HOPPING CONDUCTIVITY IN FeSi

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We measured the ac conductivity of polycrystalline FeSi at temperatures 80 mK ≤ T ≤ 450 K and frequencies 20 Hz ≤ ν ≤ 1 GHz. At temperatures T < 25 K the ac response is governed by hopping of localized charge carriers. However, the complex conductivity in FeSi cannot be described by models developed for conventional semiconductors. At higher temperatures no signs of hopping conductivity could be found. Obviously itinerant charge carriers dominate the charge transport for T > 25 K and deviations of the temperature dependence of the dc resistivity from a thermally activated behavior which occur below 90 K are not due to Anderson localization but probably to Kondo-like behavior. Below 4 K the dielectric constant increases by an order of magnitude signaling a reentrant transition into a metallic state.

1. Introduction

Since many years FeSi attracts considerable interest due to its unusual magnetic behavior (see ref. [1] and references therein). The magnetic susceptibility $\chi(T)$ exhibits a maximum at approximately 500 K with a Curie-Weiß like behavior above and a dramatic decrease below this temperature [1]. However, no signs of magnetic ordering have been detected. Various models have been proposed to explain this unusual behavior [1, 2].

Renewed interest in this material arose due to the fact that some of its properties (including $\chi(T)$) reveal striking similarities with the behavior of Kondo-insulators (KI) [3, 4], which led to the suggestion that FeSi belongs to this class of materials. KI are closely related to Heavy-Fermion Systems (HFS) which are characterized by a strong hybridization of the band states with localized (usually 4f or 5f) magnetic moments leading to high effective masses of the conduction electrons. However, unlike in normal metallic HFS the KI exhibit semiconducting behavior at low temperatures. It is widely believed that in KI a hybridization gap is prerequisite of the semiconducting properties. The special interest in FeSi arises due to the fact that it seems to be the first d-electron material exhibiting Kondo-lattice behavior.

An optical study on FeSi revealed a band gap of about 700 K at low temperatures, which fills in with increasing temperatures and has almost completely vanished at an unexpectedly low temperature of 200 K [5]. The spectral weight distribution was interpreted in the framework of a KI behavior [5]. However, Degiorgi et al. [6] who performed optical and microwave investigations in a very broad frequency range claimed that the electronic properties are that of a conventional semiconductor and can be explained without assuming a Kondo lattice picture for FeSi. At low temperatures and microwave frequencies they find a decrease of $\sigma(\nu)$ with decreasing frequencies, which they interpret as evidence for Anderson localization of the charge carriers.

The temperature dependence of the dc resistivity in FeSi reveals a rather complicated behavior with clear deviations from an Arrhenius type behavior at temperatures below 100 K [7, 8, 9] indicative for localization effects [8, 9]. The most striking feature is the tendency of $\rho(T)$ to saturate at temperatures below ~10 K [8, 9], which can be explained assuming a reentrant transition into a metallic state [9]. The authors of Ref. [9] conclude from their results on magnetic, thermal and transport properties of FeSi that at low temperatures both itinerant *and* localized electrons coexist.

The purpose of this paper is to clarify the question of localization in FeSi by measuring the complex ac conductivity. Such measurements are an ideal tool to investigate hopping conductivity, which is the dominant transport mechanism between localized states. We measured the ac conductivity of polycrystalline FeSi samples at frequencies 20 Hz ≤ ν ≤ 1 GHz and temperatures 80 mK ≤ T ≤ 450 K. At temperatures T <

20 K we find experimental evidence for hopping conductivity. These results, however, cannot be interpreted in the framework of models developed for conventional semiconductors.

2. Experimental details

Polycrystalline samples of FeSi have been prepared by melting of high purity iron (99.99 %) and silicon (99.9999 %) in an argon-arc furnace. The samples have been characterized by X-ray investigations yielding a cubic structure with a = 4.51 Å. No indications of impurity phases were detected.

