Observation of Spin-Polarized Photoelectron Diffraction

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We report the first observation of spin-polarized photoelectron diffraction in core-level emission from antiferromagnetic $KMnF_3$. The Mn $3s$ multiplet splitting provides an internal source of polarized electrons, and spin-polarized photoelectron diffraction effects of up to 17% are seen in the $^5S/^7S$ intensity ratio. These effects are found to be very sensitive to both emission direction and temperature. Short-range antiferromagnetic order is found to persist up to approximately 3 times the Néel temperature.

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The possible use of core s-level multiplet splittings in transition-metal atoms[1] as internal sources of spin-polarized photoelectrons has been discussed previously.[2,3] Such measurements would thus not require an external spin detection system, but only an energy analyzer. Quantitative estimates of the degree of *spin-polarized photoelectron diffraction* (SPPD) thus expected for the example of Mn $3s$ emission from a single crystal of antiferromagnetic $KMnF_3$ have been made very recently by Sinković and Fadley (SF).[3] These calculations were based upon spin-dependent plane-wave scattering factors for Mn^{2+} allowing specifically for $3d$-photoelectron exchange and a simple single-scattering cluster model of photoelectron diffraction.[4] SF show that the exchange-induced anisotropies in scattering are greater for forward scattering, the case of greatest importance in angle-resolved photoelectron diffraction. They also point out that the multiplet-split ^5S-^7S doublet seen in $3s$ emission may exhibit changes in its intensity ratio of as much as 8% due to spin-dependent final-state scattering and diffraction. Measurements at photoelectron kinetic energies E_{kin} of $\lesssim 100$ eV are also found to maximize these predicted SPPD effects. Finally, photoelectron diffraction in general is expected to be dominated by the first few spheres of near-neighbor atoms[4–7] so that SPPD will inherently be very sensitive to short-range magnetic order.

In this Letter, we present experimental results for $KMnF_3$ in which SPPD is observed for the first time. These results also show that short-range magnetic order persists up to ~ 3 times the Néel temperature $T_N = 88$ K for this material. The general use of SPPD as a new tool for studying short-range magnetic order is also discussed.

A single crystal of $KMnF_3$ was cut and mechanically polished to within 0.5° of the (110) surface. The specimen was mounted on a high-precision two-axis goniometer (cf. Ref. 4) equipped with a liquid-He–compatible cold finger. This was placed in a VG ESCALAB5 spectrometer operating at ultrahigh-vacuum conditions of $\leq 5\times 10^{-11}$ Torr; its angular acceptance was approximately $\pm 6°$. This system was further modified to provide both Al $K\alpha$ ($h\nu = 1486.6$ eV, FWHM $= 0.8$ eV) and Mo $M\zeta$ ($h\nu = 192.6$ eV, FWHM $= 1.6$ eV) radiation, as well as a low-energy electron flood gun (HP 18623A) for neutralization of photoelectron surface charging. *In situ* surface preparation was accomplished by Ar-ion bombardment and high-temperature annealing plus evaporation cleaning at up to 970 K. Ultimate surface impurities were reduced to C (≤ 1.6 monolayers) and O (≤ 0.8 monolayer) as estimated from Al-$K\alpha$–excited core peak intensities. The surface stoichiometry in K, Mn, and F was also found to be very close to that of $KMnF_3$ ($K_{0.7-1.0}M_{1.00}F_{2.5-3.0}$) in x-ray photoemission spectra obtained at both normal and grazing photoelectron emission, with the latter being much more surface sensitive.[4] LEED measurements were not possible because of the insulating character of the specimen, but a high degree of near-surface order of the $KMnF_3$ lattice was verified by the presence of strong core-level photoelectron diffraction effects in K, Mn, and F azimuthal scans at both high and grazing takeoff angles with respect to the surface. These high-energy Al-$K\alpha$–excited data also were very stable with temperature cycling *and* very well described by single-scattering cluster calculations assuming the known $KMnF_3$ crystal structure. The analogous C-1s and O-1s azimuthal scans showed no such diffraction features, however; thus these impurities were present in a thin, amorphous overlayer that is not expected to produce any directional anisotropy in photoelectron scattering. The overall surface stoichiometry, including overlayer impurities, was *very* stable (to within $< 5\%$) over periods of days in the vacuum system and also with cooling to cryogenic temperatures, so that successive low- and high-temperature runs were always made without any detectable change in the specimen surface.

