

## Ultraviolet laser photoemission spectroscopy of FeSi: Observation of a gap opening in density of states

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The temperature ( $T$ ) dependent gap formation in the density of states (DOS) of FeSi has been investigated by angle-integrated laser photoemission spectroscopy (PES). With decreasing  $T$ , the evolution of a small gap ( $\sim 60$  meV) at the Fermi level is observed in the DOS, indicating a  $p$ -type semiconducting character of this compound. The Fermi edge, which has been controversial in all past PES studies, is extremely small at 5 K in accordance with transport and optical experiments. The  $T$  dependence of the gap, which gets smeared out quickly at high  $T$  as in optical conductivity spectrum, suggests the existence of a strong scattering mechanism beyond thermal excitations.

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FeSi is a well-known semiconductor which shows unconventional physical properties indicative of its characteristic electronic structure. Its puzzling nature most directly shows up in the magnetic susceptibility. While obeying the Curie-Weiss law at high temperature, it starts decreasing on lowering temperature, and exhibits a maximum at 500 K.<sup>1,2</sup> The effective magnetic moment at low temperature decreases with an activation energy  $\Delta_m \sim 80$  meV. Neutron diffraction measurement, however, had ruled out any possibility of magnetic ordering at low temperature.<sup>3</sup> The resistivity, on the other hand, shows a metal-to-semiconductor crossover on decreasing temperature across 300 K, with its low-temperature behavior characterized by an activation energy of  $\Delta_c \sim 60$  meV. The optical conductivity spectrum also shows a charge gap ( $\Delta_{\text{opt}} \sim 80$  meV) comparable in size, which quickly closes at  $\sim 200$  K on increasing temperature.<sup>4</sup> These properties are to some extent explained by the local-density-approximation (LDA) band calculation,<sup>5</sup> which predicts a feature of narrow-gap semiconductor with the gap ( $\sim 0.1$  eV) between the valence and conduction band edges with high density of states (DOS). However, to quantitatively account for their temperature dependence, a mechanism beyond a simple Fermi-Dirac-type thermal smearing seems necessary, as discussed in the models considering the enhanced spin fluctuation,<sup>6</sup> strong correlation<sup>7,8</sup> (including Kondo Insulator<sup>9,10</sup>), or thermally induced lattice disorder.<sup>11</sup> In any of these models, the fine details of the DOS at and near the Fermi level ( $E_F$ ), namely, the gap size, shape, and width of the gap edges, as well as its temperature dependence are important keys to understand the physical properties of FeSi.

In order to elucidate such electronic structure near  $E_F$ , a

number of valence band photoemission spectroscopy studies have been performed so far.<sup>12-15</sup> In spite of careful measurements with sufficiently high energy resolution compared to the expected gap size ( $2\Delta \sim 60-80$  meV), the results are not conclusive about the nature of the gap. Chainani *et al.*<sup>12</sup> and Saito *et al.*<sup>13</sup> had observed a slight shift ( $\sim 5$  meV) of the Fermi edge, indicative of a tiny (pseudo-)gap opening, which had been attributed to localized states in the gap. Breuer *et al.*,<sup>14</sup> on the other hand, reported a  $\sim 30$  meV gap structure formation below  $E_F$ , but with a residual well-defined Fermi edge which is due to a metallic surface caused by sample surface disorder. Angle-resolved photoemission spectroscopy<sup>16</sup> revealed a drastic temperature dependence of a sharp quasiparticle peak with a narrow band dispersion ( $\sim 30$  meV), indicative of a renormalization effect. However, this study did not report the observation of a clear gap structure.

In this study, we have performed a UV-laser excited photoemission spectroscopy (laser-PES) study to finely elucidate the temperature dependence of the near- $E_F$  electronic structure of FeSi. Using extremely high energy resolution and bulk-sensitivity of laser-PES, we have succeeded in observing the gap formation in the DOS on decreasing temperature. In our photoemission spectra, FeSi shows up as a  $p$ -type semiconductor with a gap of about 60 meV, whose chemical potential is located at the top of the valence band. We also discuss the consistency of our data with earlier transport and optical studies.

