

Impurity band in p -type β -FeSi₂

E. Arushanov,* Ch. Kloc, and E. Bucher

Faculty of Physics, University of Konstanz, P.O. Box 5560, D-78434 Konstanz, Germany

(Received 17 February 1994)

The results of transport measurements on p -type β -FeSi₂ single crystals in the temperature range of 30–300 K are presented and explained assuming the existence of an impurity band and an additional deep acceptor level. The values of the activation energies of the shallow and deep acceptors, their concentrations, as well as the concentration of the compensating donors and the density-of-states effective hole mass were calculated.

β -FeSi₂ has received considerable attention as a very attractive material for light detectors and photovoltaic applications,¹ and for the development of new optoelectronic devices.² Transport phenomena measurements were carried out on p -type β -FeSi₂ polycrystalline sintered samples³ and on thin films,^{4–7} and the temperature dependencies of the Hall coefficient, conductivity, and Hall mobility were determined.^{3–7}

The observed variation of the Hall voltage on magnetic field was explained in assuming that β -FeSi₂ behaves as a ferromagnetic material below 100 K.⁵ To explain the temperature dependence of the normal Hall coefficient, a two-valence band model was proposed.⁵ The separation between the valence bands was estimated to be equal to 1 meV.

A maximum value of the Hall mobility of up to 4 cm²/V s at 300 K,⁶ and up to 25–50 cm²/V s at low temperature,^{6,7} was obtained.

The observed and expected low mobilities lead to the conclusion that electronic applications of β -FeSi₂ are limited.^{4–6} It was also assumed that improved sample preparation could not increase the mobilities, because the low mobilities observed are caused by an unusually strong electron-phonon scattering in the band-edge states.⁸

We report results of transport measurements on p -type β -FeSi₂ single crystals. The importance of growing and measuring the properties of β -FeSi₂ single crystals lies in the possibility of obtaining more reliable data about the physical properties of the material of interest and its parameters. Our experimental results are discussed assuming the existence of an impurity band in the samples investigated.

β -FeSi₂ needlelike single crystals were grown by chemical vapor transport using iodine as a transport agent. The as-grown crystals showed n -type conductivity. To change the conductivity type from n - to p -type, aluminum was used as a doping agent.

The resistivity ρ and Hall coefficient R were measured in the temperature range from 30 to 300 K in dc magnetic fields, H up to 6600 Oe. The samples studied were both as-grown single crystals and crystals etched in a solution of HF:HNO₃:H₂O (1:1:20) for 1 min. The contacts were made by soldering with In. The results ob-

tained do not depend on the character of the surface treatment.

The $R(1/T)$ temperature dependence shows an exponential growth with decreasing temperature and a well-pronounced maximum at low temperatures (Fig. 1) which is a characteristic sign of the presence of a conduction in a band formed by shallow impurity levels.^{9–12} The decrease of the shallow-impurity concentration leads to an increase of the magnitude of the Hall coefficient maximum R_{\max} and its shift to lower temperatures. However, it is worth mentioning that the value of R_f , the smallest value of R at low temperatures ($p_f = 1/eR_f$ is the concentration of holes in the impurity band in the carrier freezing region) is much less than R_d , which corresponds to the depletion of the impurity states at the

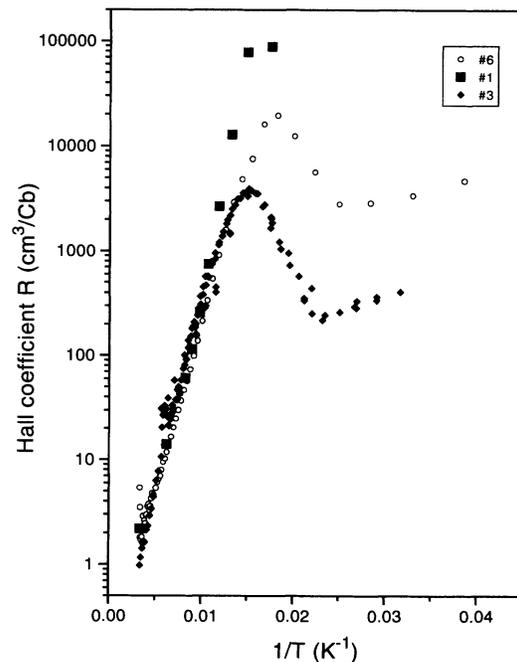


FIG. 1. Temperature dependence of the Hall coefficient $R(T)$ of p - β -FeSi₂. Here and hereafter the numbers of the curves correspond to the sample numbers.

