Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Inelastic exchange scattering in electron-energy-loss spectroscopy: Localized excitations in transition-metal and rare-earth systems

S. J. Porter, J. A. D. Matthew, and R. J. Leggott
Department of Physics, University of York, York YO1 5DD, United Kingdom
(Received 11 January 1994)

Cross sections for quasiatomic excitation by exchange scattering of electrons are calculated in the Born-Ochkur approximation for $3p$-$3d$ and $3d$-$3d$ transitions in transition-metal systems, and for $4d$-$4f$ and $4f$-$4f$ transitions in rare earths. The energy dependence of the spin polarization of $3p$-$3d$ and $4d$-$4f$ losses in reflection electron-energy-loss spectroscopy from ferromagnetic surfaces involves a balance of small-angle spin-dependent inelastic processes accompanied by a high-angle elastic scattering, and large-angle spin-flip exchange scattering without the need for elastic scattering. Both $3d$-$3d$ excitations, e.g., in transition-metal compounds, and $4f$-$4f$ excitations in rare earths involve spin-flip transitions whose scattering amplitudes g fall off with momentum transfer q such that the full width at half maximum $q_{1/2}$ (in a.u.) is given by $q_{1/2}\langle r_{nl}\rangle \sim 2$, where $\langle r_{nl}\rangle$ is the expectation value of r for the $3d$ or $4f$ electron. The angular width of the spin-flip differential cross section is then much greater than for dipole transitions, a pattern that helps to account for how these intra-atomic transitions compete with dipole processes for primary energies in excess of 100 eV.

For primary electron energies significantly larger than the excitation or loss energy, electron-energy-loss spectroscopy is usually dominated by dipolar processes involving scattering of the incident electrons through a small angle: observation of the loss electron in reflection mode then requires an additional large-angle elastic scattering. This single stage process [Fig. 1(a)] is generally much less probable than an inelastic + elastic scattering [Fig. 1(b)] due to the dominance of near forward inelastic scattering. When electrons interact with an atom having a net spin, the outcome of the scattering process will depend on whether the spin of the incoming electron is parallel or antiparallel to the atomic spin: if atomic spins near a surface are aligned as in a ferromagnetic system, the electron scattering cross sections will produce both spin polarization in the scattered beam if the incident beam is unpolarized (see, for example, $3p \rightarrow 3d$ in the electron energy losses of amorphous Fe alloys[1]) and spin asymmetry in the scattering of spin-up and spin-down electrons.

These phenomena arise from exchange terms in the inelastic-scattering cross sections. Treating the scattering of the incident electron and the promotion of an oriented electron into an empty state as a two-electron problem, i.e., neglecting multiplet effects in the partially filled shell, the scattering may be described in terms of a direct amplitude $f(\theta)$ and an exchange amplitude $g(\theta)$, where θ is the scattering angle. For $3p \rightarrow 3d$ transitions in ferromagnetic Fe or Mn[1] or $4d \rightarrow 4f$ transitions in ferromagnetic rare earths, the polarization is then given by

$$P=\frac{|f|^2+|g|^2-|f-g|^2}{|f|^2+|g|^2+|f-g|^2} \, . \tag{1}$$

In systems with open shells it is also possible for incident electrons to induce dipole forbidden intermultiplet excitations, e.g., $3d^n$-$3d^n$ or $4f^n$-$4f^n$ transitions, which

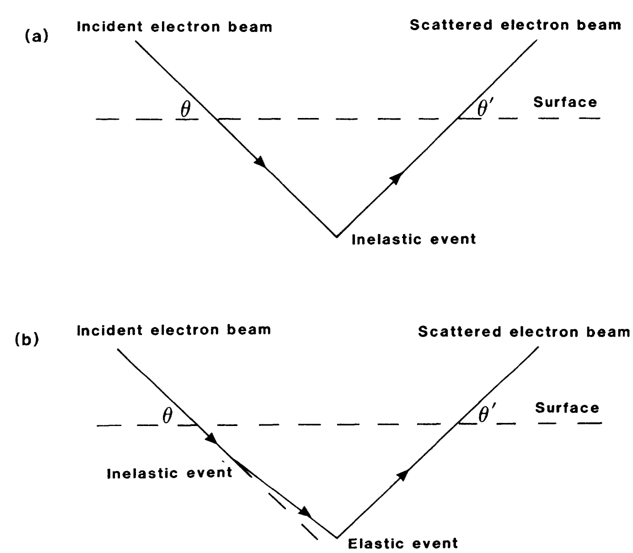

FIG. 1. (a) A large-angle inelastic-scattering event; (b) a small-angle inelastic scattering followed by large-angle elastic scattering.

require a spin flip.[2–5] The differential cross section is then proportional to $|g|^2$.

