Theory of Spin-Polarized Secondary Electrons in Transition Metals

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We show that in contrast to the secondary-electron intensity distribution, the spin polarization, $P(E)$, yields useful information about the electron-electron interaction. The ratio of lifetimes of majority- to minority-spin electrons can be determined directly from the measured values of $P(E)$ by

$$\frac{\tau_\uparrow(E)}{\tau_\downarrow(E)}=\frac{1-p_B}{1+p_B}\,\frac{1+P(E)}{1-P(E)},$$

where p_B is the bulk magnetization.

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Rapidly increasing interest in the spin-dependent properties of magnetic metals has been evident for several years. In particular, the spin polarization of excited electrons has been measured in Fe,[1] Co,[1] and Ni[2,3] as well as in related glasses such as $Fe_{81.5}B_{14.5}Si_4$.[4] These metals are subjected to monoenergetic electrons or photons with energies of 30 eV or more and the polarization of the resulting low-energy secondary electrons is measured. The shape of the polarization distribution of the secondaries is quite similar in all cases. At energies greater than a few electronvolts above the vacuum level the polarization is close to the bulk value but exceeds it by a factor of 2 or 3 at zero energy as shown in Figs. 1 and 2.

The total number of secondary electrons at a given energy, i.e., the secondary-electron distribution, is unfortunately insensitive to details of the electron-electron interaction and experimental measurements have not yielded much insight into the nature of the interaction. Our purpose is to report the first theory of the spin-polarization distribution of the secondaries. We show that experimental measurements provide direct information about the electron-electron interaction and we explain the large spin polarization at low energies which has not been understood.

The essence of the physics is the following. The electron cascade process might be expected to produce secondaries with the same magnetization as the bulk because the vast majority of secondaries are electrons scattered out of the metal ground state. However, in these materials, there are an excess of unfilled minority-spin d states over unfilled majority-spin d states and excited minority-spin electrons can scatter into the former.[5] Minority-spin electrons are scattered out of a given energy at a faster rate than majority-spin electrons. Thus, a net majority polarization is established due solely to the difference in mean-free paths. This effect increases at low energies where the scatter-

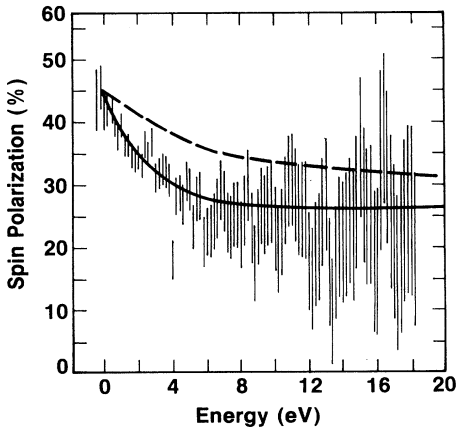

FIG. 1. Spin polarization of the secondary electrons in Fe. Measured values are from Ref. 1. Dashed line is calculated spin polarization with constant matrix elements. Solid line is calculated spin polarization with exchange matrix element, M_4, assumed energy dependent according to Eq. (7).

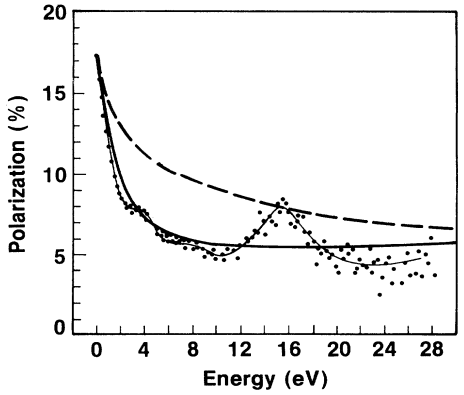

FIG. 2. Same as Fig. 1, but for Ni with measured values from Ref. 2.

ing into empty d states is emphasized by the relatively small number of free-electron states into which scattering can occur. The connection between the spin polarization of the secondaries and the empty d states has been discussed in the experimental papers,[1,2] and our results confirm the importance of this effect.

