Spin-polarized photoelectron diffraction

B. Sinković and C. S. Fadley
Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822
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The use of multiplet-split s levels in magnetic atoms or ions for spin-polarized photoelectron diffraction or extended x-ray absorption fine-structure experiments is discussed. Over the range 50–500 eV, spin-dependent scattering factors for Mn^{2+} show exchange-induced asymmetries of as high as 8%, with significantly larger effects expected for forward scattering as compared to backscattering. Single-scattering-cluster photoelectron diffraction calculations for Mn $3s$ emission from antiferromagnetic $KMnF_3$ show net effects ranging from 8% at 50 eV to 1% at 400 eV.

Spin-polarized electron-emission experiments making use of external spin detectors[1] and spin-polarized electron-diffraction experiments involving external polarized electron sources[2] are now well developed as powerful tools for studying magnetically ordered materials. In this Brief Report, we present the first quantitative theoretical analysis of a third type of spin-dependent measurement: spin-polarized photoelectron diffraction (SPPD) based upon an *internal* source of polarized electrons as produced by the well-known multiplet splittings of core-level binding energies in transition-metal ions.[3,4] The model used to describe the scattering and diffraction is the single-scattering-cluster (SSC) approach that has been shown in several prior studies to rather well describe various types of photoelectron diffraction at energies $\gtrsim 100$ eV.[5] We use this model to determine the degree of spin asymmetry expected in such angle-resolved photoemission measurements, and the extent to which such data can provide unique information concerning short-range magnetic order. We also discuss the possibility of performing very closely related spin-polarized extended x-ray absorption fine-structure (SPEXAFS) studies in which individual photoelectron peaks are used as monitors of the EXAFS signal.[4]

The example considered is photoemission from the Mn $3s$ level of the highly ionic antiferromagnet $KMnF_3$. Figure 1(a) shows the Mn $3s$ doublet observed, together with the single-configuration multiplets primarily responsible for each peak and the predominant photoelectron spin polarization thus expected. A detailed consideration of the angular momentum coupling in the total ^6P final state of ion + photoelectron shows the spin-down ^7S peak to be $\frac{5}{7}$ or 71.4% polarized and the spin-up ^5S peak to be 100% polarized.[4] Additional satellite peaks and correlation effects are not expected to alter these polarizations appreciably due to the monopole nature of these excitations.[3(b)] These two peaks thus represent convenient internal sources of nearly fully polarized electrons for which spin-dependent scattering and diffraction could occur during photoelectron escape from the specimen.

The $KMnF_3$ crystal structure is shown in Fig. 1(b), and it is clear that emission along different directions should involve anisotropic spin effects. For example, for emission along [101], the first Mn^{2+} scatterer encountered has its spin (and magnetic moment) parallel to the emitting Mn^{2+} ion, whereas for emission along [100] or [1$\bar{1}$1] the first scatterer is antiparallel to the emitter. This is true regardless of whether the emitter is spin up or spin down. Thus, some change in the doublet intensity ratio as a function of direction might be expected due to spin-dependent exchange scattering by the Mn3d electrons. We will focus entirely on exchange scattering here, as spin-orbit effects will tend to cancel in an angle-resolved photoelectron diffraction measurement on such an antiferromagnetic system due to the equal numbers of emitters with up and down moments.

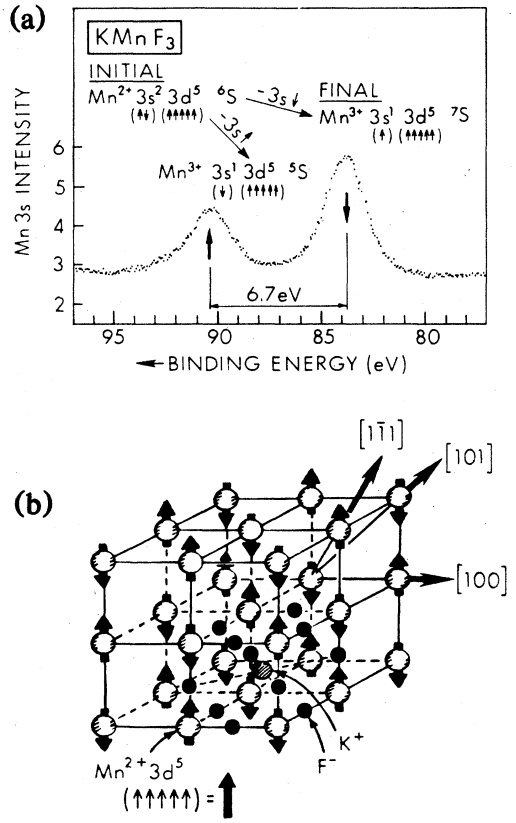

FIG. 1. (a) The multiplet-split Mn $3s$ spectrum of $KMnF_3$, with the initial and final states and the predominant photoelectron spin orientations indicated. (b) The perovskite crystal structure of $KMnF_3$, with the antiferromagnetic ordering of Mn^{2+} ions occurring below $T_{Néel} = 88$ K also indicated. (A slight lattice distortion away from perovskite at these lower temperatures can be neglected for the present discussion.)