THEORY

In this paper, we examine the properties of f and g for $3p \rightarrow 3d$ transitions in Fe and $4f^7$-$4f^7$ transitions in Gd within a simple quasiatomic scattering model, the Born-Ochkur approximation,[6,7] where for incident energy $E_p = k_i^2/2$ a.u. and incident wave vector $\mathbf{k}_i$; f and g are given by

$$f = -\frac{2}{q^2} I(q) , \tag{2a}$$

$$g = -\frac{2}{k_i^2} I(q) , \tag{2b}$$

where $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is the momentum transfer and $I(q)$ the transition amplitude, is given by

$$I(q) = \int \psi^*_{n'l'} e^{i\mathbf{q}\cdot\mathbf{r}} \psi_{nl} d\mathbf{r} , \tag{3}$$

where $\psi_{nl(n'l')}$ is the initial (final) state wave function. The excitation energy $\Delta E = (k_i^2 - k_f^2)/2$, and the approximation is valid for $E_p \gg \Delta E$. When the scattering angle is small,

$$P \simeq \frac{g(\theta)}{f(\theta)} = \frac{1}{4} \left[\frac{\Delta E}{E_p} \right]^2 . \tag{4}$$

Figure 2 plots P as a function of θ for $3p \rightarrow 3d$ transitions in Fe($\Delta E = 56$ eV) at $E_p = 90$, 227, and 1321 eV. At small scattering angles, P is small and arises from differences in the direct scattering amplitudes for spins parallel ($f - g$) or antiparallel (f) to the oriented atom direction[1] rather than spin-flip transitions. $P \rightarrow 1$ in the range 60°–75°, corresponding to conditions when $|\mathbf{q}| = |\mathbf{k}_i|$ and $f = g$. This is an artifact of the simplification implicit in the

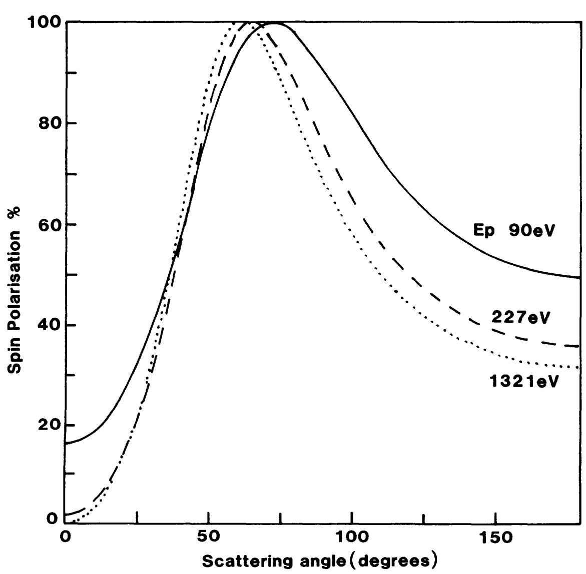

FIG. 2. The spin polarization P versus scattering angle for $3p \rightarrow 3d$ transitions in ferromagnetic iron for primary energies 90, 227, and 1321 eV.

Born-Ochkur exchange correction, and higher-order theories will yield somewhat smaller values. In addition, the first Born approximation is known to be erratic in its prediction at high scattering angles. However, Born-Ochkur gives a good approximation to the spin asymmetry in H ionization[8] by electrons for $E_p \geq 80$ eV, and this simple theory gives general insight into the spin dependence of scattering. When P is large ($g \sim f$), spin-flip transitions have assumed considerable importance, but the peak in P contrasts strongly with the rapid falloff in the conventional first-order Born cross section

$$\frac{d\sigma}{d\Omega} \propto (\theta^2 + \theta_0^2)^{-1} , \tag{5}$$

where $\theta_0 = \Delta E/(2E_p)$. $(d\sigma/d\Omega)^{\text{1ST BORN}}_{3p\rightarrow 3d}$ has fallen to half its maximum value at $\theta = 18°$, 7°, and 1.2°, respectively, at the energies shown, so that high polarization events have low cross section even at $E_p = 90$ eV. The pattern is then one of low polarization with a high inelastic forward scattering cross section and of high polarization and low inelastic cross section at higher scattering angle. This implies that the balance between low-angle loss accompanied by a single high-angle elastic scattering [Fig. 1(b)] or multiple elastic scattering, and high-angle losses is delicate and highly dependent on both experimental geometry and the state of order at the surface. This is discussed in detail by Porter and Matthew[9] for $p \rightarrow d$ and $d \rightarrow f$ transitions in transition-metal systems and rare earths, respectively.

