Electronic band structure of $\epsilon - FeSi$(100)

Electronic band structure of ε-FeSi(100)

G R Castro†, J Alvarez‡, M E Dávila§, M C Asensio§ and E G Michel†

† Departamento de Física de la Materia Condensada and Instituto Universitario de Ciencia de Materiales 'Nicolás Cabrera', Universidad Autónoma de Madrid, 28049 Madrid, Spain
‡ ESRF BP 220, 38043 Grenoble Cedex, France
§ LURE, Bâtiment 209D, Université Paris-Sud, F-91405 Orsay, France and Instituto de Ciencia de Materiales, CSIC, 28049 Madrid, Spain

Abstract. The electronic band structure of single-crystalline ε-FeSi(100) has been probed by angle-resolved ultraviolet photoemission in the energy range 27 eV ⩽ $h\nu$ ⩽ 65 eV. The bands were mapped as a function of $k_\perp$ along the ΓX direction, and compared with theoretical calculations. The area closest to the Fermi energy (binding energy ⩽ 0.25 eV) has been mapped in greater detail. A large density of states has been detected here. Two different bands were resolved for distinct polarization conditions, located close to the X point. One of them is non-dispersing, while the other presents a band width of ∼0.3 eV. The presence of these narrow, intense bands is discussed in view of a possible Kondo-insulator-based description of the electronic structure of ε-FeSi.

ε-FeSi has been investigated since the late 1930s. The magnetic susceptibility of this compound presents a peculiar behaviour: it increases with temperature above room temperature, passing through a broad maximum at ∼500 K [1]. It was recently proposed by Mason *et al* [2] that ε-FeSi might represent the first example of a Kondo-type insulator based on d-type electrons (namely, the 3d Fe band). For this reason, it has received much attention during recent years. In view of the known properties of better understood Kondo-type insulators based on rare earths [3], it might be useful to recall some of the properties of ε-FeSi. Although the easiest explanation for the magnetic behaviour could be an antiferromagnetic transition, neutron diffraction, Mössbauer effect, and Knight shift measurements failed to find any sort of ordered moments. Thus, ε-FeSi presents a unique magnetic behaviour, without being magnetically ordered. Interestingly, the substitution of ∼10% Fe atoms by Co yields a magnet with helical spin order [4]. Several models were put forward to explain the peculiar dependence of the susceptibility. Jaccarino *et al* [1] proposed two different (but in fact very similar) possibilities. In their first model they postulated the existence of two narrow bands symmetrically placed around the chemical potential. The second model involved a two-level system, with an $S = 0$ ground state separated by a gap of ∼0.06 eV from a $S = 1/2$ excited state. Both models could explain equally well the magnetic susceptibility behaviour, but Jaccarino *et al* [1] favoured the second possibility, because the first one required unphysical conditions to explain the experiment (zero bandwidth). An alternative explanation was proposed later by Takahashi and Moriya [5]. These authors introduced a strong local Coulomb interaction, which was shown to promote enhanced thermally induced spin fluctuations for a model with two narrow bands (∼1 eV), keeping a gap. This image was supported by inelastic neutron scattering measurements [6]. Mason *et al* [2] have pointed out in a recent study that the peculiar magnetic behaviour of ε-FeSi was similar to the spin-fluctuation spectrum of the Kondo

insulator CeNiSn. These authors suggested that 3d electrons of ϵ-FeSi could behave in a way similar to 4f electrons in conventional rare-earth-based Kondo insulators. In this model, the 3d electrons should hybridize with an extended, itinerant conduction band formed by Si sp^3 electrons. This would be an unexpected behaviour, since the 3d wavefunctions are usually rather broad (compared with 4f). Fu *et al* [7] proposed tentatively to include ϵ-FeSi in a more general group of 'strongly correlated insulators'. Nevertheless, the intrinsic existence of a fluctuating valence in ϵ-FeSi (a very old concept already suggested by Pauling and Soldate [8]) could fit well within this model. In spite of such objections, recent experimental data [9, 10, 11] are described well by a two-band model compatible with a Kondo insulator. From the point of view of the band structure, linear-augmented plane wave (LAPW) calculations carried out in the local-density approximation (LDA) by Mattheiss and Hamann [12] have predicted a gap of $\sim$0.11 eV and a band width roughly a factor 10 too wide (0.5 cf. 0.06 eV) to explain the thermodynamics and resistivity properties [9]. Nevertheless, and in spite of the differences between the Kondo-insulator model and the enhanced spin-fluctuation model, theoretical band structure results appear to be consistent with both. Recent augmented spherical wave (ASW) calculations carried out in the LDA scheme have also obtained a $\sim$0.1 eV band gap [7].

