Photoemission and electronic structure of cobalt

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Energy distribution curves (EDC's) of photoelectrons emitted normal to the surface have been measured for the (0001) and $(10\bar{1}0)$ single crystal faces and for evaporated polycrystalline films of cobalt. Incident photon energies of 11.83, 16.85, and 21.22 eV were used. The EDC's of the (0001) and $(10\bar{1}0)$ faces can be interpreted in terms of emission from electronic states characteristic of the one-dimensional bulk band structure along the corresponding symmetry lines. The maximum density of occupied states of the entire Brillouin zone is found to occur at -0.35 ± 0.05 eV relative to the observed Fermi level. The density of states $N(E)$ for the ferromagnetic fcc phase has been calculated self-consistently by applying the Hubbard-model Hamiltonian. $N(E)$ at the Fermi level is obtained to be 0.65 and 0.99 electron/(atom eV) for the majority-spin and minority-spin states, respectively. The calculated $N(E)$ is consistent with the overall shapes of ultraviolet and x-ray photoelectron spectra. The present experimental and theoretical results agree with the requirements of the itinerant-electron model of ferromagnetism of the Slater-Stoner-Wohlfarth theory below the Curie point.

I. INTRODUCTION

During the past few years notable progress has been made in understanding the peculiar nature of the electronic band structures of the $3d$ transition elements. Among the spontaneous ferromagnetic metals, iron, cobalt, and nickel, cobalt has received least attention, and one's knowledge of its valence-band properties is most imprecise at the moment. The hexagonal-close-packed (hcp) room-temperature phase of Co consists of two atoms per unit cell, and therefore twice as many energy bands exist in the hcp lattice as in the bcc or fcc lattices. In addition, cobalt is considered to be a typical itinerant ferromagnet.[1] In the band model of the ferromagnetism due to Slater,[2] Stoner,[3] and Wohlfarth,[4] the exchange interaction between the itinerant electrons produces an average Hartree-Fock molecular field which is different for the two electron-spin directions and thereby causes a splitting of the bands below the Curie point. The presence of the exchange splitting in the hcp phase leads to a very complicated band scheme of cobalt.

A brief review is given below to show that new investigations of Co are necessary to improve and clarify the present day conception of the electronic band properties of this metal.

Some results of soft-x-ray emission[5,6] and x-ray photoelectron emission[7-9] (XPS) measurements of polycrystalline Co are available in the literature. However, the resolution of these techniques appears to be insufficient for a detailed analysis of the band structure in this case. To the author's knowledge, only two high-resolution ultraviolet photoemission spectra (UPS) obtained from clean Co polycrystalline surfaces for the incident photon energies $\hbar\omega$ of 10.2 and 40.8 eV have been previously reported.[10,11] There exist no XPS or UPS studies of Co single crystals in the literature.

Photoelectron spin polarization (photo-ESP) measurements[12-14] of Co show a positive polarization for electrons ejected from the vicinity of the Fermi level as opposed to the negative polarization predicted by theory. The wavelength dependence of the spin polarization in the valence band also disagrees with calculations. These observations have been proposed as experimental proof that the Slater-Stoner-Wohlfarth theory of ferromagnetism is inadequate to account for photoemission from Co.

Furthermore, the question of the existence of a magnetically "dead" layer on the surface of ferromagnetic Fe, Co, and Ni films was raised by Liebermann *et al.*[15] on the basis of their magnetization measurements. By contrast, Shinjo *et al.*[16] have not found any indication of magnetically dead layers in their Mössbauer experiments for an electroplated ^{57}Co source. Photoemission from nonmagnetic layers could contribute to the UPS spectra of a ferromagnetic sample, and the effect might be observable.

As far as we know, in all theoretical work concerning the band structure of Co, the analysis of the paramagnetic state has been extended to the ferromagnetic state by assuming a rigid splitting of the paramagnetic bands to meet the requirement of the Bohr magneton number of the atom.[17-22] However, the validity of this approximation is highly questionable because the exchange splitting depends both on the symmetry of the state and on the crystal momentum.

In the following sections we present new UPS data for two Co hcp single-crystal faces and for evaporated polycrystalline films. The density of states of the high-temperature fcc ferromagnetic

structure of Co has been calculated self-consistently, and the results are shown here.

