Low-temperature magnetic, thermal, and transport properties of FeSi

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We have measured the ac susceptibility, specific heat, resistivity, and thermal conductivity of single-crystalline samples of FeSi in various temperature ranges between 0.04 and 300 K. The unequivocal result emerges from the ac susceptibility data, and is that there is no evidence for any magnetic ordering, at least down to 40 mK. The specific heat contains a linear contribution visible between 1.5 and 3.5 K, and a slow upturn below 1.5 K. This latter feature, and the observed Curie behavior of the ac susceptibility can both be quantitatively accounted for within a model of Anderson-localized states associated with impurities, at the level 10^{19} cm^{-3}. However, the electrical conductivity, which is nowhere activated, appears to saturate below about 5 K, which would suggest a metallic state. We draw attention to numerous similarities between our data and previously published data for the rare-earth compound SmB_6.

I. INTRODUCTION

FeSi is a cubic compound with space group $P2_13$ and has hitherto widely been referred to as a narrow-gap semiconductor. It has excited interest for over half a century, mainly because of its unusual magnetic behavior. The magnetic susceptibility $\chi(T)$ as measured, for example, by Jaccarino *et al.*[1,2] shows a Curie-Weiss-like $1/T$ dependence above about 550 K, but falls off sharply towards zero below this temperature. Subsequent neutron-scattering investigations have revealed no evidence for magnetic order, however.[3] Both single particle and many-body approaches have been used to try to explain this. Jaccarino *et al.* were able to describe the observed temperature dependence of the susceptibility very well by assuming a surprisingly simple and, in their view, unrealistic, single-particle model of two infinitely narrow bands, located symmetrically above and below the Fermi level, separated by an energy gap Δ, and with each band able to hold two electrons per Fe ion. The empirically determined gap parameter Δ given by their fitting $\chi(T)$ is 0.13 eV.

Very recently, Mattheiss and Hamann[4] calculated the band structure of FeSi, using the linear augmented-plane-wave (LAPW) method in the local-density approximation. They found an indirect gap of 0.11 eV, which they note is very close to the empirical gap of 0.13 eV found by Jaccarino *et al.* In addition they found that the gap appears in the Fe ($3d$) manifold. They note, however, that the calculated band structure is not at all similar to the model of Jaccarino *et al.* While the calculated and empirical gap values Δ are comparable, and while the calculated bands are sharply peaked around the Fermi energy, the calculated conduction-band width is about five times greater than Δ, not vanishingly small by comparison, and, further, there is room, per peak in each band, only for about one electron per Fe ion, not two, as the simple model requires. Mattheiss and Hamann concluded that the result of single-particle band calculations is completely unable to account for the observed temperature dependence of the FeSi susceptibility.

Two many-body approaches have been considered previously. Motivated by the unrealistic assumptions of the model of Jaccarino *et al.*, Takahashi, Tano, and Moriya,[5] and also Evangelou and Edwards,[6] developed many-body descriptions of the magnetic behavior of FeSi. Both calculations are based on the same model band structure,[7] and both, while including realistic conduction-band widths of about 1 eV and on-site Coulomb correlations, account for the temperature dependence and magnitude of the magnetic susceptibility. The physical picture of temperature-induced paramagnetic local moments was subsequently confirmed by the observation of thermally activated spin fluctuations in FeSi by neutron diffraction.[8]

The same neutron-scattering data revealed both a Q (momentum transfer) independent $\chi'(Q,0)$ and a strongly Q-dependent $\chi''(Q,\omega)$, a feature also observed in the rare-earth compound CeNiSn.[9] This unusual feature implies a vanishing intersite magnetic interaction in the limit of zero energy. From recent optical measurements of the frequency-dependent conductivity $\sigma(\omega)$, Schlesinger *et al.*[10] claim that, as the temperature is lowered, the loss of magnetic moment is accompanied by an extensive redistribution of the charge excitation spectrum, just as it happens in the case of a Kondo lattice. In the latter case, the local spins couple to the entire conduction band. In addition, it was claimed that at low temperatures the conductivity sum rule is not satisfied unless an energy range many times the gap energy is encompassed, which suggests the presence of an additional energy scale, as would be provided by the on-site Coulomb correlations.

Given the sum total of these indications that the electronic structure of FeSi is not explicable in a single-particle scheme, and given also the possible opportunity

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of shedding light on many-body aspects of electronic properties of a d-transition-metal compound that might be related with features of correlated-electron behavior in f-electron materials, it seemed worthwhile to perform a comprehensive series of low-temperature thermal, magnetic, and transport measurements, as far as possible on one high-quality single crystal. To our knowledge, no complete data set of this kind has yet been presented.

II. EXPERIMENTAL

We have measured the specific heat, thermal conductivity, electrical resistivity, and ac magnetic susceptibility in varying ranges of temperature between 0.04 K and room temperature. All measurements, except for the ac susceptibility, were performed on the same single-crystalline sample, a particularly important matter in the case of FeSi, the composition of which can vary from 49 to 50.5 at.% Si.[11] For the ac susceptibility measurements, another crystal from the same batch was used. Our samples were grown in an Antimony flux and both samples were needle shaped. The principal specimen weighed 18.4 mg and measured $0.5\times0.5\times8$ mm, while that used for the susceptibility measurements weighed only 4.0 mg.

