

Spin Polarization of Photoelectrons from Cesium Fe, Co, and Ni

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The electron-spin polarization (ESP) of photoelectrons from cesiated Fe, Co, and Ni films has been measured for photon energies $h\nu < 6$ eV at 4.2°K. The photo-ESP was *positive* (magnetic moment parallel to the magnetization) independently of Cs coverage and photon energy. For Ni and Co and coverage parameters θ near to 1 (monoatomic layer) the photo-ESP approaches 0 at photon energies near the photothreshold ϕ . However with Fe, the photo-ESP is rather independent of θ , even for $h\nu$ approaching ϕ . At higher photon energies a common trend of the spectra is observed: The photo-ESP approaches the average polarization $P = n_B/n$ with photon energies exceeding ϕ only by 2 to 3 eV, which correlates with the d band-width observed in recent ultraviolet photoemission and x-ray photoemission spectroscopy.

I. INTRODUCTION

In recent years photoemission spectroscopy is increasingly used as a tool for studying the electronic structure of solids. The energy-distribution curves (EDC) of photoelectrons emitted from thin films of noble metals have been interpreted successfully on the basis of the joint density of states¹ including, in more refined calculations, the matrix elements for the optical transitions.² Eastman found good agreement between experimental peak location and predictions of the Hartree-Fock calculations even for the ferromagnetic transition metals Fe, Co, and Ni.³

However, experiments testing crucial features of the Stoner-Wohlfarth-Slater (SWS) band theory of ferromagnetism have been performed recently and have shown the following discrepancies with theoretical predictions: (i) The electron-spin polarization (ESP) from polycrystalline Ni and Co⁴ has the wrong sign and does not show the predicted dependence on photon energy. (ii) The temperature dependence of the Ni d peak position is much smaller than expected from band theory.^{5,6} (iii) The sign and magnitude of the spin polarization of electrons within 1 meV above E_F as determined by spin-dependent tunneling into ferromagnetic Ni and Co are in disagreement with the SWS theory.^{7,8} (iv) The widths of the d band peak obtained from high-energy photoemission experiments (especially for Ni) are smaller than predicted.^{9,10}

The discrepancies between the predictions of the one-electron approximation for the photoemission process based on the existing band-structure calculations and ESP measurements have already been discussed for Co.¹¹ Since both the direct and non-direct transition models for the optical process do not seem to be able to explain the results, one must question whether the available band structures contain the essential characteristics necessary for

the understanding of ferromagnetism in Co, or in neighboring Fe and Ni.

New theories including many-body effects during the excitation process or assuming a many-body ground state have been recently proposed by Anderson,¹² Baltensperger,¹³ Doniach,¹⁴ and Kim.¹⁵ The present status of these approaches is such that no quantitative statements can be made. It is obvious that for a complete understanding of the experimental situation one also needs the data for Fe and Ni. These data are presented in this work and they support the conclusions drawn from the measurements on Co. The following information is required: (a) What is the influence of cesiation on the ESP of the photoemitted electrons, especially for photon energies near threshold? (b) What is the dependence of the ESP on photon energy? (c) How large must the energetical excitation depth be in order to observe the average polarization $P = n_B/n$ (n_B is the number of Bohr magnetons per atom and n is the number of s and d electrons per atom)?

With this information it will then be possible to make a detailed comparison between predictions of the band theory and the photo-ESP data, especially in the case of Ni, where calculations assuming both direct¹⁶ and nondirect optical transitions are available.

II. EXPERIMENTAL

The Fe, Co, and Ni films were obtained by electron-gun evaporation from 99.999%-pure material. They were deposited onto a stainless-steel substrate and covered with Cs from a zeolite source as shown in Fig. 1. The distance between the crucible and the substrate was 7.5 cm. The heating elements and the Pt thermometer were used to maintain the temperature of the substrate around 500°K during evaporation or to anneal the films deposited onto cold substrates. The pressure rose during evaporation to 1×10^{-8} Torr and immediately afterwards

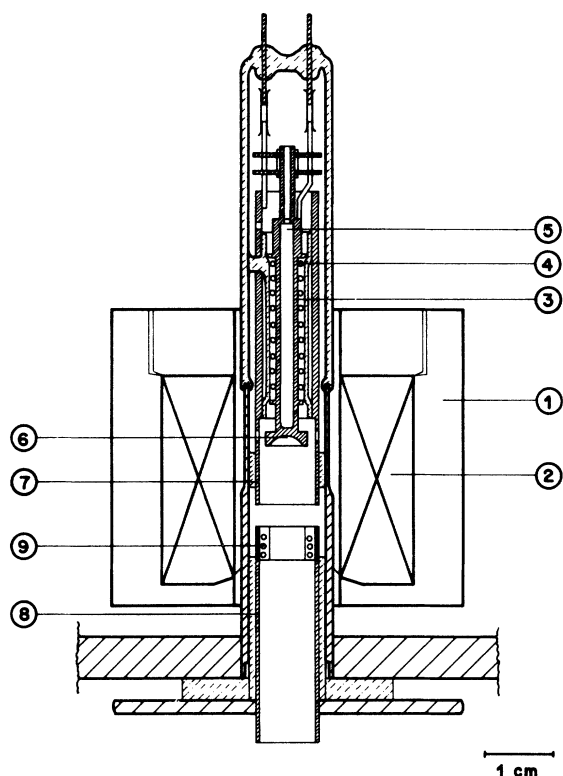


FIG. 1. Photocathode for the production of spin-polarized electrons from Cs-covered Fe, Co, and Ni films: (1) iron shield, (2) superconducting coil, (3) sample holder, (4) heating element, (5) Pt thermometer, (6) magnetic film (photocathode), (7) and (8) extraction electrodes, and (9) zeolite source of Cs ions.

