Photoemission spectroscopy across the semiconductor-to-metal transition in FeSi

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Abstract. High-resolution angle-resolved photoemission spectroscopy (ARPES) was performed on high-purity FeSi single crystals. Since a high quality of the surface is obligatory to obtain reliably the correct band structure, special care was taken for the in situ preparation. Comparison of the experimental data with band structure calculations in the local density approximation shows that the self-energy resulting from electronic correlation effects leads to a strong renormalization of the energy bands in the vicinity of the Fermi energy. Temperature-dependent ARPES investigations reveal that at elevated temperatures the self-energy is strongly $\vec{k}$-dependent due to scattering of thermally excited particles and holes near the gap. From the ARPES results, it is obvious that the physical properties of FeSi are due to the high DOS at the edge of the renormalized band gap, but are not determined by a Kondo scenario.

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1. Introduction

One of the most intensively discussed topics in condensed-matter physics has been the field of metal-to-insulator transitions [1]. An issue of special importance is the understanding of materials with transitions that are driven by electronic correlation effects. Among such materials are the Kondo insulators or heavy-fermion semiconductors [2, 3]. For these materials the high-temperature phase is reminiscent of the Kondo effect, in which the conduction electrons interact with the degrees of freedom associated with dilute magnetic moments. However, at low temperatures the lattice properties of the impurities become important and they cannot be seen as dilute any longer. In the limit of one conduction electron per local moment, the ground state then becomes insulating with a gap that is strongly renormalized.

In this context, FeSi has been of high experimental and theoretical interest for over 60 years. The magnetic susceptibility, which shows a Curie–Weiss-like \(1/T\)-dependence above 500 K, decreases with lowering temperature and finally ends in a non-magnetic ground state [4]. In the electrical resistivity at low temperature, a semiconducting \(T\)-dependence is observed, whereas metallic behavior occurs above room temperature [5]. The crossover from an insulator to a metal is also apparent in optical measurements where the band gap vanishes at temperatures above \(\approx 150\) K [6, 7]. Since FeSi displays a behavior which has, so far, only been observed in f-electron containing Kondo insulators, FeSi itself has often been claimed to be the first 3d system which also belongs to this class of materials [2, 8, 9].

In agreement with the experimental data, single-particle band structure calculations using the local density approximation (LDA) result in a non-magnetic semiconductor with a band gap that is slightly larger than the measured values [10]. Introducing the on-site Coulomb repulsion by LDA + U, it was found that FeSi is energetically close to a ferromagnetic metallic phase [11]. However, similar results can be obtained by the inclusion of temperature dependencies in the LDA calculations [12]. Since current band structure calculations predict bandwidths that are much too large to describe the properties of FeSi correctly, different models were proposed with two narrow peaks in the density of states (DOS) on either side of the band gap [8, 13]. The peaks correspond to two localized Hubbard bands that couple to each other leading to a strong renormalization.

The most direct way to shed light on the electronic structure including many-body effects of a material is angle-resolved photoemission spectroscopy (ARPES) [14]. In recent ARPES measurements a sharp peak very close to the Fermi energy has been observed which is attributed to Fe 3d states and is strongly temperature dependent [15]–[21]. In some details, however, these experiments lead to contradicting results due to different sample and surface qualities.
In addition, the energy resolution was, in some cases, not sufficient to give clear answers to the question of the electronic nature of these states. Therefore, highly resolved ARPES experiments were performed on FeSi single crystals with a very low impurity concentration and with carefully in situ prepared single-crystalline surfaces. In our previous work, we showed in combination with LDA calculations that electronic correlations strongly renormalize the bands in the vicinity of the Fermi energy [21]. However, we could also show that despite strong electronic correlations FeSi does not belong to the class of Kondo insulators. Here we show temperature-dependent measurements on the same samples. Our results reveal that the crossover from an insulating to a metallic state is due to a $\vec{k}$-dependent self-energy and that the characteristic energy scale of the system is probably the renormalized band gap $\Delta$.