The resistivity $\rho(T)$ was measured as a function of temperature between room temperature and 1.5 K, using a standard four-wire low-frequency ac technique, with bare platinum or copper wires fixed to the sample by conducting silver paint. Excitation frequencies were in the range of 100 Hz to 1 KHz, with excitation currents as low as 10 μA. We checked that the measured resistivities were independent of frequency, and that the current did not cause significant joule heating. Initially, the sample was fixed to a paper-covered copper heat sink by GE-7031 varnish along the whole of one side, but it was found that results below about 200 K were not quantitatively reproducible from run to run, with the sample and contacts remounted and remade each time. The differences were qualitatively consistent with the view that the sample was subject to compression during cooling, due to GE-7031 having an integrated thermal expansivity several times greater than that of FeSi.[12] Reproducible results were finally obtained by fixing the sample at one end, or in the center with as thin a layer of Ge-7031 as would hold it in position.

The low-frequency and low-field ac susceptibility was measured by a conventional mutual inductance technique in the temperature range between 0.04 and 0.7 K. Measurements were made at a frequency of 82 Hz and with an excitation field amplitude of 0.1 Oe. The in-phase component χ' and the out-of-phase component χ'' were measured with a two-phase lock-in amplifier. A low-noise signal transformer was used to match the impedance of the pickup coil with that of the lock-in amplifier. With this experimental setup, it was not possible to move the sample during a run, and so the cell background contribution to the measured susceptibility could only be determined from a separate run without the sample. Because the sample is very small and proved to be almost nonmagnetic, the relative error introduced by this method for background determination is unacceptably large. In order to determine the size of any temperature-independent part of the sample susceptibility, the ac susceptibility of the same small sample was again measured in a magnetometer in which it was possible to move the sample during a run, but in which it was necessary to measure in an excitation field of 0.1 T and at temperatures between 2 and 6 K. We made the assumption that the temperature-independent part measured in this way could be extrapolated to the temperature region below 1 K.

The specific-heat data were obtained with a relaxation-type technique in the temperature ranges between 0.06 and 0.85 K, and 1.5 and 8.5 K. The sample was fixed by 0.4-mg Apiezon grease to a sapphire disk onto which a heater and germanium-gold thermometer had been evaporated. The disk and sample were weakly coupled thermally to a copper heat sink held at constant temperature. The heat capacity of the addenda, including the grease, was determined in each temperature range by a preliminary run without the sample. Between 0.5 and 1 K and at 9 K, the total heat capacity of the addenda was comparable to that of the sample, with a correspondingly large uncertainty in the absolute value of the data in those regions of temperature.

The thermal conductivity was measured using a standard steady-state technique monitoring the thermal gradient along the sample in the same temperature range as was covered with the specific-heat measurements. For the sample thermometers, Allen-Bradley carbon resistors[13] were used above 1 K and Matsushita carbon resistors[13] were used below. The original resistors were ground to a thickness of approximately 0.2 mm, then wrapped in 0.1-mm-thick Ag foil and set in Stycast 2850 epoxy. Narrow extensions of the foil were wrapped around the sample at points 5 mm apart along the long axis and fixed to it with GE-7031 varnish, as was the heater at one end of the sample. Temperature differences between the fixing points of between 1% and 4% of the mean sample temperature were used. Thermal leaks by radiation or conduction through the heater and thermometer wires in parallel with the sample are estimated to have been less than 0.3% throughout the measurement range of temperature.

III. RESULTS AND ANALYSIS

The resistivity data are shown in Fig. 1 on a log-log scale. The room-temperature value of the resistivity, 140 $\mu\Omega$ cm, is comparable to the value reported by Schlesinger *et al.*, to within their measurement error.[10] It is consistent with a description of FeSi as a dirty metal at this temperature, although with an elastic mean-free-path of order 3.5 Å if we assume one carrier per FeSi formula unit. This would mean around one scattering site per ten FeSi formula units. We shall show below that we believe the structural disorder in our sample to be principally of point defect type, and that these defects are present at vastly lower concentration levels than would be necessary, with one carrier/FeSi, to limit the mean-free-path to 3.5 Å. Thus, this mean-free-path seems unreasonably

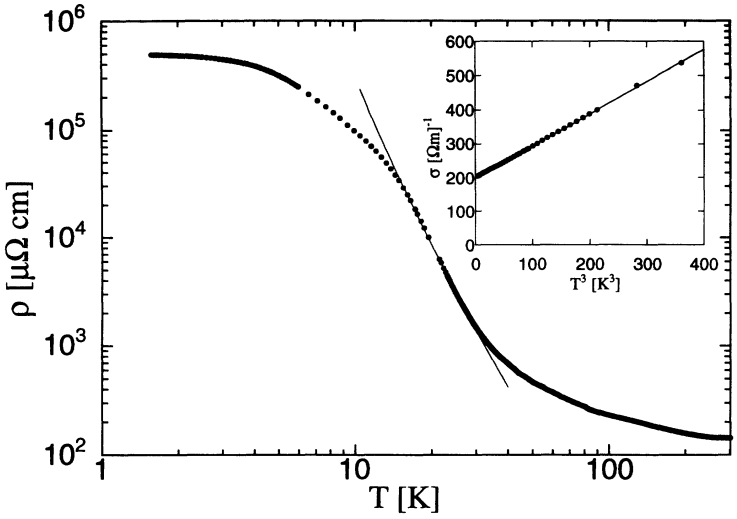

FIG. 1. The resistivity $\rho(T)$ of FeSi between 1.5 and 300 K. The line is a fit, in the region 15–30 K, to an expression appropriate to a variable-range-hopping mechanism: $\rho \propto \exp(T_0/T)^{1/4}$. Inset is shown the conductivity, $\sigma(T)$ vs T^3 between 1.5 and 6 K.

short if due solely to elastic scattering arising from disorder, and so we propose that it is being limited by inelastic collisions. Schlesinger *et al.* reached the same conclusion for their own sample.