fell to 3×10^{-10} Torr. Cesium and annealing were performed in 10^{-10} -Torr range. The magnetic domains of the films were aligned perpendicularly to the surface by an external magnetic field generated by a superconducting coil. The light from a Xe-Hg lamp was focused onto the magnetic film after passing through a monochromator and the photoemitted electrons were extracted from the magnetic field in a way such as to form an electron beam. The photoelectrons were then accelerated in several stages to 100 keV. At this energy Mott scattering was performed in order to measure $\langle \sigma_z \rangle$ of the beam. σ_z is the z component of the Pauli spin operator $\vec{\sigma}$. The measured right-left asymmetry of the scattered intensities from a thin gold foil is proportional to the spin polarization $\langle \sigma_z \rangle$ of the incident beam. Further details of the apparatus and of the experimental technique employed are given in Refs. 4 and 17.

III. RESULTS AND DISCUSSION

A. Cesium

The work function Φ of the films could be varied between 3.8 and 2.2 eV. The value 2.0 ± 0.1 eV

corresponds to the Φ of pure-Cs metal as deduced from Fowler plots.¹⁸ θ is defined as the coverage parameter: for $\theta = 1$ we have a fully packed first adsorbate layer and for $\theta = 0$ the pure-metal surface. A work function Φ of 2.2 eV corresponds to a nearly complete Cs monolayer.

In Fig. 2 we show the observed influence of the annealing and Cs adsorption on the work function of Ni films. Curve 1 represents the Fowler plot of an amorphous Ni film evaporated onto a substrate kept at 20 °K: $\Phi = 4.4 \pm 0.1$ eV. Curve 2 is obtained after annealing the same film at 300 °K: $\Phi = 4.2 \pm 0.1$ eV. Curve 3 after cesiation at 300 °K: $\Phi = 3.7 \pm 0.1$ eV, and curve 4 after annealing the cesiated film at 500 °K: $\Phi = 3.0 \pm 0.1$ eV. One would expect an increase of the value of Φ after annealing of the amorphous film⁴ rather than a decrease. The decrease is likely due to presence of alkali atoms or ions which remain in the region of the photocathode after the *first* evaporation from the zeolite; during the annealing process a small amount of these can reach the photocathode.

The alkali atoms on the ferromagnetic substrate might influence the observed photo-ESP in the following ways: (i) photoionization of the adatoms; (ii) elastic and inelastic scattering of the photoelectrons originated in the substrate; (iii) spin-exchange collisions between adatoms and photoelectrons from the substrate; and (iv) alteration of

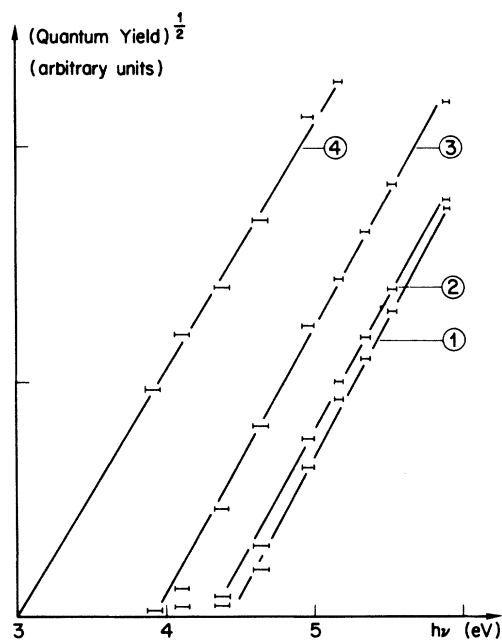


FIG. 2. Dependence of the quantum yield on cesiation and thermal treatment: (1) after evaporation onto a substrate kept at 20 °K, (2) after annealing at 300 °K, (3) after cesiation at 300 °K, and (4) after annealing the cesiated film at 500 °K.

d -level position in the first atomic layer of the ferromagnetic substrate (and, as a consequence, of its magnetic state). We discuss briefly these four points.