Single crystals of FeSi were grown by a floating-zone method as described elsewhere.<sup>17</sup> Measurements were performed using a photoemission spectrometer system constructed with the Scienta R4000 electron analyzer and an

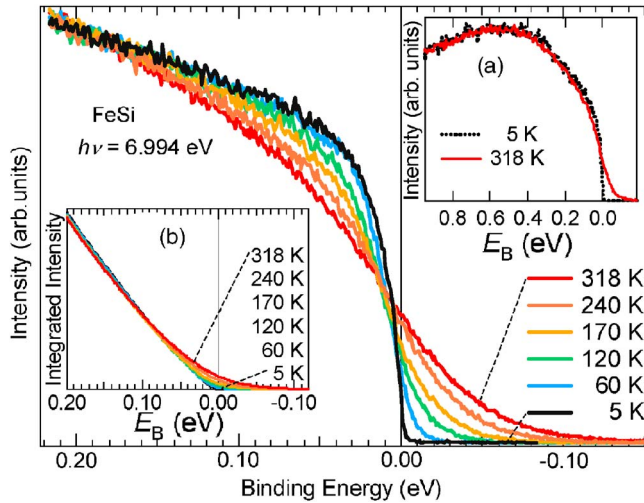


FIG. 1. (Color online) Temperature dependence of the photoemission spectrum  $I(E_B)$  for FeSi. Inset (a) shows the spectra in a wider energy region ( $-0.2 \leq E_B \leq 0.9$  eV) for the lowest (5 K) and highest (318 K) temperature. Inset (b) shows the integrated intensity  $S(E_B) = \int_{-0.18}^{E_B} I(E'_B) dE'_B$  for each temperature.

ultra-violet ( $h\nu = 6.994$  eV) laser for the incident light.<sup>18</sup> The escape depth of the photoelectron in this energy region (i.e., kinetic energy of 2–3 eV) attains a large value of  $\sim 100$  Å,<sup>19</sup> which enables us the bulk-sensitive measurements. The temperature was precisely controlled from room temperature down to 5 K using a flow-type He liquid refrigerator. The base pressure of the chamber was below  $\sim 5 \times 10^{-11}$  Torr throughout the measurements. A clean sample surface was prepared by fracturing *in situ* at 5 K. The energy resolution for temperature-dependent measurement was  $\Delta E \sim 3.7$  meV. The Fermi level ( $E_F$ ) of the sample was determined precisely within error of  $\delta E_F = \pm 0.3$  meV by referring to that of the Au film evaporated on the sample substrate. The reliability of the temperature-dependent spectra was carefully checked by measurements carried out in a temperature cycle.

Figure 1 shows the temperature dependence of the photoemission spectra near the Fermi level for FeSi. The inset (a) shows the photoemission spectra at 5 and 318 K for a wider binding energy ( $E_B$ ) region. These spectra have a broad peak at  $\sim 0.5$  eV, which is known to be due to Fe3d nonbonding states from high-energy photoemission spectroscopy studies.<sup>20</sup> Since the temperature dependence is very weak for  $E_B \geq 0.2$  eV region, the photoemission intensity is normalized at  $E_B = 0.2$  eV throughout this study. At 318 K, the spectrum is very similar to that of a conventional metal with a clear Fermi edge. Upon lowering the temperature, however, the intensity at  $E_F$  gradually starts to decrease and is transferred to higher  $E_B$ , suggestive of a gap opening at  $E_F$ . When cooled down to 5 K, we clearly observe a spectrum with  $E_F$  lying at the top of the valence band, indicative of a *p*-type semiconductor.