2. Experimental

For the crystal preparation, iron granules (Alfa Aesar 99.98%) and high-purity silicon pieces ($\rho_n = 300 \ \Omega \ cm$, $\rho_p = 3000 \ \Omega \ cm$) were melted using a single arc oven. From the pre-reacted polycrystalline FeSi button, a single crystal was grown using the tri-arc Czochralski method. X-ray powder diffractometry using the Riedveld method confirmed that the material was single-phase FeSi in the cubic B20 structure. The single crystals were oriented by the Laue technique and by low-energy electron diffraction (LEED). The purity of the samples can be estimated from the low-temperature paramagnetic susceptibility; assuming that this residual magnetization originates from magnetic moments of uncompensated Fe$^{3+}$ [6, 22], the Curie constant corresponds to a comparatively low impurity concentration of $\approx 0.17\%$. The high-resolution ARPES experiments have been performed using a SCIENTA R4000 analyzer in combination with a monochromatized GAMMADATA VUV5050 lamp at a photon energy of $h\nu = 21.2$ eV (He I$_\alpha$). Since the sample temperature and experimental resolution are very important for the presented data analysis, we carried out an exact calibration of the energy resolution with the help of superconducting V$_3$Si similar to [23]. The sample temperatures could be determined by a fit of the Fermi edge of a polycrystalline metal sample that was mounted next to the FeSi sample. For the measurements presented here, the energy resolution of the set-up was $\Delta E = 4.1$ and 6.8 meV, dependent on the particular analyser settings. The excitation energy-dependent measurements were carried out on the X09LA beamline at the Swiss Light Source. In order to gain sufficient intensity for a band mapping, the resolution was set to $\sim 20$ meV. The base pressure of the UHV systems was in the low $10^{-10}$ mbar range increasing to $8 \times 10^{-10}$ mbar during the experiments with the discharge lamp, due to He leakage.

3. Theory

Density functional calculations were performed with the electronic structure code CRYSTAL [24] and employing the local density approximation (LDA). A local basis set was used with a [6s5p2d] basis for Fe and a [5s4p1d] basis set for Si as described in [25]. The $\vec{k}$-point sampling net was chosen as $8 \times 8 \times 8$.

In various LDA calculations for FeSi [10, 12], [25]–[27], it was found that the LDA describes the band gap reasonably well, with a gap of the size of $\sim 100$ meV. The band structure computed with the present approach is shown in figure 1. The density of states, total as well as projected on the iron, iron d, and the silicon states, is displayed in figure 2. It becomes obvious that around the Fermi energy the states are mainly Fe d like.
Besides mapping the band structure, photoemission spectroscopy is able to reveal true many-body processes that influence the properties of a solid. More precisely, the many-body interactions enter the spectral function $A_k(E)$ directly via the complex self-energy $\Sigma(E, \tilde{k})$ [14, 28]. In the case of a vanishing velocity of the photo hole perpendicular to the surface (which holds in general for very flat bands or low-dimensional systems), its imaginary
part \( \text{Im} \Sigma \) is directly accessible from the linewidth \( \Gamma \) (FWHM) of the photoemission peaks, where \( \Gamma = |2 \text{Im} \Sigma| \). The real part \( \text{Re} \Sigma \), on the other hand, is determined from the shift of the peak maximum relative to the single-particle energy. Thus, \( \text{Re} \Sigma \) can be extracted from the ARPES spectra only by assuming a single-particle energy \( \varepsilon_k \) from band-structure calculations. However, \( \text{Re} \Sigma \) can also be derived directly from \( \text{Im} \Sigma \) by a Kramers–Kronig transformation. The importance of self-energy effects in ARPES is described in detail in [29, 30]. In general, the energy dependence of \( \Sigma \) leads to an asymmetric line shape that has also been observed, e.g. in solids showing electron–phonon coupling [31] and Fermi-liquid behaviour [29].

