PHYSICAL REVIEW B VOLUME 14, NUMBER 9 1 NOVEMBER 1976

Density of states of ferromagnetic and paramagnetic Ni and Fe studied by photoelectron spectroscopy with 21.2- and 40.8-eV photon energies

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(Received 12 January 1976)

We present in this paper photoemission measurements on Ni and Fe which could partly be viewed as an extension of the measurements on nickel by Rowe and Tracy with $\hbar\omega < 5$ eV and by Pierce and Spicer with $\hbar\omega < 11.7$ eV at temperatures below and above the Curie temperature. We use photon energies of 21.2 and 40.8 eV which give electron energy distributions which, in a more direct way, show the shifts expected from the early band model of ferromagnetism when the temperature is varied through the Curie temperature. Iron is included because the shifts should be larger than for nickel owing to the larger exchange splitting. However, no such energy shifts are detected.

I. INTRODUCTION

The mechanism responsible for the ferromagnetic properties of the transition metals has caused a great deal of controversy.[1] The itineracy of the electrons responsible for the magnetic properties is the focal point of the arguments. For instance, the $4f$ ferromagnetic metals have been most successfully described by a localized model while the $3d$ metals have been described better by an itinerant model.[2] The different models have however merged to the extent that, for instance, spin waves which earlier were described only in a localized model can now be described in an itinerant model which includes correlation.

In the itinerant model an energy band is thought to be split into two bands, containing either spin-up or spin-down electrons. Figure 1 shows a calculated density of states for the nonmagnetic case of iron, where, in the ferromagnetic case, $E_F^{\downarrow}$ and $E_F^{\uparrow}$ correspond to the Fermi energy of the down- and up-spin electrons, respectively. The ferromagnetic density of states is then obtained by adding the two contributions, keeping $E_F^{\downarrow}$ and $E_F^{\uparrow}$ on a common Fermi energy. In a more realistic model, the energy splitting between the two bands ΔE_{ex} is not constant over the bandwidth, nor do the bands look exactly alike. The energy separation ΔE_{ex},[3] is the so-called exchange splitting, which represents the difference in exchange energy and correlation effects between the two bands. If ΔE_{ex} depends on the magnetization,[2,4] it implies that above Curie temperature the two bands would have merged to a common band and thus give a different density of states. A ferromagnetism of this type is dependent on a high density of states at the Fermi surface, such that the energy needed to move the electrons above E_F will be smaller than the energy gained from the exchange term while having more electrons with parallel spin. Nickel and iron fulfill this demand.[5]

In a localized model where the magnetic moments are situated on the atoms the argument is not as straightforward, but passing through the Curie temperature would have no large effects on the energy bands (see Sec. V).

This rough sketch[6] gives a motivation for a photoelectric study of the ferromagnetic materials below and above the Curie temperature. Such studies have previously been reported on cesiated nickel by Rowe and Tracy[4] for photon energies between 4 and 5 eV, and by Pierce and Spicer[7] on clean nickel using photon energies between 7.7 and 10.7 eV. The main point made in these reports is that a band model cannot adequately explain ferromagnetism in nickel. We extend these experiments to clean nickel and iron at photon energies 21.2 and 40.8 eV. For iron the shifts expected in a band model should be larger than for nickel owing to the

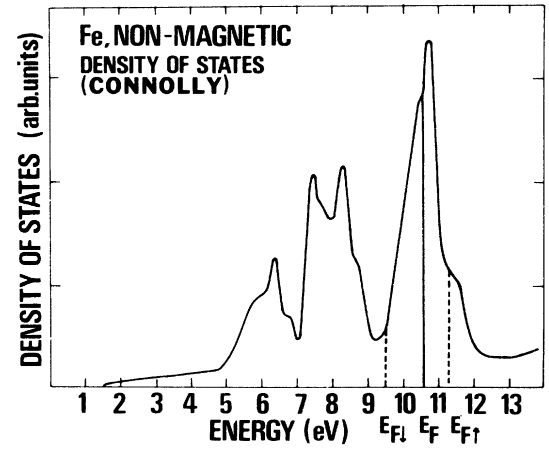

FIG. 1. Iron, nonmagnetic density of states as calculated by Connolly (Ref. 22). $E_F^{\downarrow}$ and $E_F^{\uparrow}$ correspond to the Fermi energy of the down- and up-spin electrons respectively, in the ferromagnetic case.

larger exchange splitting in iron.[3] Another objective of this work was to achieve electron energy distribution curves (EDC's) from the clean surfaces of nickel and iron, since, especially for iron, good experimental data are rare.

