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Photoelectron spectroscopy study of the bulk band structure of FeTi

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Photoelectron spectroscopy with synchrotron radiation ($7 \lesssim h\nu \lesssim 90$ eV) has been used to examine the bulk band structure of the intermetallic compound FeTi. Four features are observed in the photoelectron energy distributions at initial-state energies of about 1.0, 1.7, 2.7, and 3.5 eV below E_F. Interpretation is guided by the calculations of Papaconstantopoulos and of Yamashita and Asano. It is shown that though there is generally good agreement between experiment and theory, theory predicts that the density-of-states features occur at ~ 0.25 eV higher binding energy than observed. The Ti and Fe $3p$ cores are shown to have binding energies of 33.2 ± 0.15 and 53.1 ± 0.15 eV, that of Ti being shifted to higher binding energy by ~ 0.6 eV relative to elemental Ti while that of Fe remains unchanged within experimental uncertainty.

INTRODUCTION

The FeTi system has attracted recent interest because it is representative of transition-metal intermetallic compounds in general and because it is a promising material for the storage of hydrogen. Both aspects have interested us and we have undertaken an experimental examination of the electronic structure of FeTi for a comparison with band-theoretical results and to establish a basis from which studies of the interaction of interstitial hydrogen with the lattice can proceed.

As an intermetallic compound, FeTi orders with the CsCl crystal structure [two simple cubic lattices displaced with respect to each other by $\frac{1}{2}$ a $(1,1,1,)$] for 1:1 stoichiometry. FeTi has a valence of 6 and is one of several alloys which are isoelectronic to elemental Cr, e.g., VMn, FeTi, and ScCo. A wide variety of other intermetallic systems also display the CsCl structure and have interesting and diverse physical properties (e.g., the shape memory of TiNi, various magnetic properties). Indeed, there is a very large literature for these systems.[1]

Systems with CsCl structure were among the first intermetallic compounds studied using band theory, in part because of their tractable crystal structure and in part because of the wealth of existing information relating to these materials. FeTi itself has been examined by Yamashita and Asano,[2] who used a self-consistent Korringa-Kohn-Rostoker (KKR) formalism, and Papaconstantopoulos,[3] who chose the self-consistent augmented-plane-wave (APW) method to determine the electronic band structures for FeTi. The calculations have been compared to recent Fermi-surface,[4] specific-heat,[5] isomer-shift,[6] and x-ray-emission measurements[7] in Refs. 2 and 3.

In this paper, we present the results of a photoelectron spectroscopy (PES) study of stoichiometric, ordered FeTi and compare our results with the predictions of Yamashita and Asano[2] and of Papaconstantopoulos.[3] We will also compare these PES results to analogous results for elemental Cr. Insights about the electronic structure gained from optical reflectance and thermoreflectance measurements will be presented elsewhere.[8]

EXPERIMENTAL TECHNIQUE

Large polycrystalline buttons of FeTi were prepared by arc melting. Samples were sliced from the buttons using a diamond saw, they were polished mechanically and electrolytically for metallographic examination and were subsequently annealed at 1000 °C for 336 h to promote grain growth and single-phase homogeneity. Metallographic examination revealed grains of 1 mm characteristic dimension, and nearly single FeTi (~6% second phase). Samples for photoelectron spectroscopy studies ($\sim 2 \times 2 \times 10$ mm^3) were then cut from these annealed slices. Shallow starter grooves for subsequent cleaving were cut normal to the long axis. Finally, they were electropolished and were attached to copper sample holders.

FeTi is very hard but is also brittle. The brittle property was exploited to advantage in the PES studies because the samples could be cleaved or fractured immediately before the measurements began. The cleaving and all the subsequent measurements were done *in situ* at pressures better than 6×10^{-11} Torr. Immediately after each cleave, the sample was translated a few centimeters to the mutual focus of a commercial double-pass cylindrical-mirror electron-energy analyzer (pass energy 25 eV) and the focused ra-

diation beam from Tantalus I, the 240-MeV electron storage ring at the University of Wisconsin-Madison. The radiation was monochromatized with the Synchrotron Radiation Center toroidal grating monochromator. Photoelectron energy distribution curves (PED's) were taken with photon energies ranging from 7 to 90 eV using s-polarized radiation and an angle-integrated cylindrical mirror analyzer.[9]