Because of the presence of the substrate, the valence level of the adatoms becomes broadened so that the atoms are never completely ionized. The degree of occupancy of this level (and therefore the degree of neutralization of the positive core) is determined by its relative position compared to the Fermi level E_F of the substrate. Using a self-consistent treatment of a jellium model for the metallic substrate-adsorbate system (an approach valid especially for $\theta \gg 0$, where the interaction of the adatoms can no longer be neglected) Lang¹⁹ showed that the density of negative charges lying outside the metal surface increases with θ . Since in photoemission the spatial excitation depth x_s is relatively small (approximately 20–30 Å for an excitation energy of 4–6 eV above E_F), the photoexcitation of the negative charge may have a decisive influence on the observed photo-ESP, especially for photon energies $h\nu$ near threshold Φ . The yield of the transition metals goes to zero approximately as $(h\nu - \Phi)^2$ for $h\nu \rightarrow \Phi$. The total photoionization cross section σ_{ph} of the Cs atoms is, on the other hand, essentially different from 0 especially for $h\nu \rightarrow \Phi$. On increasing $h\nu$, σ_{ph} goes through a minimum for photon energies exceeding the first ionization energy by about 1 eV.²⁰ Thus, the photoemission from the Cs is especially important near Φ . The polarization of the Cs levels due to the presence of the ferromagnetic background cannot be assumed *a priori* to be negligible, at least not for small- θ values. However, at higher- θ values, when formation of Cs molecules is conceivable, the spin polarization of the adsorbed layer may be neglected.

As Penn²¹ pointed out, the influence of the adatoms on the yield Y_s from the substrate may have the form of an antiresonance, i. e., at given photon energies Y_s may be reduced by an extra scattering from the adatoms. The antiresonant contribution may then enhance the role of the photocurrent originating from the adsorbate layer in the ESP measurement.

Elastic and inelastic *spin-exchange* interactions between the photoelectrons from the ferromagnetic substrate and the Cs adatoms could completely determine the polarization of the electrons emitted into vacuum, especially for those electrons having small kinetic energies. The total cross section for the spin-exchange collisions of free electrons with Cs atoms increases to values much larger than 1×10^{-14} cm² for kinetic energies smaller than 0.5 eV.²²

Regarding point (iv) of this discussion, we remember that in increasing θ from 0 the density of conduction electrons in the first atomic layer of

the substrate decreases. It has been suggested by Liebsch *et al.*²³ that if the s -electron density n_s^s at the surface is lower than the one in the bulk ($n_s^b > n_s^s$), then the d bands of the first atomic layer shift downward in energy leading to a decrease of the magnetization value in the case of Ni. But the basic underlying assumption is that the interaction of the d electrons with the nucleus is more strongly affected by a variation of n_s than the intra-atomic d - d interaction. An enhancement of this interaction will probably generate an energy shift which goes in the opposite direction.

Independently of these open questions, one would expect qualitatively quite different effects from the cesiation of Fe and Co and Ni, since the first is a weak ferromagnet while Co and Ni are strong ferromagnets. With these remarks in mind we now analyze the experimental data.

B. Fe

In Fig. 3 we compare the dependence of the photo-ESP on the external magnetic field strength, for (a) a pure polycrystalline Fe film with work function $\Phi = 4.7 \pm 0.1$ eV and (b) for a cesiated Fe film with work function $\Phi = 3.2 \pm 0.1$ eV. Curve (a) is obtained using the full spectrum of the Xe-Hg lamp, corresponding therefore to an energetical excitation depth ϵ_a of about 0.8–1 eV below E_F . Curve (b) is obtained using monochromatic light with wavelength 316 nm (3.92 eV); in this case $\epsilon_b \leq 0.8$ eV and therefore comparable to ϵ_a . Curves (a) and (b) correspond to the magnetization curve of an Fe film magnetized perpendicularly to the surface. We observe saturation of the ESP for $B \sim 20$ kG. The saturation values are $P_s^{(a)} = 54\%$ and $P_s^{(b)} = 45\%$. Since $\epsilon_a \cong \epsilon_b$ to a good approximation, the measured decrease $P_s^{(b)}/P_s^{(a)} = 0.83$ remains a question. Using the simple approximation that the photocurrent from the Cs adatoms is negligibly polarized, one obtains

$$P = (P_{Fe}I_{Fe} + P_{Cs}I_{Cs}) / (I_{Fe} + I_{Cs}) = P_{Fe} / (1 + c),$$

with $c = I_{Cs}/I_{Fe}$; P_{Fe} and P_{Cs} are the ESP of the photoelectrons emitted from the Fe and from the adsorbate layer, and I_{Fe} and I_{Cs} the corresponding photocurrents. The c value corresponding to curve (b) of Fig. 3 is ~ 0.2 .

It is known that cesiation can generate patch effects at a metal surface and that with photoemission one determines the lowest value of the work function rather than an average as given by the Kelvin contact-potential method. Closer comparison between curves 3(a) and 3(b) shows that even in the case of Cs-covered surfaces the deviations of the experimental points from an ideal (dashed) magnetization curve are relatively small. The patch effects may contribute to deviations having electron optical origin, but with the present ap-