highest temperatures. This feature could not be explained by assuming a two-band model (the valence and the impurity bands) only, and leads us to conclude the existence of an additional deep acceptor level.^{13,14}

The resistivity of the samples studied shows a minimum in the range of 180–240 K, and increases with decreasing temperature (Fig. 2). The $1/T$ dependence of the resistivity is nearly exponential in the two temperature ranges. The slope change of the $\rho(1/T)$ curves is observed near the temperatures corresponding to the maximum of the Hall coefficient.

The temperature dependence of R/ρ is given in Fig. 3. At room temperature the mobility ranges between 10 and 20 cm^2/Vs . As the temperature decreases, R/ρ increases, reaches a maximum, and then decreases. With decreasing concentration the mobility maximum shifts to lower temperatures. The absolute magnitude of the maximum increases. The mobility maximum observed is 1200 cm^2/Vs at 74 K, which is 25–50 times higher than the maximum values previously reported.^{6,7}

The observed features of $R(T)$ indicate the presence of both shallow and deep acceptor levels. For a semiconductor containing acceptor levels with two activation energies ϵ_1 (shallow level) and ϵ_2 (deep level), the concentration p of free holes is given by¹⁵

$$p + N_d = \frac{N_{A_1}}{1 + \frac{\gamma p}{N_v} \exp \frac{\epsilon_1}{kT}} + \frac{N_{A_2}}{1 + \frac{\gamma p}{N_v} \exp \frac{\epsilon_2}{kT}}, \quad (1)$$

where

$$N_v = 2(2\pi m^* kT/h^2)^{3/2}. \quad (2)$$

$N_{A_{1,2}}$ is the concentration of shallow and deep acceptor levels, respectively; N_v is the density of states in the

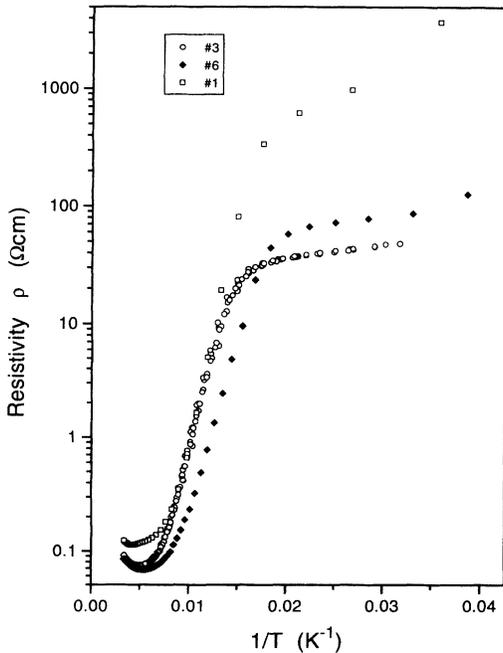


FIG. 2. Resistivity vs temperature of p - β -FeSi₂.

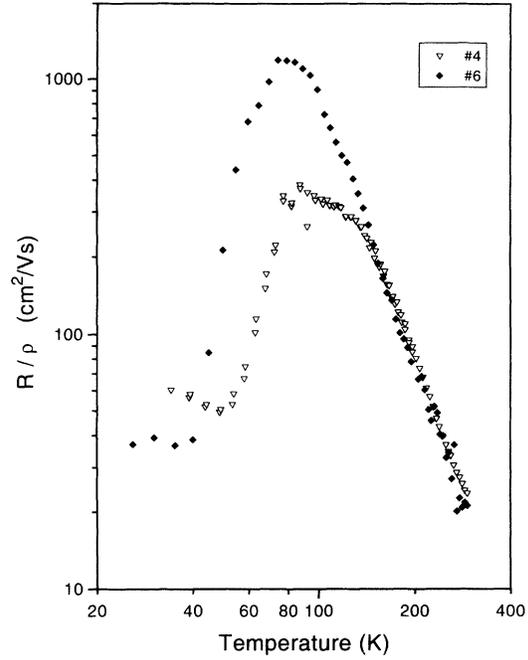


FIG. 3. Temperature dependence of R/ρ of p - β -FeSi₂.

valence band; γ is the degeneracy factor ($\gamma=2$); and N_d is the concentration of compensating donors.