II. PHOTOEMISSION MODEL

In a direct model of photoemission (i.e., k conserving), the internal distribution of excited electron $N_{\rm int}(E,\hbar\omega)$ will be given by[8]

$$N_{\rm int}(E,\hbar\omega)=\sum_{f,i}\int d^3k\,|P_{f,i}|^2\,\delta(E_f(\bar{k})-E_i(\bar{k})-\hbar\omega)\,\delta(E-E_f(\bar{k})),$$

where $P_{f,i}=\langle f|P|i\rangle$ is the momentum matrix element which governs the strength of the optical excitation.

The external distribution is given by

$$N(E_0,\hbar\omega)=\sum_{f,i}\int d^3k\,|P_{f,i}|^2\,\delta(E_f(\bar{k})-E_i(\bar{k})-\hbar\omega)\,\delta(E-E_f(\bar{k}))\,T(E_f,\bar{k}),$$

where $E_i<E_F<E_f$, and where $T(E_f,\bar{k})$ is an escape factor which is considered not to introduce any sharp structure in the distribution. The momentum matrix element will, at least for the metals considered here, introduce large distortions in $N(E_0,\hbar\omega)^{9-13}$ compared with the energy distribution of the joint density of states which is equal to $N_{\rm int}(E,\hbar\omega)$ with $P_{f,i}$ kept constant. There will also be distortions due to scattered electrons, surface photoemission, surface states, etc.

In the photon energy range considered by the previous workers,[4,7] $\hbar\omega<10.7$ eV, the density of the final states of the excited electrons will introduce a great deal of structure in the energy distribution of the joint density of states. This will make it more difficult and more uncertain to look for changes in the band structure, since changes in the density of both initial and final states are involved. With 40.8-eV photons, the excited electrons will reach a region in k space where the final states are more closely and evenly packed, and the EDC will thus reflect the density of the initial states more directly.[14,15] For $\hbar\omega=21.2$ eV, final states effects are still considered to introduce structure in the EDC (as will be discussed further in Sec. IV). Photoelectron energy distribution curves recorded with an exciting energy of 40.8 eV would thus reflect changes in the initial density of states more directly than would those recorded with an exciting energy of 21.2 eV, and lower.

Another point to take into account is that the electron-electron scattering length reaches a minimum in the vicinity of those d-band electrons excited with 40.8 eV ($E_{\rm el}\approx 40$ eV).[16,17] For 5.4-eV electrons, the scattering length in nickel l has been measured to be 11 Å by Pierce and Siegmann.[18] For For 40-eV electrons, an $l=3-5$ Å seems probable.[19] Since, in a quantum-mechanical description, the momentum broadening is indirectly proportional to the scattering length,[15] it will become important at these energies, and will introduce a smearing which will probably make it impossible to resolve finer details in the EDC. Existing data support this point.[20]

However, if the above model of photoemission is applicable to Ni and Fe and if a band model of ferromagnetism is valid, then the shifts expected of the leading peak in the density of states[21,22] (0.3–0.5 eV) owing to a transition from a ferromagnetic state to a paramagnetic state should show up as similar shifts in the EDC. (See also the discussion in Sec. V.)