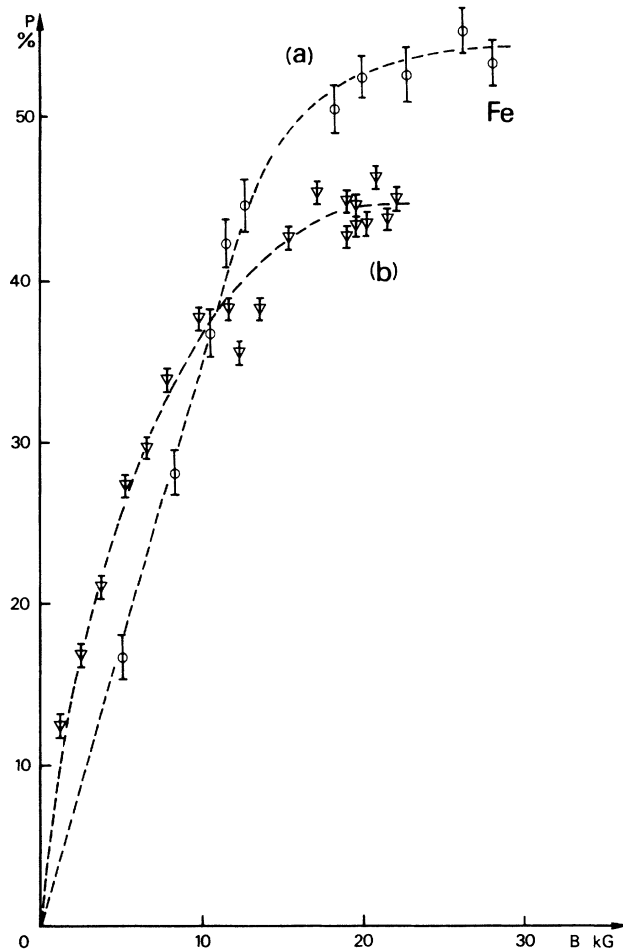


FIG. 3. Dependence of the photo-ESP on the magnetic field strength for (a) a pure polycrystalline Fe film and (b) a cesiated Fe film at 4.2°K. Vertical bars indicate the statistical uncertainty.

paratus and measurement technique these effects can be controlled and maintained within an acceptable range.

The main conclusion that we draw from curve (b) is that the electric dipole field generated by the adsorbed atoms does not strongly influence the ESP of the photoelectrons emitted from the ferromagnetic substrate when the photon energies are slightly higher than the threshold Φ .

Curves (a) and (b) of Fig. 4 show the dependence of the photo-ESP on photon energy for two representative Fe films with work functions $\Phi(a) = 3.2 \pm 0.1$ eV and $\Phi(b) = 2.35 \pm 0.1$ eV—indicated by the arrows—at a constant magnetic field $B = 13.7$ kG. Curve (c) in Fig. 4 is the result of an ESP measurement of the Fe film (b) after it remained 4 days in ultrahigh vacuum (1×10^{-9} Torr). The work function of the film, $\Phi = 2.55 \pm 0.1$ eV, increased by

about 0.2 eV compared to the freshly cesiated film. The dependence of the ESP on $h\nu$ is similar in every case: monotonically decreasing for increasing $h\nu$. The value of the ESP near photothreshold is not strongly dependent on θ . We do not observe any relevant decrease of ESP for increasing θ . On going from $\Phi = 3.2$ eV to $\Phi = 2.35$ eV the ESP changes from 42 to 40% for $\epsilon \sim 0.4$ eV. Aging the film generates a higher value of the ESP near threshold [curve (c)]. Although the influence of the Cs might be important for $h\nu \sim \Phi$, at higher $h\nu$ ($\epsilon > 0.5$ eV) one should observe the properties of the Fe substrate. The ESP reaches the average saturation value of $\sim 26\%$ expected for the Fe conduction band for energetical excitation depths ϵ of only 2.5–3 eV. In comparing these results with

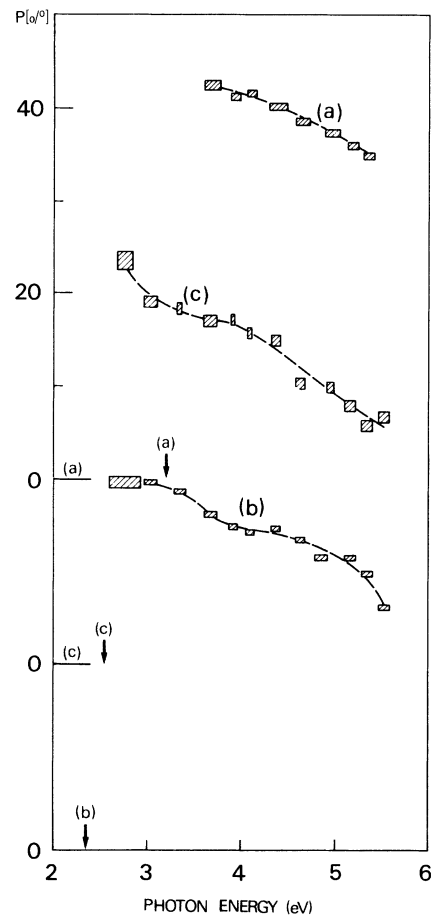


FIG. 4. Photon energy dependence of the ESP for two cesiated Fe films with work functions (marked by the arrows) $\Phi(a) = 3.2 \pm 0.1$ eV and $\Phi(b) = 2.35 \pm 0.1$ eV. Curve (c) has been obtained from film (b) 4 days after film preparation, $\Phi(c) = 2.55 \pm 0.1$ eV. The horizontal dimension of the dashed fields corresponds to the resolution of the monochromator; the vertical dimension corresponds to the statistical uncertainty.

