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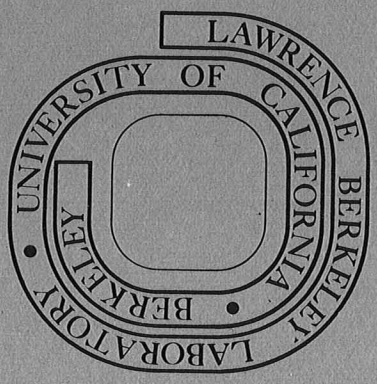

EVIDENCE FOR THE ITINERANT ELECTRON MODEL OF FERROMAGNETISM AND FOR SURFACE PHOTOEMISSION FROM ANGLE-RESOLVED PHOTOEMISSION STUDIES OF IRON*

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ABSTRACT

Angle-resolved HeI photoemission spectra of Fe(001) are reported and interpreted within the framework of a direct transition model using Callaway's ferromagnetic band structure. The generally good agreement between predicted and experimental peak positions is taken to be strong support for the itinerant electron theory of ferromagnetism. Spectra taken with nearly grazing incidence p-polarized light emphasize the one-dimensional density of states peaks, supporting Kliewer's theoretical predictions of surface photoemission. The importance of electron refraction is noted, as is the value of interpolation calculations for interpreting ARP spectra.

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The itinerant electron theory of ferromagnetism is widely accepted as describing the situation in the iron group ferromagnets on the basis of a variety of evidence. For example, de Haas-van Alphen studies show two Fermi surfaces — for the majority and minority bands — in iron, cobalt, and nickel.[1] It is highly desirable to characterize the itinerant nature of the 3d electrons more completely throughout the valence bands, as well as at the Fermi energy (E_F). In particular, direct observation of the exchange splitting throughout the Brillouin Zone would be valuable. Photoemission is clearly the method of choice for this problem. Although the exchange splitting has been the subject of numerous photoemission experiments in the past,[2] the information obtained was limited. In a really definitive study, it would be desirable to observe separate peaks arising from majority and minority spin bands and to follow their dispersion relations through the zone. We have undertaken such a study on iron. In this communication we report our first results, which: 1) exhibit for the first time continuous dispersion of separate peaks due to majority and minority bands, and 2) give clear evidence for polarization-dependent surface photoemission, as predicted by Kliewer.[3]

Angle-resolved photoemission (ARP) experiments were performed on the (001) face of an iron single crystal at the HeI photon energy of 21.2 eV. The measurements were carried out in a chamber with an ambient base pressure of 7×10^{-11} Torr, described elsewhere.[4] The sample crystal had previously been polished to 1μm smoothness and etched in H_2O_2 and oxalic acid. An atomically clean surface was prepared in situ

by repeated and simultaneous argon-ion bombardment and heating to 600°C, followed by annealing to remove surface damage. By adding a molecular sieve trap to the helium line, the running time between cleaning cycles was extended to 4 hours.

The experimental geometry and results are shown in Fig. 1. Spectra were taken at the normal emission angle ($\Theta = 0°$) and in 5° increments off normal emission toward the [100] axis ($\phi = 0°$) or "backward" toward the $[\bar{1}00]$ axis ($\phi = 180°$). The unpolarized light beam was incident in the plane containing the [100] and [001] directions, at a constant angle of 35° from the analyzer acceptance direction. Three distinct trends are clear in the $\phi = 180°$ spectra, for which the light is near normal incidence. First, the sharp peak at the Fermi energy, observed in normal emission, becomes less distinct at $\Theta = 10°$, returns at $\Theta = 15°$, and then grows to become the most intense peak in the spectrum at higher values of Θ. Second, the peak at $E_B = 2.5$ eV splits at $\Theta = 20°$; the lower E_B peak moves toward the Fermi level and eventually merges into the $E_B = 0.5$ eV peak. Finally, the peak at $E_B = 4$ eV in the near-normal emission spectra moves to lower E_B as Θ increases, merges with the peak at $E_B = 2.5$ eV at $\Theta = 25°$, and then moves rapidly to higher binding energy for $\Theta \geq 30°$.

The $\phi = 0°$ spectra exhibit two marked characteristics: 1) the peak at $E_B = 0.5$ eV is always significantly stronger than in the corresponding spectra (i.e., the same Θ) for $\phi = 180°$, and 2) the detailed peak structure is lost for $E_B \geq 1.5$ eV.

