Sample dependence of the specific heat in FeSi

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Abstract

Recently, a high-mobility surface conduction channel and in-gap states were identified in the correlated small-gap semiconductor FeSi using electrical transport measurements and high-resolution tunneling spectroscopy. Intriguingly, the mobility of the charge carriers in the surface channel is quantitatively similar to typical topological insulators, but displays a striking lack of sensitivity to the presence of ferromagnetic impurities as studied by means of a series of single crystals with slightly different starting compositions. Here, we report measurements of the specific heat of these crystals. Contributions to the specific heat observed in our crystals that are linear in temperature, suggestive of an electronic origin, lack a dependence on magnetic field but display a pronounced variation as a function of starting composition, by a factor of ∼50.

1 Introduction

FeSi is a correlated small-gap semiconductor in which an unusual temperature dependence of its electric and magnetic properties has been attracting scientific interest for several decades [1–3]. Notably, as illustrated by means of the temperature dependence of the electrical resistivity in Fig. 1(a), around 200 K a crossover is observed between a paramagnetic metal with strong spin fluctuations at high temperatures, denoted regime I, and a semiconducting state with reduced magnetic susceptibility featuring an energy gap of about 60 meV, denoted regime II [4–8]. Further decreasing the temperature below 100 K, the resistivity continues to increase at a changed slope, denoted regime III, up to a saturation on logarithmic scales at low temperatures, denoted regime IV [9,10]. The magnetic susceptibility increases by about two orders of magnitude in regimes III and IV [11]. While band structure calculations indicated that FeSi is a band insulator at low temperatures [12–14], the unusual metallization and paramagnetism may be associated with correlation-induced incoherence under increasing temperature [15]. The saturation of the resistivity was attributed to the emergence of an impurity band with ferromagnetic impurities potentially adding to the complexity of the low-temperature properties [16–18].

Recently, the emergence of a high-mobility surface conduction channel was inferred from the electrical transport properties of a series of single crystals prepared under a systematic variation of the initial iron content [19–21]. This was corroborated by high-resolution tunneling spectroscopy revealing two in-gap states in the low-temperature regime [22]. The surface channel in FeSi appears to exhibit a remarkable robustness against the presence of ferromagnetic impurities and the surface-to-bulk ratios of the charge carrier densities and mobilities. In fact, it compares quantitatively with values observed in topological insulators such as Bi_2Te_3 [23]. An open question concerns whether this robustness represents a hallmark of FeSi in general that is also reflected in further bulk or transport properties.

2 Experimental Methods

In this paper, we report a study of the specific heat of a series of optically float-zoned single crystals of FeSi that were prepared using slightly different starting compositions $Fe_{1+x}Si$ [24–26]. The magnetisation and electrical transport properties of samples cut from the same single crystal ingots were reported in Refs. [19, 21]. In addition, a single crystal with an iron deficiency $x = -0.005$ was studied. Samples cut from the start of the single crystal growth process (close to the initial grain selection) and from the end (close to the final quenched zone) may be distinguished, as summarized in Tab. 1.

Sample	Starting composition	Location in float-zoned ingot	Debye temperature Θ_D [K]	Linear coefficient γ [mJ/mol K^2]
A1	$Fe_{0.99}Si$	start	496	28.7
A2	$Fe_{0.99}Si$	end	496	22.1
AB	$Fe_{0.995}Si$	start	500	14.1
B1	FeSi	start	502	8.1
B2	FeSi	end	496	23.2
C	$Fe_{1.01}Si$	start	505	0.6

Table 1: Overview of the samples studied. For each sample, the chemical composition before float-zoning and the location from which the sample was cut within the float-zoned single crystal ingot are stated. In addition, the Debye temperature Θ_D and the coefficient γ of a contribution linear in temperature to the specific heat are given as determined in the study reported here.