II. THEORY

A. Photoemission spectra

Angle-resolved photoemission normal to a single-crystal face provides insight into the one-dimensional bulk structure along a specific symmetry line, on the assumption that the wave vector component $\vec{k}_{\parallel}$ (in this case $\vec{k}_{\parallel} \cong 0$) remains invariant when an electron propagates through the solid-vacuum interface.[23-25]

Direct transitions from bulk bands give rise to discrete spectral lines. The initial energy of these transitions usually varies with the photon energy corresponding to the shape of the participating valence bands. The observed widths of the lines depend on the angle and energy resolution of the photoelectron spectrometer and on other effects as for example momentum and lifetime broadening.[25,26] Directional photoemission may also yield information about surface effects, such as surface states and surface photoemission.[23,25,26] The selection rule on the normal component of $\vec{k}$ is relaxed for surface photoemission, and as a consequence, stationary structures are expected to appear in the spectra when they are plotted against the initial energy of electrons. It is therefore possible that under specific circumstances one can make a distinction between the bulk and surface contributions to the spectra.[25]

The electron distribution curves (EDC's) of a polycrystal are associated with the integrated electronic properties of the entire Brillouin zone. These EDC's may be very involved and cannot always be interpreted as an energy distribution of the density of states or of the joint density of states of the bulk material.[27] On the condition that surface effects are negligible, the shape of the UPS spectrum at a high photon energy resembles closely the XPS spectrum and the structure in the energy distribution of the occupied initial states.[25,26,28,29]

B. Calculation of the density of states

We have used a Hubbard-model Hamiltonian to calculate self-consistently the electronic states of ferromagnetic fcc cobalt. Since this method will be described elsewhere,[30] we will only outline the procedure as it was applied to cobalt.

The fcc band structure of Co has been calculated at an arbitrary $\vec{k}$ point of the $\frac{1}{48}$ irreducible part of the Brillouin zone according to a general interpolation scheme developed by Bross.[31] In this representation a parametrized form of Hamiltonian matrix elements is derived by using generalized Wannier functions as a basis set. In our work, the parameters were computed from eigenvalues $E(\vec{k})$ of the Co paramagnetic band complex of Ballinger and Marshall[21] along the directions of high symmetry. The extension to the ferromagnetic state was done in a similar way as was suggested by Hodges *et al.*[32]

A nine-dimensional ferromagnetic Hamiltonian matrix, where the diagonal elements include the Hubbard correlation appended to the paramagnetic Hamiltonian, was diagonalized. Two adjustable parameters, $J_{\text{eff}}^{s,p-d}$ and U_{eff}^{d-d}, associated with the ferromagnetic state, were considered. The former parameter represents the exchange interaction energy between the electrons in sp- and d-like states and was taken to be 0.054 eV. The latter parameter takes into account the intra-atomic Coulomb repulsion between the itinerant "d electrons." U_{eff}^{d-d} was determined on the basis that it should generate an appropriate average d-band exchange splitting ΔE and reproduce the input Bohr magneton number of 1.56. The Fermi level was calculated after every iteration loop.

The energy values $E(\vec{k})$ of the ferromagnetic state were determined in 916 $\vec{k}$ points of the $\frac{1}{48}$ Brillouin zone. This enables us to calculate the density of states $N(E)$ of the majority-spin and minority-spin bands. In this computation we used the method of Gilat and Raubenheimer,[33] after having formed the necessary energy gradients of the states at a given $\vec{k}$ point according to the method of Bross.[31] When constructing $N(E)$ the step length along the energy axis was chosen to be 0.0272 eV. The total $N(E)$ was determined by superimposing the $N(E)$ of the two subbands.

We realized that the band structure was unstable to ferromagnetic ordering, if $U_{\text{eff}}^{d-d} = 4.1$ eV, since the Bohr magneton number decreased continuously in consecutive iterations. On the other hand, we were forced to operate near this limit in order to obtain a reasonable agreement with experimental ΔE (Sec. V D). This phenomenon may partly be due to uncertainty in the input original eigenvalue data.[21] In practice, we had to slightly sacrifice the magneton number to keep U_{eff}^{d-d} sufficiently small. The final $N(E)$ shown in Sec. V D is calculated for $U_{\text{eff}}^{d-d} = 4.35$ eV which produced the stable magnetic moment of 1.47 Bohr magneton.