In the past, the interpretation of ARP spectra of three-dimensional lattices has been confused by the use of two inherently different models. The surface sensitivity of electron spectroscopy has lead most investigators to interpret their results in terms of a one-dimensional density of states (ODDOS) model.[5,6] In this model, only the energy and $\vec{k}_{\parallel}$, the component of crystal momentum parallel to the surface, are conserved, and the observed spectra are predicted to reflect the ODDOS along that $\vec{k}_{\parallel}$ direction. Other workers have emphasized a direct transition model in which photoemission is treated as a bulk process, with strict conservation of energy and of all three components of crystal momentum.[7,8] Recent results[7] from this laboratory have demonstrated that direct transitions from valence band initial states into final states at energies given by the plane-wave dispersion relation adequately describes the peak positions in ARP spectra obtained from copper single crystals.

In Fig. 2 we show the results of a similar direct-transition calculation on iron, for the conditions applicable to this work. The values of the initial state momenta $\vec{k}_i$ were calculated assuming strict conservation of crystal momentum. Band energies were calculated at these $\vec{k}_i$ by use of the interpolation scheme of Baker and Smith,[9] which was fitted to Callaway's[10] majority and minority spin bands independently. Corrections were made for the finite angular resolution of the detector and surface electron refraction.[11-14]

Also shown in Fig. 2 are the peak positions taken from our $\phi = 180°$ spectra. Agreement between theory and experiment is good, considering the approximations used to generate the first principles band structure

and those inherent in our use of the interpolation scheme. We conclude that the agreement shown in Fig. 2 demonstrates clearly, for the first time, that majority and minority bands follow different dispersion relations continuously through the zone. This conclusion must be tempered by two observations. First, some bands are missing in the spectra. Their absence may be due to cross-sectional effects (including, perhaps, symmetry factors). Second, it is the nature of valence-band photoemission spectra that some narrow peaks appear and can be identified but much of the underlying spectral area, which can not be explicitly accounted for, may arise via different mechanisms. Thus we feel that the above conclusion is valid even though the spectra are not completely understood.[15] It is interesting to note that theory and experiment continue to agree well even at the highest values of Θ attainable in our apparatus, where, by a simple mean-free-path argument,[11] the uncertainty in $k_\perp$ should be largest. Thus, we conclude that broadening in $k_\perp$ due to the variation in the sampling depth is unimportant in this study.

In addition to the finite mean-free-path of the excited electron, p-polarized light also leads to an uncertainty in $k_\perp$ and has been discussed at length by Kliewer.[3] The important parameter determining the amount of uncertainty in $k_\perp$ is the magnitude of the component of the vector potential $\vec{A}$ perpendicular to the surface, $A_\perp$. Taking the unpolarized incident radiation to be composed of two orthogonal linearly polarized components, one of which is s- and the other p-polarized,[16] we can define a polarization parameter, χ as the ratio of $A_\perp$ to $A_\parallel$

(the magnitude of the component of $\vec{A}$ parallel to the surface). Thus as χ increases, so should the broadening in $k_{\perp}$. In terms of the electron emission angle Θ, χ is given by $\frac{\sin|35°-\Theta|}{1+\cos(35°-\Theta)}$ for our $\phi = 180°$ spectra and $\frac{\sin(35°+\Theta)}{1+\cos(35°+\Theta)}$ for our $\phi = 0°$ spectra. Thus for our $\phi = 180°$ spectra, χ is small, its largest value (.32) occuring for $\Theta = 0°$, whereas it is much larger for our $\phi = 0°$ spectra, attaining a maximum value of .84 at $\Theta = 45°$.

On this basis, we expect our $\phi = 0°$ spectra to exhibit more ODDOS structure than our $\phi = 180°$ spectra. In fact, an ODDOS calculation similar to that used by Grandke, et al.[6] for PbS predicts a peak at $E_B = 0.5$ eV and complicated structure at $E_B = 1.5$-2.5 eV for all values of Θ, in good qualitative agreement with the data for $\phi = 0°$. However, the calculation does not fit the spectra in overall detail. Because our measurements were made at two azimuthal angles, $\phi = 0°$ and $\phi = 180°$, we can make direct comparisons between pairs of spectra with the same Θ values and thus equivalent angles between the crystalline axes and the electron propagation direction. On this basis, we conclude that the "surface photoeffect" predicted by Kliewer[3] has been observed in our $\phi = 0°$ spectra, and that it is responsible for the $E_B = 0.5$ eV peak in these spectra. Because of the magnitude of the effect it seems probable that surface photoemission and bulk photoemission have been present in previous ARP studies in which the role of the photon polarization was neglected. Future ARP investigators should be cognizant of this effect.

In summary, we can draw the following conclusions from this research:

1. Distinct, continuous dispersion relations for majority and minority spin bands have been observed throughout the d-bands of iron for the first time. This provides strong support for the itinerant electron model of ferromagnetism.

