Low-temperature properties of ϵ-FeSi from *ab initio* band theory

T. Jarlborg
Département de Physique de la Matière Condensée, University of Geneva, 24 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland
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Local-density calculations of the electronic structure as a function of temperature T and applied magnetic field H are presented for FeSi. The small band gap (6 mRy) makes FeSi change from being semiconducting at low T to being metallic at moderate T, and the exchange enhancement shows strong variations with T and H. An unusual situation, when a local field has closed the gap, is favorable for additional enhancement and spin fluctuations. Low-T properties are understood from mean-field calculations based on the band structure, but spin fluctuations have to be invoked to describe properties for T larger than about 200 K.

The cubic compound ϵ-FeSi has eight atoms per unit cell and its crystal structure in $B20$. It has been studied mostly due to its unusual magnetic properties, such as the maximum of the magnetic susceptibility at about 500 K.[1] Band calculations have shown an indirect semiconducting gap of only 4–8 mRy.[2–4] Resistivity and infrared absorption confirm the presence of a gap of about 50 meV at low temperature,[5,6] but it is essentially closed already at a temperature of 200 K. A recent work proposes that strong Kondo-like correlations and disordering of the band structure have to be present in FeSi in order to explain the rapid T variation of the optical gap.[4] The pressure dependence of the magnetic susceptibility has been found to agree with the calculated variation of the band gap.[3] Theories of spin fluctuations have been put forward to explain various T-dependent properties,[7,8] and formation of magnetic moments at high T has been detected from neutron scattering.[9] These moments are too small to be seen in spectra of x-ray photoemission,[10] but the shape of the spectra agree with the general shape of the calculated density-of-states (DOSs).

In this work we show that first-principles band results, based on the local-density approximation (LDA),[11] lend support to the idea that magnetic fluctuations become important at moderate temperatures. An adequate description of the T variation of the magnetic susceptibility and many other properties must take the fluctuations into account for $T \geq 200$ K.

For the band calculations we use the self-consistent, semirelativistic, all-electron, linear-muffin-tin-orbital (LMTO) method,[12] in which T-dependent electronic excitations are included via the Fermi-Dirac function.[13] Spin-polarized calculations including the applied magnetic field H give the Stoner enhancement of the susceptibility.[14] The atomic sphere radii in these calculations were $0.328a_0$ and $0.29a_0$ for Fe and Si, respectively. This choice gives only small discontinuities of the potential at the limits of the spheres. As noted in Ref. 4 and from comparing with the band results in Ref. 3, the bands near the gap are not sensitive to reasonable choices of sphere radii. The basis used s, p, and d for all sites, with f included in three center terms and tails.[12]

The LMTO calculations give a band structure and a gap which is very similar to what has been published earlier by use of different methods.[2–4] The calculated lattice constant, $a_0 = 4.43$ Å, is found at the minimum of the total energy E_{tot}. This is about 1% smaller than the experimental lattice constant. The bulk modulus, B, at a_0 is calculated to be 2.2 mbar, which is considerably larger than the experimental value, 1.3 Mbar, quoted in Ref. 15. It is known that LDA overestimates the bulk modulus and underestimates the lattice constant for $3d$ metals. The gap E_g is indirect, ranging from 6.1 mRy at a lattice constant of $0.98a_0$ to 5.7 mRy at $1.02a_0$. Bandwidths normally increase with pressure, and therefore gaps between different bands close with applied pressure. But here in FeSi the case is different since the gap is in the middle of the Fe $3d$ band. This may also be relevant for the fact that it is rather exceptional that E_g agree well with experiment, since LDA usually gives too small gaps in semiconductors.

The gap E_g is stable against changes in temperature. When T is increased from about 30 to 500 K (at fixed volume) the gap increases only about 0.05 mRy, despite the different electron occupation at large T. The density of states on both sides of the gap is dominated by Fe d states; cf. Fig. 1. The character of Si p and d is about $\frac{1}{10}$ of Fe d, both below and above the gap, so no real-space charge transfer is obtained by raising T. This explains the weak T dependence of the band structure itself. It is also true that the gaps within each of the two spin-polarized band structures are likewise insensitive to the temperature. However, for the physical properties it is the effective band gap (the gap which remains after an exchange-splitted band structure) which is important. As will be seen from the spin-polarized band results, properties of the effective gap depend strongly on H and T.

