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Direct observation of a narrow band near the gap edge of FeSi

C.-H. Park, Z.-X. Shen,* A. G. Loeser, and D. S. Dessau
Department of Applied Physics, Stanford University, Stanford, California 94305
and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94309

D. G. Mandrus, A. Migliori, J. Sarrao, and Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We report a high-resolution angle-resolved photoemission investigation of FeSi. The high angle and energy resolutions enable us to identify a band with spectacularly sharp features near the valence-band edge. This band shows very small dispersion but remarkable temperature dependence. The small dispersion constitutes a direct observation of a narrow band in FeSi. This finding supports a theoretical picture involving two narrow bands at the edges of a narrow gap, to account for the unusual temperature dependence of the magnetic susceptibility that makes FeSi a fascinating material.

The electronic structure and magnetic interactions in transition-metal compounds have attracted considerable attention due to the rich and unusual physical properties discovered in this family of materials. A key to the electronic structure of these materials is the correlation effects, which go beyond the one-electron picture. FeSi is a very interesting compound for many reasons. According to band calculations, FeSi is a semiconductor with a small energy gap. In fact, the magnetic susceptibility, $\chi(T)$, and electrical conductivity have a gaplike activated behavior at lower temperatures.[1] However, the band calculation alone cannot explain the unusual behavior of $\chi(T)$, or the recently reported temperature dependence of the optical conductivity data.[2–4] In particular, the magnetic susceptibility, which can be described with the Curie-Weiss law above 500 K but drops rapidly below 500 K, has intrigued solid-state physicists for a long time. Neutron scattering[5] and Mossbauer[6] experiments rule out any magnetic ordering or any spontaneous moment as causes of the unusual $\chi(T)$.

Several theoretical pictures have been put forward to account for this phenomenon. Takahashi *et al.* and Evangelou *et al.* tried to explain $\chi(T)$ with their spin fluctuation theory of itinerant electron systems, and assigned FeSi to the same class of materials as $InSc_3$ and $ZnZr_2$.[7,8] In this picture, the amplitudes of local spin-density fluctuations increase with temperature until saturation. Above this temperature, the spin fluctuations can be regarded as a set of interacting local moments and thus can explain the Curie-Weiss behavior above 500 K. With a reasonable bandwidth of 1 eV at the gap edges, as predicted by band calculations, the theory can explain this unusual $\chi(T)$ curve. Temperature-dependent x-ray photoemission spectroscopy (XPS) (Ref. 9) and neutron scattering experiments[10,11] were done to test this model, but without reaching a consensus.

On the other hand, a picture involving a very narrow band near the gap edge has also been put forward. It was originally proposed by Jaccarino *et al.*,[1] but required the band near the Fermi level to have an infinitesimally narrow width. In this form, the theory could not be correct because of the unphysical narrow band. A very narrow band was not seen in the band-structure calculation observed in the XPS and ultraviolet photoemission spectroscopy experiments, which had relatively poor energy resolution.

More recently, motivated by the fact that FeSi exhibits similar properties to some narrow-band Kondo insulators,[12] Mandrus *et al.*[13] developed a refined version of the narrow-band picture. They found that the thermodynamic properties of FeSi could be accounted for by a simple model involving two reasonably narrow (about 500 K or 40 meV) peaks in the density of states (DOS) at the edges of a narrow gap (about 900 K), eliminating the need for the δ-function-like peaks in the DOS. This is strong circumstantial evidence for a narrow band in FeSi, although the bandwidth is too small to be explained by band calculation alone. Mandrus *et al.* suggested that the narrow band is due to a strong renormalization of the band structure in FeSi, implying that this is the first Kondo material to be found without rare-earth elements.

