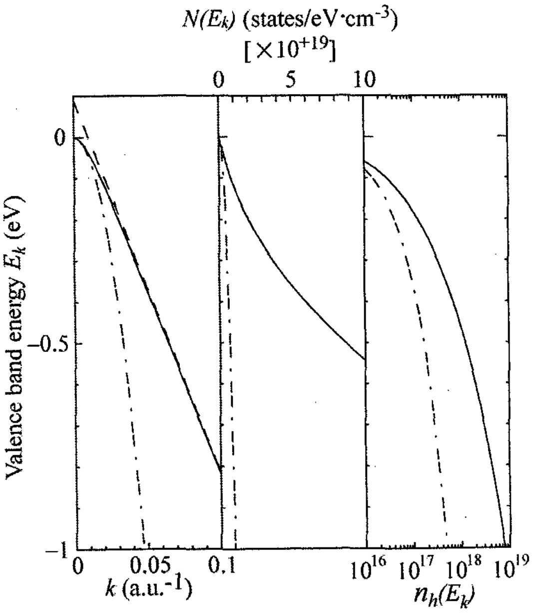

Fig.1 Valence band edge energy dispersion E_k, density of states $N(E_k)$ and hole concentration $n_h(E_k)$, occupying the states between the energies 0 and E_k. Solid, solid with dot and dotted lines show the results for the Kane's nonparabolic band (Eq. (1)), parabolic band (Eq. (2)), and k-linear band (Eq. (3)), respectively. Band parameters m_v=0.03m and Δ=180 meV are chosen.

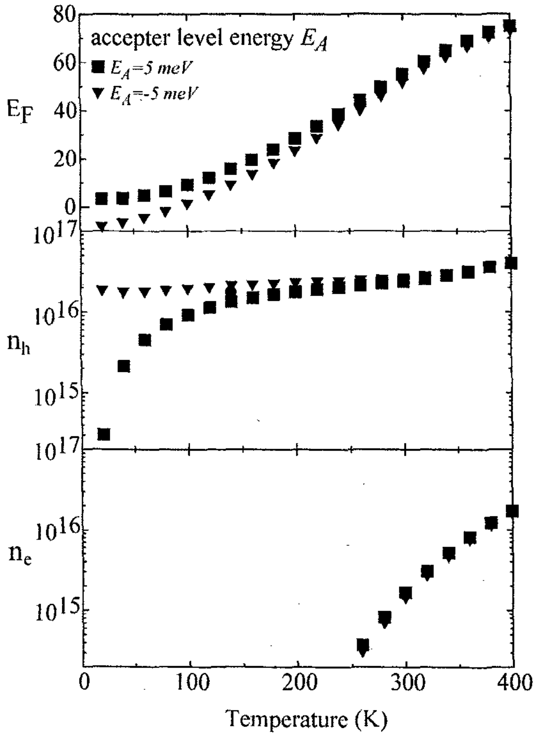

Fig.2 Typical temperature dependent behavior of the Fermi energy E_F, the electron concentration n_e and the hole concentration n_h in $CoSb_3$ cases for two different accepter levels E_A. Band parameters $m_v = 0.03m$, $\Delta = 180$ meV and accepter concentration $N_A=3\times10^{16}$ cm^{-3} are chosen.

Fig.1 shows the valence band energy dispersion E_k and the density of states $N(E_k)$ for the Kane's nonparabolic band. We have also shown the hole concentration $n_h(E_k) = \int_E^0 N(E_k)dE_k$ in Fig.1. We chose the band parameters $m_v = 0.03m$ and $\Delta = 180$ meV in $CoSb_3$, where Kane's model describes the band edge states very well [4-5]. It is seen in Fig.1 that, for small k, the energy and the density of states behaves as those in the parabolic band. However, for large k, energy E_k has a linear dispersion and this yields the E_k^2 behavior for the density of states, compared to the $E_k^{1/2}$ behavior in the parabolic case. This large density of states may yield larger Seebeck coefficient for the nonparabolic band.