III. EXPERIMENTAL

The experimental setup consists of an ion-pumped ultrahigh-vacuum chamber, equipped with a liquid-N_2-cooled sublimation pump, capable of reaching a base pressure of $(3-5)\times10^{-11}$ Torr, a differentially pumped He resonance lamp, and an electrostatic, hemispherical energy analyzer.[23] When the He lamp is operated at typical working pressures of 0.5–3.0 Torr, the pressure in the ultrahigh-vacuum chamber does not exceed 1.5×10^{-9} Torr. Residual gas analysis, with a quadrupole mass spectrometer, show that the pressure rise is entirely due to the He flow from the lamp. When the lamp is operated for maximum He II (40.8 eV) radiation, the ratio between the He I and He II radiation is approximately one.[24] The analyzer is operated in the constant resolving power mode with $E/\Delta E_{1/2}$ set to approximately 100. This analyzer is well suited for measuring the angular dependence of the emitted electron distribution, as it is small in size ($r=2.5$ cm), has a small angular acceptance, and is mounted on a turntable. The angle of incidence was set to 45°, and electrons emitted normal to the sample were analyzed.

The samples were prepared by electron-gun evaporation by depositing nickel on an ultrasmooth quartz plate, and iron on a mechanically polished molybdenum plate. Both substrates were well outgassed prior to evaporation. The film thickness was approximately 1000 Å for both materials, and it took 3–5 min to obtain these films. The evaporation pressures were typically 5×10^{-9} Torr in the beginning of the evaporation and 2×10^{-9} Torr at the end. The heating of the sample was accomplished by resistance heating with a filament designed to minimize the magnetic fields. The temperature was measured on the edge of the sample holder with a chromel-alumel thermocouple. The temperature is believed to be correct to within ± 10 °C of a stated value.

IV. RESULTS

A. Ferromagnetic state

1. Nickel

Typical energy distributions are shown in Figs. 2 and 3. The full width (FW) of the main peak, believed to represent the d band[25] in the EDC with $\hbar\omega = 21.2$ eV, is 3.0 eV (as shown in Fig. 2), and the full width at half-maximum (FWHM) is 1.6 eV (after a subtraction of secondary electrons, as shown in Fig. 2). The main peak is located at − 0.4 eV (with the Fermi energy set to zero), and a small shoulder is located at − 0.9 eV. The small bump seen above the Fermi energy in Fig. 2 is due to electrons excited with the He I line at 23.1 eV. With $\hbar\omega = 40.8$ eV, the spectrum shows a full width of 3.5 eV, and a full width at half-maximum of 1.6 eV. The main peak is also here located at − 0.4, eV and a shoulder is located at − 1.2 eV. A comparison between the EDC's recorded with $\hbar\omega = 21.2$ and $\hbar\omega = 40.8$ eV shows that even though the FW of the 40.8 eV peak is larger, which one would expect due to poorer resolution, the FWHM is about the same. This could be explained by noting that the electron scattering length should be somewhat smaller for 40-eV electrons than for 20-eV electrons (see Sec. II), and so the 40.8-eV EDC would be more influenced by the surface density of states than would the 21.2-eV EDC. Since the d-d overlap will be smaller closer to the surface due to fewer neighbors, the d band should be narrower.[26,27] This effect was not seen in our previously reported measurements on the noble metals.[28] This discrepancy could be explained if the scattering length becomes shorter in nickel than in the noble metals. (Hüfner *et al.* have, for instance, used this argument to explain the deviation in width in their results compared with theoretical density of states.[29]) Perhaps an even more likely explanation of the smaller FWHM at the higher photon energy is that (i), the density of the final states will still have an influence on the shape of the 21.2-eV EDC and (ii), that the transition probabilities (i.e., the momentum matrix elements) then will also be different for $\hbar\omega = 21.2$, and for $\hbar\omega = 40.8$ eV.

A comparison between the 21.2-eV EDC from a fresh nickel film, the results of Eastman,[25] and the calculated density of states by Wang and Callaway,[30] is shown in Fig. 4. We note three facts: (i) compared with the results of Eastman, we do not see