For spin-flip transitions within a configuration, e.g., $4f$-$4f$ transitions in the rare earths, Born-Ochkur leads to

$$\frac{d\sigma}{d\Omega} \propto \left| \int |\psi_{nl}|^2 e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2 . \tag{6}$$

Here the one-electron wave function ψ_{nl} of both the initial and final states is the same, and so $d\sigma/d\Omega$ is proportional to the x-ray atomic scattering for the excited electron. The differential cross section peaks in the forward direction as for dipolar losses but falls off much more slowly with angle. Expanding $e^{i\mathbf{q}\cdot\mathbf{r}}$ and approximating the matrix element by a parabolic function of q, $d\sigma/d\Omega$ falls off to half its maximum value at $\theta_{1/2}$ given by

$$\theta_{1/2} \approx 2 \arcsin \left[\left[\frac{3(1 - 2^{-1/2})}{4E_p \langle r_{nl}^2 \rangle} \right]^{1/2} \right] , \tag{7}$$

where $\langle r_{nl}^2 \rangle$ is the expectation value of r^2 for the electron in both its initial and final state. Higher order terms in the expansion increase this value slightly (by $\sim 10\%$ for $E_p = 100$ eV in Gd). Figure 3 compares the differential cross sections for $4f$-$4f$ transitions in Gd at three typical primary energies. $(d\sigma/d\Omega 0)_{\theta=0}$ varies as E_p^{-2}, and the total $4f$-$4f$ cross section varies as E_p^{-3} as noted by Joachain.[10] In contrast to the $4f^7$-$4f^7\,{}^1G$ loss ($\Delta E = 4.5$ eV), dipolar losses at the same ΔE have fallen to half maximum by 1° for $E_p = 100$ eV so that in a reflection loss experiment these will again be a balance between double- and multiple-scattering (loss + elastic) and single inelastic-scattering events. The sensitivity of the ratio of $4f^7$-$4f^7$ losses in Gd to geometry, primary energy, and surface order is consistent with this conclusion. Only for inelastic low-energy electron-diffraction events are the low angle exchange events, i.e., non-spin-flip processes, likely to predominate.

For the corresponding spin-flip cross sections for $3d$-$3d$ transitions in ionic Mn compounds ($\Delta E = 3$ eV), $(d\sigma/d\Omega)_{\theta=0}$ is lower than for Gd (five electrons instead of seven) and $(d\sigma/d\Omega)$ falls off more quickly with angle since $\langle r^2_{\mathrm{Mn}\,3d}\rangle = 1.64$ a.u.^{2} is greater then $\langle r^2_{\mathrm{Gd}\,4f}\rangle = 0.89$ a.u.^{2}—see Froese Fischer.[11] In terms of momentum transfer the results may be expressed by a kind of "uncertainty" style relationship

$$\Delta q_{1/2}\langle r_{nl}\rangle \sim 2 , \quad (8)$$

where $\Delta q_{1/2}$ is the momentum transfer at which the transition *amplitude* g has fallen to half its $\theta=0$ value and $\langle r_{nl}\rangle$ is a measure of the size of the electron orbital. These results are also relevant to d-d transitions involving spin flip where the levels are further split by a crystal field.[12–15] Indeed the recent results of Gorschlüter and Merz[13] on d-d excitations in NiO(100) and CoO(100) are consistent with significant contributions from high-angle losses without elastic scattering.

Although higher order theories would modify the simple pattern outlined here, the Born-Ochkur model provides a good general guide to the angular distribution of electron exchange scattering for quasiatomic $3p$-$3d$ and $4d$-$4f$ excitations in transition metals and rare earths. Likewise, $4f$-$4f$ transitions in rare earths and $3d$-$3d$ transitions in ionic transition-metal compounds should be reasonably well described provided $E_p \gg \Delta E$. Although Stoner excitations[16,17] and d-d transitions in paramagnetic model systems[18] are less quasiatomic and show marked bandlike character, the results presented here usefully complement the dielectric descriptions of spin-flip processes developed, for example, by Modesti *et al.*[17] and Mills.[19] It must, however, be emphasized that this simple model does not treat the behavior of the *individual* multiplet transitions and a more detailed theory would predict some differences in the variation of cross sections with energy and angle for different loss components, as is indeed observed by Matthew *et al.*[3] and Kolaczkiewicz and Bauer *et al.*[4] The pioneering calculations of Moser and Wendin[20] using the distorted-wave approximation