Mo-$M\zeta$–excited Mn $3s$ spectra such as those in Fig. 1 were studied at various specimen temperatures

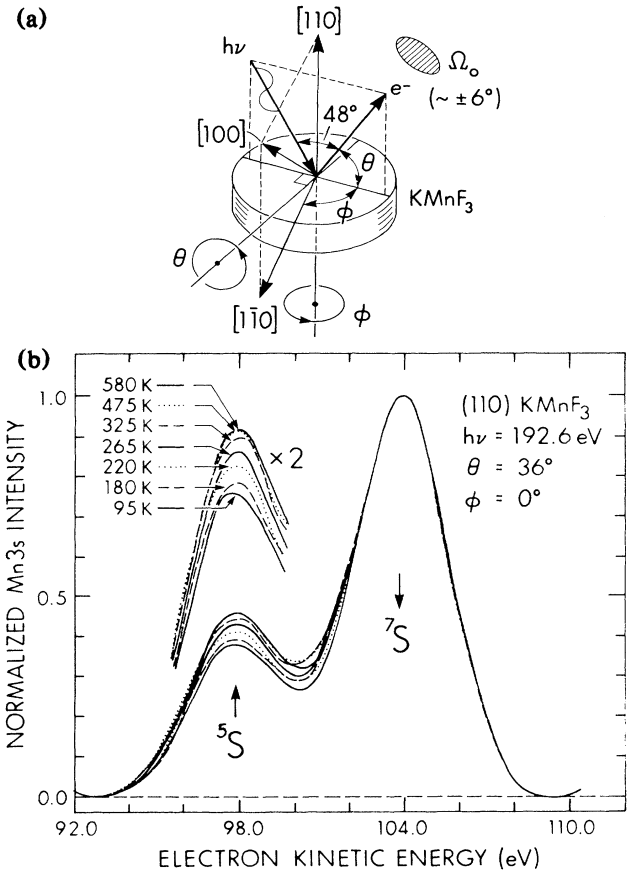

FIG. 1. (a) Experimental geometry for photoemission from a (110) surface of $KMnF_3$, with pertinent angles defined. The radiation is unpolarized. (b) Mn $3s$ spectra at several temperatures, with normalization to the ^7S or "spin-down" peak. Mo $M\zeta$ radiation at 192.6 eV is used for excitation. Emission is along $\theta = 36°$, $\phi = 0°$.

between 95 K (just above the Néel temperature) and 580 K, and at various emission directions as defined by θ (relative to the specimen surface) and ϕ [relative to the $[1\bar{1}0]$ aximuth in the (110) surface]. Figure 1(a) defines the experimental geometry. The resultant relatively low photoelectron kinetic energies of 98.0 eV (^5S peak) and 104.0 eV (^7S) should yield higher SPPD effects,[3] but also higher surface sensitivity because of the shorter inelastic attenuation lengths involved. All spectra were taken in the constant-retard-ratio mode to yield true peak relative intensities and also an essentially linear background under the $3s$ spectral region. In general, ambient-temperature reference spectra were taken before and after runs at lower or higher temperatures without any specimen movement to check for possible hysteresis effects, and none were observed. The intensity and shape of the background under the $3s$ region were also found to be independent of temperature, and so did not introduce any spurious variations of peak relative intensities. Also, the peak shapes of the individual components in the Mn $3s$ doublet were found to be essentially constant with both emission direction and temperature. Minor changes in the $KMnF_3$ crystal structure away from cubic perovskite occurring at 92 and 187 K[8] principally involve the nonmagnetic F atoms, and are not expected to influence significantly the photoelectron diffraction patterns studied here. In fact, no noticeable changes in the $^5S/^7S$ ratio were seen in the vicinity of these temperatures. Five emission directions were studied, although only results for the two showing the largest SPPD effects are discussed in detail here.

Figure 1(b) shows the Mn $3s$ doublet of $KMnF_3$ for emission at $\theta = 36°$, $\phi = 0°$ and at seven temperatures. The spectra have been normalized so as to have the same height for the ^7S peak at lower binding energy.[9] The ^7S peak is expected to consist of photoelectrons 71% spin polarized antiparallel to the spin of the emitting Mn^{2+} ion; the ^5S peak by contrast should consist of photoelectrons 100% polarized parallel to the spin of the emitting ion.[2,3] The $\theta = 36°$, $\phi = 0°$ direction is also of interest because SF predict for this case a maximum SPPD effect at 100 eV in the negative direction: That is, the $^5S/^7S$ ratio at temperatures low enough to exhibit short-range antiferromagnetic order should be lower relative to analogous ratios at temperatures high enough to destroy magnetic order fully. This is, in fact, the direction of the effect seen in Fig. 1(b), where the ^5S relative intensity increases steadily from 95 K ($1.08T_N$) to about 475 K ($5.40T_N$), and is constant above this temperature. By contrast, peak positions, shapes, and widths change very little as temperature is changed.