2. Although direct transitions are of primary importance in predicting peak positions in ARP spectra of iron for near-normal incidence light, p-polarization leads to $k_\perp$-broadening and surface photoemission, as predicted by Kliewer.[3] Clear evidence for this effect was obtained in the form of spectra taken at $\phi = 0°$ which exhibited ODDOS characteristics.

3. Electron refraction at the surface, which was implicit in all of our direct transition calculations is important and must be taken into account.

4. Finally, off-normal ARP has been treated systematically and rigorously in this work, by carrying out appropriate interpolation calculations. To our knowledge this represents the first approach of this kind in metals. The significance of this approach is that it allows the experimenter to study dispersion relations along arbitrary directions in the Brillouin Zone, using a single photon energy, rather than being confined to a single value of k along those symmetry lines for which band structure calculations are available.

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FIGURE CAPTIONS

Fig. 1. Experimental geometry and spectra. Note that the angle between light incidence and electron emission is fixed at 35°. Θ and ϕ are the spherical polar and azimuthal angles, respectively, measuring the electron emission direction with respect to the sample normal. Energy resolution was $\approx$0.1 eV, and the angular resolution was $\pm 5°$.

Fig. 2. Direct transition calculations for peak positions as functions of Θ for $\phi = 180°$, with the experimental peak positions superimposed. Corrections have been made for finite angular resolution and refraction of the photoelectrons at the surface.