In this paper, we report results of our high-resolution angle-resolved photoemission data from FeSi. Although our data collected at room temperature in angle-integrated XPS mode are virtually identical to earlier work,[9] low-temperature angle-resolved investigation yields some of the most spectacular spectra we have observed in a solid-state material. In particular, we observed at low temperature a very sharp and intense peak at the valence-band maximum (VBM), which shows a much smaller dispersion than that predicted by band calculations. The peak has a very asymmetric line shape, which varies dramatically with temperature and emission angle. The data have two implications. First, they are consistent with the picture of FeSi as a highly correlated material with a very narrow band near the band edge. This constitutes a direct observation of a narrow band at the valence-band edge of a highly correlated insulator. Second, the data provide an example of strong temperature-dependent photoemission data near the (pinned) Fermi level. We hope to stimulate more work towards understanding temperature-dependent photoemission data from unusual materials.

The angle-resolved photoemission spectroscopy (ARPES) experiment on FeSi was performed using a Vacuum Science Workshop system with the undulator beamline 5-3 of the Stanford Synchrotron Radiation Laboratory, as described elsewhere.[14] A single crystal of FeSi was transferred into the chamber, and cleaved by a knife edge *in situ*, in a vacuum of 5×10^{-11} torr, in order to yield a fresh surface. Even though

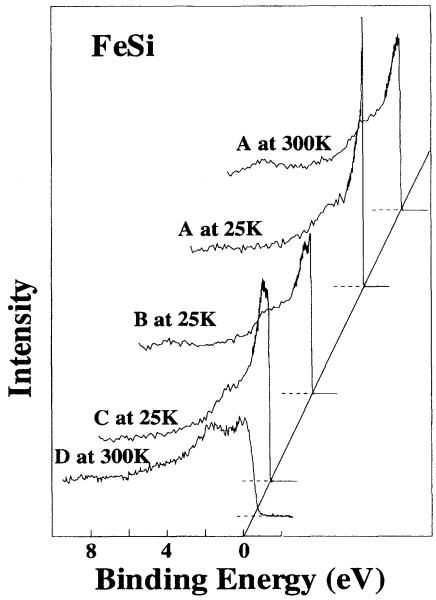

FIG. 1. *A* at 300 K and *A* at 25 K were taken at the same analyzer angle, but at different temperatures. *B* at 25 K and *C* at 25 K were taken at different angles from *A*. All spectra were taken with 24-eV linearly polarized photons. *D* at 300 K is XPS at room temperature.

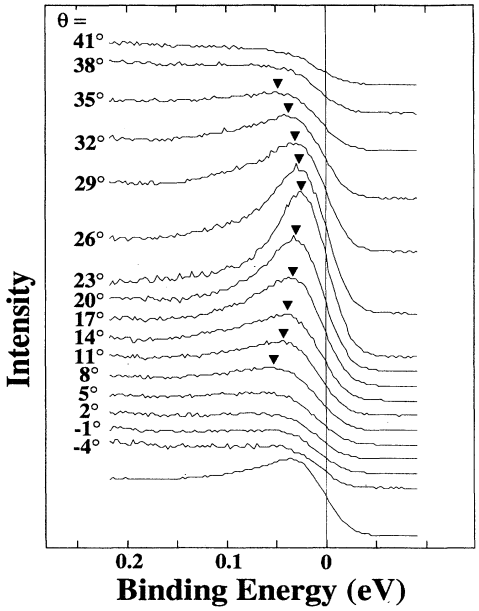

FIG. 2. The stack of data shows the angular dispersion of the sharp peak. The triangles roughly indicate peaks, in order to clarify the dispersion. θ is the analyzer angle from which the data were collected. $\theta=0$ when the analyzer is about normal to the [100] plane. As θ increases, it tilts toward the [110] plane.

the cleaved surface does not have a well-defined crystal plane, we observed a very sensitive angular dependence near the Fermi level. The samples were oriented so the [100] direction was about 45° from the incident photons. A gold sample was electrically connected so that the Fermi level of the sample could be inferred from a gold spectrum. The combined photon and electron energy resolution was approximately 35 meV at 24-eV photon energy and the angular resolution of the detector was $\pm 1°$. The data were taken in better than 5×10^{-11} torr base pressure. For our angle-integrated data, we performed XPS on FeSi in a Surface Science electron spectroscopy for chemical analysis system. The data were taken at room temperature, with monochromatized 1487-eV photons. The same fracturing method was used on a single crystal, and the sample was cleaved in 1×10^{-7} torr. The overall resolution was about 0.6 eV and the base pressure was about 1×10^{-9} torr when the data were taken.