As the temperature falls, there is a monotonic rise in resistivity through three and a half orders of magnitude by the lowest measured temperature of 1.5 K. On a linear scale there is a shoulder in the data at $T \approx 120$ K, and we observe a tendency to saturation below 10 K. In between, although the resistivity rises very steeply, it is nevertheless not possible, over any extended range of temperature, to describe the data with a usual activated behavior, i.e., $\sigma \propto \exp(-\Delta/2k_BT)$, as would apply to a conventional semiconductor. A fit to an expression of the form $\sigma \propto \exp[(T_0/T)^{1/4}]$, appropriate to a variable-range hopping mechanism, is possible in this region, and we shall return to a consideration of this later. Below 6 K, the conductivity is well fitted by a sum of a constant and a cubic-in-T contribution, as shown in the inset to Fig. 1. In this range we find $\sigma = \sigma_0 + aT^3$ with $\sigma_0 = 200\ (\Omega\text{m})^{-1}$ and $a = 0.94\ (\Omega\text{mK}^3)^{-1}$.

Here we observe that the tendency to saturation of $\rho(T)$ below 5 K suggests that the FeSi sample, far from being a semiconductor, is metallic in character in that temperature regime. This, following a steep rise in resistivity with decreasing temperature suggests in turn that the saturation arises through the formation of an impurity band. For an estimate of the corresponding impurity concentration, we assume that the standard Boltzmann formulation of the metallic conductivity in a cubic solid is valid, so that

$$\sigma = \frac{e^2}{12\pi^3\hbar} \int \mathbf{L}_k \cdot d\mathbf{S}_k \ , \tag{1}$$

where $d\mathbf{S}_k$ is an area element of the Fermi surface, and $\mathbf{L}_k$ is the mean-free-path vector. This is true for any shape of Fermi surface. The band-structure calculations of both Mattheiss and Hamann[4] and Fu, Krijn, and Doniach[14] predict a conduction-band minimum along the ΓM direction, which means a valley degeneracy ν of 12. The low conductivity means that a free-electron approximation is probably reasonable, i.e., we assume that there are carriers enough only to occupy the lower tip of the conduction band. Thus, we find a conductivity given by

$$\sigma = \frac{e^2}{12\pi^3\hbar} \nu 4\pi \left[\frac{3\pi^2 n}{\nu} \right]^{2/3} \mathbf{L} \ , \tag{2}$$

where n is the itinerant charge-carrier concentration. If we invoke the Ioffe-Regel condition, and assert that $L \geq a$, where $a = 2.2$ Å is the FeSi nearest-neighbor distance, then we find, if we insert $\sigma = \sigma_0$, that $n \leq 3.7 \times 10^{17}$ cm^{-3} at $T = 0$. This would mean that each charge carrier occupies a spherical volume with a diameter of at least 170 Å. We note here that although these carriers presumably originate from impurities, the concentration of the impurity sites may be greater than 3.7×10^{17} cm^{-3}.

The thermal conductivity $\lambda(T)$ data are consistent with an estimate of 3.7×10^{17} cm^{-3} or less free charge carriers. They are shown in Fig. 2, in which is included the electronic contribution $\lambda_{e-\text{WF}}$ to $\lambda(T)$, which has been calculated under the assumption that the Wiedemann-Franz (WF) rule is valid. We have already noted that the resistivity at room temperature indicates the dominance of inelastic scattering, at least at that temperature, which actually invalidates the use there of the WF rule. However, in the most usual circumstance in which inelastic scattering dominates, that is at temperatures higher than the regime where impurity scattering dominates, but nevertheless much smaller than the Debye temperature, so that inelastic electron-phonon scattering is through small angles, the WF rule is still correct to within a factor 2 or so. It is clear from Fig. 2 that $\lambda_{e\text{-WF}}$ is four to five orders of magnitude smaller than λ throughout the temperature range where both conductivities were measured. Providing the caveat just mentioned holds good, there must, therefore, be a vastly dominating phonon contribution to the thermal conductivity, as one would expect for a single crystal and a charge-carrier concentration of only 3.7×10^{17} cm^{-3}.