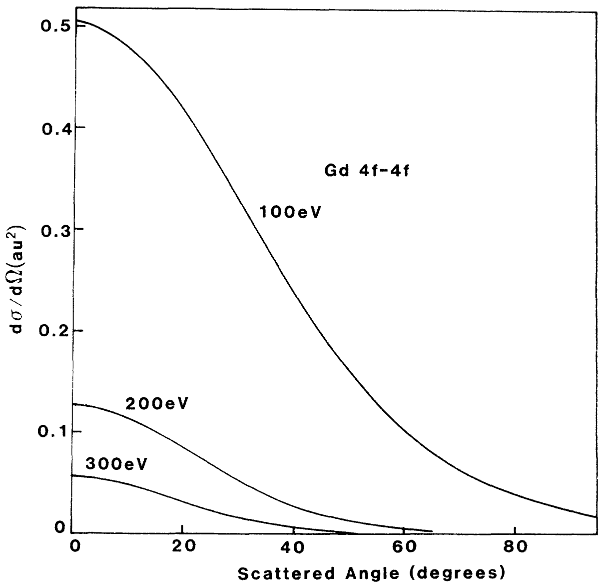

FIG. 3. The differential scattering cross section versus scattering angle for $4f$-$4f$ transitions in Gd at $E_p = 100$, 200, 300 eV.

predict *L-S resolved results* for La $4d \rightarrow 4f$ and $3d \rightarrow 4f$ transitions and Th $4d \rightarrow 5f$ and $4f$-$5f$ transitions, but make no explicit spin-polarization predictions. Clearly such approaches provide a way forward for the problems investigated here, but the simple scaling patterns inherent in the Born-Ochkur approximation provide useful initial tests of spin-polarized loss data.

SUMMARY

The Born-Ochkur approximation is shown to give useful insights into exchange scattering in electron-energy-loss spectroscopy in the reflection mode. Both the polarization induced in dipolar transitions and spin-flip transitions are much less forward scattering dominated than for nonexchange scattering and as a result experimental observations will include both single inelastic-scattering events and multiple-scattering events where low-angle inelastic scattering is combined with elastic scattering.

[1] D. Mauri, R. Allenspach, and M. Landolt, Phys. Rev. Lett. **52**, 152 (1984).

[2] F. Della Valle and S. Modesti, Phys. Rev. B **40**, 993 (1989).

[3] J. A. D. Matthew, W. A. Henle, M. G. Ramsey, and F. P. Netzer, Phys. Rev. B **43**, 4897 (1991).

[4] J. Kolaczkiewicz and E. Bauer, Surf. Sci. **265**, 39 (1992).

[5] A. Gorschlüter, R. Stiller, and H. Merz, Surf. Sci. **251/252**, 272 (1991).

[6] V. I. Ochkur, Zh. Eksp. Teor. Fiz. **45**, 734 (1963) [Sov. Phys. JETP **18**, 503 (1964)].

[7] V. I. Ochkur, Zh. Eksp. Teor. Fiz. **47**, 1746 (1964) [Sov. Phys. JETP **20**, 1175 (1965)].

[8] M. J. Alguard, V. W. Hughes, M. S. Lubell, and P. F. Wainwright, Phys. Rev. Lett. **39**, 334 (1977).

[9] S. J. Porter and J. A. D. Matthew (unpublished).

[10] C. J. Joachain, *Quantum Collision Theory* (North-Holland, Amsterdam, 1983).

[11] C. Froese Fischer, *The Hartree Fock Method for Atoms* (Wiley, New York, 1977).

[12] K. Akimoto, Y. Sakisaka, M. Nishijima, and M. Onchi, J. Phys. C **11**, 2535 (1978).

[13] A. Gorschlüter and H. Merz, Phys. Rev. B **49**, 17 293 (1994).

[14] J. P. Kemp, S. T. P. Davies, and P. A. Cox, J. Phys. Condens. Matter **1**, 5313 (1989).

[15]A. Freitag, V. Staemmler, D. Cappus, C. A. Ventrice, K. Al Shamery, H. Kuhlenbeck, and H.-J. Freund, Chem. Phys. Lett. **210**, 10 (1993).
[16]J. Kirschner, Phys. Rev. Lett. **55**, 973 (1985).
[17]S. Modesti, F. Della Valle, R. Rosei, E. Tosatti, and J. Glazer, Phys. Rev. Lett. **31**, 5471 (1985).
[18]G. A. Mulhollan, X. Zhang, F. B. Dunning, and G. K. Walters, Phys. Rev. B **41**, 8122 (1990).
[19]D. L. Mills, Phys. Rev. B **34**, 6099 (1986).
[20]H. R. Moser and G. Wendin, Phys. Rev. B **44**, 6044 (1991).