Concerning the crystalline structure, ϵ-FeSi crystallizes in a simple cubic lattice (*B*20, space group T^4-$P2_1$3) [8]. It contains four FeSi molecules in the unit cell, and due to its low symmetry, it is especially difficult to visualize. The only symmetry operation (in addition to the cubic ternary axes), are screw axes along the cubic directions. We refer the reader to references [8, 12, 13] for more details on the crystallographic structure of ϵ-FeSi.

We aim in this article to characterize the electronic band structure of single-crystalline ϵ-FeSi(100) by angle-resolved ultraviolet photoemission (ARUPS), with the aim of establishing a comparison with theoretical calculations and determining the relevant features of the band structure of ϵ-FeSi(100) along the ΓX direction. Previous photoemission results concentrated in other properties, and not the band topology itself, either due to lack of angular or energy resolution, or because the samples were polycrystalline [14, 15, 16, 17]. In a recent study, Park *et al* [11] have observed dispersion effects for single crystalline samples fractured in vacuum, but they concentrated on the near Fermi edge region and its temperature dependence. The adequacy of existing models to explain the valence band topology of ϵ-FeSi can shed light on the fundamental properties of this intriguing compound.

The experiments have been carried out in an ultrahigh vacuum (UHV) chamber located at the SuperAco storage ring of the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE) in Orsay (France). It was equipped with facilities for low-energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS), and ARUPS. The ARUPS spectra were recorded with a hemispherical analyser mounted on a UHV goniometer. The combined photon and energy resolution (as measured from the width of the Fermi edge of a polycrystalline metallic sample) was 90 meV at 32 eV, and the angular resolution was $\pm$0.5°. The base pressure of the system was 1×10^{-10} mbar. The position of the Fermi level was obtained from reference measurements on a Mo foil in electric contact with the sample end and close to it. The ϵ-FeSi(100) mirror-polished single-crystalline sample was cleaned by cycles of Ar sputtering followed by a long-time anneal at 500 °C. These preparation conditions were established from previous quantitative Auger electron spectroscopy (AES) experiments [18]. In those studies, AES and ion scattering spectroscopy (ISS) were used to investigate the dependence of the surface composition on the preparation method (sputtering energy and annealing conditions). The conditions selected in this work guarantee the formation of a stoichiometric, well-ordered ϵ-FeSi(100) surface. Samples prepared by this method consistently displayed a sharp 1×1 LEED pattern, without traces
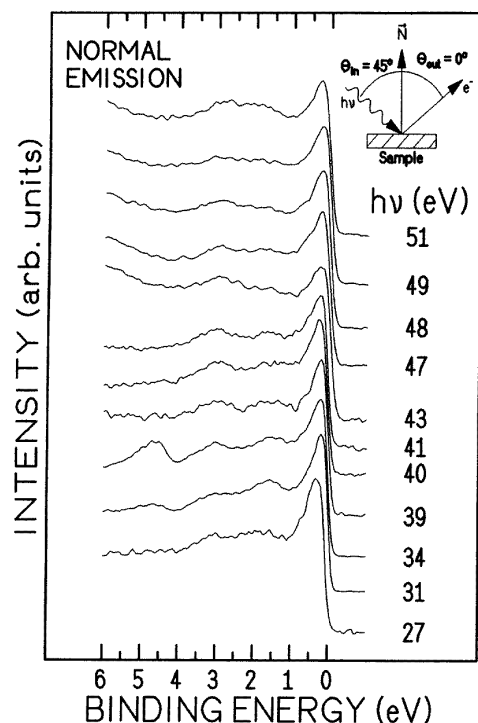
Figure 1. Selected normal emission ARUPS spectra for different photon energies. The angle of incidence of light was 45°.

of contamination.