It should be emphasized that the present computation was carried through exactly in the same way as that for ferromagnetic fcc nickel.[30] We have completely ignored the fact that Co possesses one d hole more than Ni, and some approximations known to be good for Ni may not be so for Co.

III. EXPERIMENT

The single crystals were spark cut along the (0001) and (10$\bar{1}$0) faces and were oriented to within an accuracy of 0.5°, as deduced from Laue diffraction patterns. After mechanical and electrolytical polishing the samples were cleaned *in situ* by repeated cycles of argon bombardment and heating procedures. Care was taken not to exceed the critical temperature of about 700 K in order to avoid the phase transition from hcp to fcc.

Polycrystals were prepared from a 99.9975% pure cobalt wire by means of evaporation. Films of 10–30 nm thickness, monitored by a quartz crystal oscillator, were deposited at an evaporation rate of about 0.4 nm/sec upon a polycrystalline silver foil. We did not determine the crystallographic structure of the films but presumably it was mainly hcp with possibly (10–20)% fcc phase present; this was the admixture found by Eastman[10] with the aid of electron diffraction studies of his evaporated Co films under very similar preparation conditions. A small amount of the fcc phase in hcp should not influence the profile of the EDC's, since the density of states of the two close-packed structures are substantially the same.[20,21]

The spectra were induced by using the rare-gas resonance lines of 21.22 (He), 16.85 (Ne) and 11.83 (Ar) eV. The angle of incidence of the light was 80°. The base pressure in the preparation chamber was about 7×10^{-8} Pa, but during the evaporation the pressure increased to about 7×10^{-7} Pa. The working pressure in the analyzer chamber with the gas lamp on was 3×10^{-8} Pa.

The instrumental resolution was better than 0.06 eV for all measurements. A detailed description of the apparatus used here is given in Ref. 34.

Our experimental configuration allows electrons to be counted only if they enter the average analyzer acceptance cone of 10° full opening normal to the surface; i.e., we measure electron emission with $\vec{k}_{\parallel} \cong 0$ for single crystals. Accordingly, in the present case the bands to be studied lie along the symmetry directions $\Gamma - \Delta - A$ and $\Gamma - \Sigma - M$ perpendicular to the (0001) and (10$\bar{1}$0) faces, respectively.

A constant background has been subtracted from all spectra. The raw UPS data have been corrected for the instrumental transmission function and for the doublet lines of Ne and Ar.

IV. PHOTOEMISSION RESULTS

The corrected EDC's for the (0001) and (10$\bar{1}$0) single-crystal faces are shown in Figs. 1 and 2. The corresponding band structures according to calculations of Batallan *et al.* are given in Figs.

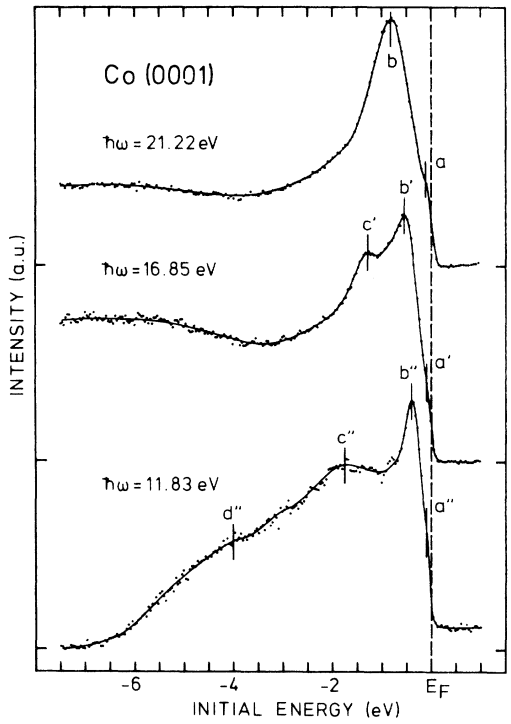

FIG. 1. Energy distribution curves of photoelectrons emitted normal to the (0001) single-crystal face.

