HOPPING CONDUCTIVITY AND SPECTRUM OF LOCALIZED CARRIERS IN $\beta$-FeSi$_2$:Mn

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Abstract

Resistivity measurements of Mn-doped p-type $\beta$-FeSi$_2$ single crystals are presented and analyzed with the different hopping conductivity models. Both the Mott and the Shklovskii-Efros regimes of the variable-range hopping (VRH) conductivity are observed as well as the universal scaling behavior of the resistivity. The characteristic and transition temperatures and widths of the impurity band and of the Coulomb gap, $\Delta$, in the density of states (DOS) are obtained, indicating existence of a rigid gap, $\delta$, in the spectrum of DOS, in addition to $\Delta$, which points out to the polaronic nature of the charge carriers in the investigated compound.

1. Introduction

In recent time, semiconducting iron disilicide ($\beta$-FeSi$_2$) has attracted much attention as a promising material for optoelectronic devices on Si substrates and high-temperature thermoelectric materials [1]. The transport properties of undoped and Al-, Co-, and Cr-doped $\beta$-FeSi$_2$ single crystals have been studied so far (see [2, 3] and references therein). Some optical, electrical, and magnetic properties of $\beta$-FeSi$_2$:Mn films and single crystals have been reported [4, 5].

In this work, we investigate variable-range hopping (VRH) conductivity of $\beta$-FeSi$_2$ single crystals doped with Mn, which is expected to yield valuable information on the energy spectrum of the localized charge carriers.

2. Results and discussion

The $\beta$-FeSi$_2$ needle-like single crystals doped with Mn were grown by chemical vapor transport using iodine as a transport agent and a Si/Fe ratio in the transport ampoule of 2.0 or 1.5. The doping concentration was determined by spark mass spectroscopy at radio frequency excitation (see Table I). The resistivity, $\rho (T)$, was measured by the standard dc technique between 5 - 300 K.

As can be seen from the top panel of Fig. 1, temperature dependence of the resistivity in the investigated samples has an activated character, including two intervals with different slopes of the function of $\rho (1/T)$. The high-temperature slope is connected to the band conductivity, whereas the low-temperature one to the hopping conductivity over the localized states of the impurity band. One can also see that low-temperature slope is not constant but varies
Table I. The doping levels, the values of the characteristic \((T_{04} \text{ and } T_{02})\) and transition \((T_{v4} \text{ and } T_{v2})\) temperatures for the Mott and the Shklovskii-Efros VRH conductivity regimes, respectively, and widths of the impurity band \((W)\), of the Coulomb \((\Delta)\) and of the rigid \((\delta)\) gaps.

<table>
<thead>
<tr>
<th>Sample no. (FeSi(_x))</th>
<th>Mn doping wt % (at %)</th>
<th>(T_{04}) (K)</th>
<th>(T_{v4}) (K)</th>
<th>(T_{02}) (K)</th>
<th>(T_{v2}) (K)</th>
<th>(W) (meV)</th>
<th>(\Delta) (meV)</th>
<th>(\delta) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L20 (FeSi(_2))</td>
<td>1 (0.11)</td>
<td>281</td>
<td>62</td>
<td>11.6</td>
<td>6.4</td>
<td>7.78</td>
<td>0.37</td>
<td>0.17</td>
</tr>
<tr>
<td>L20a (FeSi(_2))</td>
<td>1 (0.11)</td>
<td>407</td>
<td>60</td>
<td>8.2</td>
<td>7.2</td>
<td>8.33</td>
<td>0.33</td>
<td>0.23</td>
</tr>
<tr>
<td>L39 (FeSi(_2))</td>
<td>2 (0.42)</td>
<td>241</td>
<td>55</td>
<td>11.9</td>
<td>7.3</td>
<td>6.84</td>
<td>0.40</td>
<td>0.18</td>
</tr>
<tr>
<td>L21 (FeSi(_{1.5}))</td>
<td>1 (0.11)</td>
<td>357</td>
<td>69</td>
<td>8.2</td>
<td>7.2</td>
<td>8.95</td>
<td>0.33</td>
<td>0.22</td>
</tr>
<tr>
<td>L22 (FeSi(_{1.5}))</td>
<td>1 (0.11)</td>
<td>116</td>
<td>45</td>
<td>10.3</td>
<td>7.2</td>
<td>4.90</td>
<td>0.37</td>
<td>0.11</td>
</tr>
</tbody>
</table>