As a check for the surface quality and stoichiometry, the line shape of Fe 3p and Si 2p core levels was measured at $h\nu = 130$ eV. The results agree well with previous experiments [19], and are not shown here. A line shape analysis of these core levels, quantitative AES, and ISS experiments all support a 1:1 Fe:Si stoichiometry of the surface region. Thus, the bulk contribution to the photoemission results comes from a well-ordered, stoichiometric sample.

The electronic band structure of ε-FeSi was systematically probed in the photon energy range 27 eV $\leqslant h\nu \leqslant$ 65 eV. Under normal emission conditions, this corresponds to a $k_\perp$ range which allows two sweeps over a ΓX range (i.e. one full Brillouin zone). Since the $B20$ structure has a very low symmetry and does not include any mirror plane, we do not expect that any mirror-based selection rule is strictly fulfilled. Nevertheless, bands were probed under p and s polarization geometries (in the last case also for $A\|\overline{\Gamma X}$ and $A\|\overline{\Gamma M}$). Some peaks showed intensity variations for the different vector potential geometries, without complete extinction. Figure 1 presents selected spectra for a light incidence angle of 45° and normal emission. The valence band is dominated by a sharp peak close to the Fermi energy. This peak is due to Fe 3d states, which extend down to ∼3 eV binding energy [12] (BE). Between 3 and 6 eV BE, Fe–Si hybridized states are expected, while Si 3s states should appear below ∼6 eV BE [12]. The BE versus photon energy relation from figure 1 (and for other experimental geometries) has been converted in a conventional BE versus $k_\perp$
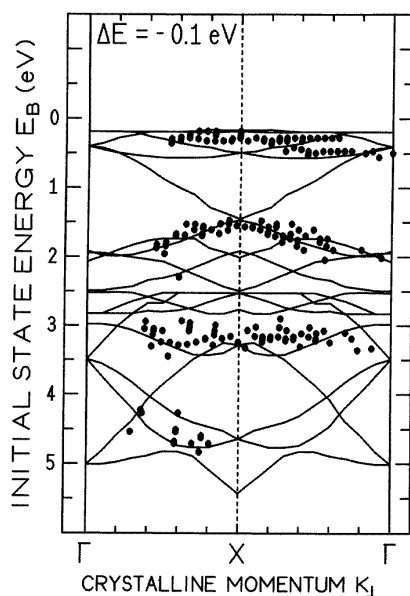
Figure 2. Measured binding energies versus $k_\perp$ for the ΓX direction of ϵ-FeSi(100), calculated using a direct transition model with a free-electron final-state band. An inner potential of 13.1 eV was used. The data were measured between the third and fourth Brillouin zones. The continuous lines have been taken from [12], and are shifted by 0.1 eV towards lower binding energy.

plot in figure 2. To this end we assumed a simple model with a free-electron-like final-state and parabolic dispersion. The inner potential used was $V_0 = 13.1$ eV. For this value a correct behaviour around symmetry points is obtained. It is roughly equal to the BE at the bottom of the valence band [12]. Changes of V_0 up to ± 2 eV would introduce an error in $k_\perp$ of $\pm 3\%$ at most.