The change in the $^5S/^7S$ or "spin-up/spin-down" ratio is conveniently measured as a percentage change in the intensity $I(\uparrow)$ of the spin-up peak after the normalization of Fig. 1(b), or

$$S_{\text{expt}}(\text{LT}) = 100\{I(\uparrow)_{\text{LT}}[I(\downarrow)_{\text{HT}}/I(\downarrow)_{\text{LT}}] - I(\uparrow)_{\text{HT}}\}/I(\uparrow)_{\text{HT}},$$

where $I(\downarrow)$ is the intensity of the spin-down peak, HT refers to a sufficiently high reference temperature that the ratio has become constant (e.g., 580 K for the $\theta = 36°$, $\phi = 0°$ data), and LT refers to some lower temperature. (Values of S_{expt} defined in this way can be compared directly to S_I as defined in SF because of the relatively small percentage effects involved.) Such S_{expt} values as derived from the data of Fig. 1 are shown in Fig. 2, together with a similar set of values obtained with emission along [100] or with $\theta = 45°$, $\phi = 0°$ (that is, only 9° away from

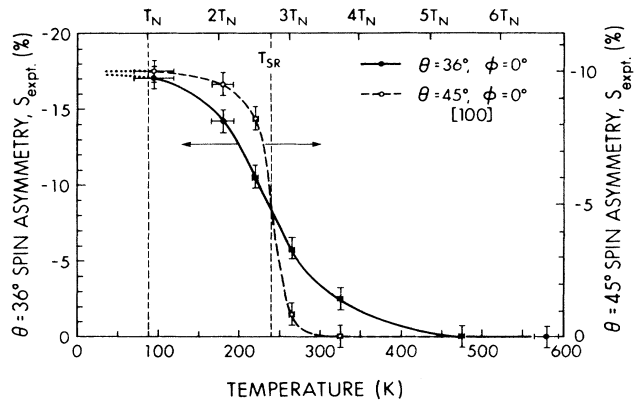

FIG. 2. Experimental spin asymmetries S_{expt} for Mn $3s$ spectra from (110) $KMnF_3$ as a function of temperature. HT refers to a sufficiently high reference temperature that the peak ratio $I(\uparrow)/I(\downarrow)$ has become constant, and LT to an arbitrary lower temperature at which S_{expt} is determined. Data for two emission directions are shown: $\theta = 36°$, $\phi = 0°$ [cf. Fig. 1(b)] and $\theta = 45°$, $\phi = 0°$.

the first set of data). The forms of both curves are fully reproducible, with estimated errors of $< \pm 1\%$. Both curves exhibit SPPD effects of about the same order at temperatures near T_N (-17% for $\theta = 36°$ and -10% for $\theta = 45°$), and also saturate to zero effect at the highest temperatures studied. The $\theta = 45°$ data show a much more abrupt falloff at $T = 240 \pm 5$ K $\simeq 2.73 T_N$ than those for $\theta = 36°$, but both sets of data agree in showing maximum negative slope at this temperature. (The more abrupt transition for $\theta = 45°$ is also fully reproducible in three separate measurements.) Thus, both of the curves in Fig. 2 are fully consistent with a disappearance of SPPD effects due to the breakdown of *short-range* Mn^{2+} magnetic order as T is increased. The origin of the difference in shapes of the two curves is not yet clear, but it may be that, for $\theta = 45°$, the SPPD effect is dominated by nearest-neighbor Mn^{2+} ions along the [100] direction of emission [cf. Fig. 1(a) here and Fig. 1(b) in SF], whereas for $\theta = 36°$, both nearest neighbors and more distant neighbors are important. Thus, some sort of smearing of the transition could be effected in the latter case. Whatever the explanation for this difference in shape, neither curve is at all in agreement with simple Debye-Waller-type effects on diffraction intensities, as these would not be expected to saturate at low or high temperatures *or* to yield a sharp falloff such as that exhibited for $\theta = 45°$.

The temperature of maximum negative slope in Fig. 2 can thus be termed a short-range-order temperature T_{SR}. It is furthermore very suggestive that our T_{SR} value is extremely close to the Θ value of 238 K in the Curie-Weiss magnetic susceptibility for $KMnF_3$.[10] Although this close agreement between T_{SR} and Θ may be somewhat coincidental, the microscopic origin of Θ also relates to short-range order: It is calculated as the sum of all near-neighbor exchange interactions acting on a given atomic site.[11] (The nature of our experiment may make the present T_{SR} value more surface sensitive, however.)