That is, for photoelectrons detected in either member of the $3s$ doublet, the spin-orbit effect, which is proportional to $\mathbf{s}\cdot\mathbf{L}$ ($\mathbf{s}=e^-$ spin, $\mathbf{L}$=photoelectron orbital angular momentum), will have opposite signs for the two different types of contributing emitters. Such a cancellation does not occur for exchange, however, due to its dependence on $\mathbf{s}\cdot\mathbf{S}$ ($\mathbf{S}=3d$ spin).

In order to account for the effects of exchange on the Mn^{2+} scattering factors, a special muffin-tin calculation of partial-wave phase shifts was performed so as to include the $3d^5$ charge density $\rho_{3d}(r)$ in calculating the Slater exchange contribution to the potential for the case of photoelectron spin parallel to the Mn^{2+} moment, or to exclude $\rho_{3d}(r)$ in calculating exchange for photoelectron spin antiparallel to this moment. The exchange potential was finally calculated in the usual way as being proportional to $\alpha\rho(r)^{1/3}$, where α is a proportionality factor and $\rho(r)$ the total charge density (with or without ρ_{3d}, as appropriate). Two choices have been used for α: $\alpha=\frac{2}{3}$, as is standard in many bound-state atomic and molecular calculations; and $\alpha=\alpha(\epsilon)$=a function of electron kinetic energy ϵ, as used previously in analyzing spin-polarized low-energy electron diffraction (LEED) data.[6] The latter choice should be more accurate for higher-energy electrons, although other models have also been used to describe such continuum exchange scattering.[7] Scattering factors for the nonmagnetic K^+ and F^- ions were calculated in the usual way from muffin-tin partial-wave phase shifts. Other assumptions and inputs for the SSC calculations are discussed elsewhere.[5] Although multiple-scattering effects may be present in such diffraction curves, particularly at lower energies of $\lesssim 200$ eV, prior studies with the SSC method[5] suggest that it should provide very good estimates of such spin-dependent phenomena, particularly as the $3d$ exchange represents only a small perturbation to the total scattering potential.

We begin by considering the spin dependence of scattering factors for Mn^{2+} as a function of electron energy, which is summarized in Fig. 2. Here, $f_\uparrow(\theta)$ indicates a scattering factor for photoelectron spin parallel to the Mn^{2+} moment and $f_\downarrow(\theta)$ implies photoelectron spin antiparallel to this moment. The percentage spin asymmetry in these scattering factors is defined as

$$S_f(\theta)=(|f_\uparrow(\theta)|^2-|f_\downarrow(\theta)|^2)/(|f_\uparrow(\theta)|^2+|f_\downarrow(\theta)|^2)\times 100$$

where θ is the scattering angle. Curves of S_f are shown for both the forward scattering case ($\theta=0°$) that will dominate $|f(\theta)|$ at higher energies $\gtrsim 400$ eV, and the backscattering case ($\theta=180°$) that should become more important at lower energies. Backscattering is also the only case of relevance in a SPEXAFS experiment. Also shown for comparison are the forward scattering S_f results for neutral atomic Fe of Mathew;[7] these are based on the Born-Ockhur approximation. These curves make it clear that the use of the more accurate $\alpha(\epsilon)$ rather than $\alpha=\frac{2}{3}$ considerably reduces the forward scattering S_f values, whereas much less difference between the two approximations is seen in backscattering. Considering now only the $\alpha(\epsilon)$ curves, we note that forward-scattering spin asymmetries are significantly higher than those in backscattering, with ratios of $\gtrsim 2\times$. Also, the backscattering S_f values are unique in showing a change in sign at 300 eV. Thus, a measurement such as photoelectron diffraction that tends to emphasize *forward* scattering would appear to be inherently better suited to observing