with temperature suggesting VRH conductivity with a law \(\rho(T) = \rho_{0p}\exp((T_{0p} / T)^{1/p})\) [6], where \(p = 4\) describes the Mott-VRH and \(p = 2\) the Shklovskii-Efros (SE)-VRH conductivity regimes, \(\rho_{0p} = A_p T^{4/p}\) is the prefactor \((A_p\) is independent of \(T)\) and \(T_{0p}\) is the characteristic VRH temperature, which can be written as \(T_{04} = \beta_4 / [k_B \alpha^3 g(\mu)]\) and \(T_{02} = \beta_2 \varepsilon^2 / (k_B \kappa \alpha)\). Here \(\beta_4 = 21\) and \(\beta_2 = 2.8\) are numerical constants, \(\kappa\) is the dielectric permittivity, \(\alpha\) is the localization radius of charge carriers and \(g(\mu)\) is the density of the localized states (DOS) at the Fermi level, \(\mu\) [6]. The Mott-VRH conductivity takes place when the DOS at the Fermi level is constant, whereas the SE-VRH conductivity is realized when the DOS has a parabolic gap with width \(\Delta\) due to the long-range Coulomb correlations of the localized electrons in the energy range between \(\mu - \Delta\) and \(\mu + \Delta\) [6].

Fig. 1. The plots of \(\rho\) vs. \(T^{-1}\) (upper panel), \(\ln(\rho / T^{1/4})\) vs. \(T^{-1/4}\) (middle panel), and \(\ln(\rho / T^{1/2})\) vs. \(T^{-1/2}\) (bottom panel). The lines are to guide the eye (top panel) and the linear fits (middle and bottom panels).
As follows from the middle and the bottom panels of Fig. 1, in our Mn-doped samples both the Mott- and the SE-VRH conductivity can be found in different intervals of the low-temperature part of \( \rho \) (7). The characteristic temperatures \( T_{04} \) and \( T_{02} \), as well as the prefactor coefficients \( A_4 \) and \( A_2 \), are obtained with linear fits of the plots \( \ln (\rho / T^p) \) vs. \( 1 / T^p \) (\( p = 4 \) and 2), whereas the onset temperatures \( T_{v4} \) and \( T_{v2} \) are determined by onsets of the linear behavior of the corresponding plots following the fitting lines (see the middle and the bottom panels of Fig. 1). These data are collected in Table I. The width of the impurity band, \( W \approx k_B (T_{v4} / T_{04})^{1/4} \), and \( \Delta \approx 0.5 k_B (T_{v2} / T_{02})^{1/2} \) [6] have been evaluated and are listed in Table I as well.

Generally, the temperature dependence of the hopping resistivity can be expressed by a scaling equation of the form \( \ln (\rho / \rho_0) = A f(T/T_x) \), where \( A \), \( T_x \) and \( \rho_0 \) are sample-dependent constants and \( f(x) = \left\{ 1 + \left[ (1 + x)^{1/2} - 1 \right] \times \left[ (1 + x)^{1/2} - 1 \right]^{-1/2} \right\} \) is a universal crossover function [7]. In our samples the prefactor \( \rho_0 \) depends on temperature. Therefore, in Fig. 2 we plot \( \ln (\rho / A_4 T^{1/4}) / A \) vs. \( \ln (T/T_x) \) for the data of five studied samples. The values of \( A_4 \) have been already determined (Table I) and those of \( A \) and \( T_x \) are estimated for each sample as fitting parameters from non-linear least-squares fit of the dependence \( \rho (T) \). As expected from the scaling model [7], we find that the temperature dependence of the resistivity in the VRH regime can be represented by a universal curve (see Fig. 2). It has been shown earlier that the corresponding resistivity data of \( \beta \)-FeSi\(_2\):Cr [2] and \( \beta \)-FeSi\(_2\):Co [3] fall on a universal curve, too. The same scaling behavior has been observed also in various compounds other than \( \beta \)-FeSi\(_2\), such as CdSe [7], CuInSe\(_2\), and CuInTe\(_2\) [8]. The deviation from such behavior with increasing \( T \) observed in Fig. 2 of this work, as well as in Refs. 2 and 3, is connected to completion of the hopping conductivity and transition to the band one, where the model [7] becomes inapplicable.

Fig. 2. \( \ln (\rho / A_4 T^{1/4}) / A \) vs. \( \ln (T/T_x) \) for five Mn-doped samples with different parameters \( A \) and \( T_x \). The solid line is the function \( f(x) \).