Three other emission directions also were studied at low and high temperatures to determine the approximate degree of variation of S_{expt} with direction. The data for $\theta = 36°$, $\phi = 42°$, which are expected to exhibit the same degree of surface sensitivity as those at the same polar angle of $\theta = 36°$, $\phi = 0°$, gave *no* detectable effect (i.e., $S_{expt} < 1\%$). For two more bulk-sensitive directions near normal emission ($\theta = 90°$, $\theta = 85°$ and $\phi = 0°$), small effects of $\sim -6\%$ and $\sim -5\%$, respectively, were found. The previously discussed amorphous nature of the thin impurity overlayer precludes associating this very strong directional sensitivity with any sort of overlayer scattering and diffraction, although such directionally random scattering could tend to mix emission from different directions, and thus could make all of the S_{expt} values given here somewhat lower in magnitude than the corresponding clean-surface values. The added effect of spin depolarization due to overlayer scattering will not affect the present measurements unless it also changes electron energies by very large values comparable to the multiplet splitting. Thus, these additional results also strongly indicate direction-dependent SPPD effects such as those predicted previously by SF (cf. Fig. 3 in Ref. 3). The agreement between maximum S_{expt} values and these prior calculations is not quantitative, but this is not surprising in view of the simple single-scattering cluster model used, the assumption of plane-wave scattering at each ion, and the use of a single energy of 100 eV for both photoelectron peaks. More accurate calculations are presently underway. It is encouraging, however, that approximately the correct magnitudes of SPPD effects are predicted by SF (for example, $\sim -3\%$ to -5% versus the $\sim -17\%$ observed at $\theta = 36°$, $\phi = 0°$), although the experimental values are ~ 3–6 times larger than estimated. Another point of agreement is the strong negative effect in both theory and experiment at $\theta = 36°$, $\phi = 0°$, as mentioned previously. The fact that only zero or negative S_{expt} values have so far been observed is also not inconsistent with theory, which in SF shows larger negative effects than positive at 100 eV, and only negative effects at 50 eV.

Thus, we conclude that the results of Figs. 1 and 2 represent the first observation of SPPD. Implicit in this conclusion is also that the two multiplet peaks are indeed very strongly spin polarized, as previously assumed.[2,3] The data for S_{expt} also exhibit a very strong dependence on emission direction, as expected. Final-

ly, the forms of both curves in Fig. 2 clearly show that short-range antiferromagnetic order within the first few spheres of Mn^{2+} ions does not fully disappear until temperatures of as high as $\sim 3.0T_N$–$4.5T_N$. These results are thus consistent with neutron diffraction data for $KMnF_3$,[12] which suggest the existence of spin waves at up to ambient temperature, even though an unambiguous analysis of the higher-temperature neutron results was not possible.

Such SPPD effects thus should provide a very useful new probe of antiferromagnetic and ferromagnetic systems that is rather uniquely sensitive to short-range order. The only condition required is that a reasonably well split *core* s-level doublet of predominantly spin-polarized peaks exists, but this should be met by a number of $3d$ metals and their compounds, as well as by rare-earth metals and their compounds. Spin-resolved ligand-field–split *valence* levels[13] also should exhibit SPPD, although a pair of spin-up and spin-down reference peaks may not be as easily distinguishable as in the core s-level case, so that such effects may be more difficult to observe unambiguously. Analogous spin-polarized extended x-ray-absorption fine-structure (EXAFS) measurements in which spin-up and spin-down core s-level peak intensities are separately monitored to determine the EXAFS[2,14] are also in principle possible. However, it has been pointed out by SF that such backscatter-dominated spin-polarized EXAFS effects are expected to be significantly smaller than those in angle-resolved SPPD of the type discussed here. Spin-polarized EXAFS also may be more difficult to interpret because of changes in the magnitude and sign of the exchange-produced spin asymmetry of the scattering factor as electron energy is swept.[3]

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[9]The $^5S/^7S$ ratios found here with Mo $M\zeta$ excitation lie in the range (0.40–0.45)/1.0, whereas those obtained with Al $K\alpha$ excitation are slightly higher at (0.50–0.52)/1.0 (Refs. 1 and 3). This relatively small difference may be due to a somewhat more adiabatic character in the lower-energy Mo $M\zeta$ excitation process, but does not affect any of our conclusions. The magnitude of the ^5S-^7S splitting is essentially the same for the two cases, however, at 6.5–6.7 eV.

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