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The effect of a multivalley energy band structure on the thermoelectric figure of merit

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Résumé. — Les coefficients de qualité thermoélectrique sans dimension de semiconducteurs à vallées multiples \((ZT)_{mv}\) ou à vallée unique \((ZT)_{sv}\) sont ici comparés. La diffusion des phonons acoustiques et celle des impuretés ionisées sont prises en considération. Bien qu’il soit avantageux pour les applications thermoélectriques d’utiliser un semiconducteur à vallées multiples, l’effet bénéfique est réduit par l’augmentation de la concentration des porteurs et la présence de diffusion inter-vallées. Lorsque la concentration des porteurs est optimale pour le coefficient de qualité thermoélectrique, le coefficient \((ZT)_{mv}/(ZT)_{sv}\) pour l’alliage silicium-germanium est réduit d’environ 40 %.

Abstract. — A comparison is drawn between the dimensionless thermoelectric figure of merit of a multivalleyed semiconductor \((ZT)_{mv}\) and one having a single valleyed structure \((ZT)_{sv}\). In the analysis both acoustic phonon scattering and ionized impurity scattering are considered. Although it is advantageous to employ a multivalleyed semiconductor in thermoelectric applications it is concluded that the beneficial effect of a multivalleyed structure is reduced with increase in carrier concentration and the presence of intervalley scattering. At a carrier concentration which optimizes the thermoelectric figure of merit, the ratio \((ZT)_{mv}/(ZT)_{sv}\) for silicon-germanium alloy is reduced by approximately 40 percent. It has been generally accepted for some considerable time that a semiconductor which possesses a multivalley energy band structure should exhibit a higher value of the thermoelectric figure of merit \(Z\) than a similar material which has only a single valley. A comparison of the measured \(Z\) values for thermoelectric semiconductors supports this view. Multivalleyed semiconductors such as bismuth telluride, lead telluride and silicon-germanium alloys are the best materials over their temperature ranges of operation [1]. Previous analyses have shown that in the non-degenerate limit and neglecting intervalley scattering of the charge carriers, the figure of merit increases monotonically with the number of valleys \(N_v\) [2, 3]. In practice thermoelectric semiconductors are doped to relatively high carrier concentrations in order to optimize the materials thermoelectric properties. In the region of optimum doping, a multivalley energy band structure and the intervalley scattering may have a significant effect on the figure of merit compared to that in the non-degenerate limit. In this note we report the results of our calculations into the effect of intervalley scattering on the figure of merit of a multivalleyed semiconductor, as a function of carrier concentration \(n\).
(expressed in terms of reduced Fermi energy $\xi$). Assuming conduction in a single band semiconductor (electron or hole) the dimensionless figure of merit for a multivalleyed semiconductor $(ZT)_{mv}$ (with $N_v$ equivalent valleys) can be expressed as [1, 4]

$$\begin{align*}
(ZT)_{mv} &= \frac{(\alpha'_e)^2 (\sigma'_e)_{mv}}{1 + (\sigma'_e \xi)_{mv}} \\
\text{where} \\
\alpha'_e &= \delta(\xi) - \xi \\
\delta(\xi) &= \frac{(s + 5/2) F_{s+3/2}(\xi)}{(s + 3/2) F_{s+1/2}(\xi)} \\
\xi(\xi) &= \frac{(s + 7/2) F_{s+5/2}(\xi)}{(s + 3/2) F_{s+1/2}(\xi)} - \delta^2.
\end{align*}$$

The reduced electrical conductivity $\sigma'_e$ is given by

$$\sigma'_e = \beta \frac{F_{s+1/2}(\xi)}{(s + 1/2)!}$$

where

$$\beta = \frac{2(2\pi k_B)^{3/2} k_B^4 A'}{eh^3}$$

$$A' = T^{5/2} m^{3/2} \mu/\lambda_L.$$ 

The various symbols have the same meaning as in reference [1].

Assuming that the reduced Seebeck coefficient $\alpha'_e$ is independent of the number of valleys and that the effect of intervalley scattering manifests itself primarily through the carrier mobility and electrical conductivity, the effect of a multivalley energy band structure on $ZT$ can conveniently be discussed in terms of the ratio [5]

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} = \left(\frac{\sigma'_e}{\xi} \right)_{sv} \left\{ 1 + (\sigma'_e \xi)_{sv} \right\}$$

In the non-degenerate limit, $-\xi \gg 1$ and in the absence of intervalley scattering

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} = N_v.$$ 

The ratio $(ZT)_{mv}/(ZT)_{sv}$ can be evaluated as a function of the reduced Fermi energy or the carrier concentration, with $\xi$ and $n$ related by:

$$n = 4\pi \left(\frac{2k_B}{\hbar^2}\right)^{3/2} N_v m^*_{1/2} T^{3/2} F_{1/2}(\xi).$$

Here $m^*$ corresponds to the effective mass for a single valley i.e. $(m_1^* m_2^* m_3^*)^{1/3}$ where $m_1$, $m_2$ and $m_3$ refer to the components of the effective mass tensor along the principal directions.