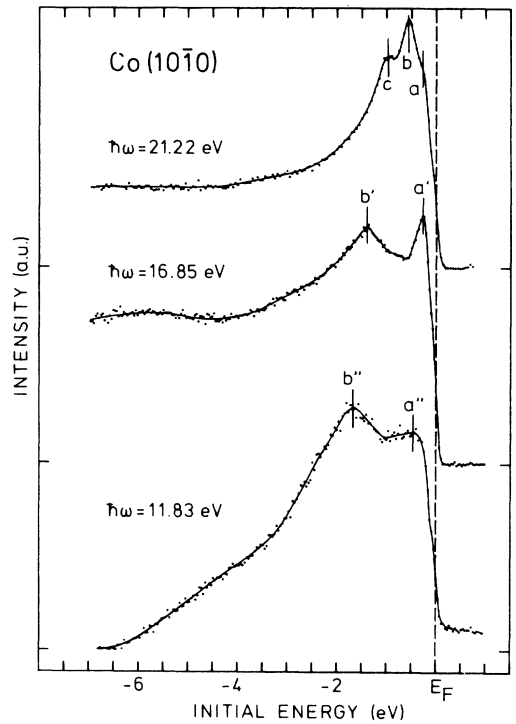

FIG. 2. Energy distribution curves of photoelectrons emitted normal to the (10$\bar{1}$0) single-crystal face.

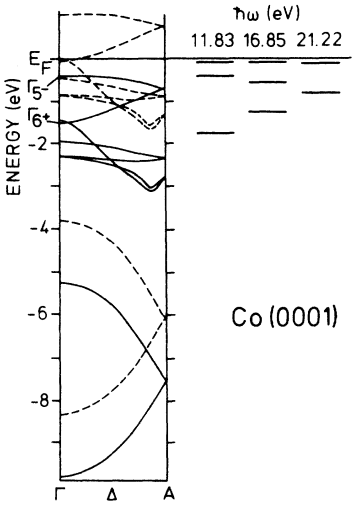

FIG. 3. Ferromagnetic band structure (Refs. 22 and 35) along the Γ-*A* symmetry line and the initial energy levels of the observed transitions.

3 and 4.[22,35] The initial energy levels of the main structures of the observed photoemission are indicated on the right-hand side of the band diagrams of Figs. 3 and 4. The EDC's of a polycrystal are shown in Fig. 5. Characteristics of all spectra are listed in Table I.

The EDC's are plotted against the initial energy E_i electrons. The Fermi level $E_F = 0$ eV, chosen to be the reference point of the energy scale, is observed in the spectra; the Fermi edge (total width = 0.2 eV) emerges most clearly in emission from the (0001) face at $\hbar\omega = 21.22$ eV. The location of E_F in these and our earlier measurements over a period of one year has remained stable within ± 0.05 eV. By virtue of this stability of the spectrometer, E_i relative to E_F can be determined in a dependable way.

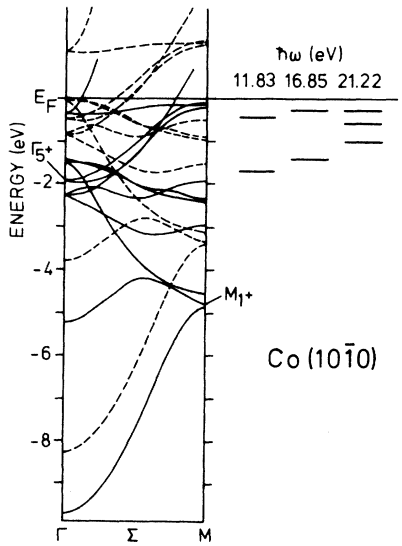

FIG. 4. Ferromagnetic band structure (Refs. 22 and 35) along the Γ-*M* symmetry line and the inital energy levels of the observed transitions.

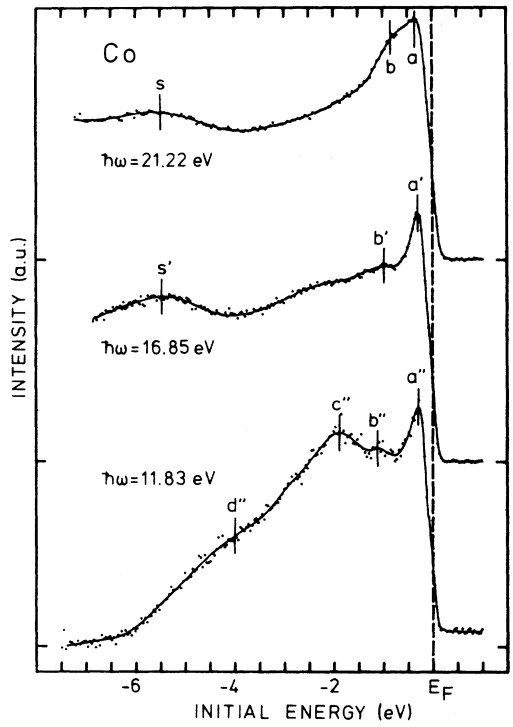

FIG. 5. Energy distribution curves of photoelectrons emitted from an evaporated Co film.