We find that the temperature dependence of the thermal conductivity follows a power law reasonably well

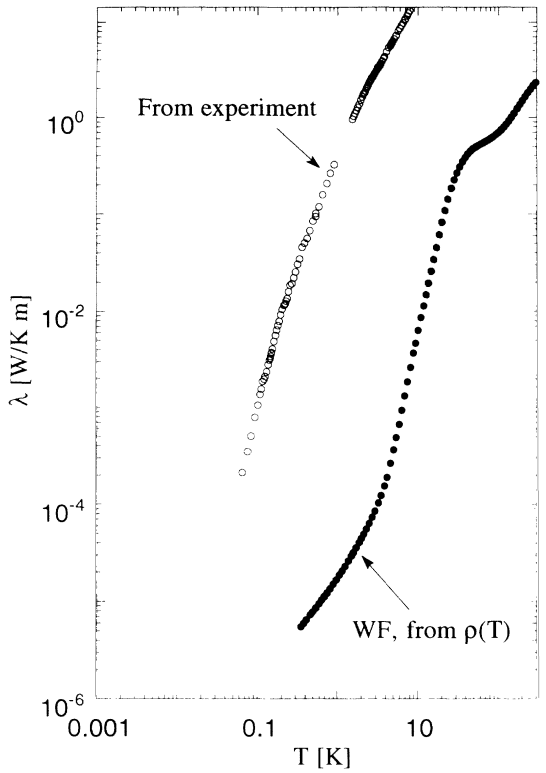

FIG. 2. The thermal conductivity $\lambda(T)$ of FeSi for temperatures below 8 K. We also show the Wiedemann-Franz $\lambda(T)$ as calculated from the electrical resistivity data.

throughout the measured temperature range. For $T<0.2$ K, $\lambda\approx 2.4T^{3.4}$ W/K m, while $d\lambda(T)/dT$ declines with increasing temperature.

We may estimate the effective mass of the charge carriers if we assume that the sample does undergo an insulator to metal transition with decreasing temperature and that this occurs when the Mott criterion for this,

$$n^{1/3}a^*_{\rm eff}\geq 0.25 \tag{3}$$

is satisfied, where $a^*_{\rm eff}$ is the effective Bohr radius. For $n=3.7\times 10^{17}$ cm^{-3} we require $a^*_{\rm eff}=35$ Å if a transition is to occur. Since, on the insulating side of the transition,

$$a^*_{\rm eff}=\frac{m_e}{m^*}\varepsilon_1 a_0\ , \tag{4}$$

where a_0 is the Bohr radius, ε_1 is the static dielectric constant, and m_e is the free-electron mass. If we use $\varepsilon_1=380\pm 10$, as deduced by DeGiorgi *et al.*[15] from an extrapolation to dc of far-IR reflectivity measurements down to 6 K and to below 100 cm^{-1} on the same sample that was used for the dc conductivity measurements, we obtain $m^*\leq 5.7m_e$. This compares with an estimated conduction-band mass, at the band edge along the ΓM direction, of $2-5m_e$, which may be calculated from Fig. 3 of Ref. 4.

These numbers have two immediate implications. One is that, according to Mott, $a^*_{\rm eff}$ implies a minimum metallic conductivity $\sigma_{\rm min}$ given by

$$\sigma_{\rm min}\approx\frac{Ce^2}{\hbar a^*_{\rm eff}}\approx 1700-3400\ (\Omega{\rm m})^{-1}\ , \tag{5}$$

where C is a constant between 0.025 and 0.05.[16] This minimal conductivity is 8.5–17 times bigger than what we actually observe. In view of the simplifying assumption of spherical pockets of the Fermi surface, this discrepancy may not be significant but has been noted in another similar case as well (see Sec. IV).

Another implication of a metallic interpretation of the conductivity at the lowest measured temperatures is that there should be a linear-in-T contribution to the specific heat. Within the framework described above, where we have assumed 12 degenerate spherical Fermi surface pockets along the ΓM directions, and we use the values for n and m^* deduced from the conductivity, we find $\gamma=4.6\times 10^{-4}$ J/mol K^2. We do see a nonzero linear contribution to the specific heat, and, remarkably, it is within a factor 2–3 of this calculated value. Nevertheless, even if the metallic interpretation is correct, such close agreement may well be largely fortuitous, given the simplifications involved in calculating γ from σ.

Our specific-heat data $C_p(T)$ are shown in Fig. 3, and in Fig. 4 on a logarithmic scale. In Fig. 5 we plot C_p/T

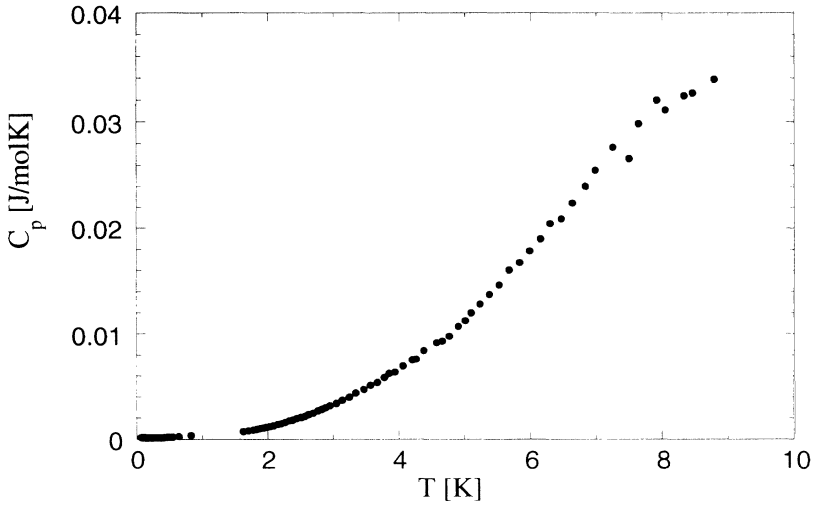

FIG. 3. The specific heat $C_p(T)$ of FeSi for $0.06<T<9$ K.