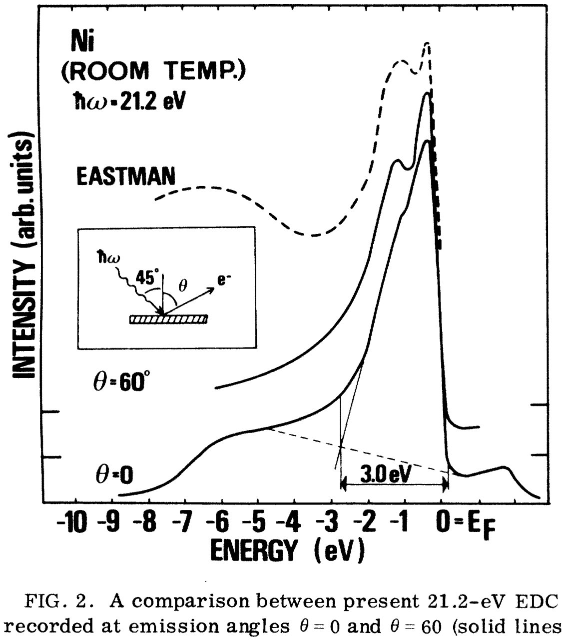

FIG. 2. A comparison between present 21.2-eV EDC's recorded at emission angles $\theta = 0$ and $\theta = 60$ (solid lines), and the result of Eastman with $\hbar\omega = 21.2$ eV (Ref. 25). The small bump seen above the Fermi energy is due to electrons excited with the He I line at 23.1 eV.

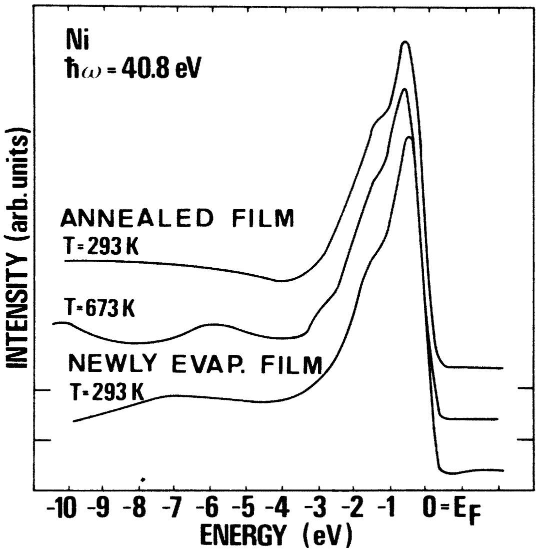

FIG. 3. EDC's from Ni with $\hbar\omega = 40.8$ eV. The lowest is from a newly evaporated film at room temperature, the one in the middle was recorded at $T = 673$ K, and the one at the top is from an annealed film, recorded at room temperature. The main difference between the EDC's is the higher background from the heated films.

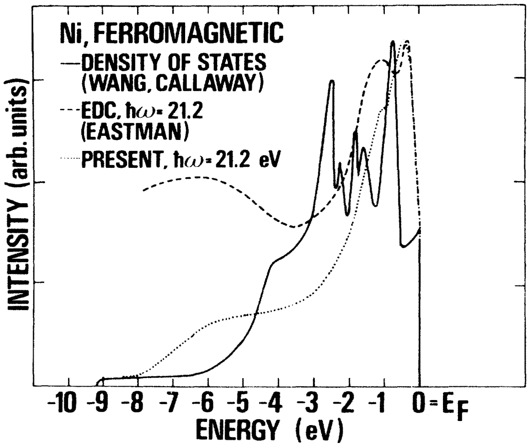

FIG. 4. A comparison between the present 21.2-eV EDC from Ni, the experimental result of Eastman, with $\hbar\omega = 21.2$ eV (Ref. 25), and a calculated density of states by Wang and Callaway (Ref. 30). Note the poor agreement between the theoretical and experimental results.

the peak centered at -1 eV, (ii) the number of low-energy electrons is much lower in the present result than in Eastman's, and (iii) the agreement between the experimental results and the theoretical density of states is not striking.

The first point could be explained by noting that the emission of the electrons in the present result was along the normal of the sample. Changing this emission angle from 0 to anywhere above 30° from the normal will have drastic effects on the EDC. Figure 2 also shows an EDC recorded with an emission angle of 60°, and here this peak is clearly seen. We believe that this angular effect is due to a preferential orientation of the crystallites in the film. Such effects have been observed by Koyama and Hughey[31] on gold. Since this angular effect is not seen in the 40.8-eV EDC, it is not entirely due to structure in the initial density of states, but rather to structure in the joint density of states. It is worthy of mention that the origin of the high-energy peak also has been attributed to a localized surface state.[32]

The small number of low-energy electrons, especially as seen in the 40.8-eV EDC, small also compared with the more recent results of Page *et al.*,[33] suggests that the surface is free of contamination.