In interpreting the angular dependence of experimental photoemission spectra one must be aware of the fact that during the photoemission process only the \( \vec{k} \)-component parallel to the surface (\( k_\parallel \)) is conserved. The perpendicular component \( k_\perp \) is not conserved and has to be approximated in order to be compared with the LDA calculations. A common method is to assume a free electron final state for the emitted photoelectron [14, 20, 32]. The wave vectors can then be determined by

\[
\begin{align*}
  k_\parallel &= \frac{\sqrt{2m}}{\hbar} \sqrt{E_{\text{kin}}} \sin \Theta, \\
  k_\perp &= \frac{\sqrt{2m}}{\hbar} \sqrt{E_{\text{kin}} + V_0 - \frac{\hbar^2}{2m} k_\parallel^2},
\end{align*}
\]

where \( m \) is the free electron mass. The parameters \( V_0 \) and \( E_{\text{kin}} \) are the inner potential and the kinetic energy of the photoelectrons (see [14] for a more detailed explanation). A good way to estimate the value of \( V_0 \) is to vary the photon energy in normal emission. As can be seen from (1) and (2) this means one is following directly the \( k_\perp \)-direction. \( V_0 \) has to be chosen in such a way that the experimental band structure fits best to the calculated one. Especially the periodicity of the bands has to be reproduced which can be seen most clearly at the zone boundaries.

4. Results and discussion

Because of the surface sensitivity of photoemission spectroscopy—especially in the VUV range—special care must be taken for the surface preparation. A common method to obtain clean surfaces is to cleave the sample \textit{in situ}. For ionic crystals or layered compounds, where the cleaving planes are well defined due to weak forces between the layers, this technique provides nice single-crystalline surfaces [30], [32]–[34]. However, in three-dimensional crystals with predominantly covalent bonding character, like in FeSi, there are no such predefined cleaving planes. For these materials, cleaving attempts often result in a surface consisting of a mixture of various crystalline directions, or the surface can be totally disordered and then has to be treated as polycrystalline [35]. In both cases only the angle-integrated density of states (DOS) can be probed.

Another method to prepare clean surfaces \textit{in situ} is to sputter the surface with Ar\(^{+}\)-ions. The main risk of this method is that the sputtering cross-sections change with the atomic mass and, thus, the stoichiometry of the crystal is possibly altered. Although the sputter process usually leads to clean surfaces, the quality of as-sputtered surfaces is far from being single crystalline. Nevertheless, single crystallinity can be restored by annealing the surface after sputtering for an appropriate time. Besides annealing, the thermal treatment itself is another method to prepare a
Figure 3. Photoemission spectra \((h\nu = 21.2\,\text{eV}, \text{He I}_\alpha, T = 10\,\text{K})\) and LEED patterns \((E_0 = 100\,\text{eV})\) of FeSi(100) surfaces used to characterize different surface preparation methods: (a) surface degradation due to absorption of oxygen, (b) valence spectra for different preparation methods, (c) LEED pattern for an annealed surface and (d) for a cleaved surface. The horizontal lines indicate the DOS of a normal metal (Fermi–Dirac distribution).

clean single-crystalline surface since it often leads to the desorption of physisorbed atoms and molecules [36].

Figure 3(a) shows the valence band spectrum of a clean FeSi (100) surface directly after \textit{in situ} cleaving and after several hours. Using a He I\(_\alpha\) source, all the data in this section were collected in the angle-resolved detector mode (\(\Gamma XRM\)-plane) but integrated afterwards over \(\pm 15^\circ\). The dominating features in the resulting spectra are bands at \(E_B < 3\,\text{eV}\) and there are no other structures visible at higher binding energies. A comparison with the LDA calculations (figures 1 and 2) reveals that this intensity originates mainly from Fe 3d-states. The sp-bands at higher binding energies have a much larger dispersion and do not appear as a sharp peak in the integrated spectrum. Despite the UHV-conditions during the experiment the surface shows degradation effects after several hours: a broad peak, that most likely corresponds to oxygen
adsorption on the sample surface, emerges below $E_B = 6 \text{ eV}$. At the same time the 3d-features lose intensity and get smeared out. The surface can be restored by annealing the sample for $\sim 30 \text{ min at 700}^\circ \text{C}$.