The variety in the shapes of the EDC's of Figs. 1, 2, and 5 is striking. This phenomenon together with the fact that emission of pronounced structures from other directions of the Brillouin zone are not seen in the spectra of a chosen symmetry direction indicate that umklapp-scattering effects do not notably influence the characteristics of photoemission in the energy region of a few eV below E_F. However, the low-energy region is

TABLE I. Compilation of the energies of spectral features.

Peak notation	Energy (eV) (0001)	(10$\bar{1}$0)	Polycrystal
a	−0.11 ± 0.06	−0.32 ± 0.06	−0.35 ± 0.05
b	−0.82 ± 0.05	−0.56 ± 0.05	−0.84 ± 0.08
c	•••	−0.97 ± 0.10	•••
a'	−0.09 ± 0.06	−0.28 ± 0.05	−0.30 ± 0.05
b'	−0.55 ± 0.05	−1.40 ± 0.08	−0.98 ± 0.08
c'	−1.27 ± 0.08	•••	•••
a''	−0.09 ± 0.06	−0.45 ± 0.15	−0.30 ± 0.05
b''	−0.40 ± 0.05	−1.70 ± 0.15	−1.1 ± 0.1
c''	−1.75 ± 0.10	•••	−1.9 ± 0.1

strongly affected by inelastic electron scattering and secondary electron emission. This was demonstrated by measuring the EDC's of a $(10\bar{1}0)$ surface which contained some etch pitches.

The intensity of the low-energy tail of the spectra increased (40–50)% relative to the spectra of the smooth $(10\bar{1}0)$ face. The structure labeled d'' in the 11.83-eV EDC of the (0001) face and of the polycrystal is mainly due to inelastic scattering effects.

The polycrystalline films may have been contaminated by a fraction of an atomic impurity layer on the surface, as concluded from the presence of a small hump at -5.5 eV in the EDC's of $\hbar\omega = 21.22$ and 16.85 eV, labeled s and s', respectively. We could not remove this hump despite several subsequent evaporations. It is interesting to note that a similar "satellite" structure appears in Fe,[7,9,36] Co,[7] and Ni,[7,37] XPS valence-band spectra, where it has been explained by the influence of final-state effects (see, e.g., Ref. 37).

V. DISCUSSION

A. Emission from the (0001) face

In Fig. 1, peaks b, b', and b'' dominate angle-resolved photoemission from the (0001) face. These peaks move towards lower energies as $\hbar\omega$ is increased, while peaks c' and c'' move in the opposite direction, which may indicate their origin in direct transitions. Since no final-state bands well above E_F have been published, we have made an attempt to outline such a band on the basis of the trend of the measured line shifts and of the theoretical valence-band structure[22,19,20] (see Fig. 3) and under the assumption of direct $\vec{k}$-conserving transitions. At least one final-state band in the $\Gamma - A$ direction should lie at about 20 eV in the neighborhood of the symmetry point A to account for peak b. The band should further move via the energy levels 16.3, 15.6, 11.4, and 10.1 eV when going towards the Γ point, as calculated from the initial levels and the photon energies. If this is the case then the whole of the EDC pattern of peaks b through c'' could be interpreted as due to direct transitions to this final-state band from the initial majority-spin d bands starting at Γ_{5^-} and Γ_{6^+}. The asymmetrical shape of line b also favors the assignment of this line to emission from near the A point where transitions from the initial states with an almost equal energy can contribute to structure b.