Figure 1 presents selected spectra of FeSi taken under various conditions. The XPS spectrum, *D*, gives a rough estimate of the DOS; it is consistent with previously published data,[9] and qualitatively consistent with the band-structure calculation.[3,4] While spectra *A*, *B*, and *C*, which were taken at 25 K, but at three different analyzer angles, demonstrate the large angular dependence, the difference between 25 and 300 K with the same analyzer angle *A* is also very dramatic. The peak right below the Fermi level in spectrum *A* at 25 K is among the sharpest valence-band features seen by photoemission. It is also quite asymmetric, and diminishes in the higher-temperature spectrum *A* at 300 K. In spectrum *B*, the weight of the sharp peak is reduced dramatically, and one can see double peaks. This implies that there are probably two peaks in the spectra at *A* also, and the second peak at higher binding energy is buried by the tail of the first peak. In *C*, we see the sharp peak diminished even more, and the second is clearly visible.

The data in Fig. 1 clearly show that FeSi yields spectacular photoemission spectra: an extremely sharp and intense peak at E_F, with a very asymmetric line shape and strong temperature as well as angular dependence. Although one expects photoemission features at the lowest binding energy to be very sharp because the lifetime broadening is small, sharp features are rarely seen in experiments. To have such a strong and sharp feature right at the VBM is remarkable. The existence of this sharp peak is very reproducible, but the intensity shows some variation from cleave to cleave, presumably due to surface roughness. Even the sharp peak at Fig. 1, spectra *A* is not the most intense in our data set. An analysis of the rich ARPES data from FeSi will not only help to understand the unusual properties of this material in particular, but also will lead to a better insight of the temperature-dependent photoemission spectra from highly correlated materials in general.

For a more detailed look at the peak, we show angular dispersion of the sharp feature obtained from a cleave yielding the highest peak intensity, with a magnified energy scale, in Fig. 2. From the bottom to the top curves, the feature is observed dispersing towards the Fermi level, reaching a maximum at $\theta=23°$ and then backing down after $\theta=23°$. In the $\theta=23°$ spectrum, the highest intensity peak is roughly 25 meV below the Fermi level. The width of the leading edge (10–90 % height) is comparable with our 35-meV energy resolution, and thus is mainly limited by the latter. In this spectrum, the reference Fermi level lies in this leading edge, more than halfway towards the peak. This spectrum is very similar to data from metallic samples such as the high-T_c superconductors whose line shape is highly controversial.[15,16]

We believe, however, that the quasiparticle peak is below the Fermi level at $\theta=23°$ because it has the highest intensity and energy when compared to neighboring angles; if some of the spectral function weight were above the Fermi level, then the photoemission peak's intensity would be decreased. This critical point behavior is consistent wit the fact that FeSi is a semiconductor, placing the VBM at $\theta=23°$. The energy separation between the VBM and the pinned Fermi level should be no larger than the 25 meV measured above. It is possible that the peak at $\theta=23°$ is only a local maximum, not a global VBM. If we assume that the Fermi level is in the middle of the gap, as for an intrinsic semiconductor, the data suggest that FeSi has a very narrow gap. However, we cannot rule out the possibility that the Fermi level of FeSi is pinned very close to the VBM.

