

## Spin-Polarized Photoelectrons from Fe, Co, and Ni

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This experiment shows that photoelectrons from  $3d$  ferromagnets exhibit a large spin polarization, which is in contrast to earlier investigations. The degree of polarization of electrons emitted from the neighborhood of the Fermi level was found to be +54%, +21%, and +15% for Fe, Co, and Ni, respectively. The preferential direction of the magnetic moment is parallel to the magnetization, and this provides strong evidence against the applicability of the Stoner-Wohlfarth-Slater band theory for the interpretation of photoemission data. On introducing disorder in the lattice by depositing thin films onto cold substrates, the spin polarization decreases; for Fe and Ni the decrease scales with the number of Bohr magnetons per atom.

## INTRODUCTION

The electronic structure of solids can be investigated by means of photoemission spectroscopy; for Fe, Co, and Ni, Eastman<sup>1</sup> found that all the structure observed in the energy distribution curves is qualitatively consistent with what one would expect from band-structure calculations. However, some features, crucial for the occurrence of ferromagnetism in these metals, are not clarified. Recent high-resolution photoemission measurements by Pierce and Spicer<sup>2</sup> at temperatures above and below the Curie temperature of Ni did not detect the shifting of the density of states for both spins relative to each other, as postulated by the Stoner-Wohlfarth model of ferromagnetism. This model, as well as the Slater band theory, predicts for strong ferromagnets that the preferential direction of the magnetic moment of the electrons should be antiparallel to the magnetization at the Fermi level  $E_F$ , and furthermore that the electron polarization should be a strongly varying function of the energy below  $E_F$ . It has been reported recently<sup>3</sup> that photoelectrons from Ni show sizable electron spin polarization (ESP), undetected in earlier experimental investigations.<sup>4-6</sup> The preferential direction of the magnetic moment of the photoelectrons was found to be *parallel* to the magnetization of the sample and did *not* vary with photon energy, within experimental uncertainty of  $\pm 2\%$ .

We have now performed similar studies with Fe and Co. The main purpose of this work is to point out the striking evidence that arises from the measurements against the applicability of the Stoner-Wohlfarth-Slater band theory of ferromagnetism for the interpretation of photoemission data. Furthermore, disordered films of Fe, Co, and Ni were obtained by evaporating onto a substrate kept at liquid-He temperature. These films exhibit new photoelectric and magnetic properties and the photo-ESP yields information on amor-

phous ferromagnets. Lastly, it is obvious from this experiment that polycrystalline films of Fe offer a very simple way to produce polarized electron beams.

## EXPERIMENT AND RESULTS

In Fig. 1 we show a scheme of the electron-source part of the apparatus. A thin film is prepared onto the bottom of the cylindrical insertion of the helium Dewar by electron bombardment of 99.999% pure material. For film preparation one of the ten different holes of the sample holder containing the samples is moved into the axis of the apparatus. For the measurement, a tube replaces the samples as shown in Fig. 1, and the substrate of the film is at 4.2 K. An external magnetic field  $\vec{B}$ , generated by a superconducting coil,

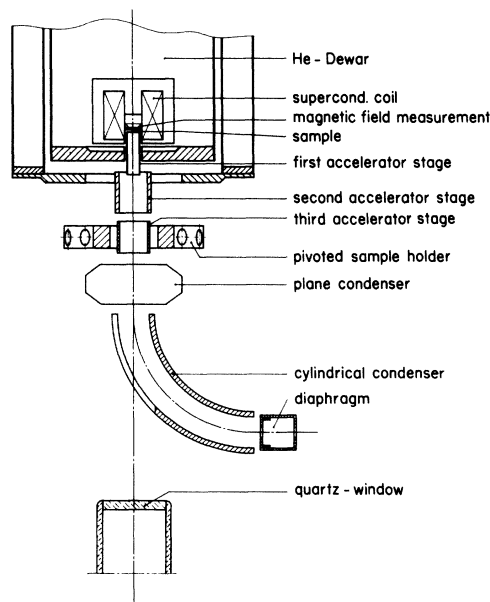


FIG. 1. Scheme of the electron source and electron-optical elements for electron-beam formation.