An interesting feature in the spectra is the stable shoulder a which indicates the beginning of the Fermi edge. We believe that this shoulder most probably is attributable to surface photoemission from electronic states right at E_F. Calculations[19,20,22] of the Fermi surface for the minority-spin bands show, indeed, that there should be three pockets around the Γ point. In the calculations of Refs. 19, 20, and 38 a majority-spin sp band also intersects the Fermi level in the $\Gamma - A$ direction. Hence, if the bulk states are extended to the surface, the electrons giving rise to the shoulder must come from either the pocket area or from the sp bands via surface photoemission. On the other hand, Höchst *et al.*[36] have suggested that the lifetime broadening is large ($\cong 0.5$ eV) for an Fe valence-band hole. One of their main criteria was the finding of great similarities between the shapes of their XPS band spectrum and our UPS spectrum for polycrystalline iron.[39] However, the comparison of these spectra is not very conclusive since a lack of prominent fine structures in the UPS is fully consistent with the profile of $N(E)$ for ferromagnetic Fe according to calculations of Singh *et al.*[40] If shoulder a is due to the lifetime broadening of line b, the broadening effect is much more appreciable than what has been supposed in general. We further note than an increase in the damping parameter[25] $\vec{k}_\perp^{(2)}$ for the 21.22-eV EDC may cause a momentum broadening of the spectral lines and lead to the shoulder at E_F. In some cases, an effect of the finite angular resolution of the spectrometer also results in a broadening of a line.

Desjonquères and Cyrot-Lackmann[41] have calculated the local density of states on the (0001) and $(10\bar{1}0)$ surfaces of the paramagnetic lattice of Co. They have obtained a narrowing in the width of the d band at the surface as compared with the bulk. The narrowing is about 0.7 eV for the (0001) face and 1 eV for the $(10\bar{1}0)$ face. The experimental d bandwidth in the $\Gamma - A$ direction, as estimated from our EDC's at $\hbar\omega = 21.22$ and 16.85 eV, is about 3.5 eV, consistent with most of the calculated bulk band structures. The equal breadths of the EDC's for $\hbar\omega = 21.22$ and 16.85 eV also indicate that band narrowing due to an increasing contribution of the surface atoms to the 21.22-eV EDC cannot be discerned. Since we have measured photoemission with $\vec{k}_\parallel \cong 0$ from the ferromagnetic structure, a direct comparison of the EDC data with the paramagnetic surface states of Ref. 41 is difficult. As shown below, the UPS spectra of the $(10\bar{1}0)$ face also agree with calculations for the corresponding bulk states at least in a qualitative way, and lend further support to the assumption that our EDC's as a whole sense the bulk properties of Co.

B. Emission from the $(10\bar{1}0)$ face

The band diagram of Fig. 4 implies that a large number of direct transitions should occur in photo-

emission of the $(10\bar{1}0)$ face. Experimentally, only very few resolved features appear in the EDC's in the d-band region, which indicates a considerable influence of broadening effects on the shape of the individual lines. No transitions are seen from the low-energy s-like bands (Fig. 2).

Similar to the case of the Γ-A direction, one can here suggest a final-state band which runs towards the Γ point, as the energy decreases, and which is able to account for all peaks of the EDC's. Structures a, a', and a'' seem to certify that the predicted one-dimensional high density of states does exist around -0.3 eV. Peaks b, c, b', and b'' follow the trend of the band doublet emanating from Γ_{5+}. However, due to the complexity of the band scheme and the split model approximation, no definite assignment to the transitions pertinent to peaks b through b'' can be given.

The 21.22- and 16.85-eV EDC's show a weak structure between -2.5 and -4.3 eV. This leads us to place the bottom of the d band below -4 eV; i.e., the d band is somewhat broader in the Γ-M direction than in the Γ-A direction. This is also expected from the band structure (Fig. 4) since the band terminating at M_{1+} has a mixture of s and d character.[22]

C. Emission from the polycrystal

The EDC's for the polycrystal (Fig. 5) are characterized by the leading peaks a, a', and a'' which are apparently related to transitions from the maximum density of states of the entire Brillouin zone. We also see that the Fermi edge emerges at the position where $N(E)$ is already decreasing. The intensity of the 21.22-eV EDC at E_F is about $\frac{1}{3}$ of the maximum intensity, a value that coincides with the corresponding intensity ratio in the 21.22-eV EDC for polycrystalline iron.[39] The contours of these EDC's for Co and Fe also resemble each other especially in the region from E_F to about -1 eV. It is interesting to notice how closely the relative density of states at E_F in both EDC's agrees with the results of electronic specific-heat measurements[42,43] which indicate almost equal $N(E_F)$ for Co and Fe.