For the present study, cubes with an edge length of 1 mm were prepared, each with two surfaces perpendicular to ⟨100⟩ and four surfaces perpendicular to ⟨110⟩. The specific heat measurements were carried out in a Quantum Design physical property measurement system at temperatures down to 1.9 K and in magnetic fields up to 14 T. The single crystal cubes were mounted on the platform of the measurement puck by means of a tiny amount of Apiezon N grease. A quasi-adiabatic large heat pulse technique was used, in which heat pulses had a size of 30% of the temperature at the start of the pulse [27]. For each specific heat curve, data were measured at 80 starting temperatures, covering the temperature regime from 1.9 K to 270 K in a logarithmic spacing, where the measurements were repeated three times at each temperature.

3 Experimental Results

A typical temperature dependence of the specific heat of FeSi is shown in Fig. 1(b), for the case of sample A2. For comparison, both the resistivity in Fig. 1(a) and the specific heat in Fig. 1(b) were measured on samples cut from the same ingot. The specific heat as a function of temperature is characteristic of a nonmagnetic crystal in which phonon contributions dominate. At low temperatures, the specific heat scales with the temperature cubed, $C \propto T^3$. At high temperatures, the phonon contribution approaches the Dulong–Petit value. No anomalies characteristic of phase transitions were observed in any of the samples in the temperature and field range investigated. A change of slope at the boundary between regimes I and II, namely around 200 K, may be associated with the emergence of additional contributions due to the strong spin fluctuations in the paramagnetic state at high temperatures.

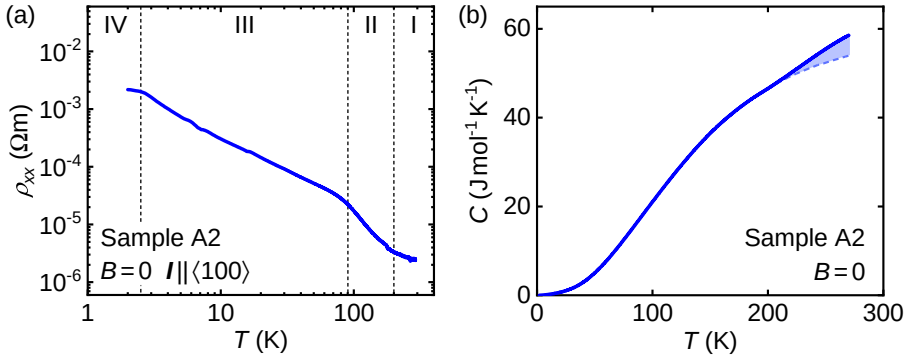

Figure 1: Temperature dependence of the low-temperature properties for sample A2 in zero magnetic field. (a) Electrical resistivity for current along ⟨100⟩ on a double-logarithmic scale. Four regimes may be distinguished as a function of temperature, denoted I through IV; see text for details. Data taken from Refs. [19,21]. (b) Specific heat of FeSi at $B = 0$. A change of slope is observed at the boundary between regimes I and II at ∼200 K. The dashed line is a guide to the eye when subtracting the additional contributions emerging at high temperatures. No anomalies are observed between the regimes at low temperatures.

For further analysis, the specific heat divided by temperature, C/T, may be considered as a function of the square of the temperature, T^2. As shown in Fig. 2(a) for sample A2, a linear fit to the data corresponds to a description of the phonon contributions to the specific heat at low temperatures in terms of a Debye model. From the slope of the fit, a Debye temperature $\Theta_D = 496$ K is inferred, consistent with other transition metal B20 compounds [28,29]. For temperatures above $\sim\Theta_D/10$, the measured specific heat starts to deviate from the low-temperature behavior, providing an excellent crosscheck that the Debye temperature has been inferred correctly. The y-axis intercept suggests a contribution linear in temperature denoted by the coefficient γ. It may be characteristic of electronic contributions to the specific heat. For sample A2, a value of $\gamma_{A2} = 22.1$ mJ mol^{-1}K^{-2} is inferred. If this contribution is of electronic origin, it may be the characteristic of relatively strong correlations for a d-electron compound. At low temperatures, a pronounced drop of C/T as a function of decreasing temperature is observed, characteristic of a freezing of degrees of freedom. In the parameter range studied, our data are insensitive to magnetic fields up to 14 T, suggesting that both the large value of γ and the freezing process at low temperatures are not linked to magnetic degrees of freedom, as may be expected, for instance, for magnetic impurities.