RESULTS AND DISCUSSION

Select photoelectron energy distribution curves (PED's) for FeTi are shown in Fig. 1 as measured for $7 \leq h\nu \leq 90$ eV. The energy positions of the PED maxima for various photon energies are shown in the inset. All energies are referenced to E_F, the Fermi level. The PED's, representing the number of photoemitted electrons at a photon energy $h\nu$, are shown in arbitrary units with the spectra normalized to the peak height of the dominant peak. For $h\nu \gtrsim 11$ eV, there is a maximum near −1 eV (peak A). A second feature (B), which is seen for $7 \lesssim h\nu \lesssim 18$ eV, appears to disperse downward from E_F, reach an extremal energy of −1.75 eV, and merge with peak A at $h\nu \approx 18$ eV. A third feature (C) at −2.75 appears only for $h\nu \gtrsim 14$ eV. For $h\nu \gtrsim 20$, a fourth feature (D) is seen at −3.5 eV. By $h\nu = 90$ eV, where the PED's show little dependence on $h\nu$, the central peak occurs at −1.1 eV, there is a broad shoulder at ~−3 eV, and the total width of the conduction bands can be taken to be ~6 eV.

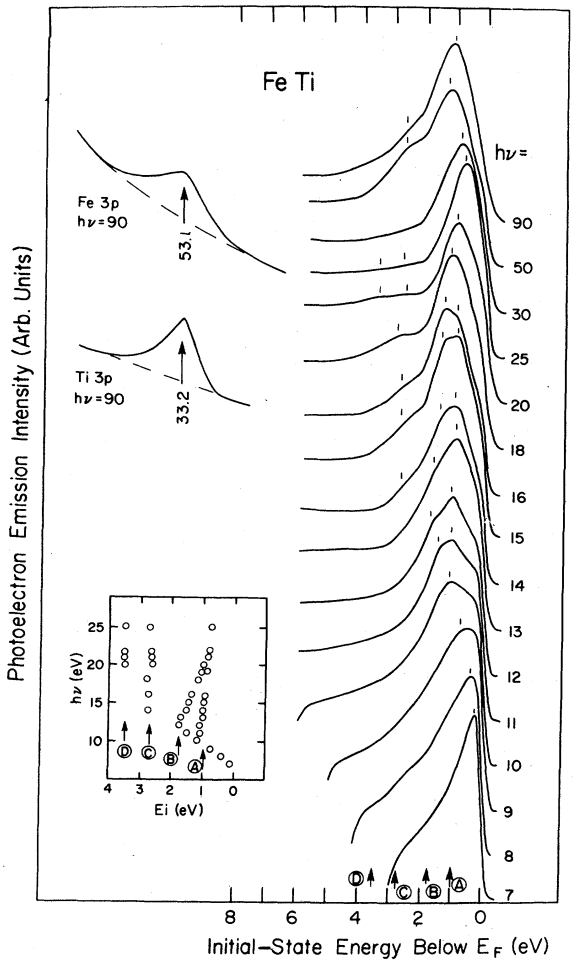

FIG. 1. Photoelectron energy distributions for FeTi for photon energies between 7 and 90 eV. The structure plot in the inset shows the $h\nu$ behavior of maxima in the PED's. Four features can be identified (arrows) at −1 eV (A), −1.7 eV (B), −2.7 eV (C), and −3.5 eV (D). Core-level features for the Ti and Fe 3p's are shown for $h\nu = 90$ eV with the same energy increments as for the conduction band.

The self-consistent energy bands calculated by Papaconstantopoulos[3] and the density of states (DOS) from both Papaconstantopoulos and Yamashita and Asano[2] are shown in Fig. 2. The calculations, based on different formalisms, gave energy bands which are in good agreement with each other. As discussed by those authors, the occupied bands are derived primarily from the Fe 3d states while the empty (antibonding) d-derived bands have primarily Ti 3d character. The Fermi level falls in a region of relatively low DOS and there is a strong resemblance to the DOS of Cr.[10,11] Yamashita and Asano also performed, in the coherent potential approximation, calculations for disordered FeTi, finding the calculated density of states to have none of the sharp DOS features characteristic of the highly stable, ordered state of FeTi (Fig. 2).

Comparison between experiment and theory, vis-à-vis the initial-state density of states, results in the interesting observation that the maxima in the experimental PED's fall very close to *minima* in the calculated density of states as predicted by either set of calculations. This is shown in the structure plot (inset of Fig. 1), where the arrows indicate experimental maxima at −1, −2.7, and −3.5 eV. The fourth feature indicated by arrow B at −1.7 eV shows more dispersion, it being deepest at $h\nu = 12$ eV. Agreement between theory and experiment would be better if the occupied Fe-derived bands were closer to E_F by roughly 0.25 eV.