The ac conductivity has been recorded in a broad frequency range using different measuring devices: For frequencies 20 Hz ≤ ν ≤ 1 MHz an autobalance bridge (HP4284) was used. This device allows the measurement with four-point contact geometry thereby avoiding any contributions of the contact resistance. In addition, all samples have also been measured using a standard lock-in four-point technique at a frequency of 19 Hz in order to check the validity of the autobalance bridge results. By varying the excitation voltage (typically 10 mV) it has been assured that possible nonlinear effects have no influence on the results and that there is no heating of the sample by the current. As contacts silver paint has been applied on the freshly polished samples. For cooling down to 1.5 K a variable-flow ^{4}He cryostat and for temperatures 80 mK ≤ T ≤ 6 K a ^{3}He-^{4}He dilution refrigerator has been used. Measurements above room temperature were performed in a nitrogen gas heating system. The high frequency data (1 MHz ≤ ν ≤ 1 GHz) were obtained using an HP4191 impedance analyzer connected to the sample in a ^{4}He cryostat by a coaxial air line. Here the sample connects inner and outer conductor of the coaxial line. From the complex reflection coefficient of this assembly the complex conductivity can be calculated after proper calibration using three standard samples to eliminate the influence of the coaxial line and the sample holder. This reflectometric method requires two-point contact configuration, which implies that the contacts may contribute to the measured response. The high frequency measurements were performed down to 1.5 K only.

3. Results and discussion

Figure 1 shows the temperature dependence of the resistivity at 20 Hz obtained in four-point technique (double logarithmic plot). Up to 1 MHz no frequency dependence could be detected, i.e. the curve of Fig. 1 resembles the pure dc resistivity. After passing a broad minimum near room temperature, ρ(T) increases approximately four decades between 300 K and 2 K. Near 70 K a shoulder in ρ(T) appears. Below 10 K ρ(T) starts to approach a saturation value, which is finally reached at 2 K. These findings agree rather well with the results of

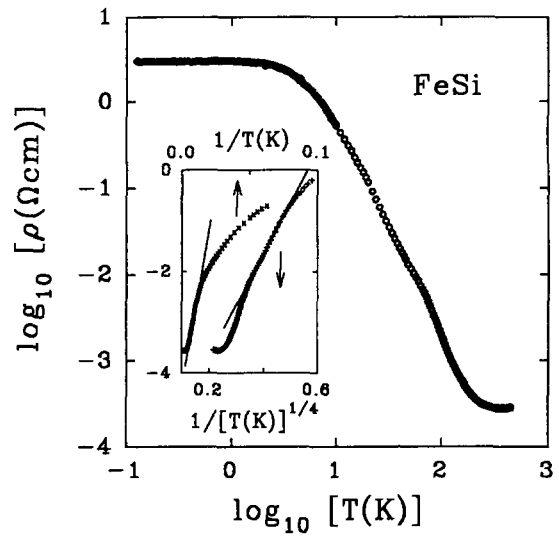

Fig. 1. Temperature dependence of the resistivity of FeSi at 20 Hz (double logarithmic plot). The inset shows the same data vs. 1/T (left curve) and vs. $1/T^{1/4}$ (right curve).

Wolfe et al. [7] and of Takagi et al. [8] obtained on polycrystals. Except for the shoulder at 70 K the characteristic features of the ρ(T) curve have also been found in recent measurements on FeSi single crystals [9].

In order to detect possible deviations of the temperature dependence of the resistivity as compared to the findings in conventional semiconductors, the inset of Fig. 1 shows ρ(T) in an Arrhenius representation (left curve). Indeed, ρ(T) behaves roughly thermally activated between 90 and 200 K with an activation energy of $E_g \approx$ 670 K, which is in good agreement with the results of Takagi et al. [8] on polycrystals and of Schlesinger et al. [5] on single crystals and agrees also well with the results from optical measurements [5, 6]. However, it should be noted that Hunt et al. [9] report resistivity measurements on single crystals in which ρ(T) reveals no activated behavior. At temperatures below 90 K the resistivity deviates significantly from an activated behavior, a finding that has been interpreted as indicative for the onset of tunneling between localized states [8, 9]. The inset of Fig. 1 shows the logarithm of the resistivity vs. $1/T^{1/4}$, which would give a straight line for Variable Range Hopping (VRH) [10]. Indeed, for 25 ≤ T ≤ 60 K a straight line can be fitted to the data. However, in our opinion this temperature range is too limited to proof VRH as dominant transport process in this temperature regime.

We were able to reproduce ρ(T) as shown in Fig. 1 in several temperature runs using different samples. For all samples, the onset of saturation of ρ(T) has been observed in the same temperature range. The variation of the absolute values of the resistivity at low temperatures never

exceeded 50%. In addition, some ρ(T) curves revealed hysteretic jumps in the resistivity around 4 K and/or a steplike anomaly near 0.6 K. It is not clear at the moment if this is an intrinsic effect or due to some small amounts of impurity phases in the sample. Further investigations on single crystals are planned to clarify these questions.