Figure 3(b) shows a comparison of the valence band spectra of single-crystals prepared with the above-mentioned methods—cleaving, sputtering and annealing (with only mild sputtering before the first annealing ($\sim 1 \text{ min}$)). The missing peak below 6 eV clearly demonstrates that the surfaces are free from oxygen in all three cases and that, therefore, all three methods are suited to obtaining a clean surface. However, the 3d-bands at the Fermi-edge show significant differences in intensity and sharpness. Since the detector mode only accesses a small region in the reciprocal space, the sharpness of these 3d-features is representative for the surface crystallinity, i.e. if some different crystalline domains exist on the surface, the spectrum is effectively integrated not only over the detector-limited angles but also over all the other domains on the surface.

Low-energy electron diffraction (LEED) provides useful information about the quality of the surface. While the as-sputtered surfaces do not yield any LEED pattern, which demonstrates that these surfaces are completely disordered, the LEED pictures ($E_0 = 100 \text{ eV}$) of the annealed and cleaved surfaces show typical patterns as depicted in figure 3(c) (top and bottom picture, respectively). The surface of the annealed sample has no or only insignificant contributions from differently oriented domains, which is demonstrated by a LEED pattern merely representing the square lattice of the FeSi (100)-surface. On the other hand, the pattern of the cleaved sample shows several additional spots that do not belong to the (100)-surface. As a consequence the broadening of the 3d features in figure 3(b) for the cleaved sample represents the admixture of other crystalline directions in addition to the (100)-surface. The sputtered surface, which is totally disordered and must be considered as poly-crystalline, shows only a flat and broad feature. These observations clearly demonstrate the importance of the surface preparation for FeSi. We want to emphasize that these findings hold also for the (111)-surface. Therefore, for all the high-resolution ARPES measurements, we have chosen a sample preparation by repeated cycles of annealing at 700 $^\circ \text{C}$ for 30 min.

In order to get an overview over the electronic structure and map it to the LDA calculations, energy-dependent ARPES measurements in normal emission along $k_\perp$ in the energy range from $h\nu = 20$ to 150 eV were performed. The energy bands in $\Gamma X$- and $\Gamma R$-direction which were obtained using a (100)- and a (111)-surface, respectively, are represented by a gray-scale plot (figure 4). The white circles specify the peak positions found in the respective energy distribution curves (EDC). FeSi appears as a semiconductor with a bunch of narrow bands ranging from $E_B \approx 50$ to 500 meV and some more dispersive bands at higher binding energies. The best agreement between the experimental bands and the calculated band structure was achieved by assuming an inner potential $V_0 = 16 \text{ eV}$ for the $k_\perp$-component of the wave vector (cf (2)).

In the $\Gamma X$-direction the periodicity of the band structure at $E_B = 1.5 \text{ eV}$ is well reproduced by the experiment. The 3d-derived bands as well as the more sp-derived bands at higher binding energies can clearly be assigned to the features in the photoemission spectra. Nevertheless, there are also peaks that lie exactly in the middle between two bands which are for higher binding energies due to the fact that the linewidth increases. Therefore, adjacent structures cannot easily be resolved and appear as one broad peak. For the bands at the Fermi edge, it is caused by an experimental resolution that is larger than the linewidth of the bands in this region, as will be discussed later. Especially for the bands that show a wide dispersion, it is not easy to derive
Figure 4. Photon energy-dependent measurements used to map the band structure (high intensities appear dark, $h\nu = 20–150$ eV). The upper panel corresponds to a FeSi(100)-surface, the lower to a FeSi(111)-surface. The white circles specify the estimated peak positions found in the respective energy distribution curves (EDC). Horizontal bands indicate two-dimensional surface states.

the correct positions of the peak maxima from EDCs. On the other hand, using momentum distribution curves (MDC) is not practicable as there are very few data points and the changing photoemission cross section [37] makes it complicated to find a correct normalization.
For the $\Gamma R$-direction, on the other hand, the agreement between theory and experiment is less obvious. Only at the $\Gamma_1$ point, the experimental data match the calculated bands at $E_B = 1.7\,\text{eV}$. For other $k$-points no peaks could be derived from the EDCs, which could be due to the large band dispersion. However, the bands at $E_B = 0.05$ and $0.4\,\text{eV}$, which are the most prominent features, cannot be assigned to any of the calculated bands. As these structures show almost no dispersion in $k_{\perp}$, we suppose that these bands are surface-related states that are not included in our LDA calculations.