The exchange (or Stoner) enhancement $S(T,H)$ is defined as the ratio between the calculated exchange splitting of the (mostly Fe d) electrons at the Fermi energy E_F, and the applied field energy (1 mRy corresponds to 230 T). It is shown in Fig. 2 for five different fields. For small fields with an energy lower than the gap energy one sees no particular field dependence. The magnetic response is absent at low T since the material is essential-

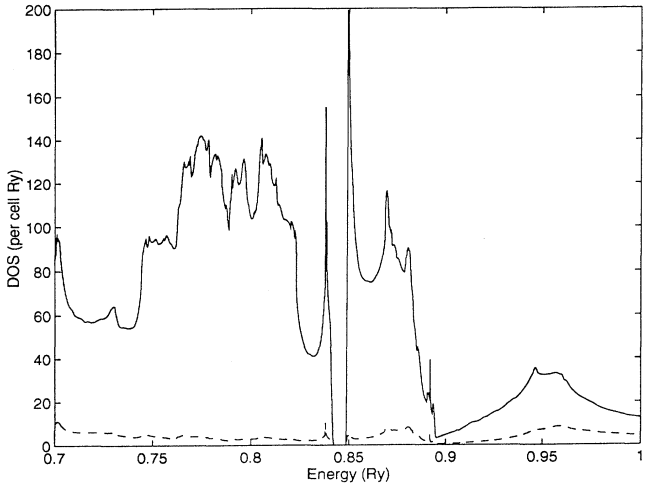

FIG. 1. Paramagnetic Fe d (solid line) and Si p (broken line) DOSs as calculated by tetrahedron integration. Units are in (Ry cell)$^{-1}$.

ly an insulator. From about 250 K and above, the occupations of electrons above the gap and holes below the gap give metallic properties, and a gradual increase of the Stoner enhancement is observed. Note that the shape of the $S(T,H)$ curve resembles measured susceptibilities in the range 50–500 K, although it has a small amplitude. (Measured results sometimes show an increase below 50 K which is extrinsic due to impurities, etc.[1,3]) A saturation is found experimentally beyond about 500 K, while the calculated $S(H,T)$ increases further.

When the exchange splitting is equal or larger than the gap energy ($\sim$6 mRy), FeSi enters into a very interesting situation: The applied field will close the gap, so that the top of the minority valence band will meet the bottom of the majority conduction band at E_F. Now magnetic excitations occur already at very low T, since the holes below E_F are in the minority band, while excited electrons

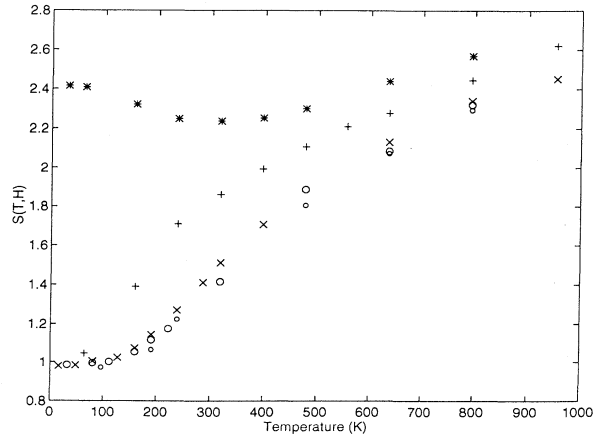

FIG. 2. The enhancement of the magnetic susceptibility $S(H,T)$ for five applied field [0.2 (o), 1 (○) 2 (×), 6 (+), and 8 mRy (*)] at different temperatures. 1 mRy corresponds to a field of 230 T.

above E_F have to go to the majority band. Therefore a change in spin character is induced by raising T at large H. As seen in Fig. 2, the high-field enhancements are much larger than at low field, because of this particular crossover of minority and majority bands. The sharp raise of the DOS on both sides of the gap makes the spin transfer important already at low T, while at larger T the effect is weakened, due to the smearing from the Fermi-Dirac function. This mechanism may also be triggered by thermal fluctuations and lead to an additional enhancement of local moments. For thermal fluctuations at 300 K, $k_BT\sim2$ mRy. The low-field Stoner enhancement at this temperature is about 1.5, and a local fluctuation of the field of 2 mRy would be enhanced to 3 mRy, which is half of the energy gap. These comparisons indicate that energies of thermal and magnetic fluctuations are not too far away from the critical value of the gap energy. Thus enhancement of the mean-field results are expected to come from fluctuations, and makes the susceptibility curve rise more steeply than $S(H,T)$ in Fig. 2. Thermomagnetic fluctuations of this type are consistent with the fact that optical measurements find no gap already at rather low T, as in Ref. 6. The fluctuations may consist of regions of several unit cells in which the internal field at a given instant is sufficient to close the gap locally.