Figure 2 shows the temperature dependence of the resistivity for frequencies above 1 MHz and below 30 K. Above this temperature ρ(T) follows the dc behavior up to approximately 200 K. Above 200 K the contact resistance significantly contributes to ρ(T) while it can be neglected at lower temperatures where the sample resistance is several decades higher. Fig. 2 reveals clear deviations of ρ(T) from the dc values at high frequencies and low temperatures. The occurrence of this frequency dependence is accompanied by a change from inductive to capacitive behavior as can be seen in the inset of Fig. 2 where the loss angle tan δ is plotted vs. temperature. This implies that from the ac conductivity point of view FeSi changes its characteristic from metallic to semiconducting behavior at low temperatures.

A decrease of the resistivity with frequency as observed in Fig. 2 is indicative for charge transport via hopping processes. To analyze this behavior in more detail Fig. 3 shows the real and the imaginary part of the conductivity $\sigma = \sigma' + i\,\sigma''$ at 2.8 K vs. frequency in a double logarithmic plot. If hopping conductivity causes the observed frequency dependence a power law increase, $\sigma' \sim \nu^s$ and $\sigma'' \sim \nu^{s'}$, should be observed with the exponents s and s' smaller than 1 [11, 12, 13]. However, $\sigma'(\nu)$ at 2.8 K is dominated by dc conductivity and shows an increase above 100 MHz only. The imaginary part σ'' clearly follows a power law with an exponent of approximately 0.75, a value typical for semiconductors [10]. Usually the dc and the ac conductivity are assumed to simply add up to the total conductivity: $\sigma' = \sigma_{dc} + \sigma_{ac}$ [11, 12]. After subtraction of the dc value from σ' a power law evolves (Fig. 3, plusses) with a slope (i.e. the exponent s) identical to that of $\sigma''(\nu)$. Such a behavior being termed "Universal Dielectric Response" (UDR) is found in a vast number of very different materials [13]. The complex conductivity can be written as:

$$\sigma' = \sigma_{dc} + \sigma_0\,\omega^s \qquad (1)$$

$$\sigma'' = \sigma_0\,\omega^s \tan(s\,\pi/2) + \varepsilon_0\,\varepsilon_\infty\,\omega \qquad (2)$$

Here σ_0 is a prefactor, ε_0 is the dielectric constant of the vacuum, and ε_∞ is the high frequency dielectric constant. The factor $\tan(s\,\pi/2)$ in (2) follows from the Kramers-Kronig transformation on (1) [14]. The second term in (2) takes the high frequency dielectric constant ε_∞ into account and leads to an approach of a slope of one for high frequencies in the double logarithmic plot of σ'' at the lowest temperatures investigated.

The exponent s can most directly be determined from the frequency dependence of σ'', which we plot for three temperatures in Fig. 4. It becomes obvious that the

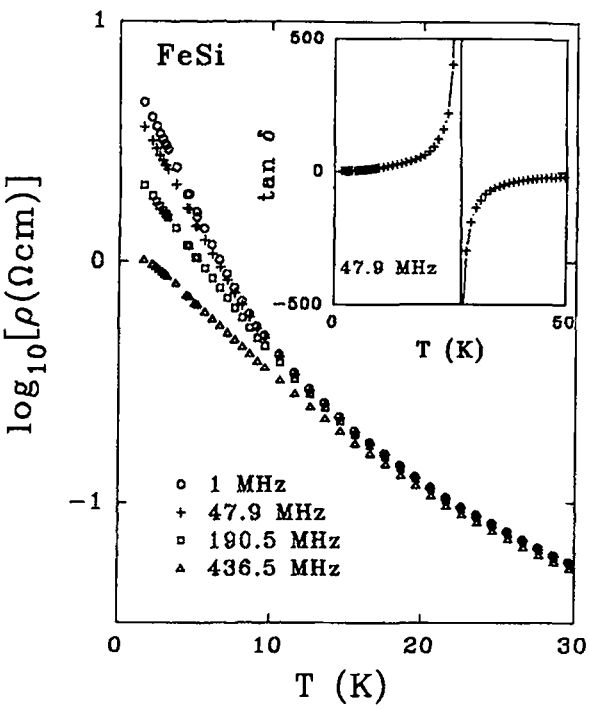

Fig. 2. Resistivity of FeSi at temperatures below 30 K for various frequencies above 1 MHz. The inset shows the temperature dependence of the loss angle tan δ at 47.9 MHz.