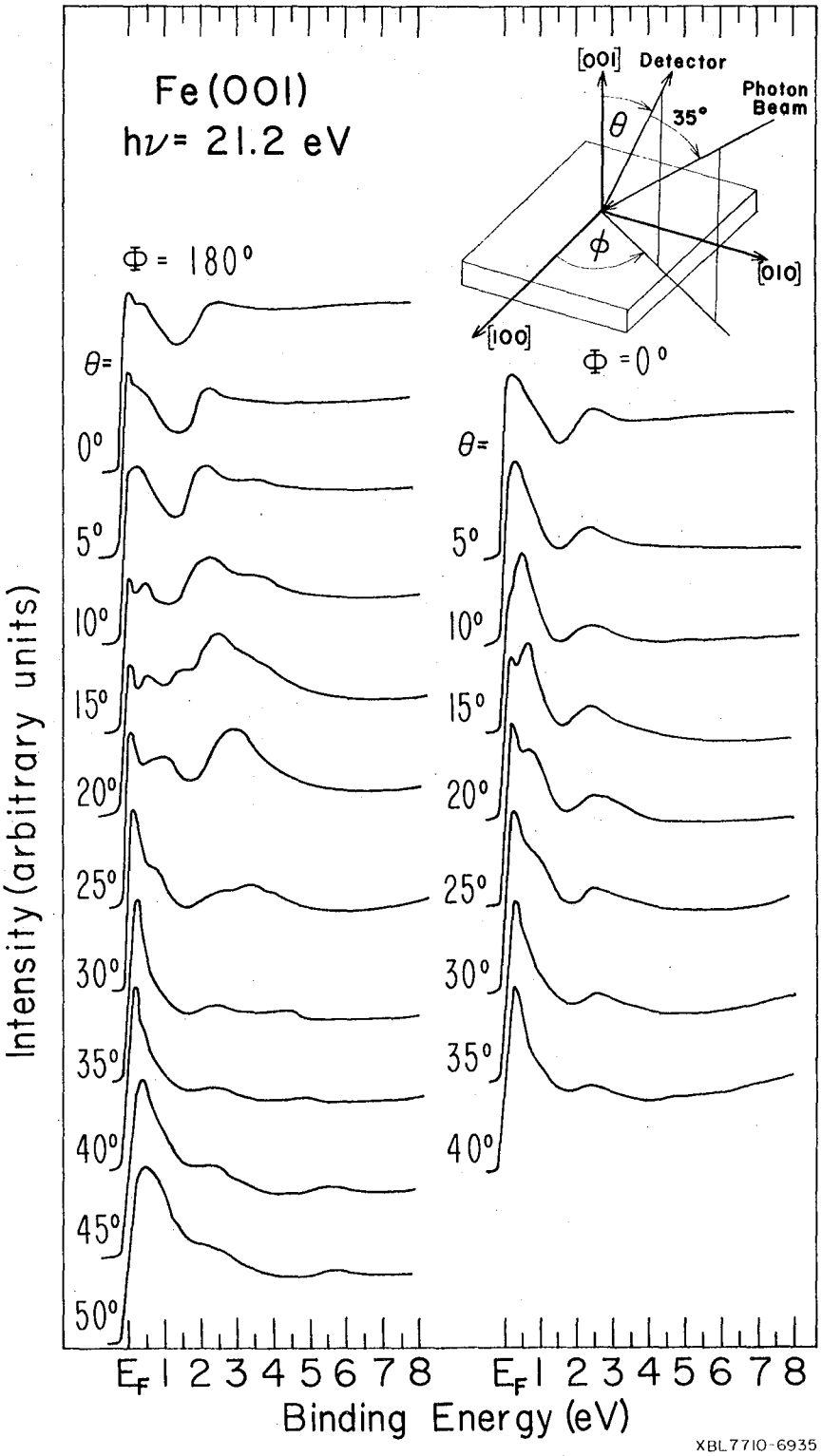

Fig. 1

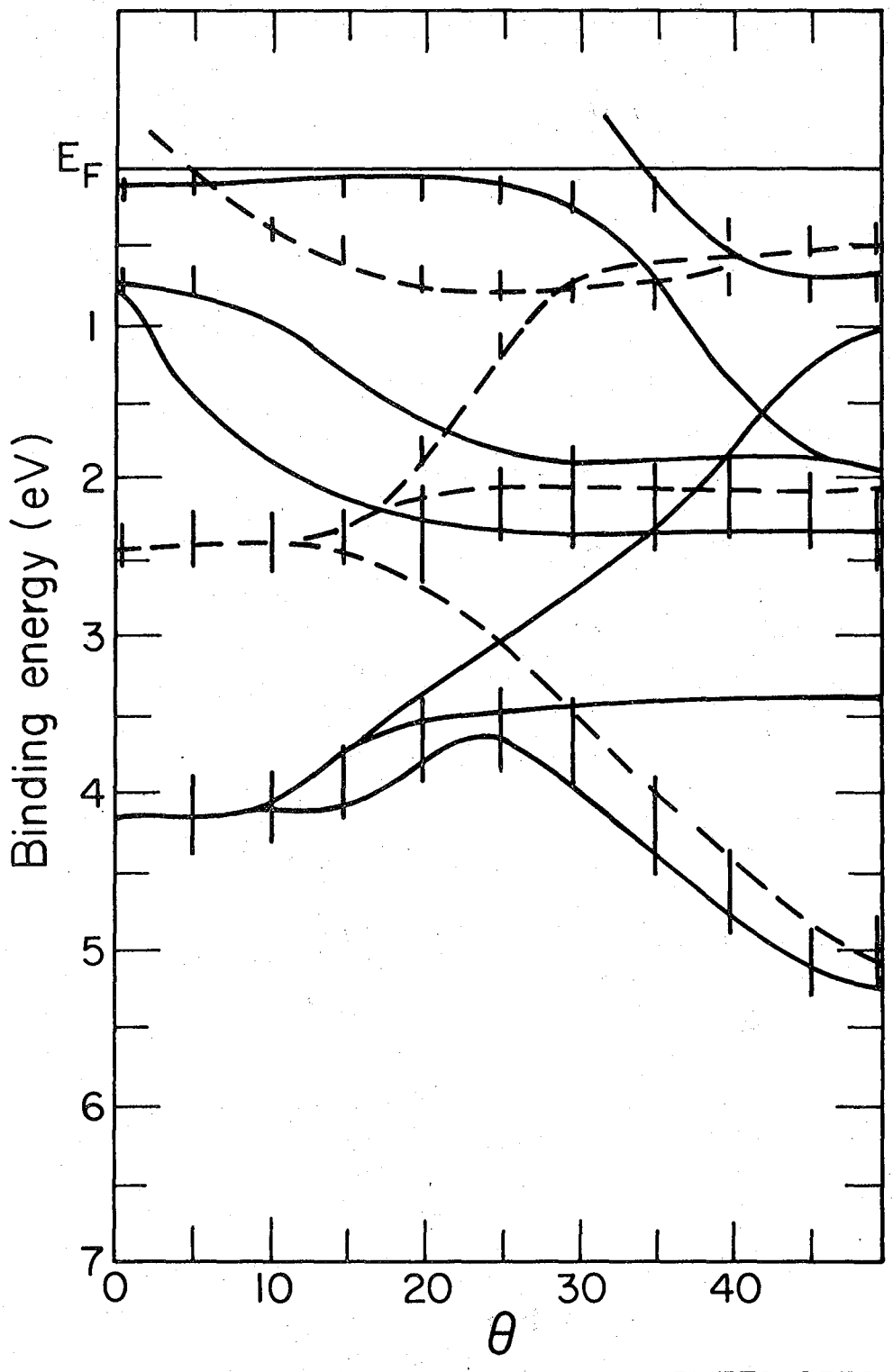

Fig. 2

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