Next we evaluate the temperature dependence of the electronic density of states (DOS) in this system. This is carried out by dividing the photoemission spectrum by the convolution of a Gaussian function (corresponding to the instrumental resolution of 3.7 meV) and the Fermi-Dirac distribution

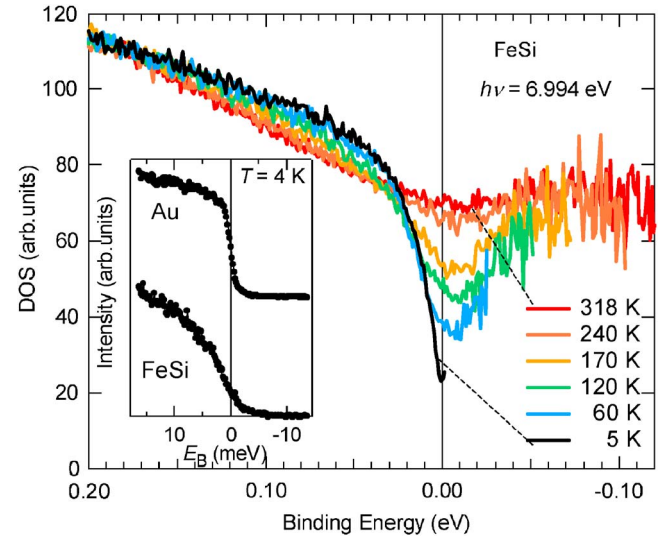


FIG. 2. (Color online) Photoemission spectrum of FeSi divided by resolution-convoluted Fermi-Dirac function for respective temperature, which represents the density of states. The inset shows the photoemission spectrum of FeSi together with Au at 5 K, measured with a higher energy resolution ( $\Delta E = 1.3$  meV).

function at respective temperature. Using this procedure, we obtain the effective DOS weighted by the transition probability not only below but also above  $E_F$  (within  $E_B \sim -5k_B T$ ), owing to the occupancy by thermally excited electrons. The DOS thus estimated are shown in Fig. 2 for respective temperatures. The DOS at 318 K seems fairly flat like a normal metal, however, a subtle pseudogap feature with its minimum at  $E_B \sim -10$  meV is already discernible. Note that the crossover temperature in this compound is 400–500 K,<sup>1,2</sup> which is well above room temperature. At 240 K, a gentle change starts and systematically develops with temperature. On decreasing the temperature, the formation of the gaplike structure centered at  $E_B \sim -10$  meV is clearly observed. At an intermediate temperature, such as 170 K, we can roughly estimate the magnitude of the gap. If we simply take the full width at the half height of the gap-edge feature, the gap size is  $2\Delta = 50$ –60 meV. It is in accord with the reported magnitudes of gaps and activation energies, though we should mention that the gap value itself is subject to the potential ambiguity arising in the process of our analysis. FeSi has been often reported as a compensated *n*-type semiconductor from Hall coefficient ( $R_H$ ) measurements.<sup>21</sup> However, recent results show that the sign of  $R_H$  is sensitively dependent on temperature.<sup>22</sup> As for the Seebeck coefficient obtained using the present crystal, it shows a positive value at low temperature ( $T \lesssim 120$  K).<sup>17</sup> These results indicate that there exist a comparable amount of *p*-type carriers in FeSi, consistent with the present result of  $E_F$  being located near the top of the valence band, and hence FeSi is dominated by *p*-type conductivity at low temperature.