At higher temperature, where the impurities are depleted,

$$p = \frac{1}{eR_d} = N_{A_1} + N_{A_2} - N_d, \quad (3)$$

where R_d is determined from an extrapolation of $R(1/T)$ to $(1/T) \rightarrow 0$.

At low temperature, where it is possible to neglect the second term on the right-hand side of Eq. (1), this expression reduces to

$$p + N_d = \frac{N_{A_1}}{1 + \frac{\gamma p}{N_v} \exp \frac{\epsilon_1}{kT}}, \quad (4)$$

and in the carrier-freezing region

$$p_f = \frac{1}{eR_f} = N_{A_1} - N_d. \quad (5)$$

At high temperature, if it is possible to disregard the first term on the right-hand side of Eq. (1), then, assuming that

$$p \gg N_d, \quad \frac{\gamma p}{N_v} \exp \frac{\epsilon_2}{kT} \gg 1, \quad (6)$$

Eq. (1) can be written as

$$p = \left[\frac{N_v}{\gamma} N_{A_2} \right]^{1/2} \exp \left[-\frac{\epsilon_2}{2kT} \right]. \quad (7)$$

In our samples the dependence of $p/T^{3/4}$ on $1/T$ is a straight line at high temperatures in accordance with Eq. (7), which confirms the assumptions made and permits us

to determine the values of ϵ_2 and $N_v N_{A_2}$. Taking into account Eqs. (2), (3), and (5), the values of N_{A_2} and m^*/m_0 were also calculated (Table I).

Due to the presence of an impurity band, an analysis of $R(T)$ at low temperature can be made on the basis of a two-band model.¹¹ If carriers in a crystal can be divided into two groups, characterized by their mobilities (μ and μ_1) and concentrations (p and p_1) which give an additional contribution to the total electrical conductivity σ_0 of the crystal, $\sigma_0 + \sigma + \sigma_1$, then according to the theory of two-band conduction

$$R = \frac{a_r p \mu^2 + a_{r_1} p_1 \mu_1^2}{e(p\mu + p_1\mu_1)^2}, \quad (8)$$

where μ , σ , and p and μ_1 , σ_1 , and p_1 are the mobility, conductivity, and the hole concentration in the main (valence) and impurity bands, respectively. If we assume that $a_r = a_{r_1}$, and take into account that $p + p_1 = p_r = \text{const}$, the equality $\sigma = \sigma_1$ is the condition for the appearance of a maximum in the $R(T)$ curves related to the presence of conduction between impurities. Then the relative magnitude of R referred to the freezing region is given by

$$\frac{R}{R_f} = \frac{(x + b^2)(x + 1)}{(x + b)^2}, \quad (9)$$

where $b = \mu/\mu_1$ and $x = p_1/p$.

Taking into account that the temperature dependence of b is considerably weaker than that of x , we may roughly consider b to be constant. Then it is easy to find that the maximum of R is given by

$$\frac{R_{\max}}{R_f} = \frac{(b + 1)^2}{4b}. \quad (10)$$

Relations (9) and (10) allow us to determine from the experimental curves $R(T)$ (Fig. 1) the concentrations p and p_1 as a function of temperature (Fig. 4). The calculation of the concentrations becomes impossible at the lowest temperature, where the Hall coefficient becomes a constant or (as in our samples) even begins to increase and becomes incorrect at high temperatures where the value of R is lower than that of R_f .

At low temperature the temperature dependence of p is determined by Eq (4), which can be written as

$$p = \frac{N_v}{\gamma} \frac{N_{A_1} - N_d}{N_d} \exp\left[-\frac{\epsilon_1}{kT}\right], \quad (11)$$

TABLE I. Parameters of p -type β -FeSi₂ single crystals.