The results of this analysis are shown as data points in figure 2, where the continuous lines have been taken from Mattheiss and Hamman's LDA–LAPW calculation [12]. The theoretical bands have been shifted by 0.1 eV towards lower BE in order to better reproduce the experimental points. This shift is within reasonable values in view of the difficulty to account for exchange and correlation effects in the calculations. In order to understand the behaviour shown by the data points, we note that, due to the low symmetry of the $B20$ structure, there exist a large number of bands split by small energies. This effect makes the bands appear to be grouped together in bunches. The energetic separation between bands within a bunch is very small ($\leqslant 100$ meV), which prevents the resolution of all the individual features. This means that the data points reflect the dispersion of each bunch of bands, and also the energetic location of areas of reduced band density. This is in fact observed in figure 2, where the overall trend of the experimental points is reasonably well reproduced by the theoretical bands. Between 2.0 and 3.0 eV BE there is an area where almost no emission is detected in the experiment, while the calculation predicts a large number of bands. Two different effects may explain this discrepancy. On the one hand, the calculated density of states (DOS) is maximum at ~ 0.8, 2.0 and 2.8 eV, in agreement with the location of the experimental points. Thus, the area between 2.0 and 3.0 eV BE has a reduced DOS. On the other hand, we note the different photoionization cross-section for d and sp electrons
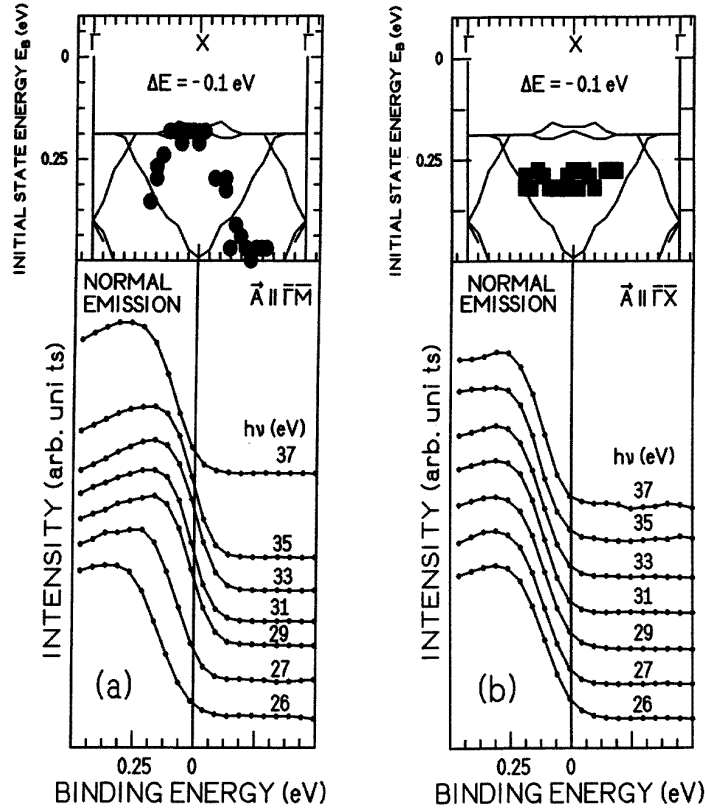
Figure 3. (a) Measured binding energies for bands close to the Fermi energy area versus $k_{\perp}$ along the ΓX direction, calculated using a direct transition model with a free-electron final-state band. An inner potential of 13.1 eV was used. The continuous lines come from [12] and are shifted by 0.1 eV towards lower binding energy. For this series the polarization was $A\|\overline{\Gamma X}$. The corresponding spectra are shown in the lower part of the panel. (b) Same as (a), but for $A\|\overline{\Gamma M}$.

in our photon energy range. This effect contributes to the depletion of bands with a higher sp content, and would indicate a decreased d content in this energy range.

The area closest to the Fermi energy has been mapped with greater detail, and the results are shown in figure 3. The band topology agrees with theoretical calculations only approximately. Depending on the orientation of the vector potential under s polarization geometry, two different bands are enhanced. Although no strict selection rule is fulfilled, we may expect enhancement of bands upon changing the excitation geometry, if they approximately satisfy adequate symmetry operations. The first band appears for $A\|\overline{\Gamma X}$ and is non-dispersing. The second, observed for $A\|\overline{\Gamma M}$, presents a maximum close to the X point. This behaviour suggests a valence band maximum (VBM) at X, related to a band enhanced for $A\|\overline{\Gamma M}$. The whole area close to the Fermi energy presents an elevated DOS (see figure 1). In principle, an increased DOS could be anticipated from single-particle DOS calculations [7, 12], and would reflect a significant localization of 3d electrons, enhanced by the increased Fe–Fe distance with respect to e.g. bcc Fe (~10%