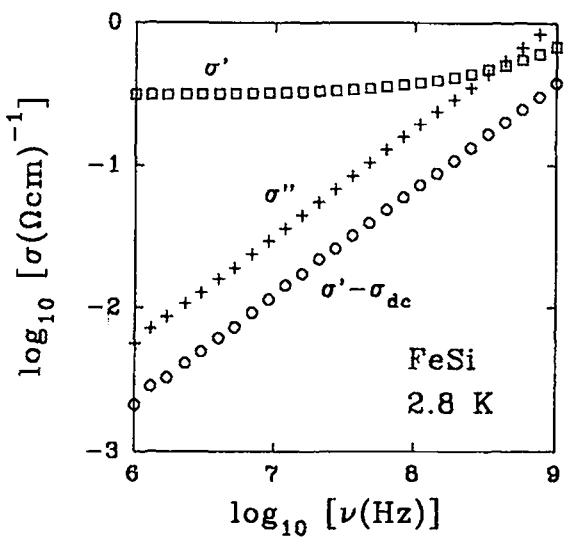

Fig 3. Frequency dependence of real and imaginary part of the conductivity of FeSi at 2.8 K (double logarithmic plot). In addition, the frequency dependence of σ' resulting after subtraction of the dc conductivity is shown.

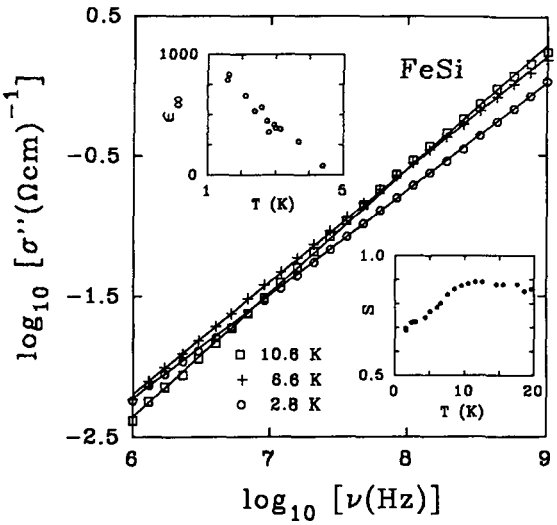

Fig. 4. Frequency dependence of the imaginary part of the conductivity of FeSi at various temperatures (double logarithmic plot). The solid lines are the results of fits using the UDR predictions (see text). The insets show the high frequency dielectric constant ε_∞ (upper) and the frequency exponent s (lower) as resulting from the fits.

frequency exponent increases significantly with temperature. This is in clear contrast to the predictions of the VRH model where s should be temperature independent [11, 12]. To check the temperature dependence of s in more detail we fitted σ' and σ'' simultaneously using eqs. (1) and (2). The experimental results can well be described for temperatures up to 20 K. Above this temperature inductive contributions to the conductivity play an important role yielding rather complicated frequency dependencies. Finally, at temperatures T > 25 K all hopping contributions have completely vanished. The temperature dependence of the exponent s is shown in the lower inset of Fig. 4. The observed increase of s with T is quite unusual and possibly points towards polaronic conduction processes [11, 12]. However, theories on polaron hopping are not able to describe the values of s higher than 0.8 that are experimentally observed above 8 K. It is important to note, that for temperatures T > 25 K, where the dc conductivity could be described by a VRH mechanism, we find no evidence for hopping in the frequency range investigated. All the conductivity is dominated by frequency-independent contributions pointing towards the importance of band-like charge carriers in this temperature regime, while for temperatures < 20 K where a power law behavior of the complex conductivity is observed the dc conductivity tends to saturate.

For the frequencies investigated the high frequency dielectric constant contributes to the conductivity for temperatures below 4.5 K only. It has a value of 80 at 4.5 K and increases by a factor of 10 when the temperature is lowered down to 1.6 K (upper inset in Fig. 4). This strong increase could indicate a transition into a metal-like state at low temperatures, an interpretation that is in accordance with speculations by Hunt et al. [9].

4. Conclusions

The ac conductivity of FeSi polycrystals has been measured for frequencies up to 1 GHz. We find clear evidence for hopping conductivity as dominant charge transport process at temperatures below 25 K. At higher temperatures the ac response of the sample changes from capacitive (semiconducting) to inductive (metallic) behavior. At the "metallic" side no sign of hopping conductivity is found i.e. the dominant charge carriers behave like band-like states. Therefore it is unlikely that the deviations from an Arrhenius behavior in $\rho(T)$ below 90 K are due to the onset of Anderson localization. Probably they are connected to the suspected Kondo-like behavior in FeSi [3, 4], leading to a temperature dependent scattering rate. However, within this interpretation the saturation of $\rho(T)$ below 10 K and the strong increase of ε_∞ for $T \to 0$ K can not be reconciled. If this increase is due to a reentrant insulator-metal transition has to be verified in further experiments.

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