In this crystal, we have not found any easy cleavage plane. The cleaved surface of the sample is a smooth curve rather than a steplike shape, which would be an indication of an easy cleavage plane. Because FeSi is a three-dimensional material, we do not know the exact value of the crystal momentum corresponding to the VBM. However, the peak has been observed very reproducibly at a certain angle between the [100] and [110] directions, as determined from the Laue pattern. We obtained similar results from other cleaved samples. Since the sample surfaces are quite different for each cleave, it is less likely that we see a surface state. Even without the knowledge of specific electron momentum, the data in Fig. 2 still give us a good estimate of the bandwidth near the VBM, because the angular range in Fig. 2 (45°) is comparable to the width of the first Brillouin zone (about 40° at the photon energy used). The dispersion seen in the data is 30 meV or less, indicating a bandwidth of that magnitude. This number is significantly smaller than the value obtained by the band-structure calculations for any band near the Fermi level (about 200–500 meV). Observation of such a narrow band near the Fermi level in FeSi supports the idea that FeSi belongs to the class of highly correlated insulators. It has been shown that a strong renormalization of the band causes a sharp peak at the gap edges.[18–21] So far, the narrow band at the gap edge has not been directly observed before in any highly correlated insulator, and its existence is indirectly inferred from other experiments.[1,13] In essence, Fig. 2 constitutes a direct observation of a narrow band in this compound.

The presence of the narrow band, most likely due to strong correlation effects, is consistent with the very unusual asymmetric line shape of the peak, and the rapid broadening of the peak with dispersion. First, if we fit the very asymmetric spectrum at $\theta=23°$ with an ansatz assuming that the higher binding energy tail is caused by particle-hole excitation in the spirit of a Doniach-Sunuji line shape, it requires very large asymmetric factor. Knowing that FeSi is not metallic, the asymmetric factor is probably another manifestation of the many-body effects in this system. This may be related to the strong renormalization of the band, unusual broadening of the peak with dispersion, and the nonconservation of the spectral weight (discussed below). The reported $3p$ core-level photoemission also indicates an abnormally large asymmetry of the line shape, which was attributed to the correlation in the d orbit.[22] Second, as shown in Fig. 2, the peak broadens more than one would expect from the small change in binding energy as it disperses away from the VBM ($\theta=23°$). One possible explanation is that the nonuniform sample surface mixes components of k, and therefore broadens the peak. However, this would contradict the sharpness of the spectra at $\theta=23°$, since it should have the same broadening as the other angles. The peak broadens as one goes above and below this angle. Knowing that the width is directly related to the lifetime of the quasiparticle, one can speculate that there may be some low-energy scattering. Such a mechanism would also explain the strong scattering implied by optical experiments, which show a fast disappearance of the gap.[2,3]

To connect electronic structure information and susceptibility, one should use the total density of states. In a typical situation, a narrow band will yield a peak in the DOS and in a simple material, angle-integrated photoemission spectra can often approximate the DOS weighted by photoionization cross sections. In a highly correlated material, however, the situation can be quite different. Much of the spectral weight can be transferred from a coherent quasiparticle peak to an incoherent background, and that makes it harder to identify a narrow band in angle-integrated data. From our angle-resolved data, one can see that it would be difficult to observe the narrow feature once it is angle integrated. With a large asymmetric tail, it broadens very quickly as it recedes from the maximum. Therefore, the fact that no strong feature has been observed in the polycrystal sample[17] can be consistent with our results.

We turn now to the remarkable temperature dependence in the photoemission data. Figure 3 shows the temperature dependence of the sharp peak at $\theta=23°$. As the temperature increases, the sharp peak reduces rapidly. To compare the spectra at each temperature while compensating for the varying photon flux, we normalized each spectrum with the height of the electron counts near 1-eV binding energy. This procedure only requires a 5–10% rescaling of the spectra as recorded.

To the best of our knowledge, the data in Fig. 3 constitute the strongest temperature dependence recorded by photoemission. Due to its potential connection to unusual phenomena such as the Kondo resonance, metal-insulator transitions, and superconductivity, temperature-dependent photoemission data near the Fermi level are of great current interest. Not only are issues such as the Kondo resonance highly controversial, but also the temperature-dependent data from Cu surfaces are not fully understood.[23,24] With the improvement of energy resolution and the proliferation of UHV low-temperature capability, it is important to establish a systematic of the temperature dependence of photoemission data. We hope that the data in Fig. 3 will stimulate more interest in this general issue, as well as a better understanding of FeSi itself. In this sense, the data in Fig. 3 provide an extreme example for the temperature-dependent photoemission data.