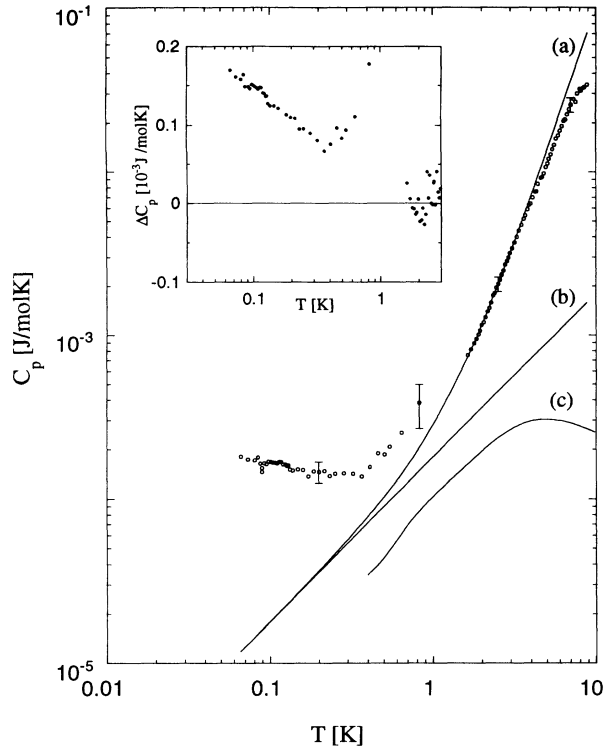

FIG. 4. The specific heat $C_p(T)$ of FeSi for $0.06 < T < 9$ K plotted on a log-log scale to emphasize the presence of the low-temperature upturn. We also show the excess specific heat ΔC below 1.5 K, obtained by subtracting from the measured specific heat the sum of the linear and cubic in T contributions, shown as (a). These are deduced from fits to the region for which $1.5 < T < 3.5$ K, as explained in the main text. The linear contribution, γT is shown as (b), while (c) is the contribution of Anderson-localized states arising from 1.0×10^{19} cm^{-3} randomly distributed impurity sites, as given by the model of Kamimura and Aoki, which considers only intrasite interactions, using parameters given by applying the same model to the susceptibility data, shown in Fig. 6.

vs T^2 for temperatures below 3.5 K and we also show the expected acoustic-phonon contribution, characterized by $\Theta_D = 313.5$ K, which we have calculated from the sound velocity at 300 K. This we deduce to be 4720 ms^{-1} from measurements at 300 K of the elastic constants c_{11} and c_{44}, by Zinoveva, Andreeva, and Geld.[17] Taken together, the data in Fig. 5 show that the Debye acoustic contribution is dominated below 10 K by another contribution, and we suggest that this may be a soft acoustic-phonon mode. In addition, the good linear fit between 1.5 and 3.5 K indicates the presence of a linear component γT, where $\gamma = 1.8\times10^{-4}$ J/mol K^2 is constant in this temperature range.

Below 0.5 K, the specific heat rises as temperature decreases. On general grounds, this must be the result of excitations of interacting Fermions within a finite number of states. After subtraction of extrapolations of the linear and cubic terms mentioned above, we find that the excess $\Delta C(T)$, shown in Fig. 4, is well described by a power law $\Delta C(T) \propto T^{\alpha}$, with $\alpha = -0.5$. Thus, $\Delta C(T)$ seems not to arise as a result of excitations within a two-level system characterized by a single interlevel energy J. As is well known, this would give a Schottky anomaly in the specific heat, with a high-temperature tail varying as T^{-2}.

Our measured ac susceptibility for $T < 1$ K, shown in Fig. 6, is well fitted by

$$\chi = \chi_0 + C/(T-\Theta) \tag{6}$$

and gives $\chi_0 = 6.81\times10^{-4}$ emu/mol, $C = 8.81\times10^{-5}$ emu K/mol, and $\Theta = 5\pm1$ mK. The background χ_0 is determined by the data above 1 K, as mentioned in Sec. II, while C and Θ are obtained from the sub-1 K data. This value of Θ is almost an order of magnitude lower than the lowest temperature at which measurements were done and should be interpreted as evidence that, within the detection limits of the susceptibility measurement, no

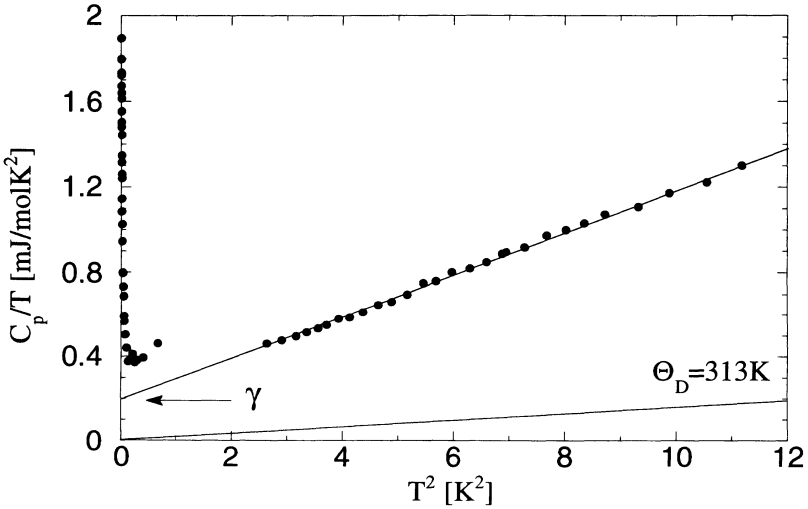

FIG. 5. $Cp(T)/T$ of FeSi as a function of T^2 for $0.06 < T < 3.5$ K. We also show the acoustic-phonon contribution.