As a conclusion from the comparison of the energy-dependent measurements with the LDA-calculations, it can be stated that the periodicity and the qualitative dispersion of the bands in the $\Gamma X$-direction (corresponding to the (100)-surface) are well reproduced by assuming an inner potential of $V_0 = 16\,\text{eV}$. The $\Gamma R$-direction (corresponding to the (111)-surface), on the other hand, gives a less good agreement because of the surface-related states.

All of the following high-resolution measurements were done using a monochromatized He-lamp on a (100)-surface. The crystal was oriented in such a way that the measured path through the Brillouin zone (see (1) and (2)) was in the $\Gamma M R$-plane. Assuming the inner potential $V_0 = 16\,\text{eV}$ deduced above, the path in $k$-space goes approximately from the $\Gamma_1$ to the $M$-point for the He I $\alpha$ spectra. But in order to get the best agreement between theory and experiment, the exact path through the Brillouin zone was calculated using (1) and (2) and from another fit of the inner potential we found that the value of $V_0 = 16\,\text{eV}$ again gives the best agreement. This is also consistent with the results from spectra using He I $\beta$ and He II $\alpha$ radiation [21].

Panel (b) of figure 5 shows a high-resolution angle-resolved dataset recorded at $T = 10\,\text{K}$. As anticipated from the $k_{\perp}$-dependent measurements and LDA, FeSi appears as a semiconductor with one very small dispersing band with a full-width at half-maximum (FWHM) of approximately $15\,\text{meV}$ and a binding energy of $20\,\text{meV}$. By fitting a parabola to the band (see red line (---) in figure 5), the effective mass can be estimated by $m^* \approx -10.5\,m_e$.

It should be noted that the width of this band is extremely small for a three-dimensional material. However, a surface localization of this band can be ruled out by the $k_{\perp}$-dependent measurements revealing a shifting of this structure when changing to a slightly higher excitation energy from He I$_\alpha$ to He I$_\beta$ (see inset in figure 7). Additionally, at higher binding energies a not so heavy, hole-like band with $E_B \approx 60\,\text{meV}$ appears. The second derivative of this intensity map shown in panel (a) reveals that the narrow band is split into two bands around $k_{\parallel} = 0\,\text{Å}^{-1}$. In order to investigate the spectral features of one band alone, the EDCs we show in the further course of this paper are taken at $k_{\parallel} = 0.14\,\text{Å}^{-1}$ as indicated by the white dashed line in (a) and the EDC in panel (c). At this $k_{\parallel}$-value, the binding energy of the hole-like band is big enough so that the small band can be observed alone.

ARPES spectra always show a DOS-background due to inelastic scattering of the photoelectrons during the photoemission process. For simple metals, this background can be estimated by a simple Fermi–Dirac distribution and can easily be subtracted. FeSi, however, with a strongly modulated density of states in the vicinity of the Fermi edge is far from being a simple metal (see figures 2 and 3). Therefore, a subtraction of a metallic background is unjustified in this case. Instead, we correct the EDCs for the background by subtracting the spectrum at the same temperature of a polycrystalline surface which was obtained by mild sputtering of a single crystal as described above. After the background subtraction, one then gets an asymmetric lineshape for the sharp band near $E_F$ as shown in panel (c) of figure 5 and the inset of figure 7. This band has no spectral weight at $E_F$ in accordance with the semiconducting nature of FeSi.
In our previous work, we could show that all those spectral features can be described by quasi-particles by using the LDA dispersion as single-particle energies $\varepsilon_f$ and incorporating an appropriate self-energy $\Sigma$ in the spectral function $A_k^<(E)$ as described above [21]. We found that the linewidths (FWHM) and the renormalization of the binding energies of the peaks (see figure 6) can be understood in the framework of a model for $d$-electron correlations in transition metals discussed in the literature [15, 20, 21, 38].