The model formulated is a general one and equation (3) can be solved by numerical integration for different scattering mechanisms. Silicon-germanium alloys are of particular interest to us and the various parameters employed in the calculations are appropriate to Si$_{70}$Ge$_{30}$. The important carrier scattering mechanisms operating in these alloys at room temperature are acoustic phonon scattering and ionized impurity scattering with associated scattering parameters $s = -1/2$ and $3/2$ respectively.
The material parameters $A'$ are given by:

$$A'_{\text{acoustic}} = \frac{(8 \pi)^{1/2} e^4}{3 k^{3/2}} \frac{C_{11} T N_v}{\varepsilon_1^2 \lambda_L m_e^*},$$

and

$$A'_{\text{impurity}} = \frac{2^{7/2} k^{3/2} C_1^2 m_e^* T^4 (N_v/m_e^*)}{\pi^{3/2} e^3 N_i \lambda_L \ln \left[ 1 + \left( \frac{3 \chi kT}{e^2 N_i^{1/3}} \right)^2 \right]}.$$

Where $\varepsilon_1$ is the acoustic deformation potential, $C_{11}$ is the longitudinal elastic constant, $\chi$ is the dielectric constant and $N_i$ is the concentration of ionized impurities (when each of the ionized impurities contribute one free electron, $N_i = n$).

Results.

The ratio $\frac{(ZT)_{mv}}{(ZT)_{sv}}$ for Si$_{70}$Ge$_{30}$ alloy at 300 K is displayed in figure 1 as a function of carrier concentration. Both acoustic phonon scattering and ionized impurity scattering are considered, but without the inclusion of intervalley scattering. Both mechanisms lead to a value of $N_v = 6$ in the non-degenerate limit and this value decreases with an increase in carrier concentration. The pattern of the decrease in the ratio $\frac{(ZT)_{mv}}{(ZT)_{sv}}$ with carrier concentration is different for each mechanism. In the acoustic scattering case the decrease in this ratio occurs over the range of carrier concentration from $10^{24}$ to $10^{26}$ m$^{-3}$, while for ionized impurity scattering the ratio remains almost constant at $N_v = 6$ up to a carrier concentration of $10^{25}$ m$^{-3}$ and then decreases rapidly with increase in carrier concentration.

The exclusion of intervalley scattering may not be justified, particularly at high temperatures, and intervalley scattering is likely to have a significant effect on the thermoelectric figure of merit. Acoustic intervalley scattering is included in our calculations by following a method due to Herring [6]. An expression is obtained for the temperature dependence of the carrier mobility

![Figure 1](attachment:image.png)

Fig. 1. — The ratio $\frac{(ZT)_{mv}}{(ZT)_{sv}}$ as a function of carrier concentration for Si$_{70}$Ge$_{30}$ alloy at 300 K. Curve 1: acoustic phonon scattering. Curve 2: ionized impurity scattering.
as a function of the ratio $W_2/W_1$, where $W_2$ and $W_1$ are measures of the strength of the carrier coupling to intervalley and intravalley acoustic modes respectively. The ratio $W_2/W_1$ is adjusted to give realistic values of the carrier mobility and the figure of merit. In figure 2 is displayed $(ZT)_{mv}/(ZT)_{sv}$ as a function of carrier concentration, assuming acoustic phonon scattering with (a) intravalley scattering, (b) intra and intervalley scattering.

The inclusion of intervalley scattering does not appreciably affect the ratio $(ZT)_{mv}/(ZT)_{sv}$ at low carrier concentrations. However, as is evident from the figure, its effect increases with increase in carrier concentration. It is concluded that intervalley scattering significantly reduces the beneficial effect of a multivalley energy band structure. At optimum doping level in silicon-germanium alloys ($n \sim 10^{25} \text{ m}^{-3}$) intervalley scattering reduces the ratio $(ZT)_{mv}/(ZT)_{sv}$ by approximately 40%.

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References