Sample No.	N_{A_1} 10 ¹⁵ cm ⁻³	N_{A_2} 10 ¹⁸ cm ⁻³	N_d 10 ¹⁴ cm ⁻³	N_d/N_{A_1} %	ϵ_1 meV	ϵ_2 meV	m^*/m_0
6	3.6	37	14	38	48	93	1.2
5	6.5	9.2	17	26	64	109	0.80
4	8.4	9.7	44	52	55	89	0.9
3	28	140	69	25	50	103	1.0
1		21				87	1.0

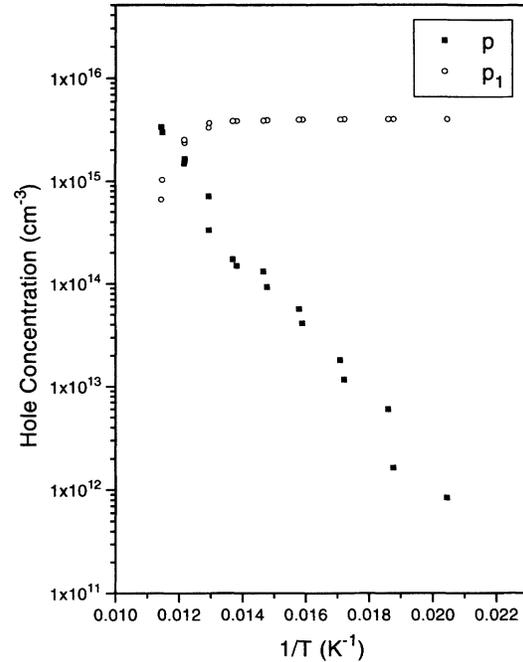


FIG. 4. Hole concentration p and p_1 vs temperature for sample No. 4.

assuming that $p \ll N_d$.

In our samples the dependence of $p/T^{3/2}$ on $1/T$ is a straight line in accordance with Eq. (11), which confirms the assumption made and permits us to determine values of ϵ_1 and $N_v(N_{A_1} - N_d)/N_d$. Taking into account Eq. (5) and the previously determined value of m^*/m_0 , the calculation of N_d was performed (Table I). The values of ϵ_1 obtained are close to those determined earlier from the temperature dependence of the Hall coefficient in thin films in the high-temperature region [80 (Ref. 6) and 100 meV (Ref. 16)]. The estimated values of m^*/m_0 are in satisfactory agreement with theoretically calculated data ($m^*/m_0 = 0.8$).⁸

The obtained set of parameters [$\epsilon_1, \epsilon_2, N_{A_1}, N_{A_2}, (m^*/m), N_d$] permitted a check of the assumptions used to obtain Eqs. (4), (7), and (11).

At the lowest temperatures a variation of the Hall voltage V_H (or R) on H was observed. It is worth mentioning that the variation of V_H on H was also observed on p -type β -FeSi₂ thin films,⁵ and was explained on the basis of the ferromagnetic nature of iron disilicide below 100 K. However, an analysis of our magnetization measurements performed on β -FeSi₂ single crystals shows that the contribution of the anomalous Hall effect to the total Hall voltage is negligible, and no evidence of a ferromagnetic phase transition around 100 K could be detected.¹⁷ The variation of V_H (or R) on H , observed in both p -type β -FeSi₂ thin films⁵ and in single crystals, could be explained in the limits of a two-band model.

In summary, we may conclude that the observed temperature and magnetic-field dependencies of the Hall coefficient in p -type β -FeSi₂ single crystals are explained by assuming the existence of an impurity band formed by

shallow acceptor levels $\epsilon_1=0.055\pm 0.010$ eV, and an additional deep acceptor level $\epsilon_2=0.10\pm 0.01$ eV.

The availability of single crystals permitted us to obtain more reliable data about β -FeSi₂. It is shown that improved sample preparation can significantly increase the mobility, in contrast to conclusions by Christensen,⁸ who suggested that the low mobilities observed in thin films and sintered samples are caused mainly by an unusually strong electron-phonon scattering in band-edge

states. In fact, the mobility of holes is up to 1200 cm²/Vs at low temperatures, i.e., up to 25–50 times higher than maximum values previously reported.^{6,7}

Therefore the conclusion of a limited electronic application of β -FeSi₂ caused by earlier observed and expected low mobilities^{4,6} may be revised.

The authors are indebted to Dr. G. Willeke for useful discussion.

*Permanent address: Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev, Moldova.

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