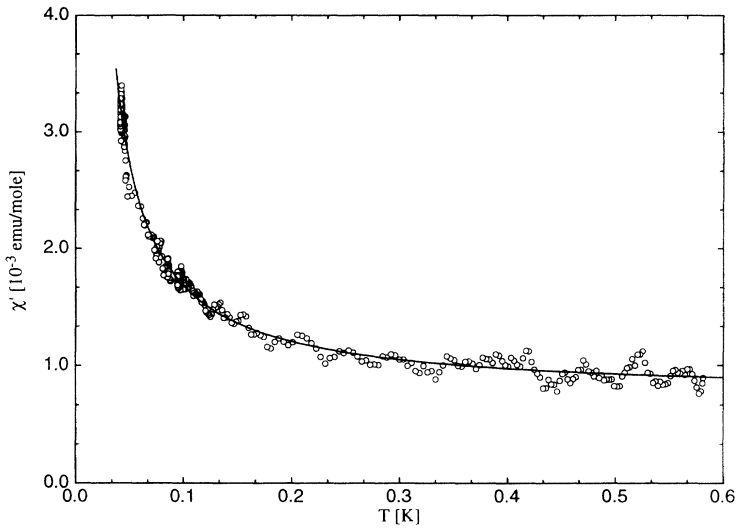

FIG. 6. ac susceptibility $\chi'(T)$ of FeSi for $T<1$ K. The solid line is a fit to $\chi'(T)=\chi_0+C/(T-\Theta)$.

magnetic order or spin-glass freezing occurs in this sample of FeSi, at least down to 40 mK. This is consistent with the neutron-scattering data taken at room temperature and at 77 K (Ref. 3) and extends the validity of the conclusion of those results downward through a further three orders of magnitude in temperature. Further, we note also that this result is consistent with the other neutron-scattering result mentioned in the introduction, that of Tajima *et al.*[8] who deduce from their data that $\chi'(q,0)$ is q independent, i.e., that there is a vanishing interaction between local moments in the system, at least at low temperatures. The low-temperature tail in the susceptibility is consistent with a 2.1×10^{18} cm^{-3}, 1.3×10^{18} cm^{-3}, or 9.1×10^{17} cm^{-3} concentration of spin $\frac{3}{2}$, 2, or $\frac{5}{2}$ impurities, respectively, as we would have if this tail reflects uncompensated iron moments from either d^7 Fe^+, d^6 Fe^{2+}, or d^5 Fe^{3+} ions, respectively. Schlesinger *et al.* are able to fit their high-temperature ac susceptibility if they suppose spin-$\frac{3}{2}$ impurities with a concentration of 0.2%, which is equivalent to 9.0×10^{19} cm^{-3}, and about 40 times greater than in our sample. In this connection, we note that excess iron at the 1% level is permitted in single-phase FeSi.[11]

IV. DISCUSSION

As a preliminary, we note that a comparison of the thermal-conductivity data below 0.2 K with the lattice specific heat suggests an absence in our sample of gross imperfections such as might scatter phonons below 0.2 K. This assertion holds so long as the following argument is reasonable. We see that $\lambda\approx2.4T^{3.4}$ W/K m for $T\leq0.2$ K. Equating this with the T^3 contribution that arises at low enough temperature through boundary scattering of phonons and using simple kinetic theory, we can estimate the temperature-independent mean-free-path of the phonons for $T\leq0.2$ K. We take the usual equation

$$\lambda(T)=\tfrac{1}{3}C_V v_s l_{\rm ph}\ , \qquad (7)$$

where C_V is the lattice contribution to the specific heat, v_s is the velocity of sound in FeSi, and $l_{\rm ph}$ is the phonon mean-free-path. We find $l_{\rm ph}=0.2$ mm, which is of the order of the macroscopic dimension of the sample perpendicular to the heat flow. Thus, we infer that our sample does not contain gross structural disorder. Rather, any disorder is most likely of point-defect type. Such defects, whether interstitial or substitutional, would not scatter phonons below 1 K.

A combination of specific heat and conductivity data, which is intriguingly similar to that presented here, has previously been observed in SmB_6.[18–20] This compound has been claimed to be an intermediate-valence material in which a hybridization gap of order 5 meV is believed to open up at temperatures of a few Kelvin. First, the conductivity of SmB_6 also saturates at low temperature, following a regime in which an $\exp(T_0/T)^{-1/4}$ dependence, again compatible with variable-range-hopping, applies, and at a value 5–10 times less than the minimum metallic conductivity calculated according to Eq. (5),[16,19,20] rather as we find here for FeSi. As far as we are aware, also for SmB_6 the origin of the residual conductivity is still an unresolved matter. Second, the lattice contribution to the specific heat below 10 K by far exceeds the Debye contribution, and a linear contribution is usually observed (although some authors have suggested that this is not an intrinsic effect[21]) together with some not well-resolved hump at even lower temperatures. Third, as in SmB_6,[22] the c_{12} elastic constant of FeSi, although positive, is much smaller than either c_{11} or c_{44}.[17] Such an anisotropy is typical of intermediate-valence compounds, where, as in SmB_6 c_{12} may even be negative. Low-temperature reflectivity data for SmB_6 also indicate that the gap has closed up at a temperature much less than the gap temperature,[23] as is claimed to be the case for the single-particle gap in FeSi (Ref. 10) although this was not confirmed for our sample.[15]

