Multi-band analyses of the conductivity, the Hall coefficient, and the Seebeck coefficient of single crystal p-type β-FeSi2

梶川　靖友

Journal of Alloys and Compounds　Volume 846

15 December 2020

https://doi.org/10.1016/j.jallcom.2020.155861

Multi-band analyses of the conductivity, the Hall coefficient, and the Seebeck coefficient of single crystal *p*-type β-FeSi$_2$

Y. Kajikawa[1]

Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan

Keywords Thermoelectric materials; Electrical transport; Impurity conduction; Hall effect

ABSTRACT

β-FeSi$_2$ is called the "environment-friendly thermoelectric semiconductor" but the origin of its high thermoelectromotive power is still unknown. In the present study, the temperature-dependence data of the electrical conductivity, the Hall coefficient, and the Seebeck coefficient on bulk single crystal *p*-type β-FeSi$_2$ samples reported in literature have been analyzed in a multi-band model. In the model, the effects of the 2nd maximum of the valence band, the 2nd minimum of the conduction band, and an acceptor impurity band are included and are proved to be important. Through the simultaneous fits to the temperature-dependence data of the three transport coefficients, the effective masses of holes at the 1st and the 2nd maximum of the valence band and those of electrons at the 1st and the 2nd minimum of the conduction band are deduced together with the energy separations among the bands. In addition, by including the temperature-dependent Hall factor for impurity hopping conduction, impurity concentrations have been significantly corrected from those previously estimated in a simple two-band model.

1. Introduction

---

[1] Tel.: +81-852-32-8903; fax: +81-852-32-8903
E-mail address: kajikawa@riko.shimane-u.ac.jp

Semiconducting β-$FeSi_2$ has been most widely investigated among other transition metal silicides as one of the most important thermoelectric materials. Recently, its use not only as bulk [1,2] or film [3] material but also as a constituent of nanocomposites [4–6] has been intensively studied. In spite of the intensive theoretical and experimental studies, however, the correct interpretation of the transport and thermoelectric properties of β-$FeSi_2$ is still a matter of debate [7–11].

One of the obstacles to correct interpretation is the complexity of the band structure. Most of band calculations for β-$FeSi_2$ show that the 1st valence band maximum (VBM) is located at the Y point while the 1st conduction minimum (CBM) is located at the Λ^* point between the Γ and Z point. It has been shown that the optical properties of β-$FeSi_2$ are significantly affected not only by the direct gap at the Y point but also by the indirect gap between the 1st VBM at the Y point and the 1st CBM at the Γ point [12]. It is, therefore, natural to consider that the transport and thermoelectric properties may also be significantly affected not only by the 1st but also the 2nd extrema of the valence or the conduction band. Up to date, however, being different from the interpretation of the optical properties, that of the transport and thermoelectric properties of β-$FeSi_2$ has been performed within a simple one-valence-band and one-conduction-band model. For precise interpretation of the transport and thermoelectric properties, the knowledge of the effective masses at the band extrema and the separation energy between the band extrema are necessary. For β-$FeSi_2$, however, even the effective masses at the 1st VBM and CBM have not been definitely determined.

In addition to the effects of the 2nd VBM or CBM, those of the impurity band should be taken into account at low temperatures. On the insulator side of metal-insulator (MI) transition, electrical conduction in the impurity band occurs via either nearest-neighbor hopping (NNH) or variable-range hopping (VRH). Hopping conduction in *p*-type β-$FeSi_2$ has already been observed in many studies [7,13–21].

The author of the present article has analyzed the temperature-dependence data of the conductivity σ, the Hall coefficient R_H, and the Seebeck coefficient S on *n*-type $CoSb_3$ in a multi-band model including plural VBM and CBM as well as an impurity band [22]. As a result, the effective masses at the band extrema as well as the separation energies among the band extrema have been deduced. In the present study, the multi-band analysis is now applied to the temperature-dependence data of σ, R_H, and S on p-type β-FeSi$_2$. For the purpose of determining the band parameters such as the effective masses and the band separations, the temperature-dependence data of σ, R_H, and S reported by Udono et al. [21] on an identical sample of p-type β-FeSi$_2$ are analyzed. Assuming a single parabolic valence band, Arushanov et al. [13] deduced the effective mass of holes in p-type β-FeSi$_2$ solely from the temperature-dependence data of the Hall coefficient below 300 K. Their deduced values of the hole effective mass are ranging from 0.8 m_0 to 1.2 m_0, where m_0 is the free-electron mass. On the other hand, also in a single-parabolic-band model, Du et al. [1] recently deduced the hole effective mass to be 4.9 m_0 from the room-temperature data of the Hall and the Seebeck coefficient with assuming only acoustic-phonon scattering as the scattering mechanism. The present multi-band analysis utilizing the temperature-dependence data of the three transport coefficients with taking into account several scattering mechanisms is expected to offer the more reliable value of the effective mass than either of the analysis utilizing the temperature-dependent Hall-coefficient data alone or that utilizing the room-temperature data of the Hall and the Seebeck coefficient with assuming a single sccatering mechanism.

Once the values of the effective masses have been determined, one can perform simultaneous fits to the temperature-dependence data of the conductivity and the Hall coefficient in a multi-band model using the values of the effective masses. Since strain due to the lattice mismatch against substrates has been shown to cause significant effects on the band structure of β-FeSi$_2$ samples epitaxially grown on Si substrates [23–26], the analyses are restricted to p-type doped bulk single crystal samples. Through the multi-band analyses, more reliable interpretations are presented for the temperature-dependence data of σ, R_H, and S on several samples of p-type doped bulk single crystal β-FeSi$_2$.

In the following, the analysis model is described in Sec. 2. In Sec. 3, in order to deduce the reliable values of the effective masses, we firstly perform the simultaneous fits of the temperature-dependence data on the three transport coefficients, namely $\sigma(T)$, $R_H(T)$, and $S(T)$, of a p-type β-FeSi$_2$ sample reported by Udono et al. [21]. Not only the effective masses at the 1st and the 2nd VBM but also other parameters related to the transport phenomena are deduced through the fits. Using the obtained values for the effective masses of holes, analyses are then performed for the data of $\sigma(T)$ and $S(T)$ reported by

Heinrich et al. [7,18] in Sec. 4. In Sec. 5, on the other hand, analyses are performed for the data of $\sigma(T)$ and $R_H(T)$ reported by Brehme et al. [15–17] and Udono et al. [20]. The summary is given in Sec. 6.

2. Analysis model

When assuming multiple valence and conduction bands together with multiple acceptor levels and a compensating donor level, the charge-neutrality condition in a *p*-type semiconductor can be written as

$$\sum_{i=1}^{p} n_{vi} + N_D = \sum_{i=1}^{q} n_{ci} + \sum_{i=1}^{r} N_{Ai}^{-} , \tag{1}$$

where n_{vi} is the hole concentration in the *i*-th valence band, n_{ci} is the free-electron concentration in the *i*-th conduction band, N_{Ai}^{-} is the ionized acceptor concentration of the *i*-th acceptor level, and N_D is the concentration of the compensating donor level.

Only the 1st acceptor level is assumed to form an impurity band, and hopping conduction there is taken into account. The total conductivity σ is then represented as the sum of contributions from respective bands by

$$\sigma = \sigma_{ib} + \sum_{i=1}^{p} \sigma_{vi} + \sum_{i=1}^{q} \sigma_{ci} , \tag{2}$$

where σ_{ib}, σ_{vi}, and σ_{ci} are the conductivities due to hopping conduction in the impurity band, free-hole conduction in the *i*-th valence band, and free-electron conduction in the *i*-th conduction band, respectively.

Furthermore, both NNH and VRH are assumed as the hopping mechanisms in the impurity band. If assuming NNH and VRH are independent phenomena, as in the previous study [27], the total hopping conductivity in the impurity band can be expressed by $\sigma_{ib} = \sigma_{NNH} + \sigma_{VRH} = en_{ib}(\mu_{NNH} + \mu_{VRH})$, where e is the elemental charge and $n_{ib} = N_A^{-} N_A^{0} / N_A$ is the effective concentration of carriers hopping in the impurity band while μ_{NNH} and μ_{VRH} are hopping mobilities for NNH and VRH, respectively. Then, Eq. (2) can be rewritten as

$$\sigma = en_{ib}(\mu_{NNH} + \mu_{VRH}) + \sum_{i=1}^{p} n_{vi}\mu_{vi} + \sum_{i=1}^{q} n_{ci}\mu_{ci} , \tag{2'}$$

where μ_{vi} and μ_{ci} are the drift mobilities of carriers in the i-th valence and conduction bands, respectively. Note that n_{ib} can be approximated as $n_{ib} \approx N_{A1}^{-}(1-K) \approx N_D(1-K)$ at low temperatures, where $K = N_D/N_{A1}$ is the compensation ratio.

Although Heinrich et al. [7] had identified the conduction mechanism at low temperatures in their Cr-doped sample as Mott VRH, they have corrected it as Efros-Shklovskii (ES) VRH in their succeeding study [18]. In the present study, ES VRH is assumed as the VRH mechanism rather than Mott VRH according to Ref. [18].

The total Seebeck coefficient is represented as the weighted average of the contributions from respective bands by

$$S = \frac{\sigma_{ib}}{\sigma} S_{ib} + \sum_{i=1}^{p} \frac{\sigma_{vi}}{\sigma} S_{vi} + \sum_{i=1}^{q} \frac{\sigma_{ci}}{\sigma} S_{ci} , \tag{3}$$

where S's are the Seebeck coefficients of carriers in the respective bands. In the present analysis, however, the Seebeck effect in the impurity band is neglected, and it is assumed that $S_{ib} = 0$.

The Hall coefficients for respective valence and conduction bands are defined as $R_{Hvi} = A_{Hvi}/(en_{vi})$ and $R_{Hci} = -A_{Hci}/(en_{ci})$, where A_H's are the Hall factors of carriers in the respective bands, while those for NNH and ES VRH in the impurity band are defined as $R_{HNNH} = A_{HNNH}/(en_{ib})$ and $R_{HVRH} = A_{HVRH}/(en_{ib})$, respectively, where A_{HNNH} and A_{HVRH} are the Hall factors for NNH and VRH, respectively. Then, the total Hall coefficient is represented by

$$R_H = \left(\frac{\sigma_{VRH}}{\sigma}\right)^2 R_{HVRH} + \left(\frac{\sigma_{NNH}}{\sigma}\right)^2 R_{HNNH} + \sum_{i=1}^{p} \left(\frac{\sigma_{vi}}{\sigma}\right)^2 R_{Hvi} + \sum_{i=1}^{q} \left(\frac{\sigma_{ci}}{\sigma}\right)^2 R_{Hci} . \tag{4}$$

The Hall mobilities for respective valence and conduction bands are defined as $\mu_{Hvi} = R_{Hvi}\sigma_{vi}$ and $\mu_{Hci} = -R_{Hci}\sigma_{ci}$ while those for NNH and ES VRH in the impurity band are defined as $\mu_{HNNH} = R_{HNNH}\sigma_{NNH}$ and $\mu_{HVRH} = R_{HVRH}\sigma_{VRH}$, respectively. Then, the total Hall mobility $\mu_H = R_H\sigma$ is represented as the weighted average of the contributions from respective bands by

$$\mu_H = \frac{\sigma_{VRH}}{\sigma} \mu_{HVRH} + \frac{\sigma_{NNH}}{\sigma} \mu_{HNNH} + \sum_{i=1}^{p} \frac{\sigma_{vi}}{\sigma} \mu_{Hvi} + \sum_{i=1}^{q} \frac{\sigma_{ci}}{\sigma} \mu_{Hci} . \tag{5}$$

As in the previous study [27], the hopping drift mobilities are assumed to be expressed as

$$\mu_i = \mu_{0i} (E_i / k_B T)^{s_i} \exp(-E_i / k_B T), \tag{6}$$

where i = 3 and ES for NNH and ES VRH, respectively, and μ_{0i}'s are temperature-independent constants. The activation energy E_3 of the drift mobility for NNH is treated as a temperature-independent constant while E_{ES} is treated as a temperature-dependent activation energy which is expressed as $E_{\mathrm{ES}} = k_B(T_{\mathrm{ES}}T)^{1/2}$. For impurity conduction, it is assumed that s_3 =3/2 according to the small-polaron theory [28–30] while s_{ES} is tentatively assumed to be 1/2.