The calculated DOS's shown in Fig. 2 have a strong maximum near −1.3 eV which can be related to the band minima along $\Sigma(110)$ and the zone face along Z. We identify this maximum as the origin of the experimental feature ($h\nu \gtrsim 20$ eV) at −1 eV. Shifting these Σ_1 and Z_1 bands upward by ~0.25 eV would affect the size of the electron hole pocket centered at M. As pointed out by

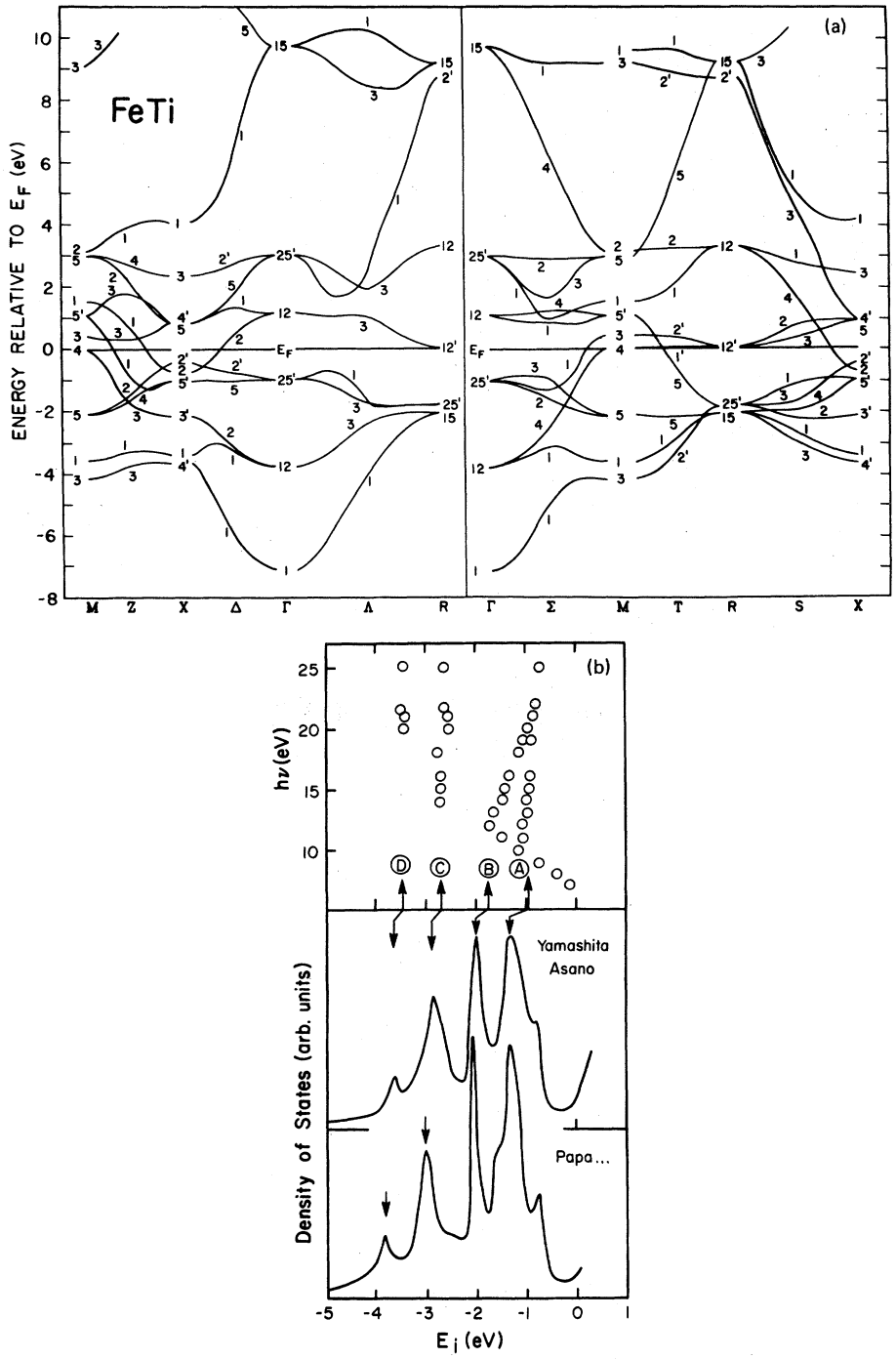

FIG. 2. (a) Calculated band structures of FeTi by Papaconstantopoulos (Ref. 3). (b) The density of states calculated from the bands of (a) (Papaconstantopoulos) compared to that calculated by Yamashita and Asano (Ref. 2) and our experimental results.