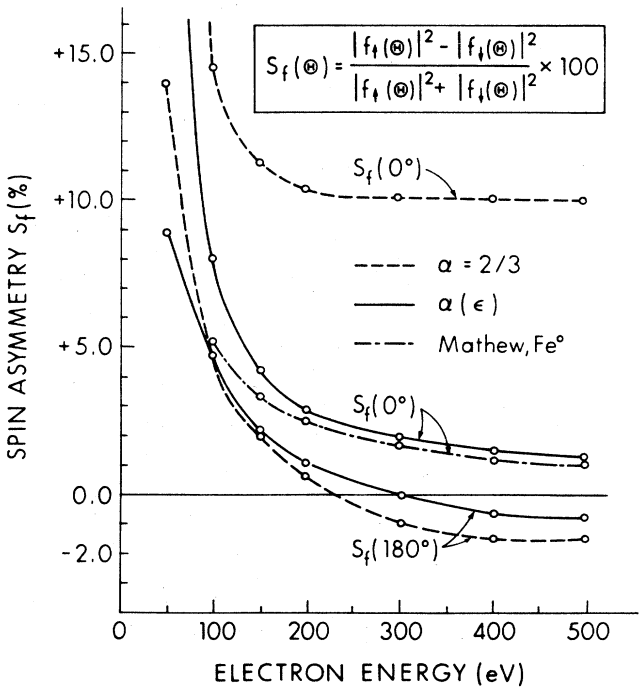

FIG. 2. The degree of spin-associated asymmetry in the Mn^{2+} scattering factor S_f as a function of electron kinetic energy. Curves of S_f are shown for both forward scattering ($\theta=0°$) and backward scattering ($\theta=180°$). Two different approximations for the Slater α parameter are compared. A curve from Mathew (Ref. 7) for Fe is also shown.

such spin-dependent effects due to both the magnitudes of as much as 5%–10% expected and the consistent direction predicted for the effect (that is, the intuitive direction in which the attractive exchange *increases* the forward-scattered flux for photoelectrons with spins parallel to the Mn^{2+} moment). The sign change in backscattering at 300 eV also could complicate the interpretation of broad-scan EXAFS data. Finally, the general form of the energy variation of $S_f(0°)$ in our results is in good agreement with that of Mathew for Fe. Comparing magnitudes between these two calculations is not directly possible, however, because the higher number of unpaired spins for Mn^{2+} (5.0 vs 2.3 assumed for Fe) is compensated by our use of a muffin-tin potential cutoff radius of 1.16 Å appropriate to touching spheres in $KMnF_3$, as compared with an effectively longer-range atomic potential of Mathew. Forward-scattering strengths are found to be particularly sensitive to the effective radius of the potential, decreasing as it decreases.

In Fig. 3 we present detailed SSC calculations of the spin asymmetry in photoelectron intensities as the polar angle of photoelectron emission is scanned in a (001) plane above a $KMnF_3$ surface with (110) orientation [cf. Fig. 1(b)]. Here, the spin asymmetry in photoelectron intensity is defined as $S_I=(I_\uparrow-I_\downarrow)/\frac{1}{2}(I_\uparrow+I_\downarrow)\times 100$, where $I_\uparrow$ and $I_\downarrow$ are the results of separate SSC calculations of the directionally dependent intensities per electron emitted with spin parallel and antiparallel to the emitting Mn^{2+} ion spin, respectively. S_I should thus provide a direct estimate of the percent change in the intensity ratio of the doublet in Fig. 1(a). Results are shown for four energies: 50, 100, 200, and 400