In a classic paper, Wolff[6] has developed a formalism for describing the cascade process that creates the secondary electrons. This theory describes the secondary distribution by means of a Boltzmann-type equation which we generalize to include spin. It will be assumed that the electron distribution in the solid is homogeneous[6] and is isotropic; this is a particularly good approximation at the low energies of interest to us. With these assumptions, our extension of Wolff's theory takes the very simple form

$$\psi(E\sigma) = S(E\sigma) + \sum_{\sigma'} \int_E^\infty dE'\, \psi(E'\sigma') F(E'\sigma', E\sigma), \quad \text{(1a)}$$

$$\psi(E\sigma) = N(\sigma)/\tau(E\sigma), \quad \text{(1b)}$$

where $N(E\sigma)$, $\tau(E\sigma)$, and $S(E\sigma)$ are the number of electrons, the lifetime, and the source function for electrons of energy E and spin σ, and $F(E'\sigma', E\sigma)$ is the probability that when an electron in the state $E'\sigma'$ is scattered, an electron is produced in the state $E\sigma$. Equation (1a) is simply a statement of detailed balance.

Because every scattering results in two scattered electrons, the original one and one from the Fermi sea, the quantity $F(E'\sigma', E\sigma)$ must satisfy the sum rule

$$\sum_\sigma \int_{\epsilon_F}^{E'} dE\, F(E'\sigma', E\sigma) = 2, \quad \text{(2)}$$

where ϵ_F is the Fermi energy. The factor of 2 in Eq. (2) is the origin of the electron multiplication. F is a function of the velocities of the incoming and scattered electrons; $F = F(\mathbf{v}', \mathbf{v}) = F(v, v'; \cos\Omega)$ where Ω is the angle between $\mathbf{v}$ and $\mathbf{v}'$. However, for the isotropic case, Wolff shows that $F(E', E) = \int d\Omega\, F(\mathbf{v}', \mathbf{v})$, i.e., F is given by the angular average of $F(\mathbf{v}', \mathbf{v})$. The polarization of the secondary electrons at energy E is given by

$$P(E) = \frac{N(E\uparrow) - N(E\downarrow)}{N(E\uparrow) + N(E\downarrow)} = \frac{(\psi^-/\psi^+) + (\tau^-/\tau^+)}{1 + (\psi^-/\psi^+)(\tau^-/\tau^+)}, \quad \text{(3a)}$$

where

$$\psi^\pm(E) = \psi(E\uparrow) \pm \psi(E\downarrow), \quad \text{(3b)}$$

$$\tau^\pm(E) = \tau(E\uparrow) \pm \tau(E\downarrow). \quad \text{(3c)}$$

We require the probability per unit time that an electron in the state $p'\sigma'$ scatters and produces an electron in the state $p\sigma$, $\omega(p'\sigma', p\sigma)$. For the case $\sigma = \sigma'$,

$$\omega(p'\sigma, p\sigma) = \frac{2\pi}{h} \sum_{kk'} f(E_{k\sigma})[1 - f(E_{k'\sigma})] |M_{p\sigma,k'\sigma}^{p'\sigma,k\sigma} - M_{k'\sigma,p\sigma}^{p'\sigma,k\sigma}|^2 \delta(E - E_{p\sigma}) \delta(E_{p'\sigma} + E_{k\sigma} - E_{p\sigma} - E_{k'\sigma})$$
$$+ \frac{2\pi}{h} \sum_{kk'} f(E_{k\bar\sigma})[1 - f(E_{k'\bar\sigma})] |M_{p\sigma,k'\bar\sigma}^{p'\sigma,k\bar\sigma}|^2 \delta(E - E_{p\sigma}) \delta(E_{p'\sigma} + E_{k\bar\sigma} - E_{p\sigma} - E_{k'\bar\sigma}), \quad \text{(4a)}$$

where $F(E)$ is the Fermi function, $\bar\sigma$ is the spin state opposite to σ, and

$$M_{p\sigma,k'\sigma'}^{p'\sigma,k\sigma'} = \langle p'\sigma k\sigma' | V | p\sigma k'\sigma' \rangle, \quad \text{(4b)}$$

where V is the electron-electron interaction.