2.2 Thermostatistical consideration

Thermoelectric properties depend on the population of electrons and holes in the conduction and valence bands, which is governed by the thermostatistics. Let us assume the existence of accepter whose energy and concentration are denoted by E_A and N_A, respectively. Then the Fermi energy E_F at the temperature T is determined by the equation,

$$n_e + N_A^- = n_h. \tag{5}$$

Here $N_A^- = N_A[1 + 2\exp\{(E_A - E_F)/k_BT\}]^{-1}$ is the number of the ionized accepter. n_e and n_h are electron and hole densities, respectively

In Fig.2, we show the typical temperature dependent behavior of the Fermi energy E_F, the electron concentration n_e and the hole concentration n_h in the $CoSb_3$ case. In lower temperature, $n_h \gg n_e$ is held and then the one band (hole) contribution to carriers is dominant. However, in higher temperature such as T=350~400K, we have the relation $n_h \approx n_e$ and then the mixed (electron and hole) carrier effects become important.

2.3 Thermoelectric-related properties

Figure of merit of the thermoelectricity Z is given by

$$Z = S^2\sigma/(\kappa_l + \kappa_e), \tag{6}$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ_l and κ_e are lattice and electronic thermal conductivities, respectively.

Quantities S, σ and κ_e are electronic transport quantities and should be treated by the same standing point. Using the distribution function under the electric field and the temperature gradient, expressions for these quantities can be derived; for the two bands model the following expressions are obtained [6, 7]

$$\sigma = \sigma_e + \sigma_h, \tag{7}$$

$$S = (\sigma_e S_e + \sigma_h S_h)/\sigma, \tag{8}$$

and

$$\kappa_e = \kappa_{ee} + \kappa_{eh} + \sigma_e\sigma_h(S_e - S_h)T/\sigma. \tag{9}$$

Here σ_i, S_i and κ_{ei} are written as

$$\sigma_i = \frac{e^2}{3}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2\tau_i(\varepsilon), \tag{10}$$

$$S_i = \frac{e}{3T\sigma_i}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2(\varepsilon-\mu)\tau_i(\varepsilon), \tag{11}$$

and

$$\kappa_{e_i} = \frac{1}{3T}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2(\varepsilon-\mu)^2\tau_i(\varepsilon). \tag{12}$$

Here $f(\varepsilon)$ is the Fermi distribution function, $\rho_i(\varepsilon)$ is the density of states, $v_i(\varepsilon) = -\frac{1}{\hbar}\nabla_k\varepsilon$ is the electron velocity, μ denotes the chemical potential, (i.e. the Fermi energy E_F) and $\tau_i(\varepsilon)$ is the relaxation time for an electron $(i=e)$ and a hole $(i=h)$. T is the absolute temperature.

For the relaxation time $\tau_i(\varepsilon)$, we use the energy dependent $\tau_i(\varepsilon)$ with the electron-acoustic phonon interaction, which is given by

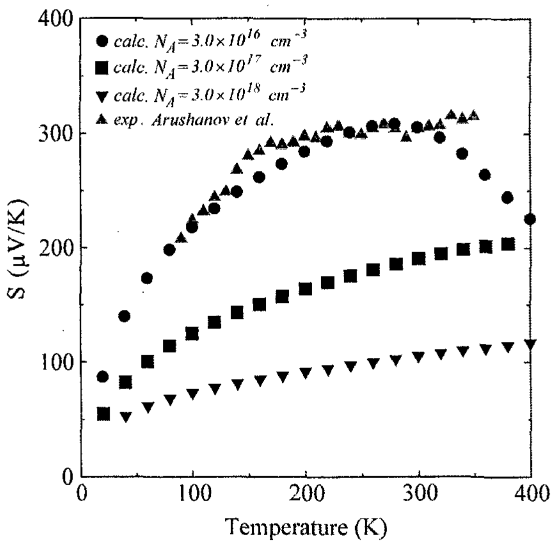

Fig.3 The calculated temperature dependence of the Seebeck coefficient for the various accepter concentrations N_A. Accepter energy E_A = -5meV is chosen.