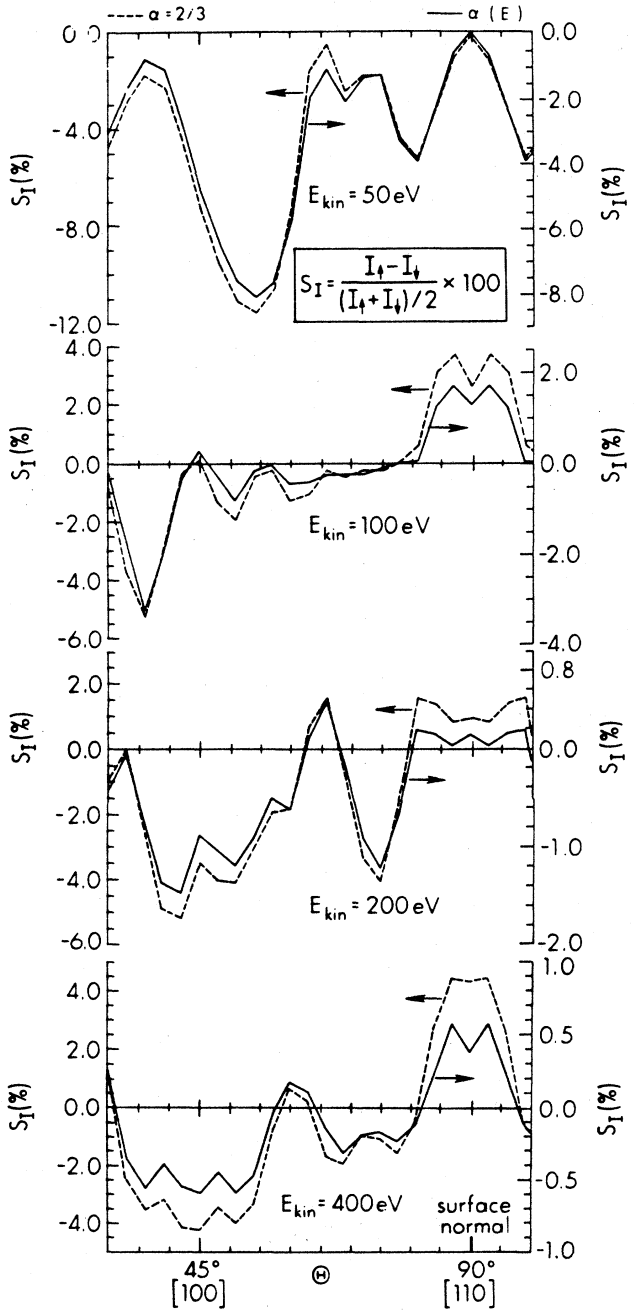

FIG. 3. Single scattering cluster (SSC) calculations of the degree of spin asymmetry in photoelectron intensity S_I for spin-up and spin-down photoelectron intensities from antiferromagnetically ordered $KMnF_3$. Polar angle scans of these intensities above a (110)-oriented surface are considered at four energies. Two approximtions for α are again compared.

eV. It is clear that significant angular-dependent changes in S_I are predicted, and that they are particularly strong at the lower energies of 50 and 100 eV. As expected from Fig. 2, the more accurate $\alpha(\epsilon)$ curves predict lower S_I values, with reductions relative to the $\alpha = \frac{2}{3}$ curves by factors ranging from ~ 0.72 at 50 eV to ~ 0.13 at 400 eV. However, the shapes of the two curves at a given energy are nearly identical for the two choices of α. If the difference $S_{I,\max} - S_{I,\min}$ with the more accurate $\alpha(\epsilon)$ is used as a measure of the maximum difference expected in such an experiment, we find 8.2% at 50 eV, 5.1% at 100 eV, 2.0% at 200 eV, and 1.2% at 400 eV. Measurements at only a few well chosen directions should suffice to verify such effects for any energy. From a criterion of precent effect, lower energies are thus preferable, although with careful measurements and good statistics, even the $\sim 1\%$–2% effects predicted at higher energies should be observable. One disadvantage of lower energies, however, is the higher secondary electron background. By contrast, for higher energies of >200 eV, the simple SSC model used here is expected to be a better approximation,[5] and secondary electrons should be less important, even if the effects are reduced in magnitude. In fact, the presence of simply interpretable forward-scattering phenomena is seen for 400 eV, where the most significant difference is between a positive S_I peak along [110] [for which the forward-scattering Mn^{2+} ions all have spins parallel to that of the emitter, as shown in Fig. 1(b)] and a negative S_I peak along [100] (for which the Mn^{2+} ion spins alternate, with the most important nearest-neighbor scatterers along this direction being antiparallel to the emitter).

Finally, we note that past analyses of photoelecton diffraction data show that it is only the first few spheres of neighboring atoms (and particularly nearest and next-nearest neighbors) that are responsible for most of the observed angular anisotropies.[5,8] Thus, the exchange-associated perturbation of these patterns discussed here is also expected to be sensitive to only very short-range magnetic order in the specimen. The observation or nonobservation of such effects thus should produce much-needed information on the presence or absence of short-range order in magnetic materials above their transition temperatures.

In conclusion, multiplet-induced spin-polarized photoelectron diffraction shows considerable promise as a new technique for studying short-range order in magnetic materials, with predicted effects in the $\sim 1\%$–8% range, and a relatively simple theoretical model that should be applicable at higher energies. Similar phenomena also should occur in analogous spin-polarized EXAFS measurements, although the percent effects are expected to be considerably smaller and the interpretation may be complicated by possible changes in the sign of the effect with energy.

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