This self-energy could be decomposed into two fractions—one Fermi-liquid like and another fraction, which is the most important for the low energetic part of $\Sigma$ (see figure 6). The low-energy behavior is described by a large coupling constant $\lambda \approx 1$ given by the slope of the real part at the Fermi energy and representing an effective band-mass renormalization of $m^*/m_0 = \lambda + 1 \approx 2$, where the single-particle band-mass $m_0$ is already rather high. The real part of the low-energy part shows a maximum at $\approx 90$ meV corresponding to a very high characteristic temperature of $T_m \approx 1000$ K. This is approximately a factor of two larger than the Debye temperature of $\theta_D = 460$ K [39] ruling out the possibility that Fermi-liquid theory, electron–phonon coupling or a combination of both can explain the physics alone. Note that the characteristic temperature could also be a bit lower, as the exact position of the maximum cannot be determined due to very few data points. However, the imaginary part shows a big increase above $E \approx 50$ meV $\sim 600$ K indicating that the characteristic temperature has at least
Figure 6. Energy dependence of \( \text{Im} \Sigma \) and \( \text{Re} \Sigma \) as determined from high-resolution ARPES measurements on a FeSi (100)-surface with He \( \text{I}_\alpha \)-radiation (see [21] for details). The broken lines (---) indicate the decomposition of \( \Sigma(E) \) into the Fermi-liquid part (FL) and the low-energy part. From the slope of \( \text{Re} \Sigma \) at \( E_F \) one can determine the coupling constant \( \lambda \). Three characteristic energy scales, the Debye temperature (\( \Theta_1 \)), the renormalized gap (\( \Delta \)) and the energy of the maximum of \( \text{Re} \Sigma \) (\( T_{\text{m}} \)) are shown by the dashed dotted lines (———). The same order of magnitude as the renormalized band gap \( \Delta \approx 60 \text{ eV} \) [6, 21], [40]–[42] or even could be \( \Delta \).

The importance of \( \Delta \)—which produces a hole in the phase-space volume for low energetic scattering processes—in combination with the unusually high DOS in the vicinity of \( E_F \) was taken into account by the model of Fu and Doniach [13]. They proposed a model for FeSi with two coupled Hubbard bands, where the chemical potential is exactly in the gap. In their calculations, the real part of \( \Sigma \) leads to a strong renormalization of the energy bands near the Fermi edge, i.e. a large contribution to \( \text{Re} \Sigma \). The linewidth increases sharply above the renormalized gap size \( \Delta \). Both facts are consistent with our data and open up the possibility that the physics of FeSi is governed by this kind of physics.

In order to shed more light on the many-body properties and clarify the role of \( \Delta \), ARPES data were taken for different temperatures from \( T = 10 \) to \( 120 \text{ K} \). The electronic correlations found to be responsible for the shape of the band structure around the Fermi level should also
Figure 7. Temperature dependence of the narrow band at $k_{\parallel} = 0.14\,\text{Å}^{-1}$ (the solid line is a guide to the eyes). The inset shows EDCs at $k_{\parallel} = 0.14\,\text{Å}^{-1}$ for two different excitation energies, and the spectrum of a sputtered surface used for background correction.

play an important role for the evolution of the spectral function with temperature, and especially for the insulator-to-metal crossover at $T \sim 100\,\text{K}$ [5]–[7]. Figure 7 shows the background corrected spectra of the narrow band near $E_F$. The EDCs are taken at $k_{\parallel} = 0.14\,\text{Å}^{-1}$ and are representative for the whole energy band in the scanned region. The evolution of the peak is as impressive as it is surprising: on the one hand, the intensity decreases by a factor of two. On the other hand, it does not broaden or show any binding energy shift. In fact, the band seems to keep its semiconducting properties up to the highest measured temperatures as no spectral intensity is seen at $E_F$. The reason for the non-broadening and sustainment of the binding energy of the band can be deduced again from the self-energy: the characteristic temperature—$\Delta$ or $T_m$—at
Figure 8. Evolution of the background DOS of a sputtered surface of FeSi with temperature. In panel (a) raw data are presented whereas panel (b) shows Fermi–Dirac normalized data. (c) Shows the intensity difference of the normalized data: \( I_{\text{diff}}(E, T) = I_{\text{norm}}(E, T) - I_{\text{norm,fit}}(E, 120 \text{ K}) \). One clearly sees the evolution of a gap at \( E_F \) and the appearance of a peak at \( E_B \approx 20 \text{ meV} \).