The EDC obtained at $\hbar\omega = 21.22$ eV shows one more structure, shoulder b. We cannot determine whether it should be related to the distribution of the density of states or to properties of the joint density of states.

At -1.3 eV a slight change occurs in the slope of the low-energy side of the main peak, the tail of which extends at least to -4 eV; the real bottom of the d band is masked by the nongenuine band structure at -5.5 eV. Eastman[11] has estimated the d bandwidth to be 3.6 eV. The L_3 and M_3 x-ray emission bandwidths[5,6] are 5 eV. Magneto-optic Kerr-effect measurements[44] result in an appreciably larger d bandwidth. Theoretical estimates vary from 4.4 to 5.7 eV.

The above-mentioned L_3 emission band reported by Hanzely and Liefeld[5] is structureless, whereas the M_3 emission band of McAlister *et al.*[6] displays several features which are absent in the UPS and XPS spectra. It seems hard to associate extra features in the M_3 emission with the genuine band structure of Co, since even the Fermi edge is not resolved in this spectrum.

The shape of the EDC obtained at $\hbar\omega = 10.2$ eV (Ref. 10) has often been considered the profile of the valence band of Co.[1,7,19,21,22] However, the nonstationary features in the EDC's of the present work point out that EDC's at low photon energies sample the structure of the joint density of states, and the $\vec{k}$-conservation rule can on no account be neglected.

In Fig. 6 an XPS spectrum[7] is compared with the UPS spectra obtained at $\hbar\omega = 21.22$ and 40.8 eV.[11] Eastman has corrected his spectrum for secondary emission effects; this has reduced the intensity of the low-energy range relative to the other spectra. The XPS spectrum shows a weakly resolved structure at -2.2 eV which coincides with the center of the broad structure from -1.3 to -4 eV in the 21.22-eV EDC. It shows that our EDC may not fully reflect the shape of $N(E)$ deep in the valence band. Judging from the notable similarities between the overall contours of the three curves in the vicinity of E_F, exluding the effect of the instrumental window broadening, we conclude that the photoexcitation matrix elements for $\hbar\omega = 21.22$ eV are roughly constant in a narrow energy interval. As a consequence, it is likely that our EDC displays a high-resolution valence-

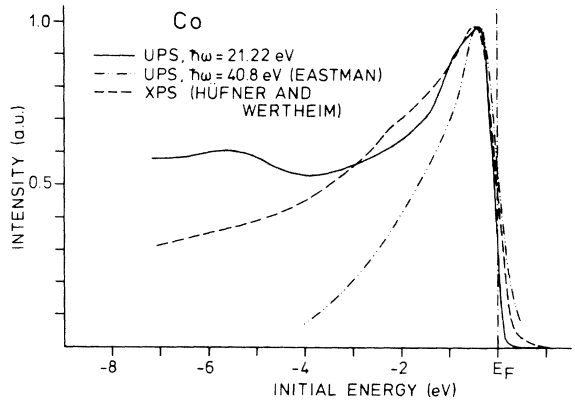

FIG. 6. Comparison of the 21.22-eV EDC with the 40.8-eV EDC (Ref. 11) and the XPS spectrum (Ref. 7) of evaporated Co films.

band profile near E_F. An important quantity, the position of the maximum density of occupied states, can now be determined with certainty to be situated at -0.35 ± 0.05 eV.

D. Properties of the band structure

In Fig. 7 we have plotted the 21.22 eV EDC of the polycrystal (mainly hcp) together with the calculated $N(E)$ of the ferromagnetic fcc structure. Although the details of the energy bands of hcp and fcc are different, integrated properties are quite similar. It is therefore reasonable to compare the EDC and $N(E)$ with each other.

Prominent low-energy structures, predicted by earlier calculations using rigid band splitting, are absent in the present $N(E)$. This observation is consistent with the UPS, XPS, and x-ray L_3 emission measurements which do not reveal any strong features in the low-energy region.