Papaconstantopoulos,[3] the Fermi-surface measurements by Kamm[4] indicated that the measured electron and hole pocket volumes at X and M, respectively, were smaller by a factor of 2.7 than those predicted.

The second sharp DOS feature shown in Fig. 2 reflects the X_3' critical point and the relatively flat third band along S (zone face diagonal) and T (zone edge). This high density-of-states feature can be associated with the extremal (−1.7 eV)

peak. For higher photon energies, the peak moves back to merge with peak A at -1 eV. At lower energies, that feature moves closer to E_F and ultimately disappears at E_F ($h\nu \approx 9$ eV). From the band structure there are several bands dispersing through E_F near M which, when account is taken of final-state effects and the joint density of states, could produce the observed dispersion.

The density-of-states maximum near -3 eV arises from contributions of the second band along Δ and Σ, particularly from the concave-downward critical points Δ_1 and Σ_1. These can be associated with the relatively weak experimental feature at -2.7 eV. The deepest feature reflects the lowest band at M and corresponds to the experimental feature ($h\nu \gtrsim 20$ eV) at -3.5 eV.

The band-structure calculations of Papaconstantopoulos[3] show a pair of relatively flat high-energy bands on the zone edge (M-T-R) and along the $\Lambda(111)$ and $\Sigma(110)$ directions. From the structure plot shown in Fig. 1, we note that peak A at -1 eV appears only for $h\nu \gtrsim 10$ eV. We have identified it with the initial-state DOS maximum along Σ, namely the Σ_1 minimum. From Fig. 2, we see that there are no final states along Σ within ~10 eV of E_F but that near $h\nu = 10.4$ eV there is a high joint density of states for transitions between the Σ_1 minimum and the relatively flat, high-lying band $\simeq 9$ eV above E_F. This predicted onset is in very good agreement with what is observed. From Fig. 1 and the structure plot, we see further that the features observed at -2.7 and -3.5 eV also have onset photon energies of $\simeq 14$ and $\simeq 20$ eV, respectively. We suggest then that these features also reflect transitions between the high DOS initial states and the high DOS final bands. This sudden onset, the correpondence between experimental features and DOS features, and the paucity of final states below ~$E_F + 10$ eV gives us some degree of k selection; it will remain for angle-resolved studies with oriented single crystals to confirm our tentative identifications.

From the results discussed above, it can be inferred that there is quite good overall agreement between theory and experiment for this representative intermetallic alloy of FeTi.

In Fig. 1 we also showed the core-level emission from the Ti $3p$ and Fe $3p$ cores as measured at $h\nu = 90$ eV. The binding energies of those cores have been determined to be 33.2 ± 0.15 eV [full width at half maximum (FWHM) 1.25 eV] and 53.1 ± 0.15 eV (FWHM 1.65 eV), respectively, referenced to E_F. Those energies can be compared to the binding energies of the same cores in elemental Ti and Fe, namely 32.6 ± 0.2 eV and 53.0 ± 0.2 eV. The binding energies of the Fe $3p$'s are unchanged to within experimental error but those for the Ti $3p$'s appear higher by roughly 0.6 eV. The band calculations show the occupied d bands are primarily Fe derived and the empty d bands are primarily Ti derived. Källne[7] has reported x-ray-emission studies of TiFe, TiCo, and TiNi and showed the Ti $2p_{1/2,3/2}$ cores to shift deeper while the Fe $2p_{1/2,3/2}$ cores remained unchanged relative to E_F upon formation of the alloy. She did not, however, observe any changes in the Ti $3p$'s, as we have.

Schlapbach and co-workers[12] have recently reported interesting results of Auger and x-ray photoemission spectroscopy studies of FeTi in which they showed surface aggregation of Fe and Ti clusters which was induced by exposure to oxygen at elevated temperatures but no segregation for unactivated TiFe. We have observed no time-dependent emission features for samples cleaved and studied at pressures below 6×10^{-11} Torr, in agreement with their findings. Preliminary chemisorption studies of H_2 on cleaved, polycrystalline FeTi show that enhanced emission at -5.5 eV occurs for exposures of as little as 1 L of H_2 (1 Langmuir = 10^{-6} Torr sec). This hydrogen feature ultimately saturates near 20-L exposure and extends from about -4 to about -8 eV. No changes in the core emission were observed. Further studies of the effects of chemisorbed O_2 on FeTi are underway.

ACKNOWLEDGMENTS

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