Also according to the small-polaron theory [28–30], the Hall factor $A_{H\mathrm{NNH}} = \mu_{HNNH}/\mu_{NNH}$ for NNH conduction is assumed to be expressed as

$$A_{HNNH} = (k_B T / I_{H3}) \exp(K_H E_3 / k_B T), \qquad (7)$$

where K_H = 2/3 and I_{H3} are temperature-independent constants. On the other hand, as in the previous study [27], the Hall factor $A_{H\mathrm{VRH}} = A_{H\mathrm{ES}} = \mu_{HES}/\mu_{ES}$ for ES-VRH conduction is assumed to be expressed as

$$A_{HES} = A_{0HES}(T_{ES}/T)^{1-s_{ES}} \exp\left[(1-\nu_{ES})(T_{ES}/T)^{1/2}\right] \qquad (8)$$

with A_{0HES} and ν_{ES} being temperature-independent constants.

The carrier concentrations in the valence and the conduction bands are respectively calculated as $n_{vi} = N_{vi} \cdot \mathcal{F}_{1/2}(\eta_{vi})$ and $n_{ci} = N_{ci} \exp(\eta_{ci})$, where $N_x = 2(2\pi m_x^{DOS} k_B T / h^2)^{3/2}$ (x = $v1$, $v2$, $c1$, or $c2$) is the effective density of states (DOS) of the x band, η_x is the reduced Fermi level with respect to the edge of the x band, $\mathcal{F}_j(\eta)$ is the normalized Fermi-Dirac integral of order j, k_B is the Boltzmann constant, h is the Planck constant, and m_x^{DOS} is the effective DOS mass, which is related to the conductivity effective mass m_x as $m_x^{DOS} = m_x M_x^{2/3}$. Here, M_x is the number of degeneracy of the x band.

For the valence bands of β-FeSi$_2$, most of band calculations [23–25,31–35] show that the 1st VBM (v_1) is located at the Y point while the 2nd VBM (v_2) located at the Λ^* point. On the other hand, some of band calculations [36–38] show that the 1st VBM is located at the Λ^* point while the 2nd VBM is located at the Y point. In the present study, v_1 and v_2 are assumed to be located at the Y and the Λ^* point, respectively. Therefore, the numbers of degeneracy of the v_1 and v_2 band are M_{v1} = 1 and M_{v2} = 2, respectively. The spin degeneracy factor for the acceptor level was taken to be 2.

For the conduction bands, all the band calculations show that the 1st CBM (c_1) is located at the Λ^* point while the 2nd CBM (c_2) is located at the Y point. Therefore, the numbers of degeneracy of the c_1 and c_2 band are $M_{c1} = 2$ and $M_{c2} = 1$, respectively. Then, the indirect gap is between the 1st VBM at the Y point and the 1st CBM at the Λ^* point while the direct gap E_g^d is between the 1st VBM and the 2nd CBM at the Y point. Figure 1 shows the sketch map of the band diagram of β-FeSi$_2$ assumed for the present analysis.

For both the indirect and the direct gap, the temperature dependence of the band-gap energies is assumed to be represented by a Bose-Einstein-type analytical expression [12,39–41]

$$E_g(T) = E_g(0) - S\langle\hbar\omega\rangle\left(\coth\frac{\langle\hbar\omega\rangle}{2k_BT} - 1\right), \tag{9}$$

where $E_g(0)$ is the energy gap at 0 K, S is a dimensionless coupling parameter, and $\langle\hbar\omega\rangle$ is an average phonon energy. According to Udono et al. [12], it is assumed that $S = 4.6$ and $\langle\hbar\omega\rangle = 29$ meV for the indirect gap while it is assumed that $S = 2.2$ and $\langle\hbar\omega\rangle = 27$ meV for the direct gap. Therefore, not only $E_g(T)$ for the indirect gap between the $c1$ and the $v1$ band but also $\Delta E_{c2}(T)$ for the energy separation of the $c2$ from the $c1$ band is temperature-dependent. On the other hand, the energy separation ΔE_{v2} of the $v2$ from the $v1$ band is assumed to be constant, being independent of temperature.

The calculation of mobilities of free carriers has been performed within a relaxation-time approximation. An early experimental study by Dimitriadis et al. [42] on p-type β-FeSi$_2$ showed that two scattering mechanisms, namely ionized-impurity and acoustic-phonon scattering, are dominant. However, Brehme et al. [16] proved the hole mobility of β-FeSi$_2$ to follow a power-law temperature dependence $T^{-\beta}$ with $\beta > 1.5$ in the temperature region of 200-300 K. In their study on p-type β-FeSi$_2$ layers, Oostra et al. [43] pointed out that the mobility does not follow the $T^{-1.5}$ behavior as expected for acoustic-phonon scattering but follows the $T^{-1.9}$ behavior in the temperature range of 100-300 K. They suggested that scattering mechanisms other than acoustic-phonon scattering are important. Filonov et al. [44] as well as Takakura et al. [45] showed that the power-law temperature dependence $T^{-\beta}$ with $\beta > 1.5$ in the high-temperature region can be obtained by including nonpolar-acoustic-phonon scattering in addition to acoustic-phonon scattering. In the present study, therefore, nonpolar-acoustic-phonon scattering is taken into account.

In addition, space-charge scattering is included, as in the previous studies on n-type GaAs [46] and InP [27]. On the other hand, while Filonov et al. [44] included neutral impurity scattering, it is not included in the present study. Takakura et al. [47] further pointed out that inter-valley scattering should be taken into account since the 1st VBM is not located at the center of the Brillouin zone but at the Y point. However, since inter-valley scattering was found to have negligible effects, this scattering mechanism was not included.

The total relaxation time τ_{total} for free holes in each valence band is assumed to be given by $\tau_{total}{}^{-1} = \tau_{ii}{}^{-1} + \tau_{ac}{}^{-1} + \tau_{npo}{}^{-1} + \tau_{po}{}^{-1} + \tau_{sc}{}^{-1}$, where τ_{ii}, τ_{ac}, τ_{npo}, τ_{po}, and τ_{sc} are the relaxation times for scattering due to ionized impurities, acoustic phonons, nonpolar optical phonons, polar optical phonons, and space charge, respectively. On the other hand, only acoustic-phonon scattering is taken into account for the calculation of the mobilities for free electrons in the conduction bands. Strictly speaking, the band dispersion near the VBM and the CBM is anisotropic. However, Zhang et al. [48] theoretically calculated σ/τ and S for β-FeSi$_2$ with including the anisotropic band dispersion to show that the anisotropies of σ/τ and S between the directions parallel and perpendicular to the c-axis are not significant as long as p-type doping is lower than 10^{21} cm^{-3}. Therefore, the calculation of τ_{ii}, τ_{ac}, τ_{npo}, τ_{po}, and τ_{sc} has been performed using the formulae for an isotropic parabolic band [49]. The formulae for the calculation of these relaxation times are described in Appendix A. The calculation of μ_{vi} and $\mu_{Hvi} = A_{Hvi}\mu_{vi}$ as well as that of μ_{ci} and $\mu_{ci} = A_{Hci}\mu_{ci}$ was also performed within an isotropic parabolic band model.

The calculation method of the hopping conductivity in the impurity band is the same as in the previous study on n-type InP [27].

The material constants used for the present calculation are summarized in Table 1, in which the values of the static and the high-frequency dielectric constants were cited from Refs. [50] and [51], respectively, while those of the longitudinal sound velocity and the Debye temperature were cited from Refs. [52] and [53].

It has been shown both experimentally and theoretically that, owing to the screening effect of neutral impurities, the static dielectric constant increases with the impurity concentration to diverge at the critical net acceptor concentration N_{NAcr} for the onset of the

MI transition [54,55]. According to Poklonski et al. [55], the static dielectric constant is assumed to be described by the form of

$$\varepsilon_{eff}(N_A^0) = \left(\varepsilon_s + 2N_A^0 / N_{NAcr}\right)\left(1 - N_A^0 / N_{NAcr}\right)^{-1} . \tag{10}$$

Since the critical net acceptor concentration for the MI transition in p-type β-FeSi$_2$ is not known, N_{NAcr} is treated as an adjustable parameter.

3. Simultaneous fits to the data of $\sigma(T)$, $R_H(T)$, and $S(T)$

Firstly, the effective masses should be determined. In the previous studies of the author on p-type [56] and n-type CoSb$_3$ [22,57], the effective masses of carriers at the 1st and the 2nd extrema of the valence and the conduction band are estimated through the simultaneous fits to the temperature-dependence data of the three transport coefficients: the conductivity, the Hall coefficient, and the Seebeck coefficient.

Regarding p-type β-FeSi$_2$, the temperature-dependence data of the conductivity, the Hall coefficient, and the Seebeck coefficient on their two samples (#Ga-1 and #Ga-2) have been reported by Udono and his co-workers in a temperature range of 10-300 K [21,58]. These samples were grown by a temperature gradient solution growth (TGSG) method using Ga solvent [20,21,58]. Between the two samples, #Ga-1 was grown using an arc-melted low-purity FeSi$_2$ solute while #Ga-2 was grown using an ampoule melted high-purity one. The Hall-effect measurement was performed in a magnetic field of 0.35 T. Similar data of $\sigma(T)$, $R_H(T)$, and $S(T)$ were obtained for both the samples. We begin with analyzing one of their samples (#Ga-2) to deduce the effective masses of holes.

For analyzing the data below 300 K, the effects of free electrons in the conduction bands may be neglected. Therefore, the simultaneous fits of the experimental data in the measurement temperature range of 10-300 K have been performed according to the present model without including the conduction bands. For these samples, good fits have been obtained assuming only a shallow acceptor level without assuming other deeper acceptor levels.

Through the fits, the values of various fitting parameters have been obtained besides effective masses. For one of their two samples (#Ga-2), the obtained values of fitting parameters related to impurities are summarized in Table 2 while those related to the 1st and the 2nd VBM are summarized in Table 3 and 4, respectively. In particular, m_{v1}/m_0 is estimated to be 0.9 ± 0.2. However, since the low temperature end of the measurement temperature range was not low enough, the values of parameters related to impurity hopping conduction cannot be definitely deduced. There exists, therefore, large ambiguity in the values of parameters related to VRH, namely $\mu_{0\mathrm{ES}}$, T_{ES}, ν_{ES}, and A_{0HES}.