the predictions of the existing Fe band-structure calculations, we can say that the ESP value near threshold shows some agreement, but we do not observe the predicted structure in the spectrum, and the energetical window $\epsilon = \epsilon^*$ for which the ESP approaches the value 26% is much smaller than expected (by a factor of the order of 2^{24-26}). ϵ^* is even smaller than the estimated width W of the d band of ferromagnetic Fe using high-resolution ultraviolet photoemission spectroscopy (UPS) ($W = 3.8$ eV) or x-ray photoemission spectroscopy (XPS) ($W = 4.2$ eV).

C. Co

In Fig. 5 we present the observed photon energy dependence of the ESP for Co. These data have been considered as a crucial test for the inapplicability of the simple SWS band theory for the interpretation of photoemission data.¹¹ The influence of the cesiation on the ESP is different from the Fe case for photon energies near threshold. On increasing θ the ESP goes to 0 as $h\nu$ approaches Φ ; in this case for $\epsilon \sim 0.2$ eV the photocurrent mainly originates from the adsorbed Cs layer. This means that with Co the polarization of the occupied broadened Cs valence level goes to 0 at higher θ values. As in Fe, the ESP reaches the expected

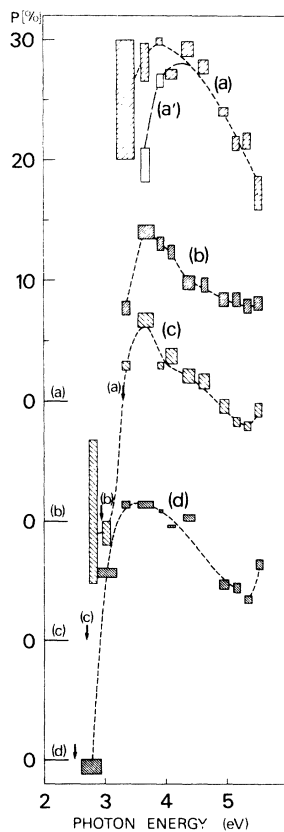


FIG. 5. Photon energy dependence of the ESP for cesiated Co films. Meaning of the symbols as in Fig. 4.

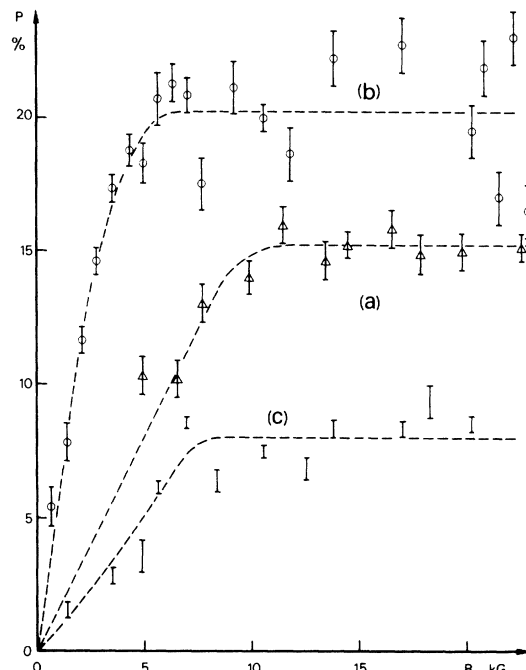


FIG. 6. Dependence of the photo-ESP on magnetic field strength for (a) a pure polycrystalline Ni film with $\Phi(a) = 4.9 \pm 0.1$ eV and two cesiated Ni films with $\Phi(b) = 3.4 \pm 0.1$ eV and $\Phi(c) = 2.4 \pm 0.1$ eV. Temperature of the substrate 4.2 °K.

average value of the conduction band, 17% for $\epsilon^* \sim 2.5$ eV, which is much smaller than expected from band-structure calculations,^{28,29} or from the 3.6 and 4.0 eV d bandwidth determined by UPS³ and XPS,²⁷ respectively.

D. Ni

In Fig. 6 we compare the dependence of the ESP on the external magnetic field strength for a polycrystalline Ni film [$\Phi(a) = 5.0 \pm 0.1$ eV] measured using the full spectrum of the Xe-Hg lamp, and for two cesiated films [$\Phi(b) = 3.4 \pm 0.1$ eV and $\Phi(c) = 2.4 \pm 0.1$ eV] using photon energies $h\nu = 3.92$ eV [curve (b)] and $h\nu = 3.35$ eV [curve (c)]. The aim of these curves is again to show that the ESP reaches saturation at $B \cong 6-7$ kG as expected and that the electron optical effects remain within an acceptable range. The ESP values of Fig. 6 are consistent with the representative spectra reported in Fig. 7, curves (a)-(d), measured at a constant magnetic field $B = 8.4$ kG; the thresholds are $\Phi(a) = 3.8$ eV, $\Phi(b) = 3.3$ eV, $\Phi(c) = 2.5$ eV, and $\Phi(d) = 2.2$ eV as indicated by the arrows. On increasing θ , Ni, as Co, exhibits a drastic decrease of the ESP near threshold and of the maximum occurring at about 0.6-0.8 eV below threshold. From Fig. 7 it follows that the ESP again reaches the