The probability that an electron in $p'\sigma$ scatters and produces an electron in $p\bar\sigma$ is

$$\omega(p'\sigma, p\bar\sigma) = \frac{2\pi}{h} \sum_{kk'} f(E_{k\bar\sigma})[1 - f(E_{k'\sigma})] |M_{k'\sigma,p\bar\sigma}^{p'\sigma,k\bar\sigma}|^2 \delta(E_{p'\sigma} + E_{k\bar\sigma} - E_{k'\sigma} - E_{p\bar\sigma}) \delta(E - E_{p\bar\sigma}). \quad \text{(4c)}$$

In the semiclassical case treated by Wolff, p, p', etc., stand for momenta $\mathbf{p}, \mathbf{p}'$ and $F(E'\sigma', E\sigma)$ is

$$F(E'\sigma', E\sigma) = W(E'\sigma', E\sigma)\tau(E'\sigma'), \quad \text{(5a)}$$

where $E' = (h^2/2m)p'^2$, $E = (h^2/2m)p^2$, and

$$W(E'\sigma, E\sigma) = \int d\Omega\, \omega(\mathbf{p}'\sigma', \mathbf{p}\sigma), \quad \text{(5b)}$$

where $d\Omega$ is an angular average and

$$1/\tau(E', \sigma') = \tfrac{1}{2} \textstyle\sum_\sigma \int_{\epsilon_F}^{E'} dE\, W(E'\sigma', E\sigma). \quad \text{(5c)}$$

Equation (5c) insures that the sum rule, Eq. (2), is satisfied.

A model for the scattering probabilities is required and we adopt Kane's random-k approximation[7] in which

momentum conservation is neglected. In our case, this model receives additional justification due to the averaging introduced by Eq. (5b). In Kane's treatment, the matrix element $M^{p'\sigma,k\sigma'}_{p\sigma,k'\sigma'}$ is replaced by its average value which will be characterized by the energy transferred in the collision and the nature of the states p', p, k, and k', whether they are free-electron-like (denoted by ϵ), or d-like (denoted by d).

Because the primary concern is with magnetic properties, and because the number of s-p electrons below ϵ_F is small compared to the number of d's, the occupied s-p states will not be distinguished from the d's. The average matrix elements are assumed energy dependent. For example, $\langle|M^{\epsilon\sigma,d\sigma'}_{l\sigma,l'\sigma'}|^2\rangle$ is taken to be $\langle|M^{\epsilon\sigma,d\sigma'}_{l\sigma,l'\sigma'}(E'-E)|^2\rangle$ if an electron is scattered from E' to E; thus, in Eq. (4a), the matrix elements are replaced by $\langle|M(E_{p'}-E_p)-M(E_{p'}-E_{k'})|^2\rangle$. The cross term of the matrix elements in (4a) will be neglected. This is justified by a previous calculation[8] that showed exchange to be important only at energies within 1 eV of ϵ_F. An additional simplification is that there are unfilled d states only for the minority-spin band. This is strictly true for Ni and Co and approximately true for Fe, where the majority-spin unfilled d states hold only about 0.2 of an electron.

With these assumptions, one obtains for E', $E>0$,

$$F(E'\sigma,E\sigma)=A_\sigma[|M_1|^2(\bar\rho_{\downarrow,\epsilon}+\bar\rho_{\uparrow,\epsilon})+|M_3|^2\bar\rho_{\downarrow,d}+|M_2|^2\bar\rho_{\sigma,\epsilon}+\delta_{\sigma,\downarrow}|M_4|^2\bar\rho_{\downarrow,d}], \tag{6a}$$

$$F(E'\sigma,E\bar\sigma)=A_\sigma[|M_2|^2\bar\rho_{\bar\sigma,\epsilon}+\delta_{\sigma,\downarrow}|M_4|^2\bar\rho_{\uparrow,d}], \quad A_\sigma=(2\pi/h)\tau(E'\sigma)\rho_\epsilon(E), \tag{6b}$$