Arushanov et al. [59] estimated the critical net acceptor concentration N_{NAcr} for the onset of the MI transition to be 3.7×10^{19} cm^{-3} for Mn-doped p-type β-FeSi$_2$. On the other hand, Udono and Kikuma [20] reported the $\sigma(T)$ and $R_H(T)$ data on three samples (#Ga4, #Ga6, and #Ga2) grown by TGSG method using Ga solvent together with an arc-melted low-purity FeSi$_2$ solute to show that all these samples exhibit non-metallic behavior with activation energies of E_A = 17-18 meV in spite of high net acceptor concentrations of $N_A - N_D = 4.1\text{-}5.3 \times 10^{19}$ cm^{-3}. Furthermore, the net acceptor concentration $N_{A1} - N_D$ was estimated to be 6×10^{19} cm^{-3} for #Ga-2 in the present study. Although this value of $N_{A1} - N_D$ exceeds $N_{NAcr} = 3.7 \times 10^{19}$ cm^{-3} estimated by Arushanov et al. [59], the conductivity of #Ga-2 still shows non-metallic behavior in the impurity-conduction temperature region. It is, therefore, clear that N_{NAcr} is larger than 6×10^{19} cm^{-3}. As shown in Table 2, N_{NAcr} was estimated to be 1×10^{20} cm^{-3} through the fits in the present study. Using this value of N_{NAcr} together with $N_{A1} - N_D = 6 \times 10^{19}$ cm^{-3}, the effective static dielectric constant was calculated to be $\varepsilon_{eff}(N_{A1}^0) \approx \varepsilon_{eff}(N_{A1} - N_D) = 77.8\,\varepsilon_0$ for #Ga-2. Ionized-impurity scattering is weakened by screening of the Coulomb force through the increase of ε_{eff}. As a result, the mobility at low temperatures is increased in #Ga-2 in comparison with the case in which the screening effect owing to the increased ε_{eff} is absent. As shown in Table 2, the ionization energy E_{A1} of the shallow acceptor level is as low as 6.5 meV. This low ionization energy is also attributed to the screening effect owing to the increased ε_{eff}.

Figures 2(a-d) show the comparison of the simulated results (solid lines) with the experimental data (open circles) of sample #Ga-2: (a) shows the conductivity as a function of the reciprocal temperature while (b), (c), and (d) respectively show the Hall mobility, the Hall coefficient, and the Seebeck coefficient as a function of the temperature. Also shown by yellow, green, and red curves are the contributions from the impurity band (*ib*), the 1st (*v*1) and the 2nd (*v*2) valence band, respectively, namely σ_x, $(\sigma_x/\sigma)\mu_{Hx}$, $(\sigma_x/\sigma)^2 R_{Hx}$, and $(\sigma_x/\sigma)S_x$, in (a), (b), (c), and (d), respectively, where $x = ib$, $v1$, and $v2$.

Arushanov et al. [13] analyzed the $R_H(T)$ data measured in the temperature range of 30-300 K on their five samples of Al-doped p-type β-$FeSi_2$ single crystal grown by chemical vapor transport (CVT). Using the higher-temperature data, they estimated $1/(eR_d) = N_{A1} + N_{A2} - N_D$ from the extrapolated value of $R_H(1/T)$ to $1/T \rightarrow 0$. Then, they estimated $1/(eR_f) = N_{A1} - N_D$ using the data in the carrier-freezing region to obtain the value of N_{A2}. Furthermore, they estimated the values of E_{A2} and $m_{v1}{}^{3/2}N_{A2}$ from the plot of $1/(eR_HT^{3/4})$ versus $1/T$ at high temperatures. Thus, it has been implicitly assumed for both free-hole and impurity hopping conduction that the Hall factor is unity, being independent of temperature. Finally, from the obtained values of N_{A2} and $m_{v1}{}^{3/2}N_{A2}$, they estimated m_{v1} for their five samples to be ranging from 0.8 m_0 to 1.2 m_0. Our estimated value of m_{v1} = 0.9 m_0 is within this range. Note, however, that their deduced values of impurity concentrations cannot be reliable since the Hall factor for impurity hopping conduction is not unity but increases to be larger than 10 with decreasing temperature.

Very recently, Du et al. [1] utilized a single-parabolic-band model to deduce the DOS effective mass of holes from the room-temperature data of the Hall and the Seebeck coefficient on the p-type polycrystalline samples of β-$FeSi_{2-x}Al_x$ (x = 0.02, 0.03, and 0.04) and $Fe_{0.92}Mn_{0.08}Si_2$. They set the scattering factor to be 0 assuming acoustic-phonon scattering as the scattering mechanism. Their deduced value for the DOS effective mass of holes is as large as 4.9 m_0. Note, however, that this value is considerably overestimated because the v_2 band with M_{v2} = 2 as well as the v_1 band with M_{v1} = 1 contributes to the Hall and the Seebeck coefficient at room temperature.

Martinelli et al. [60] calculated the principle-axis components of the effective mass tensor for holes at the Y and the Λ^* point in the framework of the full-potential *ab initio* method. They obtained (m_{xx}, m_{yy}, m_{zz}) = (0.21, 0.27, 0.27) m_0 and (1.11, 0.83, 0.81) m_0 for holes at the Y and the Λ^* point, respectively. The calculation of $(m_{xx}\ m_{yy}\ m_{zz})^{1/3}$ using these values of the tensor components yields m_{v1} = 0.25 m_0 and m_{v2} = 0.91 m_0 for the effective masses of holes at the Y and the Λ^* point, respectively. Our estimated values of m_{v1} = 0.9 m_0 and m_{v2} = 1.9 m_0 are 3.6 and 2.1 times larger, respectively, than those estimated by Martinelli et al. [60].

It can be seen in Fig. 2(a) that the contribution from the $v1$ band dominates the conductivity over most of the measurement temperature range while the contributions from the $v2$ and the impurity band become comparable to it at the highest and the lowest temperatures, respectively. Note also that, although the Seebeck coefficient is dominated by the contribution from the $v1$ band around its peak at 33 K, the contribution from the $v2$ band starts to increase at 50 K to be larger than that from the $v1$ band above 100 K.

It is interesting to note that the temperature dependence of the Seebeck coefficient observed for this p-type β-$FeSi_2$ sample is very similar to that of the absolute value of the Seebeck coefficient observed for n-type $Co_{1-x}Ni_xSb_3$ ($x = 0.003$ and 0.005) by Dyck et al. [61]. For n-type $Co_{1-x}Ni_xSb_3$, it has been proved in the previous study of the author [22] that the slight increase of the absolute value of the Seebeck coefficient with increasing temperature after its peak owing to the 1st CBM at the Γ point can be attribute to the 2nd CBM at the Σ point between the Γ and the N point. Udono et al. [21] suggested the large peak value of the Seebeck coefficient to be due to the phonon-drag effect. In the present study, however, the large peak value has been reproduced without the phonon-drag effect.

Thus, it has been shown that the $v2$ band significantly affects the transport properties (the thermoelectric property in particular) of p-type β-$FeSi_2$. This finding on p-type β-$FeSi_2$ in the present study as well as that on n-type $Co_{1-x}Ni_xSb_3$ in the previous study [22] suggests that the existence of the 2nd band with a large DOS and a small energy separation from the 1st band is crucial for the candidates of high-temperature thermoelectric materials.

The values of the energy separation ΔE_{v2} calculated by the band structure calculations for β-$FeSi_2$ are widely scattered. (Here, ΔE_{v2} corresponds to the energy separation of the 2nd VBM at the Λ^* point from the 1st VBM at the Y point.) Namely, the calculated results by Migas et al. [32] and Clark et al. [23] yielded $\Delta E_{v2} = 50$ and 170 meV, respectively while those by Eisebitt et al. [36] yielded ΔE_{v2} to be nearly zero; A negative value of $\Delta E_{v2} = -75$ meV was obtained in the calculation by Filonov et al. [37]. The estimated value of $\Delta E_{v2} = 23$ meV for Sample #Ga-2 as well as those estimated in the present study for the other samples (see Table 4) is within the scattered range of the theoretical predictions.

4. Simultaneous fits to the data of $\sigma(T)$ and $S(T)$

In this section, simultaneous fits to the temperature-dependence data of the conductivity and the Seebeck coefficient on another sample are performed using the values of the effective masses of holes at the 1st and the 2nd VBM obtained in the previous section. The acoustic-phonon deformation potential constant E_{ac} as well as the nonpolar-optical-phonon deformation potential constant E_{npo} for the 1st VBM was also fixed at the value obtained in the previous section. For the 2nd VBM, on the other hand, while E_{ac} was fixed at the value obtained in the previous section, E_{npo} was treated as an adjustable parameter.

Heinrich et al. [7,18] grew single crystal p-type β-$FeSi_2$ by a CVT reaction using Cr as a p-type dopant. They reported the $\sigma(T)$ and $S(T)$ data for their sample doped with 0.5 at. % ($\approx 4 \times 10^{20}$ cm^{-3}) Cr in a wide temperature range of 4.2-1070 K, but the $R_H(T)$ data are not available for this sample. Although the simultaneous fits have been performed to the $\sigma(T)$ and $S(T)$ data for this sample, it is rather difficult to determine the impurity concentrations without the $R_H(T)$ data. Note that, owing to the lack of the $R_H(T)$ data, there exists rather large ambiguity in deducing the impurity concentrations.

The simultaneous fits were performed firstly being restricted to the low-temperature range below 300 K, based on the present model but with the $c1$ and $c2$ band neglected. The values of the fitting parameters for the sample in this stage are summarized in Table 2, 3, and 4. As can be seen in Table 2, the net acceptor concentration $N_{A1} - N_D$ was estimated to be much lower than the critical net acceptor concentration N_{NAcr}. Therefore, the effect of the increase of ε_{eff} following Eq. (10) was neglected in the analysis on this sample.

After obtaining the simultaneous good fits to the experimental data below 300 K by adjusting the fitting parameters exept those related to the conduction bands, the $c1$ and $c2$ band have been added into the mode to extend the simultaneous fits to high temperatures. It has been noticed in this stage that the inclusion of the $c2$ band is necessary for obtaining good fits. Thus, the newly added fitting parameters in the 2nd stage are those related to the $c1$ and $c2$ band, i.e., the effective masses (m_{c1} and m_{c2}), the acoustic-phonon deformation potentials ($E_{ac}^{(c1)}$ and $E_{ac}^{(c2)}$), the energy separations at 0 K ($E_g(0)$ and $\Delta E_{c2}(0)$). Note, however, that the values of these newly added fitting parameters in the 2nd stage are not so significantly affected by the impurity concentrations obtained with rather large ambiguities in the 1st stage. Furthermore, one may wonder why the effective masses of electrons in the conduction bands can be estimated without the $R_H(T)$ data. The primitive explanation for this issue is presented in Appendix B. The values of the fitting parameters for the sample related to the 1st and 2nd CBM are summarized in Table 5 and 6, respectively.

Figures 3(a) and (b) show the comparison of the simulated results (solid lines) with the experimental data (open circles) of the sample doped with 0.5 at. % Cr: (a) shows the conductivity as a function of the reciprocal temperature while (b) shows the Seebeck coefficient as a function of the temperature. Also shown by solid lines of yellow, green, and red are the contributions from ES-VRH conduction in the impurity band, free-hole conduction in the 1st ($v1$) and the 2nd ($v2$) valence band, respectively, while shown by broken lines of green and red are those from free-electron conduction in the 1st ($c1$) and the 2nd ($c2$) conduction band, respectively.