The third point is the most intricate. We first note that the width is much smaller on the experimental curves. The easy way out is to say that because of the extreme surface sensitivity of the experimental method, we do not measure a bulk density of states, but rather a surface density of states which should be narrower.[26] However, because of the fair agreement between the EDC's of the noble metals and the calculated density of states,[28] we do not think that this is the ultimate explanation. One obvious fact, which has often been pointed out, is that when comparing experimental results with a theoretical density of states, one must not neglect such effects as that of transition probabilities and hole-lifetime broadening. Still, with these restrictions, and the momentum broadening mentioned in Sec. II, in mind, the resemblance is still not very convincing. It has been suggested by Kemeny and Shevchik[34,35] that the same effect that produces the asymmetries in the core level spectra of the metals with a high density of states at the Fermi surface, i.e., a readjustment of the Fermi sea due to the hole potential and a subsequent electron-hole pair creation, will also produce a similar effect on photoemitted *d* electrons. The similarities between the nickel $2p_{3/2}$ and the nickel $3d$ spectra are pointed out as an example and the typical low-energy tail seen in both of these two spectra is attributed to the above-mentioned effect.

The arguments given lead to the conclusion that the interpretation of the EDC's from the transition metals in terms of one-electron energy bands should be made with extreme care, or rather not at all.

2. *Iron*

The energy distribution curves for iron (Fig. 5) show a full width of 4.6 eV, which is 0.8 eV wider than the full width reported by Eastman,[25] and a full width at half-maximum of 1.4 eV for both exciting energies. Because of the constant resolving

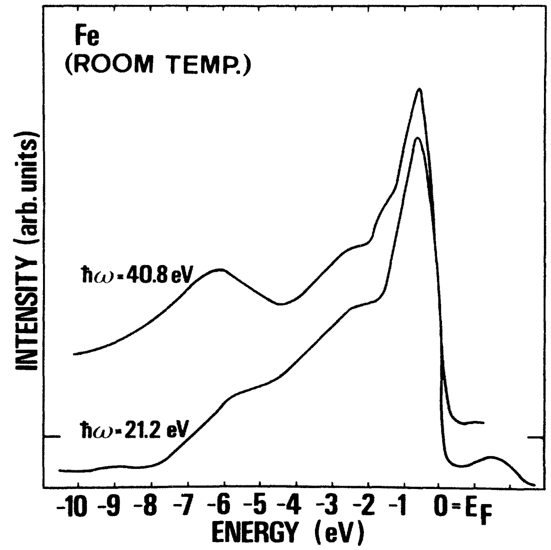

FIG. 5. EDC's from Fe as recorded with $\hbar\omega = 21.2$ eV and $\hbar\omega = 40.8$ eV from a newly evaporated film at room temperature and with normal electron emission.

power of the analyzer, one can conclude that the d-band peak excited with the higher photon energy is narrower by ≈0.2 eV. The dominating features in the spectra are the main peak at − 0.6 eV and a broad shoulder between − 2.0 and − 2.7 eV. The EDC's recorded with the two exciting energies are thus very similar, which indicates that the density of final states has only a small influence on the energy distribution of the excited electrons, and thus one might assume that the density of states in this high-energy region is rather free-electron-like. Compared with the nickel spectra, the iron spectra have slightly smaller FWHM (0.2 eV) and a significantly larger FW (≈1 eV). This smaller FWHM of iron is not in accord with the x-ray photoemission(XPS) measurements of Baer *et al.*,[36] where a systematic increase in the FWHM with the decrease of the number of electrons in d states was reported. It is not surprising, however, that the FWHM is of the same order for nickel and iron since, in a band model of ferromagnetism, there should be about the same amount of majority electrons in both materials, and it is these majority electrons that are responsible for the sharp structure (see Fig. 1). The difference in FW is probably due to the larger exchange splitting (by approximately 1 eV) in iron.