aligns the Weiss domains perpendicular to the film surface; photoemission of electrons is achieved by focusing the light of a Hg-Xe high-pressure arc through the quartz window onto the film surface. Acceleration to 3.7 keV in several stages forms a beam out of the photoelectrons. The plane condenser allows the adjustment of the beam onto the entrance of the cylindrical condenser. The cylindrical condenser deflects the electron beam out of the light beam, discriminates against photoelectrons from the acceleration stages and transforms the longitudinal spin polarization into a transversal one. The ESP detector is not shown in Fig. 1.  $\langle\sigma_z\rangle$  of the beam is measured after further acceleration to 100 keV in a scattering experiment.  $\sigma_z$  is one component of the Pauli spin operator  $\vec{\sigma}$ ; the  $z$  direction is parallel to  $\vec{B}$ , and  $\langle\sigma_z\rangle$  is the degree of ESP along  $\vec{B}$ . The spin-dependent terms in the Coulomb scattering from heavy atoms arise from  $LS$  coupling and produce a right-left asymmetry. This was discovered in 1929 by N. F. Mott and is now commonly used for detection of the spin polarization of electron beams. The scattering target is a thin gold foil, and the scattering angles are  $+120$  and  $-120$  deg. Further details are described in Ref. 7.

The photo-ESP represents an average value for a very small amount of material defined by the photoemitting surface ( $\sim 1$  mm<sup>2</sup>) and the escape depth of the photoelectrons ( $\sim 20$  Å). The information obtained from this measurement is similar to the one from a simple magnetization measurement except that we can discriminate the electrons whose spin component ( $\sigma_z$ ) we want to measure and a spectroscopy of magnetization becomes feasible. The simplest possible ESP experiment with the  $3d$  metals is to examine the spin polarization from a neighborhood of  $E_F$ ; there is no need to use monochromators for the light nor to perform energy selection of the photoemitted electrons. This arises because the work function  $\phi$  of Fe, Co, and Ni lies between 4.6 and 5.2 eV, and the intensity of the light from the lamp decreases very quickly between 5 and 6 eV, being negligible above 6 eV due to absorption in the quartz envelope of the lamp and the window of the apparatus. Furthermore, the escape probability from the material decreases quickly with  $E - E_\infty$ , where  $E$  is the energy of the photoexcited electron and  $E_\infty$  the minimum escape energy, that is, the vacuum level. All these factors together have the effect that the photoelectrons from Fe, Co, and Ni have originated mainly from states of within a few 100 meV below  $E_F$ .

During film evaporation the pressure rose to  $10^{-6}$  Torr, but immediately after evaporation fell to the  $10^{-10}$ -Torr range. The annealing of the films and the measurements were performed at a

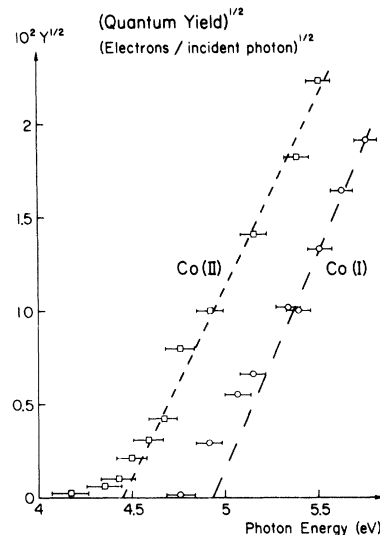


FIG. 2. Square root of the number of photoemitted electrons per incident photon,  $Y^{1/2}$ , vs photon energy for evaluation of the work function, with Co films prepared on substrate at 400 K (I) and at 4.2 K (II). Horizontal bars indicate the resolution of the monochromator.

pressure  $2 \times 10^{-10}$  Torr. The substrate temperature during film preparation was 400 or 4.2 K, and we label the two types of film that were obtained by I and II, respectively. No difference was observed between a type-II film annealed to 400 K and a type-I film.