The low-temperature conductivity can be described by ES VRH, as has been pointed out by Heinrich et al. [18]. There is a transition from ES VRH to free-hole conduction in the $v1$ band at approximately 100 K. Similar to the case of Sample #Ga-2 in the previous section, it can be seen in Fig. 3(a) that the contribution from the $v1$ band dominates the conductivity in the temperature range of 100-200 K while the contribution from the $v2$ becomes significant above 200 K. A steep increase of the conductivity above 700 K is due the onset of intrinsic conduction.

Similar transitions of the dominant contribution can be seen for the Seebeck coefficient, as can be seen in Fig. 3(b). Heinrich et al. [62] claimed that the strong temperature dependence below 150 K can be described by a T^3 law. They interpreted the dependence as the characteristic of a phonon-drag contribution [7,18,62]. In the present analysis, however, the strong temperature dependence has been reproduced without the phonon-drag effect. The steep decrease of the Seebeck coefficient with decreasing temperature below 150 K can be attributed to the steep decrease of the ratio $\sigma_{v1}/\sigma \approx \sigma_{v1}/(\sigma_{v1} + \sigma_{ib})$ in Eq. (3) due to the increase of the ratio σ_{ib}/σ_{v1} with decreasing temperature. After the peak due to the 1st VBM, the Seebeck coefficient shows a gradual increase with increasing temperature. This increase can be attribute to the contribution from the 2nd VBM. The decrease of the Seebeck coefficient above 600 K can be attribute to the onset of intrinsic conduction, as has been pointed out by Heinrich et al. [7].

Through the simultaneous fits to the $\sigma(T)$ and $S(T)$ data, the indirect band gap at 0 K was estimated to be $E_g(0)$ = 0.9 eV. Udono et al. [12,63] estimated the indirect gap at 0 K to be 0.814 eV from the optical absorption spectrum of the single crystal p-type β-FeSi$_2$ sample grown by a TGSG method using Ga solvent. Lang et al. [64] synthesized β-FeSi$_2$ nanoparticles by ion-beam-induced epitaxial crystallization followed by thermal annealing and then investigated the optical absorption spectrum at room temperature as well as the photoluminescence (PL) spectra at temperatures between 10 and 130 K. They estimated the indirect gap at 2 K to be 0.856 eV from the indirect gap at room temperature together with the temperature dependence of the PL peak. The value of $E_g(0)$ = 0.9 eV for the indirect gap obtained in the present analysis is near to the value obtained by Lang et al. [64]

Udono et al. [12] further estimated the direct gap at 0 K to be $E_g^d(0)$ = 0.939 eV while Lang et al. [64] estimated it to be 0.867 eV. The differences of these energies from the indirect gap energies lead to $\Delta E_{c2}(0)$ = 125 and 11 meV. The band calculation by Filonov et al. [37] yielded $\Delta E_{c2}(0)$ = 8 meV while those by Moroni et al. [31] and Migas et al. [32] yielded $\Delta E_{c2}(0)$ = 65 and 50 meV, respectively. On the other hand, Arushanov et al. [65] estimated $\Delta E_{c2}(0)$ to be 25 meV from the temperature dependence of the Hall coefficient for the single crystal n-type β-FeSi$_2$ sample grown by CVT. The value of $\Delta E_{c2}(0)$ = 20 meV estimated from the simultaneous fits in the present study is near to the value obtained by Arushanov et al. [65]

From the band structure calculation using the self-consistent linear muffin-tin orbital method, Filonov et al. [37] estimated m_{c1} to be 0.49 m_0 while m_{c2} was estimated to be of the order of tens in units of m_0. Martinelli et al. [60] calculated the principle-axis components of the effective mass tensor for electrons at the Y point in the framework of the full-potential *ab initio* method. They obtained $(m_{xx}, m_{yy}, m_{zz}) = (1.27, 0.83, 8.83)\ m_0$ for electrons at the Y point. These values of the tensor components yield m_{c1} = 2.10 m_0 for the effective mass of electrons at the Y point. They also found an exceedingly large value (>> m_0) for m_{c2}. Arushanov et al. [66] deduced the value of m_{c1} = 0.6 m_0 from the magnetic susceptibility measurement. Our estimated value of m_{c1} = 1.3 m_0 is between the values obtained by Arushanov et al. [66] and Martinelli et al. [60] Our estimated value of $m_{c2} = 240\ m_0$ is consistent with their results of the band calculations.

5. Simultaneous fits to the data of $\sigma(T)$ and $R_H(T)$

In this section, simultaneous fits to the data of $\sigma(T)$ and $R_H(T)$ on four samples are performed, using the values of effective masses used in the previous sections. Among the four samples, three are the samples of Cr-doped β-FeSi$_2$ grown by a CVT reaction while the other one is a sample grown by the TGSG method using Zn solvent. The acoustic-phonon deformation potential constant E_{ac} as well as the nonpolar-optical-phonon deformation potential constant E_{npo} for the 1st VBM was also fixed at the value used in the previous sections. For the 2nd VBM, on the other hand, while E_{ac} was fixed at the value used in the previous sections, E_{npo} was treated as an adjustable parameter. Since the net acceptor concentration $N_{A1} - N_D$ was proved to be much lower than the critical net acceptor concentration N_{NAcr} for all of the samples treated in this section, the effect of the increase of ε_{eff} following to Eq. (10) was neglected here.

A group of Hahn-Meintner Institute studied the electrical properties of β-FeSi$_2$ single crystal samples grown by a CVT reaction using Cr as a *p*-type dopant [15–17]. Among their studies, although Brehme et al. [17] investigated the properties of four Cr-doped *p*-type β-FeSi$_2$ samples of N1d, N2d, and N3d, and N4d, both of the $\sigma(T)$ and $R_H(T)$ data are available only for N4d. In Refs. [16] and [15], respectively, only #10 and To7 are Cr-doped *p*-type β-FeSi$_2$ single crystal. Therefore, analyses are performed here for the $\sigma(T)$ and $R_H(T)$ data on the three samples of #10, N4d, and To7. The nominal Cr concentration was 0.1 at. % ($\approx 8 \times 10^{19}$ cm^{-3}) in #10 while it was in the order of 1×10^{18} cm^{-3} in To7 [15]. For the growth of N4d, Cr was added to the starting powder in a concentration of 0.5 % [67], but it was found from energy dispersive X-ray spectroscopy (EDX) and electron paramagnetic resonance (EPR) measurements that the amount of incorporated dopants was about one order of magnitude lower [16].

The simultaneous fits to the experimental data have been performed for these three samples without including the conduction bands. It has been found that, while good fits can be obtained for #10 by assuming only ES VRH as the hopping mechanism in the impurity band, the better fits can be obtained for N4d and To7 by assuming not only VRH but also NNH. The obtained values of fitting parameters for these samples are summarized in Table 2, 3, and 4.

Arushanov et al. [67,68] analyzed the $R_H(T)$ and $\mu_H(T)$ data on two samples of #10 and N4d, assuming a single parabolic valence band with $m_{v1} = 1.0\ m_0$ together with two acceptor and one donor levels. They also assumed that $E_{npo}/E_{ac} = 2$. Their estimated values of N_{A1}, E_{A1}, N_{A2}, E_{A2}, N_D, $E_{ac}^{(v1)}$, and $E_{npo}^{(v1)}$ for #10 and N4d are also shown in parentheses in Table 2 and 3. The material constants used by them are shown in Table 1 in comparison with those used in the present analysis. Arushanov et al. [67,68] cited the values of the static and the high-frequency dielectric constants from Refs. [69] and [70], respectively, while calculated the longitudinal sound velocity by $v = (k_B\theta_D / \hbar)(V / 6\pi^2)^{1/3}$, where V is the average atomic volume. The Debye temperature was calculated using the relation of $k_B\theta_D = \langle\hbar\omega\rangle$ with the value of $\langle\hbar\omega\rangle$ = 55 meV obtained in Ref. [40] for describing the temperature dependence of the direct gap by Eq. (9).

The value used as the Debye temperature by Arushanov et al. [67,68] is not so different from that used in the present study which was estimated from analysis of specific heat by Waldecker et al. [53] On the other hand, the values used by Arushanov et al. [67,68] for the static and the high-frequency dielectric constants as well as that for the longitudinal sound velocity are significantly different from those used in the present analysis. Although Arushanov et al. [67,68] used the value calculated by the formula of $v = (k_B\theta_D / \hbar)(V / 6\pi^2)^{1/3}$ as the longitudinal sound velocity, the formula is not for estimating the longitudinal sound velocity but for estimating the average sound velocity defined as $v_{av} = [(1/3)(2/v_t^3 + 1/v_l^3)]^{-1/3}$, where v_t denotes the transverse sound velocity which is about 0.6 times of the longitudinal sound velocity v_l [52]. Tassis et al. [14] estimated the high-frequency dielectric constants by fitting the low energy part of reflectance and transmittance spectra of their six thin film samples to show that ε_∞ is in the range of 18-23 ε_0. Our used value of $\varepsilon_\infty = 18.7\varepsilon_0$ is within this range while that used by Arushanov et al. [67,68] is out of this range. Filonov et al. [71] estimated ε_s to be 26.8 ε_0. This value is near to our adopted value of $\varepsilon_s = 29.9\ \varepsilon_0$. Suzuno et al. [72] also adopted the values of $\varepsilon_s = 29.9\ \varepsilon_0$ and $\varepsilon_\infty = 23\ \varepsilon_0$ rather than $\varepsilon_s = 61.1\varepsilon_0$ and $\varepsilon_\infty = 12\varepsilon_0$ for calculating mobility in p-type β-$FeSi_2$.

Figures 4(a-c), 5(a-c), and, 6(a-c) show the comparison of the simulated results (solid lines) with the experimental data (closed circles, open triangles, and closed diamonds) of the samples: (a) shows the conductivity as a function of $T^{-1/2}$; (b) and (c) respectively show the Hall mobility and the Hall coefficient as a function of the temperature. Figures 4, 5, and 6 show the plots for #10, N4d, and To7, respectively. Also shown by solid lines of yellow and violet are the contributions from ES VRH and NNH in the impurity band, respectively, and shown by solid lines of green and red are those from free-hole conduction in the 1st ($v1$) and the 2nd ($v2$) valence band, respectively.

In Refs. [68] and [67], respectively, Arushanov et al. calculated μ_{v1} for #10 and N4d using the material parameters shown in the third column in Table 1 together with the values of fitting parameters shown in the parentheses in Table 2 and 3. They calculated μ_{v1} using Mathiesen's approximation $\mu_{v1}^{-1} = \mu_{ii}^{-1} + \mu_{ac}^{-1} + \mu_{npo}^{-1} + \mu_{po}^{-1} + \mu_{sc}^{-1}$, where μ_{ii}, μ_{ac}, μ_{npo}, μ_{po}, and μ_{sc} are the mobilities due to scattering by ionized impurities, acoustic phonons, nonpolar optical phonons, polar optical phonons, and space charge, respectively. Their calculation methods for μ_{npo}, μ_{po}, and μ_{sc} are different from those in the present study. They did not include the Hall factor and took into account only the 1st valence band without the effects of the 2nd conduction band and the impurity band. Their calculated results of μ_{v1} for #10 and N4d are shown by broken curves in Figs. 4(b) and 5(b), respectively.