The spectra in Fig. 2 show that there remains finite DOS at  $E_F$  even at 5 K. To make sure whether or not there remains a well-defined residual Fermi edge at this temperature, we performed a measurement with higher energy resolution ( $\Delta E = 1.3$  meV). The result is shown in the inset of Fig. 2

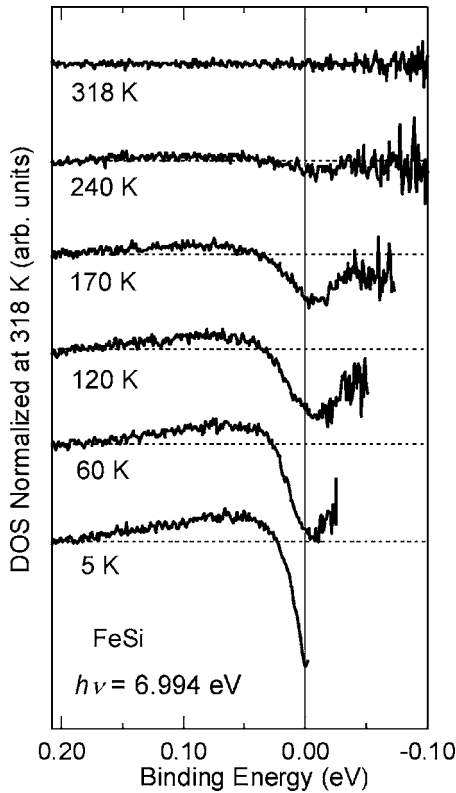


FIG. 3. Density of states for FeSi as a function of temperature, normalized to the density of states at the highest temperature ( $T=318$  K), in order to discuss the qualitative temperature dependence (see the text for details).

together with that of Au. The Fermi edge is clear in the spectrum for Au but is not well observed in FeSi. A small finite intensity discerned at  $E_F$  may be attributed to localized tail states and/or impurity band above the mobility edge, that do not participate in a coherent conduction process. Such a picture is also consistent with disorder-induced localized states as observed in the low temperature resistivity (which deviates from the thermal activation-type<sup>23</sup>) as well as in the low-frequency optical study.<sup>24</sup> Another possibility is the existence of low-density carriers introduced by impurities and/or defects. It is actually reported recently that nearly temperature-independent metallic conductivity can be observed in some samples at very low temperature ( $\leq 1$  K).<sup>22</sup> If this is the case, further cooling will be necessary in order to obtain a well-defined Fermi edge.

To see the qualitative temperature dependence in more detail, we compare the normalized DOS (Fig. 3), obtained by dividing the DOS at each temperature in Fig. 2 by the 318 K smoothed DOS. The variation of the normalized DOS is monotonic as a function of temperature. On decreasing temperature, the spectral weight at  $E_F$  starts to move to the higher  $E_B$  region forming a gap ( $2\Delta \sim 60$  meV, centered at  $E_B \sim -10$  meV) and an asymmetric broad peak at  $E_B \sim 60$  meV. The gap gets rapidly filled on increasing temperature resulting in a pseudogaplike feature, whose magnitude itself is almost temperature independent. Such gap collapse is indicative of a scattering effect strongly disturbing the semiconducting electronic structure at high temperature,

apart from the Fermi-Dirac-type thermal excitation. A number of scenarios have been suggested until now to explain the anomalous temperature dependent properties of FeSi. For example, there are models considering ferromagnetic spin fluctuation,<sup>6</sup> thermal structural disorder,<sup>11</sup> and electronic correlation<sup>7,8</sup> or in some specific cases termed Kondo insulator.<sup>9,10</sup> Our result, however, may not alone lead to a firm conclusion concerning its mechanism, since most of the models will produce to some extent a similar gap filling in DOS toward the semiconductor-metal transition.<sup>10,11</sup> In the angle-resolved photoemission spectroscopy experiment reported by C.-H. Park *et al.*,<sup>16</sup> the evolution of a sharp quasiparticle peak with a narrow band dispersion of  $\sim 30$  meV was observed, which is indicative of a strong renormalization at low temperature. The line shape of the quasiparticle peak becomes rapidly asymmetric and broader as it disperses away from the valence band maximum, suggestive of a strong incoherent part. As discussed by C.-H. Park *et al.*, these effects can smear out drastic temperature dependent effects in angle-integrated photoemission spectra.