This particular feature of the FeSi band structure makes the material sensitive to magnetic impurities. A local field is induced in the region of FeSi around the impurity leading to spin polarization and closing of the gap. This field is then enhanced by the mechanism mentioned above to give a rather important magnetic halo around the impurity site. For larger T the effect is weakened because of the Fermi-Dirac smearing. This effect resembles the Kondo effect,[4] and it is consistent with observations of enhanced susceptibility below 50 K in some samples.[1,3]

At very high temperatures it is clear that magnetic disorder is important to decrease the susceptibility. A Curie-Weiss behavior as in ferromagnets above T_c is therefore expected beyond a certain temperature. Theories for spin fluctuations give weakened susceptibility at large T due to the disordering of local moments.[8] An extrapolation of the magnetic moment from high T towards 0 K, via a Curie-Weiss law, give large estimates of the magnetic moment,[6] but such a procedure does not give the real moments at 0 K. The calculated moments at the lowest temperatures are close to zero for the low fields, while at $H=6.0$ mRy the moments are about $0.16\mu_B$ per Fe atom and about $-0.004\mu_B$ per Si atom. The Si moments and exchange splitting always show a weak antiferromagnetic tendency relative to the Fe majority spins, but the amplitudes are only a few percent of those of Fe. The similarity between measured and calculated susceptibility suggests that the T behavior is determined by the bands for moderate T, while the intensity has to be enchanced by fluctuations for $T>200$ K, in order to understand a large amplitude of the magnetic moment. The observed maximum in the susceptibility is due to strong fluctuations before magnetic disorder takes over above $\sim$500 K.

A self-consistent mean-field calculation of the electron-

ic contribution to the heat capacity $C(T)$ is done from the T variations of the total energy. FeSi at low temperature (below 50–100 K) is insulating with no electronic specific heat. Thereafter C/T increases smoothly to a saturated value of about 4 mJ/(mol K^2) around 300 K. A further increase of T does not increase the effective DOS around E_F more and C/T remains at this level. Experimentally it is difficult to separate electron and phonon contributions at these rather large T. But from the analysis which is presented in Ref. 1 the anomalous FeSi contribution is in addition to the normal specific heat of CoSi. This procedure gives a rising anomalous contribution which is peaked at 250–300 K (where C/T is read to be of the order 1 mJ/(mol K^2), in reasonable agreement with the calculated curve.

The electronic pressure P from valence electrons has been calculated as function of T. The result suggests that FeSi has an electronic contribution to the thermal expansion starting from 100–150 K. The pressure remains constant up to about 150 K. Thereafter P increases linearly with T, $P \approx 3\times10^{-6}\,(T-150)$ Mbar. With the calculated bulk modulus (2.2 Mbar with no T dependence) and neglecting other contributions, the coefficients $\alpha = 1/V\,(dV/dT) = 1/B\,(dP/dT)$, where V is the volume, is rather constant, 1.4×10^{-6} K^{-1}. Thus according to these mean-field calculations α is correlated to the gap energy, since thermal expansion starts only when thermal excitations can excite electrons across the gap.

Magnetic fluctuations tend to increase the thermal expansion further. This is concluded from the variation of P as function of magnetic moment M. The results for different fields H at low T ($k_BT < E_g$) fit to $P \approx 2\times10^{-6}H$ (Mbar if H is in T). This means that a spin fluctuation of $0.1\mu_B$ per Fe atom increases the pressure with roughly 1 kbar, when T is constant. At larger T the differences in magnetic susceptibility (and moment) between high- and low-field solutions are smaller than at low T, as seen in Fig. 2. The contribution to thermal expansion from spin fluctuations should appear at a temperature near 200 K, where other indications have shown that excitations just start across the gap. At this temperature the calculated low-field ($H < 500$ T, without fluctuations) magnetostriction is almost linear in H: $\Delta V/V = 10^{-6}H$. Measured magnetostriction has been reported to be almost quadratical in H for T below 29 K.[15] Measurements at higher temperature (or higher field) are required to see effects from fluctuations.