The above analysis of the resistivity is predicated on the view that the FeSi sample has become metallic below about 5 K. In this scenario, one could envisage the

3.7×10^{17} cm^{-3} (8 ppm) or less carriers as being localized at impurity sites at somewhat higher temperatures, but becoming itinerant at low enough temperature. From Eqs. (3) and (4), we observe that this transition could occur as a function of temperature if ε rises or m^* decreases. There is no evidence that the effective mass of the carriers drops dramatically with temperature. Indeed, our analysis above indicates a low-temperature value comparable to the band mass. The driving force for the transition should, therefore, be ascribed to a considerable increase of ε at low temperature. As mentioned above, far-IR reflectivity measurements on our sample[15] do indicate that the static dielectric constant ε_1 has attained the very large value of 380 ± 10 at 6 K.

In the following, we suggest an analysis of the ac susceptibility and specific heat for $T<1$ K, which offers an alternative explanation for these intriguing low-temperature properties in the sense that the electronic properties of FeSi are governed by a finite density of Anderson-localized states at the Fermi surface, at least down to 0.06 K. This argument arises by consideration of a model used originally to describe the structurally disordered system Si:P, where P dopants are randomly distributed in the periodic potential of the Si lattice and in the doping regime just on the insulating side next to the metallic regime. In this regime it is envisaged that carriers contributed by the dopants are Anderson localized around each dopant site. Accordingly, the electronic states are described by extended wave-functions exponentially damped within a characteristic localization length ξ. There is a nonzero density of states at the Fermi level, and hence a nonzero linear-in-T contribution to the specific heat, but these electronic states are localized, and so any contribution from them to charge conduction is of hopping type, and cannot be described by the metallic model used in the above analysis. In particular, the electrical conductivity should vanish at $T=0$. We discuss this point further below.

For the magnetic behavior of such a system, we may consider a model described by Kamimura and Aoki (KA) (see Ref. 24 and references therein), where it is envisaged that an array of randomly distributed impurity sites exists, each of which can be empty, or singly or doubly occupied by electrons. It is supposed that the one-electron energies are randomly distributed up to some maximum value W. The only parameter in this model is the ratio of W to $\bar{U}$, the mean intrasite Coulomb repulsion energy. The coexistence of localization and intrasite electron-electron interactions leads at temperatures smaller than $\bar{U}/k_B$ to a Curie-like susceptibility, despite a nonzero density of states at the Fermi level. This susceptibility is determined by the singly occupied sites

$$\chi=\frac{\mu_B^2 n_s}{k_B T} , \tag{8}$$

where n_s is the number of singly occupied sites per unit volume. This is in fact the usual Curie expression for the susceptibility of a noninteracting spin $\frac{1}{2}$ system. It is, however, a simplification of the full expression

$$\chi(T)=\frac{2\mu_B^2}{k_B T}\sum_\alpha\{2+\exp[\beta(\mu-\varepsilon_\alpha-U_\alpha)] +\exp[-\beta(\mu-\varepsilon_\alpha)]\}^{-1} , \tag{9}$$

where the summation is over states α, $\beta=1/k_B T$, μ is the chemical potential, ε_α is the one electron energy, and U_α is the Coulomb repulsion energy, which is energy dependent and given by

$$U_\alpha=\bar{U}(3\nu+1)[1-(\varepsilon_\alpha/W)]^{3\delta}\equiv U(\varepsilon_\alpha) . \tag{10}$$

The critical exponent δ is unity according to scaling theory.

If we use Eq. (8) to interpret the temperature-dependent part of Eq. (6), then we easily find that $n_s=10^{19}$ cm^{-3}, and from Eqs. (9) and (10) we find that excellent agreement with the temperature-dependent part of our data is obtained with $W/\bar{U}=0.25$, with $W=1.7$ meV and $\bar{U}=6.9$ meV. In this calculation, we assume that the density of singly occupied states is given by n_s/W, and we determine μ for each temperature.

At the same time, the continuous range of direct on-site interactions U_α will cause a broadly peaked contribution to the specific heat, which is a superposition of Schottky peaks. This will result in a specific-heat contribution approximately linear-in-T far enough below the range of peak temperatures. The linear contribution in our data is clear to see between 1.5 and 3.5 K, so in this interpretation, the range of characteristic on-site interaction energies would have to be of the order of 10 K or more. We have calculated the specific heat in the KA model, in which[24]

$$C_v(T)=\frac{\partial}{\partial T}\sum_\alpha\frac{2f(\varepsilon_\alpha)[\varepsilon_\alpha+\frac{1}{2}U_\alpha f(\varepsilon_\alpha+U_\alpha)]}{1+f(\varepsilon_\alpha)-f(\varepsilon_\alpha+U_\alpha)} , \tag{11}$$

where f is the Fermi function, and using the values for n_s, W and $\bar{U}$ deduced above from the susceptibility data. We show the result in Fig. 4 as curve (c). Clearly, the observed linear term in our specific-heat data cannot be fully accounted for in this way. The contribution to the specific heat from Anderson-localized states in numbers as indicted above is too small, by a factor 2, and moreover, peaks at about 5 K, so that it is not linear-in-T in the range where our data are linear. This supports our metallic interpretation of the conductivity data or suggests that any possible such contribution is too small to influence the experimental data noticeably.