The theoretical $N(E_F)$ is found to be 0.65 and 0.99 electron/(atom eV) for the majority-spin and minority-spin electrons, respectively. The total $N(E)$ yields a low-temperature electronic specific-heat coefficient of 3.9 mJ mol^{-1} K^{-2} in zeroth approximation. Experimental values[42,43] are 4.38 and 4.7 mJ mol^{-1} K^{-2} including various contributions of the many-body mass enhancement.[22] The effective polarization energy U_{eff}^{d-d} of 4.35 eV used in the calculation leads to an average exchange d-band splitting ΔE of 1.25 eV as determined from the separation of the two peak maxima in $N(E)$, Fig. 7. On the basis of the present UPS data and x-ray continuum isochromats,[45] one can obtain an experimental estimate for ΔE. We attribute peak a (Fig. 5) to the sharp maximum arising at -0.29 eV in the theoretical $N(E)$ of the majority-spin bands. These bands mainly cause the maximum of the total $N(E)$; the accumulation of the minority-spin electrons in this energy range does not affect the position of the maximum. The x-ray continuum isochromats,[45] which sample the empty states, exhibit a strong peak at $+0.7$ eV. Since the density of majority-spin states is practically zero just above E_F, this peak apparently belongs to the calculated local high density of minority-spin states. So the experimental exchange splitting amounts to 1.05 eV in full agreement with the "best" estimate of Wohlfarth (1.05 ± 0.3 eV).[1] Unfortunately, the accuracy of the x-ray measurements[45] is not known to us, and this numerical coincidence may be fortuitous only.

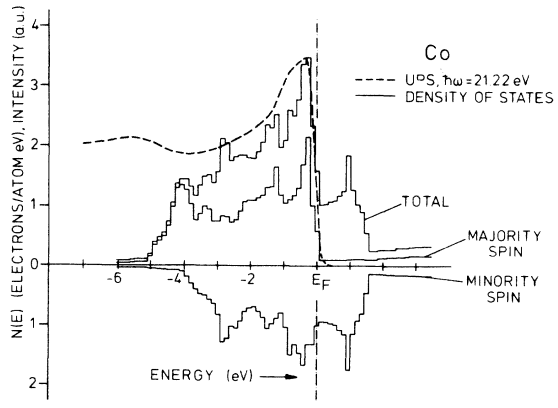

FIG. 7. Calculated density of states of the ferromagnetic fcc lattice of Co. The 21.22-eV EDC of an evaporated film is also shown.

We now have experimental values of ΔE for all three ferromagnets Fe,[39] Co, and Ni.[27] In the case of iron we have obtained $\Delta E \lesssim 1.9$ eV. For nickel, ΔE is approximately 0.3 eV as determined from an exchange band splitting believed to be observed directly in photoemission from near the L symmetry point. A close correlation of these ΔE values with the Bohr magneton numbers of the atoms is exactly what should be expected on the grounds of the Slater-Stoner-Wohlfarth theory of ferromagnetism when applied below the Curie temperature.

Our results cannot explain the results of photo-ESP experiment[12,13] on cobalt. The photo-ESP is positive (+ 21%) for electrons emitted from the vicinity of E_F. Our calculation predicts the Fermi surface spin polarization of -21%. Moreover, the d band width obtained from the photo-ESP measurements[14] is only 2.5 eV. Magneto-optic Kerr-effect spectroscopy, also used to study ESP,[44] does not show which type of electrons in Co is dominant at E_F. Recently, Chrobok *et al.*[46] have shown that the ESP in field emission experiments is extremely sensitive to emitter surface conditions.

Finally, in view of the above we conclude that magnetically dead layers are not likely to exist on the Co surface under study.

VI. SUMMARY

The EDC's of the (0001) and $(10\bar{1}0)$ faces and polycrystals can be interpreted in terms of the band structure within the framework of the direct interband transition model.

Estimates for d bandwidths are obtained. Along the Γ-A symmetry line the bandwidth is about 3.5 eV, and in the Γ-M direction more than 4 eV.

The position of the maximum density of occupied states of the entire Brillouin zone occurs at -0.35 ± 0.05 eV.

There exists an exchange splitting between the d states of opposite spins in accordance with the

Slater-Stoner-Wohlfarth theory of ferromagnetism below the Curie point. The average exchange splitting is estimated to be about 1.1 eV.

The $N(E)$ of the ferromagnetic fcc phase is calculated self-consistently. Contrary to earlier calculations, it shows that Co does not possess prominent features inside the valence band. It is consistent with the over-all shapes and the widths of UPS and XPS spectra. $N(E_F)$ is found to be 0.65 and 0.99 electron/(atom eV) for the majority-spin and minority-spin bands, respectively. The calculated negative spin polarization at E_F cannot account for the measured photo-ESP results.

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