In addition to magnetic fluctuations it is also important to note that T-dependent vibrational properties are not included in the band calculations. It is expected that band smearing and fluctuations directly related to lattice vibrations will close the gap at temperatures that are comparable or higher than the Debye temperature. For instance, a band smearing coming from fluctuations of the Madelung potential is proportional to $\sqrt{T}$ and it amounts to ~ 5 mRy at $T \approx 500$ K in $4d$ metals.[16] A broadening of this amplitude contributes to band-edge smearing as well, and may fill the narrow gap at moderate T.

Finally, we also calculate the thermoelectric power $K(T)$ at low T. As was mentioned, the bands do not change much with T, and the calculation of $K(T)$ can be done from the frozen bands with constant electron scattering time τ.[17] The T dependence of $K(T)$ enters via the derivative of the Fermi-Dirac function. The result at low T depends sensitively on the initial position of E_F, and $K(T)$ shown in Fig. 3 is for a slight hole doping $Fe_{1-\delta}Si_{1+\delta}$. This agrees well with measured data presented in Ref. 18, both concerning the T variation and the magnitudes. The rapid variation of K at low T is mainly due to the displacement of E_F with T, from the top of the valence band to the middle of the gap. The good agreement with experiment for this property is (together with resistivity data) another indication that the band structure and the gap is correct. No contribution from disorder or fluctuations are expected, since the data are restricted to low temperature.

In conclusion, we have calculated several low-temperature properties of FeSi from *ab initio* band theory. The calculated exchange enhancement gives insight to the mechanism of spin fluctuations in FeSi, although a quantitative calculation of magnetic susceptibility including dynamical effects is not done. Some other calculated properties are presented in order to suggest measurements were mean-field and fluctuation effects can be separated. The results imply that the physics of FeSi is quite different in three temperature regions. The T dependencies at low T (below about 100 K) can be understood from mean-field properties of a small-gap semiconductor. At an intermediate temperature range (about 100–200 K) the material behaves as a (poor) metal because of the important electron excitations across the gap. Mean-field calculations are still adequate, but not in the region of higher temperature when spin fluctuations become important. The spin-polarized calculations show that a key feature of the bands is that the gap can be closed by an exchange splitting. This allows for stronger T dependencies at lower T than if only Fermi-Dirac excitations across the nonpolarized gap was allowed, and it will enforce the exchange enhancement further. It also

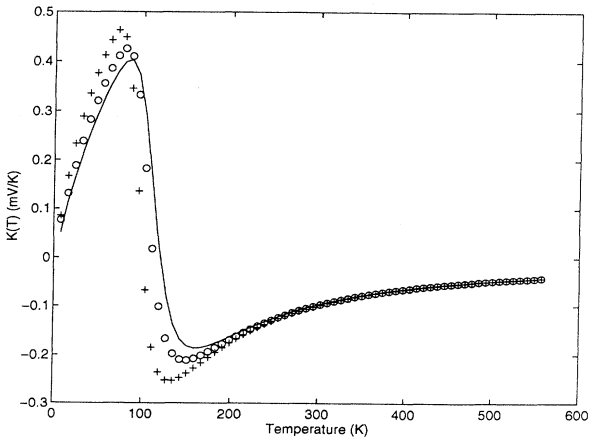

FIG. 3. The coefficient for isotropic thermopower as calculated from the frozen paramagnetic DOS. The three cases are for different hole doping, ranging from having 0.008 (solid line), 0.005 (o), and 0.002 (+) holes per unit cell.

follows that the material is sensitive to magnetic impurities.

These findings, based on parameter-free calculations, provide a complementary information to what has already been proposed for FeSi. The role of spin fluctuations have been supported by theories, in which density-of-state models and parameters for Coulomb interaction and exchange enhancements have been used to describe several T-dependent properties,[1,7] in particular the Curie-Weiss form of the susceptibility at high temperature.[8] The present work shows that the local exchange enhancement is not constant, but varies with T and H. An expected disordering of the band structure itself is proposed in Ref. 4. Here we note that atomic vibrations become important for T being close to the Debye temperature, but their interaction with spin fluctuations are yet not determined.

Some results suggest that measurements at large magnetic fields (or with dilute magnetic impurities) could elucidate the nature of the gap and its closure by exchange splitting. A large field should bring spin fluctuations towards lower temperature, according to the conclusions above. This also has an impact on the thermal expansion, where the contribution from fluctuations and disorder are separated from the pure band effects. The possibility of promoting spin fluctuations by closing the gap by an internal field makes FeSi quite unusual, since applied fields normally tend to align disordered moments and therefore also tend to suppress spin fluctuations.

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