In Fig. 4(a), it can be seen for #10 that the contribution from the $v1$ band dominates the conductivity in the temperature range of 50-80 K while the contributions from the $v2$ and ES VRH become dominant above and below this temperature range, respectively. A similar transition of the dominant contribution can be seen for the Hall mobility as well, as can be seen in Fig. 4(b). In particular, the steep increase of the Hall mobility with increasing temperature around 50 K is attributed to the transition from ES-VRH conduction to free-hole conduction. As expected from the two-band model, the Hall coefficient shows its peak at 50 K at which $\sigma_{ib} = \sigma_{v1}$ is satisfied, as shown in Fig. 4(c).

For N4d and To7, although the contribution from NNH conduction to the conductivity is not significant, as can be seen in Figs. 5(a) and 6(a), that to the Hall mobility and the Hall coefficient becomes significant in the intermediate temperature region between the ES-VRH dominant and the $v1$ conduction dominant region, as can be seen in Figs. 5(b,

c) and 6(b, c). This is due to the large values of A_{HNNH}. The calculated values of A_{Hv1}, A_{HNNH}, and A_{HES} are plotted by dotted curves of green, violet, and yellow, respectively, in Figs. 4(c), 5(c), and 6(c).

As can be seen in Fig. 6(b), the Hall mobility μ_H of To7 at its maximum is dominated not by the contribution from free-hole conduction in the $v1$ band but by that from NNH in the impurity band. This is due to the low value of μ_{Hv1} and the high value of μ_{HNNH} the latter of which is attributed to the very high value of A_{HNNH} as large as 2000 around 90 K.

Arushanov et al. [67] claimed that experimental data on Cr-doped single crystal p-type β-FeSi$_2$, including N4d, do not indicate the existence of an impurity band or the 2nd valence band. On the contrary, the data on N4d as well as those on #10 and have been well explained with assuming the existence of both an impurity band and the 2nd valence band in the present study.

It can be seen from the comparison of the present results with the results obtained by Arushanov et al. [67,68] in Table 2 that the obtained value of $N_{A1} - N_D$ in the present analysis is 25 and 150 times larger for #10 and N4d, respectively, than those obtained by Arushanov et al. [67,68] This is due to the primitive two-band model which Arushanov et al. used. In their two-band model analysis, Arushanov et al. [67,68] estimated the net concentration of the shallow acceptor level by $1/(eR_H) = N_{A1} - N_D$ using the data of R_H in the carrier-freezing region with assuming the Hall factors for the impurity conduction to be 1. In the present study, on the other hand, the Hall factor A_{HES} for ES VRH has been proved to be larger than 10 while the Hall factor A_{Hv1} for free-hole conduction in the $v1$ band has been proved to stay below 2, as can be seen in Figs. 4(c), 5(c), and 6(c). A_{HES} at 30 K is as large as 10, 200, and 500 for #10, N4d, and To7, respectively.

The large values of A_{HES} may be attributed in part to its strong dependence on magnetic field. For their another Cr-doped sample of N2d, Brehme et al. [16] showed that the Hall coefficient below 100 K increased about three times when the magnetic field was increased from 0.14 to 0.495 T. On the other hand, the dependence was reduced above 100 K and fell below the detection limit above 200 K. The strong magnetic-field dependence of R_H below 100 K can be attributed to that of A_{HES}. The $R_H(T)$ data for N4d and To7 analyzed in the present study were obtained in a magnetic field of 0.49 T. It is, therefore, expected that R_H of N4d and To7 below 100 K will also be decreased about 1/3 if measured in a decreased magnetic field of 0.14 T.

Arushanov et al. [67] further estimated the upper limit of N_D for N4d to be 1.4×10^{17} cm^{-3} with supposing $m_{v1} = 1.0\ m_0$ and $E_{A1} = 0$ meV. However, the assumption of $E_{A1} = 0$ meV is inconceivable because of the small screening effect arising from the low concentration of $N_{A1} - N_D$ in N4d, being different from the case of #Ga-2 having the high concentration of $N_{A1} - N_D$. On the other hand, our deduced value of $E_{A1} = 48$ meV for N4d is reasonable for the low concentration of $N_{A1} - N_D$ in N4d. Our deduced value of $N_D = 9 \times 10^{17}$ cm^{-3} for N4d is far beyond the upper limit of N_D estimated by Arushanov et al. [67]

Arushanov et al. [67,68] performed fitting to the mobility data by using Mathiesen's approximation $\mu_{v1}{}^{-1} = \mu_{ii}{}^{-1} + \mu_{ac}{}^{-1} + \mu_{npo}{}^{-1} + \mu_{po}{}^{-1} + \mu_{sc}{}^{-1}$, where μ_{ac} was calculated as

$$\mu_{ac} = \frac{(8\pi)^{1/2} e\hbar^4 \rho v_l{}^2}{3 m_{v1}{}^{5/2} E_{ac}{}^2 (k_B T)^{3/2}} \ , \qquad (11)$$

using $m_{v1} = 1.0\ m_0$ and $v_l = 4.994 \times 10^3$ cm/s in the 3rd column of Table 1. As a result, they obtained a value of $E_{ac} = 8$ eV for both of #10 and N4d. Eq. (11) with the use of this value of $E_{ac} = 8$ eV and the above values of m_{v1} and v_l yields $\mu_{ac} = 117$ cm^2/Vs at 300 K. On the other hand, Eq. (11) yields an approximately half the value, i.e., $\mu_{ac} = 57$ cm^2/Vs, at 300 K with the use of our deduced value of $E_{ac} = 22$ eV together with $m_{v1} = 0.9\ m_0$ and $v_l = 8.369 \times 10^3$ cm/s.

As shown in Table 2, $N_{SC}\sigma_{SC}$ (N_{SC} is the concentration of space-charge regions and σ_{SC} is their effective cross section) is estimated to be 10^4 cm^{-3} for N4d while it is estimated to be as large as 5.5×10^6 cm^{-3} for To7. In the previous studies on *n*-type GaAs [46] and InP [27], $N_{SC}\sigma_{SC}$ was estimated to be 10^4 cm^{-3} at most. Arushanov et al. [67] suggested the importance of the space-charge scattering in the low temperature region for N4d. On the contrary, it is shown for N4d in the present study that the Hall mobility at low temperatures is dominated not by the space-charge scattering but by hopping conduction and that the effect of the space-charge scattering is almost negligible. On the other hand, the low peak value of μ_{v1} of To7 at a high temperature is attributed to the large value of $N_{SC}\sigma_{SC}$. The space-charge regions may appear when the impurity concentrations or the stoichiometry between Fe and Si vary spatially owing to the inhomogeneity. The large difference of $N_{SC}\sigma_{SC}$ between N4d and To7 is speculated to be due to the difference in homogeneity.

Udono and Kikuma [20] measured the conductivity and the Hall coefficient of four samples (#Zn10-1, #Zn10-2, #Zn13, and #Zn21) of single crystal p-type β-FeSi$_2$ grown by the TGSG method using Zn solvent. Among the samples, the data in a wide temperature range of 10-700 K are available for #Zn10-1 and #Zn10-2 while only the data above 120 K are reported for #Zn13 and #Zn21. Both the samples of #Zn10-1 and #Zn10-2 showed similar data of $\sigma(T)$ and $R_H(T)$. Being different from their samples grown using Ga solvent, however, the $S(T)$ data have not been reported for these p-type samples grown using Zn solvent. The simultaneous fits to the $\sigma(T)$ and $R_H(T)$ data for sample #Zn10-2 reported in Ref. [20] have been performed using the values of the effective masses of holes and electrons obtained in the previous sections. The obtained values of fitting parameters for Sample #Zn10-2 are summarized in Table 2, 3, 4, 5, and 6.

Udono and Kikuma [20] analyzed their Hall-effect data to estimate the values of N_A and E_A within the conventional one-acceptor and one-compensating-donor model with assuming $N_D << N_A$, $A_{Hv1} = 1$, and $m_{v1} = 1.0\ m_0$. Their estimated values of N_A and E_A are also shown in parentheses in Table 2. It can be seen in Table 2 that E_{A2} obtained in the present study agrees with that obtained by Udono and Kikuma [20] while N_{A2} obtained in the present study becomes smaller owing to the addition of the shallow acceptor level.

Figures 7(a-c) show the comparison of the simulated results (solid lines) with the experimental data (crosses) of Sample #Zn10-2: (a) shows the conductivity as a function of the reciprocal temperature while (b) and (c) respectively show the Hall mobility and the Hall coefficient as a function of the temperature. The contributions from holes in the respective bands are also plotted by solid lines while those from electrons are plotted by broken lines.

It can be seen in Fig. 7(a) that, above the impurity-conduction dominant region, the conductivity is dominated not by the contribution from the $v1$ band but by that from the $v2$ band. A steep increase of the conductivity above 550 K is attributed to the onset of intrinsic conduction. The steep increase of the Hall mobility with increasing temperature around 100 K is attributed to the transition from impurity hopping conduction to free-hole conduction. On the other hand, the increases with decreasing temperature below 60

K of the Hall mobility and the Hall coefficient are both attributed to the temperature dependence of A_{HES}.

Udono and Kikuma [20] calculated the extrapolated hole concentration p_{ex} from their conductivity data by using the equation of $\sigma = e\, p_{ex}\mu_{Hex}$, where μ_{Hex} is the extrapolated Hall mobility derived from the relation of $\mu_H \propto T^{-\beta}$ with $\beta = 1.9$. Their calculated results of $1/(e\, p_{ex})$ are also plotted by open circles in Fig. 7(c). For the purpose of the comparison with p_{ex}, they calculated the intrinsic carrier concentration n_i by using

$$n_i = \sqrt{N_c N_v}\, \exp\left(-\frac{E_g(T)}{2k_B T} \right), \tag{12}$$

where $E_g(T)$ is calculated by Eq. (9). They calculated N_c and N_v with assuming $m_v = m_c = 1.0\, m_0$ and $M_v = M_c = 1$. As the energy gap E_g, they used the indirect exciton energy gap E_{gx} determined from their optical absorption measurement [12]. In Ref. [12], they obtained a value of 0.814 eV for the indirect exciton energy gap $E_{gx}(0)$ between the 1st CBM at the Λ^* point and the 1st VBM at the Y point. As a result, they find that p_{ex} agrees well with the calculated results of n_i above 500 K.

It should be noted, however, that the activation energy of the Hall carrier concentration $1/(eR_H)$ is not determined by the indirect energy gap E_{gx} but substantially by the direct energy gap $E_g^{d\Lambda} = E_{gx} + \Delta E_{v2}$ between the 1st CBM and the 2nd VBM at the Λ^* point since the contribution from the $v2$ band dominates the total Hall coefficient above 500 K rather than the $v1$ band, as can be seen in Fig. 7(c).

Through the simultaneous fits to the $\sigma(T)$ and $R_H(T)$ data in the present study, the indirect band gap $E_g(0)$ was estimated to be 0.84 eV. This value is near to the value obtained by Lang et al. [64]

6. Summary

Multi-band analyses have been performed for the temperature-dependence data of the conductivity, the Hall coefficient, and the Seebeck coefficient on six samples of bulk single crystal p-type β-FeSi$_2$. Among the six samples, four were grown by a CVT reaction using Cr as a p-type dopant while the other two were grown by a TGSG method using Ga or Zn as the solvent. The analysis results are summarized as follows:

(1) From the simultaneous fits to the $\sigma(T)$, $R_H(T)$, and $S(T)$ data of a p-type β-FeSi$_2$ sample reported by Udono et al. [21], the effective mass of holes at the 1st VBM has been estimated to be $m_{v1} = 0.9 \pm 0.2\ m_0$.