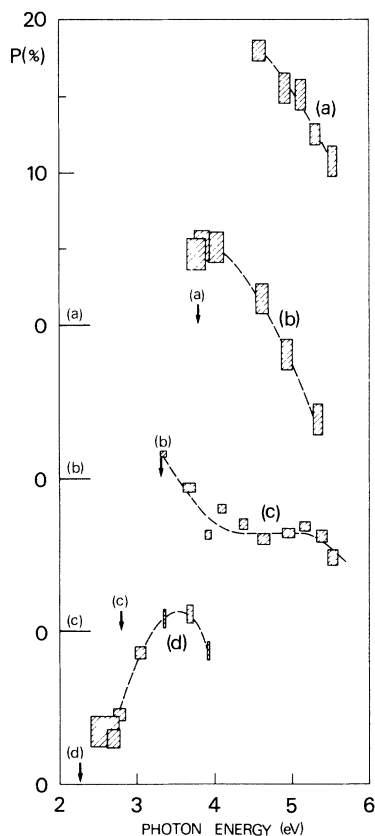


FIG. 7. Photon energy dependence of the ESP for four cesiated Ni films, with work functions $\Phi(a) = 3.8 \pm 0.1$ eV, $\Phi(b) = 3.2 \pm 0.1$ eV, $\Phi(c) = 2.8 \pm 0.1$ eV, and $\Phi(d) = 2.2 \pm 0.1$ eV.

average value expected for the conduction band of Ni, 5.5%, within 2–2.5 eV. This value of ϵ^* is much smaller than the calculated bandwidth W of the Ni d band (~ 5 eV)^{30–32} and also smaller than the experimentally estimated one (UPS: 3.3 eV,³ XPS: 2.7 eV³³). The ESP is always positive for both Co and Ni over the whole photon-energy range, even for $\theta \sim 1$. The inadequacy of the SWS band theory for the interpretation of photoemission data has been demonstrated in the case of Co and the Ni data offer a further support of this thesis. For fcc Ni, Smith and Traum¹⁶ have calculated the dependence of the ESP on photon energy using the direct transition model for the optical excitation and constant matrix elements. The same authors calculated the photo-ESP curves assuming different work functions ranging from 2 to 5 eV using the Ni band structure of Hodges, Ehrenreich, and Lang. It does not make much sense to compare directly the calculated and the experimental curves, especially because the width of the d band observed in photoemission is not in agreement with the calculated one. We mention only that, assuming no in-

fluence of the cesiation on the photo-ESP, we should observe ESP values of the order of 60–70% for $\epsilon \cong 0.7$ eV and $\Phi = 3.8$ –4 eV [corresponding to curve (a) of Fig. 7] and of the order of 40–50% for $\epsilon \cong 0.6$ eV and $\Phi = 3.3$ eV [corresponding to curve (b) of Fig. 7]. For appropriate Φ values and ϵ ranges, where the properties of the Ni substrate should be dominant, the measured Ni photo-ESP is therefore approximately three times smaller than the predicted one.

E. Photo-ESP, Density of States, and Many-Body Effects

In order to have a survey and find out possible relations between the photo-ESP data from Fe, Co, and Ni, we have plotted in Fig. 8 experimental photo-ESP curves corresponding to a common work function $\Phi = 3.2$ –3.3 eV for Fe, Co, and Ni. At the present status of the photo-ESP studies of the cesiated ferromagnetic transition metals one has to look for the general trend of the curves, rather than at finer details. The most surprising relation is the *common type* of dependence of the photo-ESP curves as a function of photon energy. We remember that Fe, Co, and Ni have different crystal structures, and if the character of the optical transition alone were so important as to determine completely the structure of the photo-ESP spectra, we would not expect such a *close similarity*. It seems that *another mechanism* is responsible for this behavior. In UPS studies and therefore also in photo-ESP

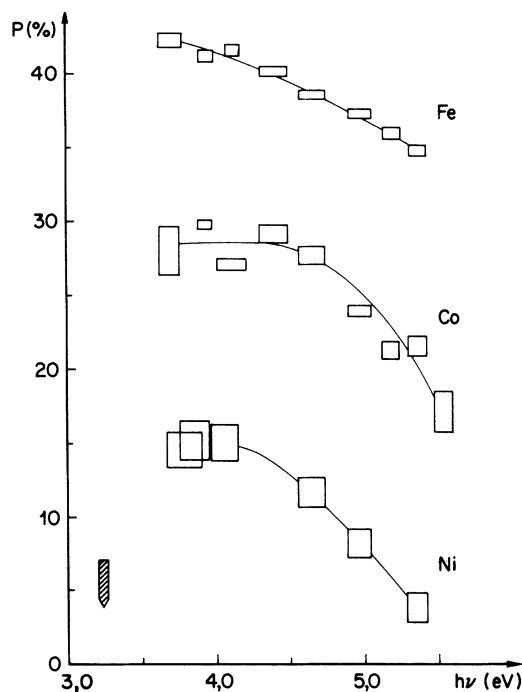


FIG. 8. Photon energy dependence of the ESP for representative cesiated Fe, Co, and Ni films with work function $\Phi = 3.25 \pm 0.1$ eV.