Although the spectra in Fig. 3 line up very well at high binding energy, the total spectral weight is not conserved. The loss, with increasing temperature, of the spectral weight below the Fermi level cannot be compensated by the tiny gain above the Fermi level. One way to look at the unconserved spectral weight is to relate this to the fact that FeSi is known to have a narrow indirect gap. The thermally depleted valence-band electrons populate the bottom of the conduc-

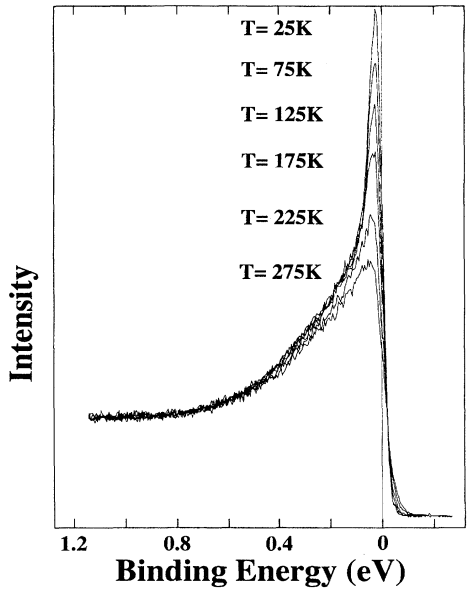

FIG. 3. The spectra were collected at an analyzer angle where the peak is sharpest at 25 K ($\theta = 23°$). This angle was measured at 25 K, then at 75, 125, 175, 225, and 275 K as the peak gets smaller.

tion band, which is located elsewhere in **k** space from the maximum of the valence band. In fact, we observed the spectral weight increasing with temperature at a different analyzer angle.

Even though the nonconserved weight can be explained up to zeroth order by the thermal electron-hole population without considering the correlation effects, it is clear that this simple idea will not explain the detailed changes with temperature. For example, the fact that the height of the peak is reduced by more than 50% over the temperature range cannot be explained by the Fermi-Dirac distribution. Recently, Fu and Doniach proposed a two-band model to explain the properties of FeSi.[25] In this model, two symmetric (Hubbard) bands with moderate on-site Coulomb interactions are allowed to hybridize. They found that the consideration of the on-site Coulomb interaction leads to a better description of the susceptibility, and a renormalization of the energy gap. For single-particle excitation spectra at low temperature, this model gives a very sharp peak and an incoherent background with a low-energy cutoff of the gap energy scale. With increasing temperature, the peak broadens very rapidly and the spectra become a single, very asymmetric feature. They also found that the peak at low temperature broadens very significantly when the energy disperses to a binding energy comparable to the gap. Although the model they are considering is very crude, we find many interesting similarities between our data and the model. The line shape of our data is very asymmetric, which is very similar to data from other highly correlated materials. The qualitative change of the peak line shape as a function of temperature and energy position found in our data is also very consistent with this physical picture. In a many-body model such as the Hubbard model, a large redistribution of the low-energy spectral weight with relatively small temperature change is possible. Within the framework of the many-body models, the extra spectral weight is either moved to other momentum, different energy, or is cut off by the Fermi function as the peak is broadened.

In conclusion, angle-resolved photoemission revealed a very narrow band at the VBM from very small dispersion (about 30 meV). These data constitute direct evidence of a very narrow band in FeSi. The spectral feature related to this band is very sharp at low temperatures, and shows a strong and very unusual temperature dependence. The significantly renormalized bandwidth, the strong temperature and angular dependence of the data, and the unusual spectral line shape can all be qualitatively accounted for by a theoretical model with strong electron-electron correlation. This framework of the electronic structure also provides an explanation for the unusual magnetic, thermodynamic properties of FeSi. This finding supports the notion that FeSi is a highly correlated insulator with a narrow band at the valence-band edge. Further, the remarkable data observed in this compound will stimulate more effort to establish a systematic understanding of temperature-dependent photoemission data from highly correlated materials.

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*Author to whom correspondence should be addressed.

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