Finally, we analyze the expression

\[
\frac{T_{02}^3}{T_{04}} = CA^2,
\]  

(1)
where \( C = \frac{3}{\pi} \beta^3 \left( \beta_4 k_B^2 \right) = 135 \text{ K}^2 / \text{meV}^2 \) is the universal constant, which can be obtained combining equations for \( T_{04}, T_{02}, \Delta \) above and using the condition of \( g(\mu) \approx g_0 \), where \( g_0 = \frac{3}{\pi} \left( \kappa^3 / e^6 \right) \Delta^2 \) is the DOS outside the Coulomb gap in the SE-VRH model [6]. This condition can be verified with expression \( g_0 / g(\mu) \approx \left[ 1 - 2\Delta / (3W) \right]^{-1} [2, 3] \), yielding the error of \( \sim 1 - 5\% \).

Equation (1) suggests the linearity of the plot of \( T_{02}^3 / T_{04} \) vs. \( \Delta^2 \), starting from the origin and having the angular coefficient \( C \). However, it is evident from Fig. 3 (crosses) that the data points do not fall on a single line, one of them deviating strongly from the linear behavior expected from Eq. (1). On the other hand, the plot containing only the rest four points exhibits a clear curvature shown by a solid line. If we try to fit this plot with a linear function of the type \( y = C'x + a_0 \) (the dashed line), we obtain \( C' = 109 \pm 15 \text{ K}^2 / \text{meV}^2 \) and \( a_0 = -10 \pm 2 \text{ K}^2 \), differing evidently from \( C \) and from zero, respectively.

A similar behavior of the plot \( T_{02}^3 / T_{04} \) vs. \( \Delta^2 \) has been observed earlier in \( \beta\)-FeSi\(_2\):Cr [2] and in \( \beta\)-FeSi\(_2\):Co [3]. This has been interpreted by existence of the rigid gap, \( \delta \), in addition to the soft Coulomb gap \( \Delta \) in the spectrum of the DOS. The origin of \( \delta \) has been attributed to a polaronic nature of the charge carriers in Cr- and Co-doped \( \beta\)-FeSi\(_2\) [2, 3]. Indeed, for hopping from one site to another site, a carrier should produce a work to annihilate polarization of the medium on the initial site and to create it on the final site, which requires a minimum possible energy available for hopping leading to \( \delta \). It is worth mentioning investigations of the high-temperature electronic properties of Co-doped [9] and Ni-doped [10] \( \beta\)-FeSi\(_2\) and the room-temperature optical properties of \( \beta\)-FeSi\(_2\) [11], which have led the authors to the conclusion about a small-polaron mechanism in these materials.

It can be shown [12] that presence of the rigid gap \( \delta \) superimposed over \( \Delta \) modifies expression for \( g_0 \) above into \( g_0 = \frac{3}{\pi} \kappa^3 (\Delta - \delta)^2 / e^6 \), provided that \( \delta \) and \( \Delta \) satisfy the relation \( 0 \leq \delta < \Delta \). Correspondingly, instead of Eq. (1) we get

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**Fig. 3.** The plots of \( T_{02}^3 / T_{04} \) vs. \( \Delta^2 \) (×) and \( (\Delta - \delta)^2 \) (O) for the investigated samples. The solid line is to guide the eye. The dashed and dotted lines are the linear fit of the data.
\[ \frac{T_0^3}{T_0^4} = C(\Delta - \delta)^2. \] (2)

As follows from Table I the values of \( \delta \) evaluated with Eq. (2) satisfy the condition of \( 0 < \delta < \Delta \). In addition, it is evident from Fig. 3 that for the plot \( T_{02}^3 / T_{04} \) vs. \( (\Delta - \delta)^2 \) the linearity is kept for all investigated samples (circles), yielding \( C' = 135 \text{ K}^2 /\text{meV}^2 \) and \( a_0 = 0 \) (dotted line). The values of \( \delta \) in Table I are close to those found in Co-doped \( \beta \)-FeSi\(_2\) [3] at corresponding values of \( W \); the origin of the correlation between \( \delta \) and \( W \) is discussed in detail in Ref. 3.

Conclusions

We have investigated resistivity of the Mn-doped p-type \( \beta \)-FeSi\(_2\) single crystals. Both the Mott and the Shklovskii-Efros variable-range hopping conductivity regimes, accompanied by the universal scaling behavior of the resistivity, are observed. The values of the characteristic and transition temperatures, as well as widths of the impurity band, of the Coulomb and of the rigid gaps in the spectrum of density of the localized states, have been determined.

References