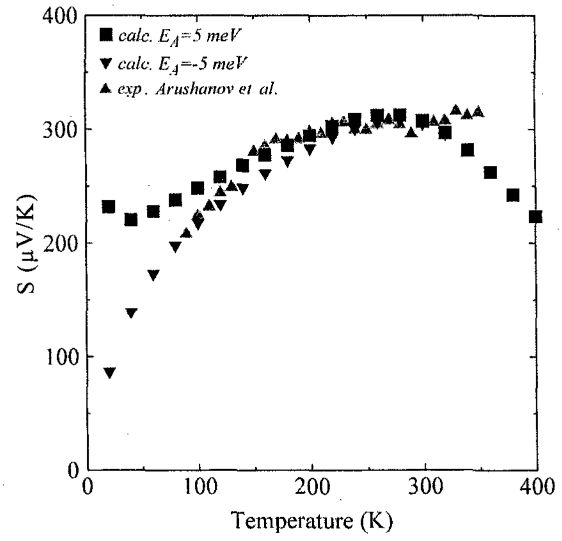

Fig.4 The temperature dependence of the Seebeck coefficient for the various two accepter energies E_A. Accepter concentration $N_A = 3\times10^{16}$ cm^{-3} is chosen.

$$\tau_i(\varepsilon)^{-1} = C E_d^2 N_i(\varepsilon) \left[(\varepsilon/\Delta)^2 + \frac{1}{3}(\varepsilon/\Delta - 1)^2\right] \Big/ [2\varepsilon/\Delta - 1]^2, \qquad (13)$$

for the nonparabolic band case [8]. Here E_d is the deformation potential and C is the constant, being related with the quantities of the elastic wave.

As an example, we choose Skutterdite CoSb$_3$, whose energy dispersion shows the predominant nonparabolic behavior, described well by the Kane's model [3-5]. Thermoelectric properties can be discussed semi-quantitatively by changing the various physical parameters such as the gap parameter $\Delta = E_g$, the accepter energy level E_A and its concentration N_A with the fixed mass value m_v =0.03m. As the origin of the energy we take the top of the valence band to be zero, according to the Kane's band expression of Eq. (1). For the experiment we refer mainly to the work of Arushanov *et al.*, which obtained large mobility value [9].

Firstly we consider the temperature dependence of the Seebeck coefficient by changing the gap parameters $\Delta = E_g$. If we take a larger gap parameter such as Δ = 500 meV, one band behavior of the monotonic increase of the Seebeck coefficient S for higher temperature appears. More reasonable smaller band gap such as Δ = 50 ~ 220 meV yields the decrease in the higher temperature region, reflecting the thermal excitation of a carrier from the valence band to the conduction band. It is noted that the value of band gap in CoSb$_3$ has not been established well, though values of 50 ~ 220 meV have been reported [3-5]. Hereafter we just fix Δ = 180 meV in the present semi-quantitative calculation.

Secondly we change the value of the accepter concentration N_A. Calculated results for the Seebeck coefficients S together with the experimental result are shown in Fig 3. For smaller concentration such as 10^{16} cm^{-3} the Seebeck coefficient has a peak structure, which yields larger values for S. For larger concentration, Seebeck coefficients become smaller in the temperature range below 400 K.

Thirdly let us see the effects of the accepter energy level E_A. Fig.4 shows the results. We notice the clear change in the Seebeck coefficients in the very low temperature region. The monotonic increase of the Seebeck coefficient for the increase of the temperature T as in the experiment [9] can be described well by the negative accepter level energy $E_A < 0$, i.e. the accepter level within the valence band (or, E_A~0, i.e., accepter level, being very chose to the valence band edge). On the other hand, for the positive accepter level energy $E_A > 0$, i.e. the accepter level inside the band gap, the Seebeck coefficient firstly decreases, takes a minimum value and then increases for the temperature increase. Actually, this behavior was realized in the experiment by Morelli *et al.* [10]. The first decrease of the Seebeck coefficient S in the very low temperature is considered to arise from the rapid increase of the hole.