where ρ_l is the density of states with orbital character $l=\epsilon$ or d. The matrix elements M_i are $M_1=M^{\epsilon,d}_{\epsilon,\epsilon}(E'-E)$, $M_2=M^{\epsilon,d}_{\epsilon,\epsilon}(E-\epsilon_F)$, $M_3=M^{\epsilon,d}_{\epsilon,d}(E'-E)$, $M_4=M^{\epsilon,d}_{d,\epsilon}(E'-\epsilon_F)$, where $M^{\epsilon,d}_{l,l'}(\omega)$ is the averaged matrix element for the scattering of a free electron into a state of type l with energy loss ω, while a Fermi-sea d electron is scattered into a state of type l', and $\bar\rho$ is the joint density of states

$$\bar\rho_{\sigma,l}(\omega)=\int dE\,\rho_{d\sigma}(E)\rho_l(E+\omega)f_{d\sigma}(E)[1-f_l(E+\omega)], \tag{6c}$$

and $l=d$ implies a minority-spin d state.

The densities of states in Eq. (6) are taken from band-structure calculations.[9] For energies greater than those reported in the calculations, a free-electron density of states is used. The matrix elements M_1 and M_2 are taken to be energy independent, in which case $M_1=M_2$ and the polarization depends on $|M_3/M_1|$ and $|M_4/M_1|$. We find empirically that the polarization is very insensitive to the choice of $|M_3/M_1|$ but depends directly on $|M_4/M_1|$ as is evident from the spin dependence of Eqs. (6a) and (6b). This ratio determines the relative probability that a minority-spin electron is scattered into an empty d state. Because of the small effect the size of M_3 has on the polarization, the somewhat arbitrary choice $|M_3/M_1|^2=0.3$ is made. The calculations are carried out for a source function $S(E\sigma)$ in Eq. (1a) that is monoenergetic and either polarized with the bulk polarization if photoexcitation has been used (as for Fe), or unpolarized if electron bombardment was used in the experiment (as for Ni).

For the case that M_4 is also energy independent, the choices $|M_4/M_1|^2=0.13$ (for Fe) and 0.19 (for Ni) result in the dashed lines in Figs. 1 and 2. These magnitudes of $|M_4/M_1|$ are consistent with M_4 being an exchange-type matrix element. These calculations show that the energy dependence of the joint density of states $\bar\rho$ is not sufficient to explain the energy dependence of τ^-/τ^+ in Eq. (3a), and the exchange matrix element M_4 must be taken as energy dependent. M_4 is extremely difficult to calculate because of the importance of screening and correlation effects, and so we parametrized M_4 by

$$|M_4(\omega)/M_1|^2=A^2/[(\omega-\epsilon_F)^2+B^2]. \tag{7}$$

For Fe and Ni, the choices $A=1.8$ and 2.9 eV and $B=3.2$ and 3.5 eV, respectively, result in the solid curves shown in Figs. 1 and 2. For energies up to about 40 eV the energy dependence of the spin-averaged mean free path is found to be almost identical to that calculated with the statistical model.[8]

The ratio $\tau_\uparrow(E)/\tau_\downarrow(E)$ can now be obtained from Eq. (3a) by use of the experimental values for $P(E)$ and the calculated values for $\psi^-(E)/\psi^+(E)$, a quantity which is quite insensitive to the choice of matrix elements. In fact, the calculations show that for energies greater than zero, $\psi^-/\psi^+\simeq p_B$, where p_B is the bulk magnetization. It will be shown elsewhere that the result[10] $\psi^-/\psi^+\simeq p_B$ depends on the condition $|M_4/M_1|^2\ll 1$ which is satisfied here. The ratio of majority-spin to minority-spin lifetimes can be obtained directly from Eq. (3a) by use of the measured values for $P(E)$ and by replacing ψ^-/ψ^+ with p_B:

$$\frac{\tau_\uparrow(E)}{\tau_\downarrow(E)}=\frac{1-p_B}{1+p_B}\frac{1+P(E)}{1-P(E)}. \tag{8}$$

Thus this ratio, $\tau_\uparrow/\tau_\downarrow$, can be obtained directly from the experimental measurements and without model calculations. $\tau_\uparrow/\tau_\downarrow$ versus energy is shown in Fig. 3 for Fe and Ni. This ratio is larger for Fe because its ratio of unfilled d states to free-electron states is larger.