larger). Nevertheless, the LDA-LAPW bands reproduced in figure 3 cannot account for the experimental points, in particular under $A\|\overline{\Gamma M}$ geometry. Recent temperature-dependent photoemission experiments [11] have shown an increase in intensity and a considerable narrowing of a feature close to E_F as the temperature is decreased. This behaviour was attributed to the highly correlated nature of ϵ-FeSi, giving rise to a narrow band close to the Fermi energy. Our results show that in fact there exist two bands close to E_F, one of them with a significant bandwidth (~ 0.3 eV). Work is in progress to elucidate whether the width or other features of these bands are temperature dependent, as may be expected for correlated states.

In conclusion, the electronic band structure of single crystalline ϵ-FeSi(100) has been mapped along ΓX. The band topology found presents reasonable agreement with band structure calculations for this compound [7, 12]. The 3d band is rather flat, and is dominated by a sharp, intense peak close to the Fermi energy. This peak is split in two different bands under adequate excitation conditions. One of them presents dispersion versus $k_\perp$. The band topology in this narrow range around E_F (~ 0.5 eV) shows significant differences with respect to theoretical calculations [7, 12]

Acknowledgments

References

[1] Jaccarino V, Wertheim G K, Wernick J H, Walker L K and Arajs S 1967 *Phys. Rev.* **160** 476
[2] Mason T E, Aeppli G, Ramirez A P, Clausen K N, Broholm C, Stücheli N, Bucher E and Palstra T T M 1992 *Phys. Rev. Lett.* **69** 490
[3] Hewson A C 1993 *The Kondo Problem to Heavy Fermions* (Cambridge: Cambridge University Press) and references therein
[4] Beille J, Voiron J and Roth M 1983 *Solid. Stat. Comm.* **47** 399
[5] Takahashi Y and Moriya T 1979 *J. Phys. Soc. Japan* **46** 1451
[6] Shirane G, Fischer J E, Endoh Y and Tajima K 1987 *Phys. Rev. Lett.* **59** 351
[7] Fu C, Krijn M P C M and Doniach S 1994 *Phys. Rev.* B **49** 2219
[8] Pauling L and Soldate M 1948 *Acta Crystallogr.* **1** 212
[9] Mandrus D, Sarras J L, Migliori A, Thompson J D and Fisk Z 1995 *Phys. Rev.* B **51** 4763
[10] Sales B C, Jones E C, Chakoumakos B C, Fernandez-Baca J A, Harmon H E, Sharp J W and Volckmann E H 1994 *Phys. Rev.* B **50** 8207
[11] Park C-H, Shen Z-X, Loeser A G, Dessau D S, Mandrus D G, Migliori A, Sarrao J and Fisk Z 1995 *Phys. Rev.* B **52** R16 981
[12] Mattheiss L F and Hamann D R, 1993 *Phys. Rev.* B **47** 13 114
[13] MnSi, CoSi and CrSi also crystallize in the *B*20 structure, of which ϵ-FeSi is the prototype. It is rather uncommon to find such a long series of transition metal silicides crystallizing in the same structure. For more details see
Taylor D and Kagle B J (eds) 1963 *Crystallographic Data on Metal and Alloy Structures* (New York: Dover)
[14] Chainani A, Yokoya T, Manimoto T, Takahashi T, Yoshida S and Kasaya M 1994 *Phys. Rev.* B **50** 8915
[15] Speier W, van Leuken E, Fuggle J C, Sarma D D, Kumar L, Dauth B and Buschow K H J 1989 *Phys. Rev.* B **39** 6008
[16] Oh S J, Allen J and Lawrence J M 1987 *Phys. Rev.* B **35** 2267
[17] Kakizaki A, Sugawara H, Nagajura I, Ishikamura Y, Komatsubara T and Ishi T 1982 *J. Phys. Soc. Japan* **51** 2597
[18] Castro G R and Ballesteros A 1988 *Surf. Sci.* **204** 415
[19] Sirotti F, De Santis M and Rossi G 1993 *Phys. Rev.* B **48** 8299