The assertion that the Anderson-localization interpretation of the susceptibility nevertheless makes sense is supported by the fact that the KA model can also account for the low-temperature rise in the specific heat in a manner consistent with the value of n_s that we deduced above from the susceptibility data. In the KA model, the rise is due, once again, to the high-temperature tail of a superposition of Schottky anomalies, this time due to intersite doublet-doublet interactions. For any given pair, the total interaction can be antiferromagnetic or ferromagnetic, and the total interaction energy will depend on the distance that separates the members of the pair.

The total contribution to the specific heat should also be peaked, with the peak position reflecting an average interaction energy. If this interpretation is correct then our data, which is not peaked by 0.06 K, implies a characteristic intersite interaction energy, which is at least two orders of magnitude smaller than the intrasite energy. The disparity of energy scales, in this sense, is a feature of the model described by Kamimura and Aoki. If we are attributing the specific-heat upturn with the degrees of freedom of spin doublets, then the associated entropy per mole of FeSi should be given by

$$\Delta S = n_s R \ln(2s+1) , \tag{12}$$

where $s=\frac{1}{2}$ and n_s is what above was called the number of singly occupied sites per unit volume. We can calculate ΔS using

$$\Delta S = \int_0^T \frac{\Delta C(T')}{T'} DT' . \tag{13}$$

From Fig. 5 it is clear that ΔC is negligible above $T=1.5$ K, and so we can set this as an upper limit to the integral in Eq. (13). We find $\Delta S=0.35$ mJ/mol K and we calculate, from Eq. (12), $n_s=6.2\times10^{-5}$/f.u. or 3×10^{18} cm^{-3}. The actual number must be somewhat greater than this, since the entire excess specific-heat hump is not within the accessible temperature range. However, it is remarkable that similar values for n_s are deduced from two independent bulk measurements, one magnetic, the other thermal.

If we accept that the susceptibility data and the low-temperature rise in the specific-heat data find a common, quantitatively coherent interpretation in terms of the KA description of Anderson-localized states at the Fermi level, arising from structural disorder due to a random array of donor sites, then we must reconcile this with our previous assertion that the conductivity, apparently saturating at low temperature, and the linear term in the specific heat above 1.5 K, are evidence for an insulator-metal transition having occurred as the temperature fell below about 5 K. If these interpretations are both valid, then both itinerant and Anderson-localized states would have to coexist on the low temperature, metallic side of the transition, so that the Fermi level would have to lie at or very close to the mobility edge, the energy which separates the two types of states. This means, in effect, that the material must remain on the verge of a metal-insulator transition, even while the conductivity saturates. The same presumably applies to previous assertions[19] that the residual conductivity in SmB_6 implies the existence of delocalized states at the Fermi level.

V. CONCLUSION

The low-temperature rise in the specific heat and the Curie-type susceptibility of our samples of FeSi have a common explanation in terms of positionally disordered Anderson-localized carriers at a level $n\approx10^{19}$ cm^{-3}. The origin of these carriers is unclear, but the presence at this level of randomly distributed impurities is certainly a reasonable scenario for FeSi, which is not a line compound. Since the sample was grown in an Sb flux, it is conceivable that the impurities are Sb donors, but this is not necessarily the case, since the sample of Schlesinger *et al.* also displays, at low temperature, a Curie tail in the susceptibility and a nonactivated resistivity, and yet was grown by vapor transport. The low-temperature rise of the dc resistivity of our sample, though it amounts to three and half orders of magnitude, is not activated in conventional semiconductor fashion, although, on cooling from room temperature, there is a temperature regime, between 10 and 30 K, in which it is well accounted for by a variable-range-hopping description. In the limit of low temperature, the resistivity saturates. If this means that itinerant charge carriers are present, and the presence of a linear contribution to the specific heat indicates that they are, then it is not clear how this can be reconciled with Anderson localization other than by assuming that the Fermi level and mobility edge virtually coincide. We have performed a simple analysis, which indicates that the number density of itinerant charge carriers is 4% that of the Anderson-localized electrons. What does seem to be a genuine bulk property of FeSi is the conclusion drawn from the ac susceptibility data, that there are no magnetic ordering phenomena in FeSi, at least down to 40 mK.

In our analysis we have neglected the complication of the possible lifting of the 12-fold valley degeneracy of perfect FeSi due to crystal fields surrounding the impurities. It does not seem appropriate to treat this problem here, since the effect on our interpretation of the data presented here would depend on the resulting degeneracy of the lowest lying state and on the energy gaps between this and higher states, none of which are known for our sample.

In this paper we have tried to distinguish between those data that are certainly characteristic of bulk FeSi and those that can be quantitatively accounted for through weak positional disorder. If this disorder does arise extrinsically, then our results suggest that caution is needed in interpreting low-temperature experiments on FeSi, since we find that impurities at the sub 0.1% level are sufficient to account both for the observed rise in specific heat below 0.4 K and also for the Curie tail seen in the susceptibility, while 10-ppm donor impurity levels would account for the saturation of the resistivity in the limit of low temperature. Finally, we point to similarities between the low-temperature properties of FeSi and SmB_6, two compounds that are not otherwise obviously related.

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