A difference between the majority- and minority-

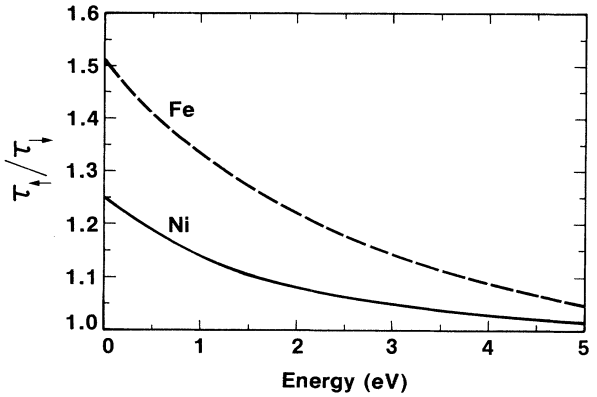

FIG. 3. Ratio of majority- to minority-spin lifetimes for Fe and Ni as determined by Eq. (8). The experimental results for $P(E)$ are taken from Refs. 1 and 2.

spin mean free paths has important implications for the interpretation of many types of spin-polarized experiments including spin-polarized photoemission and inverse photoemission, spin-polarized low-energy electron diffraction, and spin-polarized elastic scattering from amorphous materials. A spin dependence of the mean free paths implies that the polarization of electrons at a given energy in the bulk of a material differs from that measured outside the material, because in traveling to the surface more of one spin than the other is scattered out of the beam. Our results (Fig. 3) show that this effect is important only for very low energies which is a significant conclusion. In this low-energy regime it has proved difficult to carry out low-energy electron-diffraction experiments on Fe and Ni because of strong fields.

The results shown in Fig. 3 are in disagreement with previous theories which have neglected the selective scattering of minority-spin electrons into empty minority d states. Those that consider only exchange predict[8,11] almost no difference between the up- and down-spin lifetimes, while that of Beringer *et al.*[12] assumes $\tau_\uparrow/\tau_\downarrow = (1+p_B)/(1-p_B)$ independent of energy.

There have been two recent experimental papers[13,14] as well as a theoretical paper[15] that studied low-energy-loss single scattering of electrons from Fe and Ni. All three papers discuss the observed phenomena in terms of Stoner excitations, the scattering of a minority-spin electron and the simultaneous appearance of a majority-spin electron.

In general the Stoner mechanism in which a minority-spin d electron falls into an empty spin-down d state and a spin-up electron is scattered back to high energy is "balanced" by a process in which a spin-down electron is scattered back to high energy. These two processes together can be expected to result only in a spin polarization equal to that of the bulk and are completely taken into account by our theory. The case of very small net energy[13–15] loss involves the excitation of electrons very near the Fermi energy and for that case there can be a large imbalance in the number of up- and down-spin electrons. Thus the physics of those experiments[13,14] is different from that of importance in secondary-electron polarization.

We have presented the first theory of the spin polarization of secondary electrons. We demonstrated that this type of experiment (as opposed to the usual measurement of the secondary-electron intensity distribution) provides information about the electron-electron interaction in magnetic transition metals and glasses. The following results have been obtained.

(1) The theory provides the first quantitative explanation for the rapid rise observed in the spin polarization of low-energy secondaries in Fe, Co, Ni, and associated glasses.

(2) The approximate size and energy dependence of the exchange matrix element M_{ds}^{sd} relative to the direct matrix element M_{ds}^{ss} that describes the electron-electron interaction are obtained.

(3) It is shown that the ratio of the majority- to minority-spin mean free paths can be determined directly from the experimental secondary-electron polarization data.

(4) The mean-free-path difference between majority and minority spins is significant only at very low energies.

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