Figure 6 shows a comparison between the present result on iron with $\hbar\omega = 40.8$ eV, the XPS result of Hüfner and Wertheim,[37] and a theoretical density-of-states calculation by Connolly.[22] One should note the good agreement between the experimental results, although the present uv result shows a broad peak centered at − 6 eV. We believe that this peak is due to some contamination, probably oxygen, as it grows with the age of the film. The fact that it shows up in our ultraviolet-photoemission (UPS) result and not in the XPS result is attributed to the extreme surface sensitivity of photoemission with the exciting energy 40.8 eV. None of the finer structures in the theoretical density of states is observed in the experimental curves, although the overall agreement seems to be somewhat better than for nickel, especially if the experimental results are shifted downwards in energy by approximately 0.3 eV.

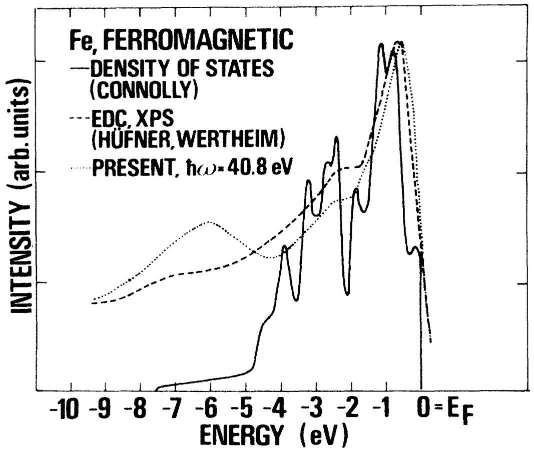

FIG. 6. A comparison between the present 40.8-eV EDC from Fe, the XPS result of Hüfner and Wertheim (Ref. 37), and a calculated density of states by Connolly (Ref. 22). Note the good agreement between the experimental results.

B. Paramagnetic state

1. Nickel

Figure 3 shows a comparison between the EDC from a newly evaporated film at room temperature, the EDC from a film heated above T_c, and the EDC from the same film cooled to room temperature again. The changes in the EDC's are small, a slight increase (0.2 eV) of the full width, and a slight shift downwards of the main peak (0.2 eV), but they do not follow the temperature variation once the film has been heated. Thus, the EDC from an annealed film, recorded at room temperature, looks different then the EDC from a newly evaporated film at room temperature. Note also that the number of secondary electrons has increased as a result of heating the sample, indicating a contamination of the surface. The conclusion is that we do not see any changes in the EDC's when going from a ferromagnetic to a paramagnetic phase, which can be attributed to a change in the magnetic properties. The small changes that we do see must be attributed to changes in the surface structure, probably due to contamination.

2. Iron

Experimentally there are some difficulties in obtaining reliable spectra when the film is heated above the Curie temperature ($T_C = 1043$ K). Around this temperature, iron has a vapor pressure which make it liable to be evaporated with a significant speed. Secondly, there are large problems with contamination. A large broad peak would almost immediately grow, centered at − 6 eV, when the heating was started.

Several series of EDC's were recorded between the temperatures 943 and 1043 K. A typical spectrum is shown in Fig. 7. We cannot see any consistent changes in the spectra which we could attribute to a change in the magnetic properties.

V. DISCUSSION

The motivation for this experiment was based on the idea that the EDC's recorded above and below

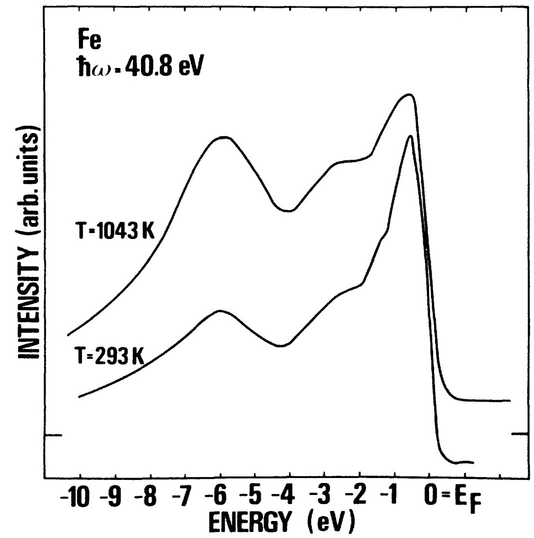

FIG. 7. A comparison between EDC's from Fe, $\hbar\omega = 40.8$ eV, at room temperature and at $T = 1043$ K. The large peak centered at -6 eV is due to contamination. No changes which we could attribute to a change in the magnetic properties could be observed.