The work function  $\phi_{II}$  of films of type II was lower than  $\phi_I$  with Fe, Co, and Ni. This agrees with the findings of Suhrmann and Wedler<sup>8</sup> and Wedler, Wölfing, and Wissmann.<sup>9</sup> In Fig. 2 we have plotted the quantum yield  $Y$ , i. e., the number of photoemitted electrons per incident photon, against photon energy  $h\nu$  for Co. Both types of Co film exhibit a quadratic dependence of  $Y$  on  $h\nu$  near threshold as expected for a metal. We obtain  $\phi_I(\text{Co}) = 4.9 \pm 0.1$  eV and  $\phi_{II}(\text{Co}) = 4.4 \pm 0.1$  eV. For Fe and Ni,  $\phi_I = 4.7$  and  $4.9$  eV, respectively, and a similar decrease of  $\phi$  for films of type II was observed. From these results and from Refs. 8 and 9, it follows that films of type I consist of polycrystalline material, whereas films of type II have some disordered or amorphous structure. Felsch<sup>10</sup> has obtained amorphous Fe and Co films in a vacuum of  $10^{-6}$  Torr only by adding small amounts of Ge, Si, or  $O_2$  and not with pure material; this should most probably be attributed to the different vacuum conditions.

In Figs. 3(a)–3(c) we show the dependence of ESP on magnetic field strength for Fe, Co, and Ni. The full spectrum of the lamp was used. The dependences in Fig. 3 are analogous to magnetization curves. Saturation ESP is reached

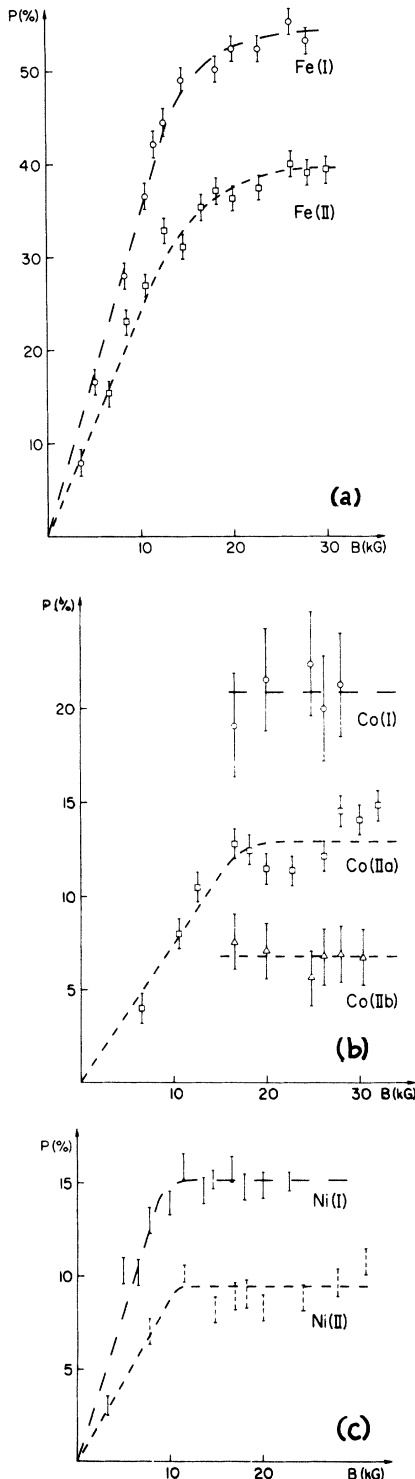


FIG. 3. Dependence of photoelectron spin polarization for polycrystalline (I) and noncrystalline (II) films of Fe (a), Co (b), and Ni (c) on the magnetic field strength at 4.2 K. Vertical bars indicate statistical uncertainty. The preferential direction of the magnetic moment is parallel to the magnetization for all three metals.

at 20, 17, and 10 kG for Fe, Co, and Ni, respectively. The highfield strength needed for saturation arises from the large demagnetizing field  $B_D$  for  $\vec{B}$  perpendicular to the film surface.  $B_D$  is of the order of the saturation magnetization of 21.5, 17.6, and 6.3 kG for Fe, Co, and Ni. The ESP values were reproducible for all three metals and for both types of film except for Co films of type II. In this latter case, the ESP was different for each sample; in Fig. 3(b) two extreme cases are shown. It must be concluded that with Co the structure of the film is not determined by the substrate temperature alone, but also by other parameters like speed of evaporation, which could not be controlled accurately enough in our experiment.