(2) Simultaneous fits to the $\sigma(T)$ and $R_H(T)$ data on all the four samples reported by Brehme et al. [15–17] and Udono et al. [20] have been well performed with common values of $m_{v1} = 0.9\ m_0$ and $m_{v2} = 1.9\ m_0$.

(3) It has been shown that the free-hole mobility in the low-mobility samples is limited by inhomogeneity while the temperature dependence of the free-hole mobility in the high-mobility samples is well described by considering ionized-impurity scattering, acoustic-phonon scattering, polar-optical-phonon scattering, and nonpolar-optical-phonon scattering.

(4) It has been shown that contributions to σ, R_H, and S from holes in the $v2$ band are significant at higher temperatures than 200 K. The separation between the 1st and the 2nd VBM has been estimated to be in the range of ΔE_{v2} = 15-35 meV.

(5) By including the temperature dependence of the Hall factor for impurity hopping conduction, impurity concentrations have been significantly corrected from those previously estimated in a simple two-band model.

(6) Through the simultaneous fits to the $\sigma(T)$ and $S(T)$ data on a p-type β-FeSi$_2$ sample in the wide temperature range of 4.2-1070 K reported by Heinrich et al. [7], the effective mass of electrons at the 1st CBM has been estimated to be $m_{c1} = 1.3\ m_0$ while that at the 2nd CBM has been estimated to be larger than 100 m_0. The indirect gap at 0 K between the 1st VBM at the Y point and the 1st CBM at the Λ^* point was estimated to be $E_g(0)$ = 0.84-0.9 eV through the fits to the data at high temperatures reported by Udono et al. [20] and Heinrich et al. [7] The strong temperature dependence of the Seebeck coefficient below 150 K has been reproduced by including the effect of the impurity band conduction without the phonon-drag effect.

In conclusion, the more reliable interpretation has been presented for the published data of $\sigma(T)$, $R_H(T)$, and $S(T)$ on the samples of p-type doped bulk single crystal β-FeSi$_2$ through the reassessment on the basis of the multi-band model. In particular, the effects of the impurity band, the 2nd VBM, and the 2nd CBM have been clarified.

Appendix A: Formulae for calculating relaxation times

The relaxation times, τ_{ac}, τ_{npo}, and τ_{sc} due to acoustic-phonon scattering, nonpolar-optical-phonon scattering, and space-charge scattering can be calculated respectively according to expressions:

$$\frac{1}{\tau_{ac}} = \frac{\left(2m^*\right)^{3/2} E_{ac}{}^2 k_B T}{2\pi\hbar^4 \rho v_l{}^2} E^{1/2}, \tag{A1}$$

$$\frac{1}{\tau_{npo}} = \frac{1}{2}\left(\frac{E_{npo}}{E_{ac}}\right)^2 \frac{\theta_D}{T}\left(e^{\theta_D/T}-1\right)^{-1} \times \left[\left(1+\frac{k_B\theta_D}{E}\right)^{1/2} + e^{\theta_D/T}\left(1-\frac{k_B\theta_D}{E}\right)^{1/2}\right]\frac{1}{\tau_{ac}}, \tag{A2}$$

$$\frac{1}{\tau_{ac}} = \left(\frac{2}{m^*}\right)^{1/2} N_{SC}\sigma_{SC}E^{1/2}, \tag{A3}$$

where ρ is the mass density, E_{ac} is the acoustic-phonon deformation potential constant, and E_{npo} is the nonpolar-optical-phonon deformation potential constant. The 2nd term in the square bracket of Eq. (A2) is present only if $E > k_B\theta_D$.

The relaxation times τ_{ii} due to ionized-impurity scattering can be calculated as

$$\frac{1}{\tau_{ii}} = \frac{\pi N_{ii}}{\left(2m^*\right)^{1/2}}\left(\frac{e^2}{4\pi\varepsilon_s}\right)^2 B_{ii}(\zeta_s)E^{-3/2}, \tag{A4}$$

where $N_{ii} = N_{A1}^- + N_{A2}^- + N_D$ is the concentration of ionized impurities. The screening function $B_{ii}(\zeta_s)$ is defined as

$$B_{ii}(\zeta_s) = \ln(\zeta_s + 1) - \frac{\zeta_s}{\zeta_s + 1}, \tag{A5}$$

$$\zeta_s = (2k\lambda_s)^2 = \frac{2m^*E}{\hbar^2}(2\lambda_s)^2. \tag{A6}$$

The screening length λ_s can be written as

$$\frac{1}{\lambda_s{}^2} = \frac{1}{\sqrt{\pi}}\frac{e^2}{4\pi\varepsilon_s k_B T}\left(\frac{2m^* k_B T}{\hbar^2}\right)^{3/2} \cdot \mathscr{F}_{1/2}(\eta). \tag{A7}$$

The relaxation time τ_{po} due to polar-optical-phonon scattering can be calculated as

$$\frac{1}{\tau_{po}} = \frac{\alpha_F}{h} k_B\theta_D\left(e^{\theta_D/T}-1\right)^{-1} \quad \text{for } 5 \le \theta_D/T \tag{A8}$$

$$\frac{1}{\tau_{po}} = \frac{\alpha_F}{h}\frac{\left(k_B\theta_D\right)^{3/2}E^{-1/2}}{\chi(\theta_D/T)}\left(e^{\theta_D/T}-1\right)^{-1} \quad \text{for } 0 \le \theta_D/T \le 5 \tag{A9}$$

where

$$\chi(x) = 1 - 0.5841x + 0.2920x^2 - 0.037164x^3 + 0.0012016x^4 \tag{A10}$$

and α_F is the dimensionless Fröhlich coupling constant defined as

$$\alpha_F = \frac{e^2}{\hbar}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right)\left(\frac{m^*}{2k_B\theta_D}\right)^{1/2}. \qquad \text{(A11)}$$

α_F is calculated to be 0.3 for holes in the $v1$ band using the values in Table 1 with m_{v1} = 0.9 m_0. Kakemoto et al. [73] calculated it to be 0.92 using different values of the parameters. Although the value of $\alpha_F = 0.3$ is less than 1/3 of that calculated by Kakemoto et al., it is still much larger than those for III-V compound semiconductors, which are within the range of 0.023 - 0.126, while it is comparable with that for ZnSe, one of II-VI compound semiconductors, which has been estimated to be $\alpha_F = 0.575$ [74].

Appendix B: Estimation of the electron effective mass from the conductivity and the Seebeck coefficient in the intrinsic region of a *p*-type sample with a known hole effective mass

In order to simplify the problem, let us consider here only one conduction band with an effective mass m_c and one valence band with an effective mass m_v. Then, the total Seebeck coefficient in the intrinsic region can be expressed as $S = (\sigma_c/\sigma)S_c + (\sigma_v/\sigma)S_v$. The Seebeck coefficient can be expressed as $S_c = -(k_B/e)(r + 2 - \eta)$ and $S_v = (k_B/e)(r + 2 - \eta)$ for free electrons in the conduction band and for free holes in the valence band, respectively [75].

Furthermore, let us consider only acoustic phonon scattering as the scattering mechanism in the intrinsic region. For acoustic phonon scattering, $r = 0$. Therefore, the total Seebeck coefficient in the intrinsic region can be rewritten as $S = (k_B/e)(2 - \eta)(\sigma_v - \sigma_c)/\sigma$. This relation together with $\sigma = \sigma_c + \sigma_v$ yields $S = (k_B/e)(2 - \eta)(2\sigma_v/\sigma - 1)$.

One can therefore estimate η as $\eta = 2 - S(e/k_B)(2\sigma_v/\sigma - 1)^{-1}$ using the calculated value of σ_v together with the measured values of σ and S. Once η has been estimated, one can estimate the mass ratio m_c/m_v using the relation of $\eta = E_g/(2k_BT) - (3/4)\ln(m_c/m_v)$ with assuming a value for E_g. The value of E_g can easily be determined from the activation energy of σ. Therefore, one can estimate the value of m_c from the measured values of σ and S in the intrinsic region without the measured value of R_H if the values of

σ_v and m_v have been estimated in advance. σ_v can be calculated using the relaxation time τ_{ac} which is calculated by Eq. (A1) with the values of m_v, E_{ac}, and v_l.

References

[1] X. Du, P. Qiu, J. Chai, T. Mao, P. Hu, J. Yang, Y.-Y. Sun, X. Shi, L. Chen, Doubled thermoelectric figure of merit in p-type β-$FeSi_2$ via synergistically optimizing electrical and thermal transports, ACS Appl. Mater. Interfaces. 12 (2020) 12901–12909.

[2] S. Le Tonquesse, Z. Verastegui, H. Huynh, V. Dorcet, Q. Guo, V. Demange, C. Prestipino, D. Berthebaud, T. Mori, M. Pasturel, Magnesioreduction synthesis of Co-doped β-$FeSi_2$: Mechanism, microstructure, and improved thermoelectric properties, ACS Appl. Energy Mater. 2 (2019) 8525-8534.

[3] T. Taniguchi, S. Sakane, S. Aoki, R. Okuhata, T. Ishibe, K. Watanabe, T. Suzuki, T. Fujita, K. Sawano, Y. Nakamura, Thermoelectric properties of epitaxial β-$FeSi_2$ thin films on Si(111) and approach for their enhancement, J. Electron. Mater. 46 (2017) 3235-3241.

[4] N.M. Liu, S.E. Rezaei, W.A. Jensen, S.W. Song, Z.F. Ren, K. Esfarjani, M. Zebarjadi, J.A. Floro, Improved thermoelectric performance of eco-friendly beta-$FeSi_2$-SiGe nanocomposite via synergistic hierarchical structuring, phase percolation, and selective doping, Adv. Funct. Mater. 29 (2019) 1903157.

[5] S. Sakane, T. Ishibe, T. Hinakawa, N. Naruse, Y. Mera, M. Mahfuz Alam, K. Sawano, Y. Nakamura, High thermoelectric performance in high crystallinity epitaxial Si films containing silicide nanodots with low thermal conductivity, Appl. Phys. Lett. 115 (2019) 182104.

[6] S. Sakane, T. Ishibe, T. Taniguchi, T. Hinakawa, R. Hosoda, K. Mizuta, M.M. Alam, K. Sawano, Y. Nakamura, Nanostructural effect on thermoelectric properties in Si films containing iron silicide nanodots, Jpn. J. Appl. Phys. 59 (2020) Sffb01.

[7] A. Heinrich, C. Gladun, A. Burkov, Y. Tomm, S. Brehme, H. Lange, Thermopower and electrical resistivity of beta-$FeSi_2$ single crystals doped with Cr, Co, and Mn, in: 14th Int.Conf. Thermoelectr., St. Petersburg, 1995: pp. 259–263.

[8] M.I. Fedorov, V.K. Zaitsev, Y. V Ivanov, V. V Popov, M.A. Khazan, Drag effects in beta-iron disilicide, in: 16th Int. Conf. Thermoelectr., 1997: pp. 291–294.

[9] M.I. Fedorov, Y. V Ivanov, M. V Vedernikov, V.K. Zaitsev, Iron disilicide as a base for new improved thermoelectrics creation, MRS Proc. 545 (1998) 155.