Here, in oreder to see the significance of the nonparabolic effect on the Seebeck coefficient S, we have performed the calculation based on the simple two parabolic model, where the expression in Eq. (2) with m_v=0.03m is used. It is found that, in the low temperature region of $T \leq$ 300 K, the parabolic model yields almost the same

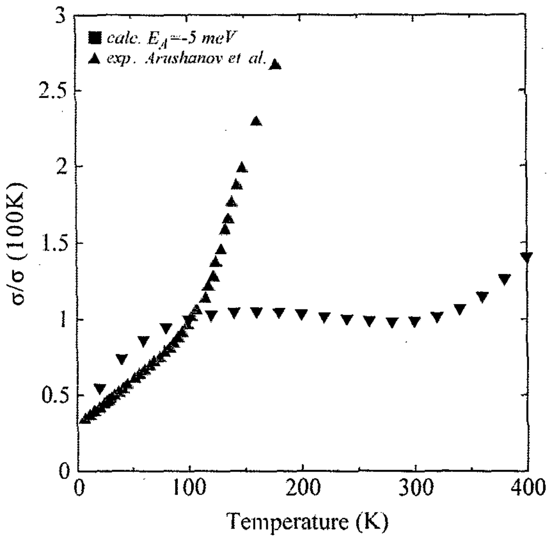

Fig.5 The temperature dependence of the conductivity σ . Accepter parameters E_A =-5 meV and $N_A = 3\times10^{16}$ cm^{-3} are chosen

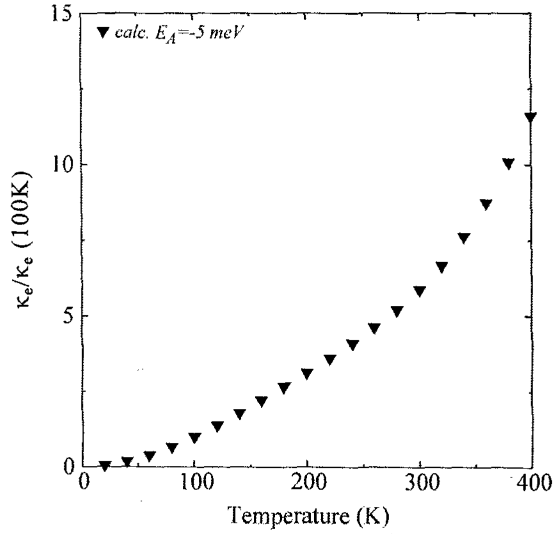

Fig.6 The temperature dependence of electronic thermal conductivity κ_e . Accepter parameters E_A=-5meV and $N_A = 3\times10^{16}$ cm^{-3} are chosen

results with the nonparabolic band model and can describe the Seebeck coefficient very well. At the only higher temperature region such as over 300 K nonparabolic effects becomes important. This situation can be understood well if we see the hole concentration 2~3×10^{16} cm^{-3}, realized in the temperature below 300K in Fig.2, dose not correspond to strongly nonparbolic part in the energy dispersion in Fig.1.

Fourthly, we show the calculated result for the conductivity σ and the electronic thermal conductivity κ_e in Fig.5 and 6. In Fig.5, we see the very different behaviors between the calculated and experimental conductivities for the temperature, being higher than 100 K ; one accepter level model seems to be insufficient to explain the experiment. In Fig.6, the increase of the electronic thermal conductivity for higher temperature is seen and there Wideaman-Franz law is hold.

Finally it is noted that we have also calculated the above thermoelectric-related transport quantities by using the two accepter level model. It has been found that the situation is much improved if the one accepter level within the valence band and another accepter level with higher energy within the band gap are assumed. However, the precise comparison with the experiment should be done by the band model based on the inclusion of other two parabolic conduction bands, which exist near the nonparabolic band [5].

Summary

In the present work, we have developed the study of thermoelectric properties, based on the Kane's nonparabolic model. Considering the thermostatistical behavior of carriers and taking the sukutterdite compound $CoSb_3$ as an example, we have calculated and discussed the Seebeck coefficient as well as electrical conductivity and electronic thermal conductivity in the same standing point. It has been shown that different behaviors of the Seebeck coefficients in experiments of the different groups can be understood by the different energy level of the accepter included in the samples. It has been also shown that one accepter model is insufficient to explain the experimental behavior of some thermoelectric -related properties all together.

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(Received October 13, 2003; Accepted January 16, 2004)