#### DISCUSSION

The main question that arises concerns the relation between the observed photo-ESP and the ESP within the material. Ultraviolet photoemission studies (UPS) by Smith<sup>11</sup> on cesiated Cu, by Eastman and Cashion<sup>12</sup> on Cu, Ag, and Au, and by Eastman<sup>1</sup> on Fe, Co, and Ni have shown that the non-stationary structure observed in the energy distribution curves (EDC's) yields strong evidence for the direct interband transition model (conservation of crystal momentum). The band density of states (DOS) has consequently no simple relation to the EDC's. However, a peak in the EDC's of Co and Ni, located at  $\sim 0.3$  and  $\sim 0.35$  eV below  $E_F$ , persists in the photon energy range 7–40 eV and is of special relevance for this experiment.<sup>1,2</sup> A photoemission spectrum calculated by Janak *et al.*<sup>13</sup> for Ni with a Korringa-Kohn-Rostoker (KKR) method including transport and escape effects shows that this peak belongs to the band DOS. If one considers the energy dependence of the emission from "s-p" and "d" states into free-electron-like conduction bands as reported in Ref. 14, one reaches the conclusion that this peak must arise from d-like states in the band DOS.

UPS of the transition metals have also shown that no special structure is present in the escape states of these elements. If the photoexcited states do not exhibit structure, their influence on the ESP is negligible; see Ref. 7.

Inelastic electron-magnon scattering might occur during the time that elapses between the photoexcitation and the evasion of surface barrier potentials. Theoretical and experimental arguments, as pointed out in Refs. 3 and 15, lead to the conclusion that this effect can be neglected. Electron-plasmon coupling, as described by Lundqvist,<sup>16</sup> is not important in the photon energy range of this experiment. Using unpolarized light, the spin-orbit coupling during the photoexcitation process can produce only a reduction of ESP and a change of sign is certainly impossible.

From these reasons it seems well established that with transition metals EDC's yield information on the ground states near  $E_F$ . This must be true so much the more for the spin with its much weaker coupling to the lattice.

If  $n$  is the number of electrons and  $n_B$  the number of Bohr magnetons per atom, the following conditions must hold:

$$n\uparrow + n\downarrow = n \quad \text{and} \quad n\uparrow - n\downarrow = n_B. \quad (1)$$

$n\uparrow$  and  $n\downarrow$  are the number of majority and minority spin electrons, respectively. In an itinerant model of ferromagnetism the Fermi energy  $E_F$  is well defined even for  $d$  electrons, and we have

$$n\uparrow = \int_0^{E_F} D\uparrow(E) dE \quad \text{and} \quad n\downarrow = \int_0^{E_F} D\downarrow(E) dE,$$

with  $D(E)$  the density of states. The majority-spin  $d$  band is full if  $n\uparrow = 5$ , and this is believed to occur in Co and Ni. We give the argument for Ni (for Co it is analogous): In order to account for the observed  $n_B = 0.5$  and assuming that the main contribution to the magnetization comes from  $d$  electrons only, we must have  $4s^1 3d^9$  and  $3d^{10}$  configurations in a 1:1 mixture. The average number of  $d$  electrons is then  $n = 9.5$ . With (1) we obtain  $n\uparrow = 5$  and  $n\downarrow = 4.5$  and the majority-spin  $d$  band is full. As a consequence, there exist only minority-spin  $d$  states at  $E_F$ , and the ESP is predicted to be negative. However, the number of assumptions to reach this conclusion is quite considerable. With Fe, the majority-spin  $d$  bands are not full.

In this situation it is conceivable that the band-structure calculations have produced negative ESP at  $E_F$  for Co and Ni and positive ESP for Fe. For Ni, we mention the calculations of Connolly,<sup>17</sup> of Hodges, Ehrenreich, and Lang,<sup>18</sup> and of Zornberg,<sup>19</sup> which all give a sign of the ESP at  $E_F$  opposite to that observed in this experiment. Recent tunneling measurements on junctions between thin superconducting Al films and Ni films by Tedrow and Meservey<sup>20</sup> showed that the ESP is positive even for states of within  $\pm 1$  meV of  $E_F$ .

For Co, the band structure calculated by Wong, Wohlfarth, and Hum<sup>21</sup> predicts  $P = -76\%$  for this experiment, taking into account the spectral energy distribution of the light, the photoelectric yield from Fig. 2, and the effective escape probability after Eastman. A similarly large negative value results from the band structure of Wakoh and Yamashita.<sup>22</sup> This is in striking contradiction to the observed

$P = +21\%$  valid for polycrystalline Co.