Another interesting result from the present photoemission results is obtained with regard to previous optical studies.<sup>4,24</sup> The qualitative temperature dependence is very similar in data obtained from the two techniques, both indicating a gap opening in the ground state and its rapid smearing on increasing temperature. However, the gap size seems to be somewhat greater in the optical conductivity spectrum ( $\Delta_{\text{opt}} \sim 2\Delta_{\text{dir}} \sim 80$  meV) than that observed in our photoemission result. Since FeSi is supposed to be an indirect semiconductor,<sup>5</sup> it may be attributed to the difference of the direct and indirect gap value. Now we consider the “sum rule” issue, which also had been considered controversial for the optical conductivity studies, i.e., whether or not the missing spectral weight due to the gap opening could be recovered in a limited energy region near the gap (e.g.,  $\hbar\omega < 8\Delta_{\text{dir}} \sim 0.3$  eV).<sup>4,24</sup> The violation of “sum rule” has been recognized as the manifestation of a strong correlation effect, which may modify the electronic structure in a wide energy range. In our case, it should be confirmed using the sum rule formulated for total electron number  $n = \int_{-\infty}^{\infty} \rho(E)f(E)dE$ , where  $f(E)$  is the Fermi-Dirac distribution function and  $\rho(E)$  is the DOS. When the temperature dependence of the chemical potential and the effect of photoionization cross section is negligible, we can apply the sum rule also for the photoemission intensity  $I(E_B)$ . The inset (b) of Fig. 1 shows the integrated intensity of photoemission spectra at respective temperatures,  $S(E_B) = \int_{-0.18}^{E_B} I(E'_B) dE'_B$ . Assuming that the chemical potential shift is small [ $\delta\mu(T) \ll E_B, 0.18$  eV] and that significant charge transfer does not occur between different elements,  $S(E_B)$  at high enough  $E_B$  should follow the sum rule. The result is, for  $E_B \geq 0.15$  region,  $S(E_B)$  for all the temperatures coincides within error. Thus, we conclude that the loss of DOS near  $E_F$  at low temperature for the most of the part is redistributed in the vicinity of the gap edge, in accord with the latest optical result.<sup>24</sup>

Thus, the present photoemission study using laser-PES successfully shows results in good accordance with other experimental probes. The first and perhaps more important rea-

son is due to the enhanced bulk sensitivity. The bulk sensitivity is estimated to be significantly higher compared to the conventional photoemission studies, owing to the low kinetic energy ( $\sim 3$  eV) of the photoelectron.<sup>18</sup> The improvement in instrumental energy resolution is also considered important in analyzing the near  $E_F$  spectra (inset of Fig. 2). In particular, since FeSi behaves like a  $p$ -type semiconductor whose  $E_F$  is fixed at the top of the narrow valence band, the DOS right below  $E_F$  is significantly large. Such an electronic structure, the possibility of surface modifications, and the smallness of the gap—this combination made it difficult to discriminate the intrinsic electronic structure around the Fermi edge and its temperature dependence till now. With the bulk sensitivity and high resolution as distinguishing characteristics, UV-laser photoemission spectroscopy seems to be a very promising probe for the study of unconventional systems.

In conclusion, we have performed a temperature depen-

dent photoemission measurement to finely elucidate the near- $E_F$  electronic structure of FeSi. The UV laser as a light source enabled us the extremely high energy resolution and bulk-sensitive measurement, by which we have succeeded in observing the gap formation in the density of states with decreasing temperature. The photoemission spectrum we obtained indicates that FeSi behaves as a  $p$ -type semiconductor with the indirect gap of about 60 meV. The well-defined Fermi edge is absent at 5 K, however, a tiny but finite DOS remains at  $E_F$  indicative of the disorder induced localized electronic state or possible impurity band. Our result shows a good correspondence with the results of transport and optical studies, solving the long-standing incompatibility among the photoemission spectroscopy results and the other physical properties.

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