the Curie temperature would show changes that could be related to the changes in magnetic properties if four conditions were met. These conditions are (i) ferromagnetism in nickel and iron can be described in an itinerant electron model with an exchange splitting that depends on the magnetization, (ii) the photoemission technique gives an adequate picture of the one-electron density of states, (iii) an evaporated film is ferromagnetic all the way to the surface, and (iv) the differences between the ferromagnetic and paramagnetic density of states are large enough to be detected with our experimental technique.

The last condition is fulfilled since the shift of the leading peak should be, at least, several tenths of an electron volt.[38] Our experimental uncertainty is less than that.

There has also been some discussion of magnetically dead layers close to the surface.[39] Since the probing depth of our technique is very short (see Sec. II), this would explain why there is no change in the EDC's in going from a ferromagnetic to a paramagnetic phase. This explanation is, however, not plausible, since recent measurements shows that even an extremely thin film (1–2 Å) can be ferromagnetic.[39,40]

Condition (ii) was, to some extent, discussed in Sec. IV. It is clear from earlier results[28] that for the noble metals, the photoemission technique gives a picture of the one-electron density of states (although somewhat distorted). The situation is less clear for the transition metals, where the agreement between experimental EDC's and theoretical densities of states have not been convincing. This is manifested in the results from photoelectron-spin-polarization measurements by Bänninger *et al.*[41] on nickel, and by Busch *et al.*[42] on cesiated cobalt, where the spin polarization is found to be the opposite of what would be expected from a theoretical density of states. (However, taking k conversation into account might account for the experimental results on nickel, as discussed by Smith and Traum.[43]) Many-particle solutions have also been given, for instance, by Doniach[44] and Anderson.[45] In Doniach's model the transition probabilities turn out to be quite different for the majority than for the minority electrons, due to the relaxation around the hole left by the outgoing electron. In the Anderson model, the Hartree-Fock ground state is corrected for many-body interactions. We cannot judge whether, for these materials, the excitation itself distorts the one-electron band picture, whether the one-electron band picture is valid at all, or whether the EDC actually gives a fairly accurate picture of the density of states. This last assumption was, naively, used as a working hypothesis.

If condition number two is fulfilled, the null result of the experiment implies that the first condition is not fulfilled. There are several theoretical arguments that would support such a conclusion. Slater[4] has pointed out that the energy splitting between the spin-up and spin-down electron bands has no connection with the Curie temperature, and thus the anticipated temperature dependence should not be seen. Harrison[46] gives a model where local moments are formed on each atom, and these are then broadened into bands. He explicitly states that the large change in the density of states should not appear. Above the Curie temperature, the local moments persist, but are disordered, and the difference expected in the density of states should be of the order of kT_C rather than of the order of ΔE_{ex}. The disorder will complicate the bands, as in liquids, and therefore we think that angular-dependent photoemission measurements on single crystals of nickel and iron, where only a small part of the Brillouin zone is investigated, would be relevant.

It should be pointed out that these "no-change" results were obtained much earlier by Spicer and Blodgett[47] on nickel ($\hbar\omega < 11.8$ eV) in 1965, and by Fadley and Shirley[48] on nickel and iron (XPS) in 1969. However, the experimental techniques and equipment were not satisfactory in light of later experiences, and further investigation of these results was justified.

In view of the crucial role of the second condition in interpreting this experiment, further work is in progress using single crystals rather than polycrystalline films, in order to clarify the connection between the EDC and the one-electron density of states in the transition metals.

ACKNOWLEDGMENT

This work was partially supported by The Swedish National Research Council (NFR) under contract No. 2761-017.

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