Comparing the specific heat of different samples, as shown in Fig. 2(b) in terms of C/T as a function of T^2 in zero magnetic field, several characteristics appear to be the same for all

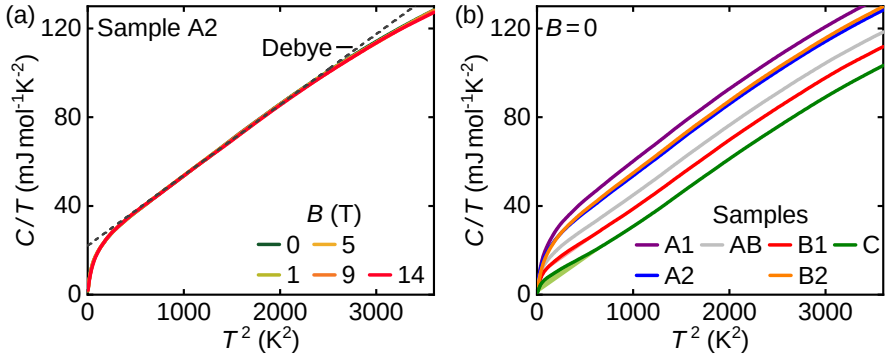

Figure 2: Specific heat divided by temperature as function of the square of the temperature. (a) Data on sample A2 for different magnetic fields. The dashed gray line is a linear fit corresponding to the Debye model. At low temperatures, specific heat contributions freeze out. Data in magnetic fields up to 14 T essentially track each other. (b) Zero-field data for different samples. A distinct shift is observed, suggesting significant variations of the γ coefficients with small changes of composition.

compositions. First, the phonon contribution in C/T versus T^2 may be described by linear fits with essentially identical slope, all yielding a Debye temperature around $\Theta_D = (500 \pm 5)$ K. This finding indicates that the small variations of the starting composition do not affect the crystal structure on a fundamental level. Second, all samples exhibit a drop of C/T vs. T^2 for temperatures approaching zero, suggestive of a freezing of degrees of freedom at low temperatures. This process sets in gradually and the onset does not appear to scale in an obvious way with the initial starting composition, in contrast to the onset of saturation in the resistivity between regimes III and IV [19, 21, 22]. Third, in all samples studied, the specific heat is insensitive to applied magnetic fields up to 14 T (not shown).

In contrast, representing the most prominent difference between samples, the y-axis intercept, which represents the coefficient γ, varies strongly. Compositions with higher initial iron content tend to exhibit smaller coefficients, ranging from $\gamma_{\mathrm{A1}} = 28.7$ mJ mol^{-1}K^{-2} to $\gamma_{\mathrm{C}} = 0.6$ mJ mol^{-1}K^{-2}. Such fundamental changes for different initial iron contents are hard to reconcile with electronic and magnetic properties that remain unchanged on a qualitative level, as reported in Ref. [21]. This discrepancy suggests that contributions to the specific heat may depend delicately on subtle details of the electronic structure, such as kinks and crossings, asking for further investigation to be identified. Similar discrepancies are also observed when comparing specific heat data from previous studies [20, 22]. As an additional sample-dependent aspect, for samples B1 and C which exhibit small values of γ, the Debye and linear contributions increase for decreasing temperatures, as indicated by colored shading, before freezing sets in below ∼10 K. For the other samples, the specific heat observed experimentally never exceeds the sum of the Debye and the linear contributions. For convenience, the Debye temperatures and γ coefficients for all samples studied are summarized in Tab. 1.

4 Conclusions

In summary, the specific heat of the correlated small-gap semiconductor FeSi was studied for a series of single crystals prepared from slightly different starting compositions. A pronounced dependence of the coefficient γ is observed, differing by a factor of ∼50 between samples with high and low initial iron content. The specific heat is insensitive to magnetic fields up to 14 T, the highest field measured. Our findings suggest that the specific heat, in contrast to the

high-mobility surface conduction channel, may be sensitive to subtle details of the electronic structure.

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