experiments the final state reached in the measurement involves a hole in the conduction band: This fact may be of decisive importance as pointed out by Fadley and Wohlfarth.³⁴ The question whether the measurements then test band properties of the electrons is pertinent. If the hole is strongly *localized* the single-atom behavior would be dominant and to try to find out any relation between the predictions of the SWS band theory and the photo-ESP data does not make much sense. In this case the interaction of the hole with the surrounding electrons is the most important process and what one observes is then the energy spectrum of the hole state left behind.¹¹

There is no doubt about the existence of the many-body effects, but it is difficult at present to assess quantitatively their *importance*, although the discrepancies between experimental results and existing Hartree-Fock calculations suggest they may be large. If the changes induced in the one-electron spectrum by the many-body interactions are such that the density of states differs appreciably from the one-electron approximation, then the role played by the different excitations generated by the suddenly photoemitted electron must be clarified on the basis of *realistic models* for the transition metals. As pointed out by Anderson,¹² if the renormalization is of a certain magnitude, then the itinerant theory of ferromagnetism is purely academic and for fundamental *numerical* calculations the approach of Hubbard, Kanamori, Gutzwiller, and Brandt³⁵ would be more adequate. Following this proposal, Edwards and Hertz³⁶ obtained a first qualitative result consisting of an intermediate coupling theory which should be applicable to Ni. Unfortunately, no quantitative estimates of the distortions of the majority spin band induced by the electron-magnon interactions is available at present. The role of the many-body effects may also be relevant for the interpretation of the conventional photoemission data on the basis of the *direct* transition model; even if the corrections to the one-electron spectrum were not large, it is possible that the small degree of localization of the hole state left behind could prevent K conservation from being an important selection rule. But then it remains to explain why on going to higher photon energies (up to 40 eV) one observes variations in amplitudes and shape of the energy distribution curves. It is difficult to attribute this fact either to an energy dependence of the matrix elements for the optical transition from the *d* band or to variations of the escape depth x_s of the hot electrons.

IV. CONCLUSIONS

It has been shown by the present work that it is possible to obtain polarized photoelectrons from

cesiated ferromagnetic photocathodes. The degree of photo-ESP depends both on the photon energy and on the Cs coverage parameter θ . For low values of θ and $h\nu$ values slightly higher than threshold Φ , the observed photo-ESP can be related to the one measured for pure polycrystalline samples. For higher- θ values the influence of the cesiation on the photo-ESP for photon energies near threshold is different in the case of Fe, Co, and Ni; the photo-ESP is not strongly sensitive to variations of θ in the case of Fe, but goes to 0 for $\theta \rightarrow 1$ and $h\nu \rightarrow \Phi$ with the two strong ferromagnets, Co and Ni. We have discussed this behavior and shown that one must be careful in identifying this effect with properties of the electrons in the ground state in both the metallic substrate or adsorbate system: spin exchange collisions, for instance, are known to be very important at low kinetic energies of the electrons.

The dependence of the photo-ESP on photon energy is similar for Fe, Co, and Ni; the energetic depth ϵ^* below the Fermi level for which one expects to observe the average polarization of the conduction band of Fe (26%), Co (17%), and Ni (5.5%) is much smaller than the *d* bandwidth predicted by the existing band-structure calculations. We find $2 \leq \epsilon^* \leq 3$ eV, decreasing in going from Fe to Ni. If all the *d* electrons contribute to the magnetic moment of these metals, we would expect ϵ^* to be approximately equal to the bandwidth. But the general trend of the photo-ESP curves shows that the most important contribution to the magnetic moment is generated by the electron states lying in a small energy range near the Fermi level. Furthermore, the incompatibility of the experimental data with the existing Hartree-Fock calculations support the suggestions concerning the importance of many-body effects in ferromagnetic transition metals as the ones proposed by Anderson,¹² Baltensperger,¹³ Brandt,³⁵ Doniach,¹⁴ Edwards and Hertz,³⁶ and Kim.¹⁵ If the single-atom behavior is dominant in the photoemission process then the photo-ESP data are not sensitive to the long-range exchange interactions postulated by the SWS band theory of ferromagnetism. The present stage of the many-body theories does not permit any numerical estimates of the importance of the many-body interactions.