[10] M.I. Fedorov, V. V Popov, I.S. Eremin, V.K. Zaitsev, Kinetic coefficients of the semiconducting phase of $FeSi_2$ at low temperatures, Phys. Solid State. 42 (2000) 1236–1239.

[11] M.I. Fedorov, G.N. Isachenko, Silicides: Materials for thermoelectric energy conversion, Jpn. J. Appl. Phys. 54 (2014) 07JA05.

[12] H. Udono, I. Kikuma, T. Okuno, Y. Masumoto, H. Tajima, S. Komuro, Optical properties of beta-$FeSi_2$ single crystals grown from solutions, Thin Solid Films. 461 (2004) 182–187.

[13] E. Arushanov, C. Kloc, E. Bucher, Impurity band in p-type beta-$FeSi_2$, Phys. Rev. B. 50 (1994) 2653–2656.

[14] D.H. Tassis, C.L. Mitsas, T.T. Zorba, M. Angelakeris, C.A. Dimitriadis, O. Valassiades, D.I. Siapkas, G. Kiriakidis, Optical and electrical characterization of high quality beta-$FeSi_2$ thin films grown by solid phase epitaxy, Appl. Surf. Sci. 102 (1996) 178–183.

[15] W. Henrion, S. Brehme, I. Sieber, H. von Känel, Y. Tomm, H. Lange, Optical and electrical properties of iron disilicide with different degree of structural perfection, Solid State Phenom. 51–52 (1996) 341–346.

[16] S. Brehme, K. Ivanenko, Y. Tomm, G.-U. Reinsperger, P. Stauss, H. Lange, Hall effect investigation of doped and undoped beta-$FeSi_2$, Mat. Res. Soc. Symp. Proc. 402 (1996) 355–360.

[17] S. Brehme, P. Lengsfeld, P. Stauss, H. Lange, W. Fuhs, Hall effect and resistivity of beta-$FeSi_2$ thin films and single crystals, J. Appl. Phys. 84 (1998) 3187–3196.

[18] A. Heinrich, H. Griessmann, G. Behr, K. Ivanenko, J. Schumann, H. Vinzelberg, Thermoelectric properties of beta-FeSi$_2$ single crystals and polycrystalline beta-FeSi$_{2+x}$ thin films, Thin Solid Films. 381 (2001) 287–295.

[19] Y. Murakami, Y. Tsukahara, A. Kenjo, T. Sadoh, Y. Maeda, M. Miyao, Impurity conduction in ion beam synthesized beta-FeSi$_2$/Si, Thin Solid Films. 461 (2004) 198–201.

[20] H. Udono, I. Kikuma, Electrical properties of p-type beta-FeSi$_2$ single crystals grown from Ga and Zn solvents, Thin Solid Films. 461 (2004) 188–192.

[21] H. Udono, H. Suzuki, K. Goto, S. Mashiko, M. Uchikoshi, M. Issiki, Solution growth and low-temperature thermoelectric properties of single crystalline beta-FeSi$_2$, in: Proc. Ict 07 Twenty-Sixth Int. Conf. Thermoelectr., 2008: pp. 241–244.

[22] Y. Kajikawa, Multi-band analysis of thermoelectric properties of n-type Co$_{1-x}$Ni$_x$Sb$_3$ ($0 \leq x \leq 0.01$) over a wide temperature range of 10-773 K, J. Alloys Compd. 664 (2016) 338-350.

[23] S.J. Clark, H.M. Al-Allak, S. Brand, R.A. Abram, Structure and electronic properties of FeSi$_2$, Phys. Rev. B. 58 (1998) 10389–10393.

[24] L. Miglio, V. Meregalli, O. Jepsen, Strain dependent gap nature of epitaxial beta-FeSi$_2$ in silicon by first principles calculations, Appl. Phys. Lett. 75 (1999) 385–387.

[25] D.B. Migas, L. Miglio, Band-gap modifications of beta-FeSi$_2$ with lattice distortions corresponding to the epitaxial relationships on Si(111), Phys. Rev. B. 62 (2000) 11063–11070.

[26] K. Yamaguchi, K. Mizushima, Luminescent FeSi$_2$ crystal structures induced by heteroepitaxial stress on Si(111), Phys. Rev. Lett. 86 (2001) 6006–6009.

[27] Y. Kajikawa, Significant effects of the D$^-$ band on the Hall coefficient and the Hall mobility of n-InP, Phys. Status Solidi B-Basic Solid State Phys. 257 (2019) 1900354.

[28] L. Friedman, T. Holstein, Studies of polaron motion, Ann. Phys. 21 (1963) 494.

[29] P. Nagels, Hall effect for small polaron LiNbO$_3$, in: C.L. Chien, C.R. Westgate (Eds.), Hall Eff. Its Appl., Plenum, NewYork, 1980: pp. 253–280.

[30] H. Böttger, V. V Bryksin, Hopping Conduction in Solids, Akademie-Verlag, Berlin, 1985.

[31] E.G. Moroni, W. Wolf, J. Hafner, R. Podloucky, Cohesive, structural, and electronic properties of Fe-Si compounds, Phys. Rev. B. 59 (1999) 12860–12871.

[32] D.B. Migas, L. Miglio, W. Henrion, M. Rebien, F. Marabelli, B.A. Cook, V.L. Shaposhnikov, V.E. Borisenko, Electronic and optical properties of isostructural beta-FeSi$_2$ and OsSi$_2$, Phys. Rev. B. 64 (2001) 75208.

[33] J.I. Tani, H. Kido, Electronic structure of beta-Fe(Si$_{2-x}$Ge$_x$) ternaries, J. Solid State Chem. 169 (2002) 19–23.

[34] Z.J. Pan, L.T. Zhang, J.S. Wu, First-principles study of electronic and geometrical structures of semiconducting beta-FeSi$_2$ with doping, Mater. Sci. Eng. B-Solid State Mater. Adv. Technol. 131 (2006) 121–126.

[35] J. Chai, C. Ming, X.L. Du, P.F. Qiu, Y.Y. Sun, L.D. Chen, Thermodynamics, kinetics and electronic properties of point defects in beta-FeSi$_2$, Phys. Chem. Chem. Phys. 21 (2019) 10497–10504.

[36] S. Eisebitt, J.E. Rubensson, M. Nicodemus, T. Boske, S. Blugel, W. Eberhardt, K. Radermacher, S. Mantl, G. Bihlmayer, Electronic-structure of buried alpha-FeSi$_2$ and beta-FeSi$_2$ layers - soft-X-ray emission and absorption studies compared to band-structure calculations, Phys. Rev. B. 50 (1994) 18330–18340.

[37] A.B. Filonov, D.B. Migas, V.L. Shaposhnikov, N.N. Dorozhkin, G. V Petrov, V.E. Borisenko, W. Henrion, H. Lange, Electronic and related properties of crystalline semiconducting iron disilicide, J. Appl. Phys. 79 (1996) 7708–7712.

[38] A.B. Filonov, V.E. Borisenko, W. Henrion, H. Lange, Electronic and optical properties of semiconducting iron disilicide, J. Lumin. 80 (1999) 479–484.

[39] C. Giannini, S. Lagomarsino, F. Scarinci, P. Castrucci, Nature of the band-gap ofpolycrystalline beta-FeSi$_2$ films, Phys. Rev. B. 45 (1992) 8822–8824.

[40] E. Arushanov, E. Bucher, C. Kloc, O. Kulikova, L. Kulyuk, A. Siminel, Photoconductivity in n-type beta-FeSi$_2$ single-crystals, Phys. Rev. B. 52 (1995) 20–23.

[41] A.G. Birdwell, T.J. Shaffner, D. Chandler-Horowitz, G.H. Buh, M. Rebien, W. Henrion, P. Stauss, G. Behr, L. Malikova, F.H. Pollak, C.L. Littler, R. Glosser, S. Collins, Excitonic transitions in beta-$FeSi_2$ epitaxial films and single crystals, J. Appl. Phys. 95 (2004) 2441–2447.

[42] C.A. Dimitriadis, J.H. Werner, S. Logothetidis, M. Stutzmann, J. Weber, R. Nesper, Electronic-properties of semiconducting $FeSi_2$ films, J. Appl. Phys. 68 (1990) 1726–1734.

[43] D.J. Oostra, C.W.T. Bullelieuwma, D.E.W. Vandenhoudt, F. Felten, J.C. Jans, Beta-$FeSi_2$ in (111)Si and in (001)Si formed by ion-beam synthesis, J. Appl. Phys. 74 (1993) 4347–4353.

[44] A.B. Filonov, I.E. Tralle, D.B. Migas, V.L. Shaposhnikov, V.E. Borisenko, Transport property simulation of p-type beta-$FeSi_2$, Phys. Status Solidi B-Basic Solid State Phys. 203 (1997) 183–187.

[45] K. Takakura, T. Suemasu, Y. Ikura, F. Hasegawa, Control of the conduction type of nondoped high mobility beta-$FeSi_2$ films grown from Si/Fe multilayers by change of Si/Fe ratios, Jpn. J. Appl. Phys. Part 2-Letters. 39 (2000) L789–L791.

[46] Y. Kajikawa, Reappraisal of conduction and Hall effect due to impurity Hubbard bands in weakly compensated n-GaAs, Phys. Status Solidi B-Basic Solid State Phys. 255 (2018) 1800063.

[47] K. Takakura, H. Ohyama, K. Takarabe, T. Suemasu, F. Hasegawa, Hole mobility of p-type beta-$FeSi_2$ thin films grown from Si/Fe multilayers, J. Appl. Phys. 97 (2005) 93716.

[48] X.J. Zhang, Y.L. Yan, Y.X. Wang, Large anisotropy of electrical conductivity induced high thermoelectric performance of p-type $CrSi_2$, J. Alloy. Compd. 581 (2013) 413–417.

[49] D.C. Look, Electrical Characterization of GaAs Materials and Devices, Wiley, New York, 1989.

[50] H. Kakemoto, Y. Makita, S. Sakuragi, T. Tsukamoto, Synthesis and properties of semiconducting iron disilicide beta-$FeSi_2$, Jpn. J. Appl. Phys. Part 1-Regular Pap. Short Notes Rev. Pap. 38 (1999) 5192–5199.

[51] C. Stuhlmann, J. Schmidt, H. Ibach, Semiconducting iron disilicide films on Si(111) - A high-resolution electron-energyloss spectroscopy study, J. Appl. Phys. 72 (1992) 5905–5911.

[52] J. Tani, M. Takahashi, H. Kido, First-principles calculations of the structural and elastic properties of beta-$FeSi_2$ at high-pressure, Intermetallics. 18 (2010) 1222–1227.

[53] G. Waldecker, H. Meinhold, U. Birkholz, Thermal conductivity of semiconducting and metallic $FeSi_2$, Phys. Status Solidi. 15 (1973) 143–149.

[54] S. Abboudy, Estimation of the effective dielectric response from hopping activation energy in the vicinity of insulator-metal transition in semiconductors, Int. J. Mod. Phys. B. 10 (1996) 59–65.

[55] N.A. Poklonski, S.A. Vyrko, A.G. Zabrodskii, Electrostatic models of insulator-metal and metal-insulator concentration phase transitions in Ge and Si crystals doped by hydrogen-like impurities, Phys. Solid State. 46 (2004) 1101–1106.

[56] Y. Kajikawa, Analysis of high-temperature thermoelectric properties of p-type $CoSb_3$ within a two-valence-band and two-conduction-band model, J. Appl. Phys. 115 (2014) 203716.