which considerable changes of \( \text{Im} \Sigma(E) \) and \( \text{Re} \Sigma(E) \) are expected is one magnitude higher than the highest temperature in the measurements. This is also consistent within the model of Fu and Doniach [13]: the \( T \)-dependence of the linewidth shows a simple \( \Gamma \propto e^{-\beta \Delta} \) behaviour and, thus, the lifetime of the quasiparticles is determined by scattering off thermally excited particles and holes near the Fermi energy. However, this theoretical scattering rate is strongly dependent on \( \varepsilon_k \). That means that the metal-to-insulator transition must be searched for at different \( \vec{k} \)-points, i.e. at points where the renormalized gap is minimal. Due to the limitations of a fixed excitation source we can reach those points in reciprocal space only in the subtracted background DOS which is shown in panel (a) of figure 8.

In order to get the actual DOS, the effects of the Fermi–Dirac distribution which suppresses the PES spectra at \( E_F \) have to be taken into account. A common method is to divide the whole spectrum by a Fermi-function with an effective temperature accounting for the thermal and resolution broadening [28, 35]. The Fermi–Dirac normalized spectra are shown in panel (b) of figure 8. From this figure it can be already seen that with increasing temperature the DOS changes: with falling temperatures, the formation of a gap-like structure is clearly observed. The low-temperature data show that the gap in the DOS is a bit smaller than the gap seen in the angle-resolved measurements. Additionally, it can be seen that the minimum of the DOS is at negative binding energies and moves towards \( E_F \). This can be understood by the fact that for FeSi the sign of the Hall coefficient (\( R_H \)) is sensitively dependent on the temperature [18, 22] and thus the position of the Fermi energy changes relative to the top of the valence band. This can be seen as well in other recent PES experiments [18, 20].

In order to investigate the quantitative change in the density of states we made a least-squares fit to the DOS at 120 K and subtracted it from the normalized spectra (see panel (c) of figure 8). Two interesting anomalies can be seen in the vicinity of the Fermi edge: firstly, a gap
opens at $E_F$ with decreasing temperature, and secondly, a peak emerges at the same binding energy $E_B = 20$ meV where the band in angle-resolved measurements appears. Together with the angle-resolved data it can be concluded that the highly correlated 3d-band is shifted only at some $\vec{k}$-points and becomes the conduction band at elevated temperatures. However, our measurements reveal that the whole band is not affected. This observation is supported by recent bulk-sensitive angle-resolved measurements on a (111)-surface [20] that show a shifting of the same band at one position along the $\Gamma R$-direction. According to our band structure calculations the band comes closest to $E_F$ at this particular $\vec{k}$-point. The bottommost band above the Fermi edge is lowered so that this raises the opportunity for additional scattering processes due to thermally occupied carriers along that direction. We therefore suggest—similar to [13]—that the self-energy is strongly $\vec{k}$-dependent, caused by scattering processes of thermally induced carriers at some points in reciprocal space and that the characteristic energy is the renormalized band gap $\Delta$. We want to point out that even though this temperature dependence is qualitatively similar to that of f-electron Kondo insulators [43, 44] the ground state electronic structure of FeSi can be explained by normal band-structure calculations and self-energy effects and, thus, FeSi does not belong to this category of correlated materials.

5. Conclusion

Our combined LDA and ARPES studies have shown that the band structure of FeSi can be described by strongly renormalized single-particle properties. These correlations lead to a strong renormalization of the bands and the band gap. However, the renormalized gap $\Delta$ plays an important role and thus the electronic correlations go beyond mere Fermi-liquid-like interactions. Temperature-dependent measurements show that the gap in the DOS vanishes with increasing temperatures due to scattering of thermally excited particles and holes near the Fermi energy. The semiconductor-to-metal transition occurs only at particular places in the Brillouin zone and, therefore, the self-energy is strongly $\vec{k}$-dependent over a wide temperature range. We also demonstrated that careful surface preparation is very important in order to obtain the correct bulk band structure for this compound.

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