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- ¹D. E. Eastman, in *Techniques of Metal Research VI* (Interscience, New York 1972); N. V. Smith, *Phys. Rev. B* **3**, 1862 (1971); W. F. Krolikowski and W. E. Spicer, *Phys. Rev. B* **2**, 478 (1970), and references cited therein.
- ²A. R. Williams, J. F. Janak, and V. L. Moruzzi, *Phys. Rev. Lett.* **28**, 678 (1972).
- ³D. E. Eastman, *J. Phys. (Paris)* **32**, C1-293 (1971).
- ⁴G. Busch, M. Campagna, and H. C. Siegmann, *Phys. Rev. B* **4**, 746 (1971).
- ⁵D. T. Pierce and W. E. Spicer, *Phys. Rev. Lett.* **25**, 581 (1970); *Phys. Rev. B* **6**, 1787 (1972).
- ⁶J. E. Rowe and J. C. Tracy [*Phys. Rev. Lett.* **27**, 799 (1971)] repeated the experiments of Pierce and Spicer, but using cesiated films: the measured d peak shift of 0.04 eV, even correcting for possible thermal effects, is over three times smaller than predictions of existing band calculations.
- ⁷P. M. Tedrow and R. Meservey, *Phys. Rev. Lett.* **26**, 192 (1971); *Solid State Commun.* **11**, 333 (1972).
- ⁸In the field-emission experiments of W. Gleich, G. Regenfus, and R. Sizmann [*Phys. Rev. Lett.* **27**, 1066 (1971)], the polarization is found to be positive or negative, according to how a monocrystalline Ni wire is etched electrolytically. The data of this work were interpreted by B. A. Politzer and P. H. Cutler [*Phys. Rev. Lett.* **28**, 1330 (1972)] as a proof of the validity of the Hartree-Fock approach. However, Gleich *et al.* do not observe magnetic saturation, which must occur if the electron optics work satisfactorily. The scattering asymmetry as a function of magnetic field strength showed "large fluctuations" and the authors reach the conclusion that rotation of the electron spin takes place. The conjectured spin rotation represents an "intriguing problem" and, apart from other problems such as surface conditions, needs clarification before taking these values too seriously.
- ⁹D. E. Eastman, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972).
- ¹⁰S. Hüfner, G. K. Wertheim, N. V. Smith, and M. M. Traum, *Solid State Commun.* **11**, 323 (1972).
- ¹¹G. Busch, M. Campagna, D. T. Pierce, and H. C. Siegmann, *Phys. Rev. Lett.* **28**, 611 (1972).
- ¹²P. W. Anderson, *Philos. Mag.* **24**, 203 (1971).
- ¹³W. Baltensperger, *Helv. Phys. Acta* **45**, 203 (1972).
- ¹⁴S. Doniach, *AIP Conf. Proc.* **5**, 549 (1972).
- ¹⁵D. J. Kim (private communication).
- ¹⁶N. V. Smith and M. M. Traum, *Phys. Rev. Lett.* **27**, 1388 (1971); and private communication.
- ¹⁷G. Busch, M. Campagna, and H. C. Siegmann, *J. Appl. Phys.* **41**, 1044 (1970).
- ¹⁸N. V. Smith and G. B. Fisher, *Phys. Rev. B* **3**, 3662 (1971).
- ¹⁹N. D. Lang, *Phys. Rev. B* **4**, 4234 (1971).
- ²⁰V. W. Hughes, R. L. Long, Jr., M. S. Lubell, M. Posner, and W. Raith, *Phys. Rev. A* **5**, 195 (1972).
- ²¹D. R. Penn, *Phys. Rev. Lett.* **28**, 1041 (1972).
- ²²D. M. Campbell, H. M. Brash, and P. S. Farago, *Phys. Lett. A* **36**, 449 (1971).
- ²³A. Liebsch, K. Levin, and K. H. Bennemann, *Bull. Am. Phys. Soc.* **16**, 584 (1971).
- ²⁴S. Wakoh and J. Yamashita, *J. Phys. Soc. Jap.* **21**, 1712 (1966).
- ²⁵K. J. Duff and T. D. Das, *Phys. Rev. B* **3**, 192 (1971); *Phys. Rev. B* **3**, 2294 (1971).
- ²⁶M. Yasni, E. Hayashi, and M. Shimizu (private communication).
- ²⁷C. S. Fadley and D. A. Shirley, Symposium on Electronic Density of States, Gaithersburg, Md., 1969 (unpublished).
- ²⁸E. P. Wohlfarth, *J. Appl. Phys.* **41**, 1205 (1970).
- ²⁹S. Wakoh and J. Yamashita, *J. Phys. Soc. Jap.* **28**, 1151 (1970).
- ³⁰L. Hodges, H. Ehrenreich, and N. D. Lang, *Phys. Rev.* **152**, 505 (1966).
- ³¹E. I. Zornberg, *Phys. Rev. B* **1**, 244 (1970).
- ³²J. W. Connolly, *Phys. Rev.* **159**, 415 (1967).
- ³³Y. Baer, P. F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, *Phys. Scr.* **1**, 55 (1970).
- ³⁴C. S. Fadley and E. P. Wohlfarth, *Comments Solid State Phys.* **4**, 48 (1972).
- ³⁵J. Hubbard, *Proc. R. Soc. A* **281**, 401 (1964); J. Kanamori, *Prog. Theor. Phys.* **30**, 275 (1963); M. C. Gutzwiller, *Phys. Rev.* **137**, A1726 (1965); U. Brandt, *Z. Phys.* **244**, 217 (1971).
- ³⁶D. M. Edwards and J. A. Hertz, *Phys. Rev. Lett.* **28**, 1334 (1972).