With Fe, the band-structure calculations are in agreement with this experiment. The degree of polarization at  $E_F$  is predicted to range from +30 to +50%; see, for instance, Wakoh and Yamashita<sup>23</sup> and Maglic and Mueller.<sup>24</sup>

The discrepancy between the predictions of the band-structure calculations and the results of the ESP experiment just in the cases of Co and Ni, which are believed to be among the most typical examples of itinerant ferromagnetism, must mean that the Stoner-Wohlfarth-Slater band theory of ferromagnetism is not able to explain photoemission data.

It should be noted that with a localized spin-moment model there will be no negative ESP in agreement with the observations, but it is also clear that Co and Ni cannot be understood in a simple localized picture. One must await more theoretical work to solve this problem.

The theory should explain the following experimental facts: The values of the saturation magnetization yield an average ESP in the conduction band given by  $\bar{P} = n_B/n$ , where  $n$  is the total number of  $s$  and  $d$  electrons per atom. We have  $\bar{P} = +28, +19, \text{ and } +5\%$  for Fe, Co, and Ni, respectively. The photo-ESP  $P$  for states in the neighborhood of  $E_F$  is *higher* than  $\bar{P}$  and of the *same* sign.  $P$  and  $\bar{P}$  are both related to the filling of the  $3d$  shell, but there exists no direct correlation.

On going from polycrystalline to noncrystalline material,  $n_B$  and  $P$  both decrease with Fe and Ni. It is  $n_{B(\text{II})}/n_{B(\text{I})} = 0.7$  for Fe after Felsch<sup>10</sup> and  $n_{B(\text{II})}/n_{B(\text{I})} = 0.60$  for Ni after Tamura and Endo,<sup>25</sup> From Fig. 3 we see that the photo-ESP is reduced by the same factor for Fe and Ni films of type II. Co might not behave in the same manner since Felsch<sup>10</sup> reported no reduction of  $n_B$ , whereas we find that  $P$  is smaller for films of type II.

A monoatomic layer of HCs reduces the work function of Fe to about 2 eV, and it is known that the EDC's are not affected seriously. We conclude that the ESP should not be affected as well, and therefore a laser can be used to obtain a high current of polarized photoelectrons, which might be useful for other experiments.

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## Study of Pure and Doped Cobaltous and Nickelous Oxide\*

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We give results for a number of "critical" tests intended to eliminate some of the structural models which have been proposed for nickelous and cobaltous oxide prepared at temperatures of order 300 to 400 °C. For the case of cobaltous oxide we are able to eliminate all of the proposed models, leaving us with no completely satisfactory explanation of the striking properties of this material. The importance of the semiconducting properties of these oxides is demonstrated by measurements of the ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  observed in the Mössbauer patterns as a function of the *p*-type dopant lithium and the *n*-type dopants chromium and gallium. When the Li doping is raised sufficiently, it is possible to completely suppress the  $\text{Fe}^{2+}$  resonance at room temperature.

### I. INTRODUCTION

The highly ideal Mössbauer isotope  $\text{Fe}^{57}$  has opened extensive study of the transition-metal oxides in recent years.<sup>1-12</sup> The physical properties of samples prepared at low and high temperatures have been radically different, and considerable debate has taken place over the structure of the low-temperature preparations. Anion and cation vacancies, microcrystals, and pores have been invoked to account for the observations. None of these taken by themselves is adequate to account for all of the experimental data, and it would appear from our present data that even a combination of these suggestions is not capable of satisfactorily accounting for the striking properties of cobaltous oxide.

Much of the focus for the model debate has been the paper which we published,<sup>9</sup> where we attempted to correlate a large amount of data taken by x-ray, chemical, and Mössbauer techniques. To contrast

the low-temperature preparation from the high, we adopted the notation forms I and II for the high- and low-temperature preparations, respectively. We tried to explain the then-existing data by assuming a very high Schottky-defect density, where  $\text{Fe}^{3+}$  is stabilized by the transfer of an electron from iron to an anion vacancy. Although we noted that the x-ray patterns precluded the possibility for any long-ranged order to the proposed Schottky defects, the model was interpreted by many as a two-phase model, a term which was not used in our original publications.<sup>9</sup> This was probably due to our speculation that there might be short-range order to the vacancy arrangement, and also because of an error<sup>9</sup> which we made in calculating the densities of our form-II samples. Our model was not a two-phase model, however, but rather a point-defect model where we assumed that all of the observed properties could be accounted for by assuming a large and equal density of anion and cation vacancies. Shortly after the publication of our