[57] Y. Kajikawa, Refined analysis of the transport properties of $Co_{1-x}Ni_xSb_3$ according to a model including a deep donor level and the second lowest valleys of the conduction band, J. Alloys Compd. 621 (2015) 170.

[58] H. Suzuki, H. Udono, I. Kikuma, Thermoelectric properties of solution grown beta-$FeSi_2$ single crystals, Mater. Trans. 47 (2006) 1428–1431.

[59] E. Arushanov, K.G. Lisunov, H. Vinzelberg, G. Behr, J. Schumann, O.G. Schmidt, Hopping conductivity in Mn-doped beta-$FeSi_2$ single crystals, J. Appl. Phys. 104 (2008) 053720.

[60] L. Martinelli, E. Grilli, D.B. Migas, L. Miglio, F. Marabelli, C. Soci, M. Geddo, M.G. Grimaldi, C. Spinella, Luminescence from beta-$FeSi_2$ precipitates in Si. II: Origin and nature of the photoluminescence, Phys. Rev. B. 66 (2002) 85320.

[61] J.S. Dyck, W. Chen, J.H. Yang, G.P. Meisner, C. Uher, Effect of Ni on the transport and magnetic properties of $Co_{1-x}Ni_xSb_3$, Phys. Rev. B. 65 (2002) 115204.

[62] A. Heinrich, A. Burkov, C. Gladun, G. Behr, K. Herz, J. Schumann, H. Powalla, Thermopower and electrical resistivity of beta-$FeSi_2$ single crystals and polycrystalline beta-$FeSi_{2+x}$ thin films, in: 15th Int.Conf. Thermoelectr., Pasadena, 1996: pp. 57–61.

[63] H. Udono, I. Kikuma, T. Okuno, Y. Masumoto, H. Tajima, Indirect optical absorption of single crystalline beta-$FeSi_2$, Appl. Phys. Lett. 85 (2004) 1937–1939.

[64] R. Lang, L. Amaral, E.A. Meneses, Indirect optical absorption and origin of the emission from beta-$FeSi_2$ nanoparticles: Bound exciton (0.809 eV) and band to acceptor impurity (0.795 eV) transitions, J. Appl. Phys. 107 (2010) 103508.

[65] E. Arushanov, C. Kloc, H. Hohl, E. Bucher, The Hall-effect in beta-$FeSi_2$ single-crystals, J. Appl. Phys. 75 (1994) 5106–5109.

[66] E. Arushanov, M. Respaud, J.M. Broto, C. Kloc, J. Leotin, E. Bucher, Magnetic properties of beta-$FeSi_2$ single crystals, Phys. Rev. B. 53 (1996) 5108–5111.

[67] E. Arushanov, Y. Tomm, L. Ivanenko, H. Lange, Hole mobility in Cr-doped p-type beta-$FeSi_2$ single crystals, Phys. Status Solidi B-Basic Solid State Phys. 210 (1998) 187–194.

[68] E. Arushanov, J.H. Schon, H. Lange, Transport properties of Cr-doped beta-$FeSi_2$, Thin Solid Films. 381 (2001) 282–286.

[69] U. Birkholz, H. Finkenrath, J. Nagele, N. Uhle, Infrared reflectivity of semiconducting $FeSi_2$, Phys. Stat. Sol. 30 (1968) K81.

[70] A. Borghesi, A. Piaggi, A. Stella, G. Guizetti, G. Nava, G. Santoro, Optical and vibrational properties of Cr and Fe disilicides, in: E.M. Anastassakis, J.D. Joannopoulos (Eds.), Proc. 20th Int. Conf. Phys. Semicond., World Scientific, Singapore, 1990: p. 2001.

[71] A.B. Filonov, D.B. Migas, V.L. Shaposhnikov, V.E. Borisenko, W. Henrion, M. Rebien, P. Stauss, H. Lange, G. Behr, Theoretical and experimental study of interband optical transitions in semiconducting iron disilicide, J. Appl. Phys. 83 (1998) 4410–4414.

[72] M. Suzuno, Y. Ugajin, S. Murase, T. Suemasu, M. Uchikoshi, M. Isshiki, Effect of using a high-purity Fe source on the transport properties of p-type beta-$FeSi_2$ grown by molecular-beam epitaxy, J. Appl. Phys. 102 (2007) 103706.

[73] H. Kakemoto, Y. Makita, Y. Kino, S. Sakuragi, T. Tsukamoto, Small polaron of beta-$FeSi_2$ obtained from optical measurements, Thin Solid Films. 381 (2001) 251–255.

[74] T. Ohyama, K. Sakakibara, E. Otsuka, M. Isshiki, K. Igaki, Cyclotron-resonance studies of electronic-properties in ZnSe, Phys. Rev. B. 37 (1988) 6153–6163.

[75] B.M. Askerov, Electron Transport Phenomena in Semiconductors, World Scientific, 1994.

Table 1

Material parameters.

Parameter	Present study	Arushanov et al. [68]
Mass density ρ (g/cm^3)	4.93	4.93
Static dielectric constant ε_s	$29.9\varepsilon_0$ [50]	$61.6\varepsilon_0$
High-frequency dielectric constant ε_∞	$18.7\varepsilon_0$ [51]	$12\varepsilon_0$
Longitudinal sound velocity v_l (10^5 cm/s)	8.369 [52]	4.994
Debye temperature θ_D (K)	630 [53]	640

Table 2

Values of parameters related to impurities. Values estimated for #10, N4d, and #Zn10-2 in Refs. [68], [67], and [20], respectively, are shown in parentheses.

Sample	#Ga-2	Cr 0.5%	#10	N4d	To7	#Zn10-2
Dopant or solvent	Ga	Cr	Cr	Cr	Cr	Zn
$N_{A1} - N_D$ (10^{18} cm^{-3})	60	1.8	0.05 (0.002)	0.3 (0.002)	1.0	0.08
N_{A1} (10^{18} cm^{-3})	70	2.9	0.09 (0.01)	1.2 (0.142)	3.6	1.05
N_D (10^{18} cm^{-3})	10	1.1	0.04 (0.008)	0.9 (0.14)	2.6	0.97
$K = N_D/N_{A1}$	0.14	0.38	0.44 (0.8)	0.75 (0.99)	0.72	0.92
N_{A2} (10^{18} cm^{-3})		8	100 (130)	150 (290)	80	0.7 (1.2)
N_{NAcr} (10^{18} cm^{-3})	90					
E_{A1} (meV)	8.5	72	35 (30)	48 (0)	54	54
E_{A2} (meV)		85	84 (85)	116 (144)	100	123 (123)
$\mu_{0\mathrm{ES}}$ (cm^2/Vs)	0.08	0.6	18	1.4	0.19	1.0
T_{ES} (K)	60	200	70	35	90	100
ν_{ES}	0.8		0.8	0.92	1.1	-1
A_{0HES}	270		5.5	140	300	1
μ_{03} (cm^2/Vs)				0.7	0.08	1
E_3 (meV)				24	22	17
I_{H3} (meV)				0.04	0.02	1.0
$N_{SC}\sigma_{SC}$ (10^5 cm^{-1})	23	4	0.1	0.1	50	8

Table 3

Values of parameters related to the 1st VBM.

Sample	#Ga-2	Cr 0.5%	#10	N4d	To7	#Zn10-2
m_{v1}/m_0	0.9	0.9	0.9	0.9	0.9	0.9
			(1.0)	(1.0)		(1.0)
E_{ac} (eV)	22	22	22	22	22	22
			(8)	(8)		
E_{npo} (eV)	60	60	60	60	60	25
			(16)	(16)		

Table 4

Values of parameters related to the 2nd VBM.

Sample	#Ga-2	Cr 0.5%	#10	N4d	To7	#Zn10-2
m_{v2}/m_0	1.9	1.9	1.9	1.9	1.9	1.9
ΔE_{v2} (meV)	23	35	20	25	15	15
E_{ac} (eV)	2	2	2	2	2	2
E_{npo} (eV)	15	25	25	25	50	15

Table 5

Values of parameters related to the 1st CBM.

Sample	Cr 0.5%	#Zn10-2
m_{c1}/m_0	1.3	1.3
$E_g(0)$ (eV)	0.9	0.84
$E_{ac}^{(c1)}$ (eV)	1.8	13

Table 6

Values of parameters related to the 2nd CBM.

Sample	Cr 0.5%	#Zn10-2
m_{c2}/m_0	240	120
$\Delta E_{c2}(0)$ (meV)	20	20
$E_{ac}^{(c2)}$ (eV)	1	1

Figure captions

Fig. 1. Sketch map of the band diagram of β-FeSi$_2$ assumed for the present analysis.

Fig. 2. Comparison of the simulated curves (solid lines) for the temperature dependence of (a) the electrical conductivity σ, (b) the Hall mobility μ_H, (c) the Hall coefficient R_H, and (d) the Seebeck coefficient S with the experimental data (open circles) for #Ga-2 of Ref. [21]. The calculated results of the contributions from the impurity band (*ib*), the fist VBM (*v*1), and the 2nd VBM (*v*2) are also plotted by yellow, green, and red lines, respectively.

Fig. 3. Comparison of the simulated curves (solid lines) for the temperature dependence of (a) the electrical conductivity σ and (b) the Seebeck coefficient S with the experimental data (open circles) for the sample of Ref. [18]. The inset in (a) shows the expanded plot for the high temperature region. The calculated results of the contributions from carriers in the impurity band (*ib*), the fist VBM (*v*1), and the 2nd VBM (*v*2) are also plotted by solid lines of yellow, green, and red, respectively, while those from electrons in the 1st CBM (*c*1) and the 2nd CBM (*c*2) are plotted by dotted lines of green and red, respectively.

Fig. 4. Comparison of the simulated curves (solid lines) for the temperature dependence of (a) the electrical conductivity σ, (b) the Hall mobility μ_H, and (c) the Hall coefficient R_H with the experimental data (closed circles) for #10 of Ref. [17]. The calculated results of the contributions from the respective bands are also plotted by solid lines. The dotted curves of green and yellow in (c) represents the calculated results of A_{Hv1} and $A_{H\mathrm{ES}}$, respectively. A broken curve in (b) shows the calculated results of μ_{c1} by Arushanov et al.

Fig. 5. The same as Fig. 4 but for N4d of Ref. [16]. The dotted curves of green, violet, and yellow in (c) represents the calculated results of A_{Hv1}, $A_{H\mathrm{NNH}}$, and $A_{H\mathrm{ES}}$, respectively.

Fig. 6. The same as Fig. 5 but for To7 of Ref. [15].

Fig. 7. Comparison of the simulated curves (solid lines) for the temperature dependence of (a) the electrical conductivity σ, (b) the Hall mobility μ_H, and (c) the Hall coefficient $|R_H|$ and the Hall factor with the experimental data (crosses) for #Zn10-2 of Ref. [20]. The calculated results of the contributions from ES VRH, NNH, the fist VBM (*v*1), and the 2nd VBM (*v*2) are also plotted by solid lines of yellow, violet, green, and red, respectively, while those from electrons in the 1st CBM (*c*1) and the 2nd CBM (*c*2) are

plotted by broken lines of green and red, respectively. The inset in (a) shows the expanded plot for the high temperature region. Open circles in (c) represent the calculated results of $1/(e\, p_{ex})$ by Udono and Kikuma [20].