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D-ORBITAL DIRECTED PHOTOEMISSION FROM MANGANESE FLUORIDE SINGLE CRYSTALS USING AlKα RADIATION*  

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ABSTRACT  

Angle-resolved photoemission energy distributions (PED's) were obtained from valence bands of MnF₂ single crystals using AlKα radiation. A pronounced variation in the PED's was observed as the electron take-off angle was varied relative to the crystalline axes, for the (111) crystal face. The observed variation is attributed to the t₂g and e_g symmetry properties of the manganese 3d initial state wavefunctions and is well described by an angle-dependent transition-matrix model. The results are in good agreement with the multi-configurational Hartree-Fock calculations of Viinikka and Bagus.  

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I. INTRODUCTION

Angle-resolved x-ray photoemission (ARXPS) has recently been shown to yield strong directional variations in valence-band spectra with respect to the crystalline axes of single-crystal samples. Two approximate models have been produced to explain the observation of this effect in noble metals, and the validity of the two models has recently been discussed.

In this paper we report ARXPS results obtained for valence bands of manganese fluoride (MnF$_2$) single crystals using AlK$_\alpha$ radiation (h$\nu$ = 1486.6 eV). MnF$_2$ differs from the metallic samples studied previously in being a salt: a ligand field theory interpretation of its electronic energy levels should apply, with the effects of band broadening being small. Thus the d bands in manganese fluoride are narrow and atomic-like. One of the approximate models mentioned above, the angle-dependent transition-matrix model, provides a clear prediction for ARXPS from the system, because MnF$_2$ has octahedral symmetry and clearly defined t$_{2g}$ and e$_g$ energy levels. Thus the correct prediction of angular variations in the spectra from Mn$^{2+}$ 3d-derived valence bands in MnF$_2$ is a test that the transition matrix element model must pass if it is to be taken seriously in other systems (e.g., metals). In this paper we show that the model gives very good agreement with experiment for MnF$_2$. The satisfactory application of the angle-dependent transition-matrix model in this study thus provides further evidence that ARXPS is directly related to the symmetry properties of the initial-state wavefunctions.
A cluster molecular orbital calculation on the MnF$_6^{4-}$ unit of the MnF$_2$ crystal is a useful method of understanding the valence bands of this compound. A simple CNDO calculation of such a cluster reveals that the valence bands consist of an overlapping band of principally F(2s) character at highest binding energy, an overlapping band of principally F(2p) character some 18 eV lower in binding energy and finally at lowest binding energy the t$_{2g}$ and e$_g$ orbitals of principally metal character (an average of 85% Mn(3d) character in this calculation). These results are confirmed by the valence band photoelectron spectrum of MnF$_2$, for which the XPS spectrum has been published and discussed. The ARXPS spectrum reported and discussed in this paper shows a pronounced variation in photoemission energy distributions with electron-emission angles relative to the crystalline axes, for the (111) crystal face. In the angle-dependent transition model these differences can be explained in terms of the variation of the relative t$_{2g}$ and e$_g$ intensities. The curve analysis of a range of ARXPS spectra provides additional information which allows the positions of the overlapping t$_{2g}$ and e$_g$ components to be obtained with more accuracy than that of a single non-ARXPS spectrum. Comparison of these results with cluster molecular-orbital calculations provides a powerful test of these calculations.

II. EXPERIMENTAL

High-resolution x-ray photoelectron spectra were obtained using a Hewlett-Packard 5950A, modified for ultra-high vacuum operation, using monochromatized AlKα radiation. The resolution of the spectrometer
has been measured as 0.55 eV. 11

Single crystals of MnF$_2$ were cleaved along the (111) face and oriented using the Laue back-reflection method. Manganese fluoride has the rutile structure, which is non-cubic; thus the Laue photograph will vary with unit-cell parameters. Analysis of the Laue photographs was facilitated by use of a computer program which calculated and plotted theoretical Laue patterns for manganese fluoride for various crystal surfaces. The MnF$_2$ single crystal was mounted on a holder which allowed the crystal to be rotated under vacuum with the (111) crystal face exposed to the x-rays. This axis of rotation lay at right angles to the z axis and parallel to this face (Fig. 1). The crystal holder was placed in the spectrometer in one of two orientations. In the first, which we shall term the "z+" orientation, the crystal z direction made an angle $0 < 90^\circ$ with the outgoing photoelectrons accepted in the analyzer. In the second orientation, which we call z-, $\theta$ lay between $90^\circ$ and $180^\circ$. The exact arrangement is shown in Fig. 1. The same crystal sample was used for each set of ARXPS studies. The sample chamber pressure was in the range $(5 \times 10^{-10} < P < 5 \times 10^{-9})$. In situ analyses for carbon and oxygen contamination were performed by examining the O(1s) and C(1s) core regions, yielding, in most cases, low levels of these contaminants. To minimize sample charging which can lead not only to binding energy shifts, but also to inhomogeneous line broadening, 12 the samples were bathed with low-energy electrons from an electron flood gun. 13,14 The flood gun settings were determined empirically by plotting the F(1s) full width at half-maximum (FWHM) vs. the flood-gun voltage and current settings. The F(1s) FWHM values were recorded in each ARXPS
study to detect any changes in instrument resolution or line broadening caused by sample charging. Only small changes were observed.

There was a higher contamination level on the crystal surface than in the previously published XPS study, since the crystal could not be cleaved in situ because of the requirement for crystal orientation using Laue photography, and because special care had to be taken not to disorder the crystal surface (to test the effect of disordering the surface ARXPS studies were made with crystals whose surface had been extensively scratched). For the same reason cleaning by argon-ion bombardment was not employed, except in a few cases in which a very short bombardment at very low energy was used. Great care had to be taken in changing the crystal angle because of the fragility of the crystals.

The nominal electron take-off angle from the crystal face for maximum intensity is 35.5°; thus ARXPS studies at this angle had the best statistical accuracy. We estimate the angular accuracy for positioning the samples to be ±3° with a spectrometer solid angle of acceptance of ±(4±1)°.

III. RESULTS AND DISCUSSION

The ARXPS results for the same MnF₂ single crystal are shown in Fig. 2 for three values of the angle θ in the z+ orientation and three values in the z- orientation. Figure 2 shows the lowest binding energy portion of the valence band XPS spectrum of MnF₂. Two distinct peaks are readily observed, the one at higher binding energy being assigned to F(2p) electrons, and the one at lower binding energy being assigned
to Mn(3d) electrons, in agreement with the simple cluster calculation discussed above and earlier assignments. We shall assume for this analysis that the photoemission energy distribution from the F(2p) level is angle-independent. This assumption is justified at least approximately both because no variation of the F(2p) peak shape with angle is observed and because little could be expected, given the number of inequivalent fluorine sites relative to any particular direction. Of course the F(2p) peak need not be simple (and apparently is not, judging from its square-topped appearance), as the F(2p) shell is subject both to (non-cubic) crystal fields and to exchange interaction with Mn\(^{2+}\) ions. For the purposes of this paper, however, we shall regard the F(2p) peak as playing only a fiducial role. The Mn(3d) band peak has a clear asymmetry, which is more pronounced for some of the ARXPS results in Fig. 2 than for others. We assign this asymmetry to the overlapping \(t_{2g}\) and e\(_g\) photoelectron peaks. It is clear from Fig. 2 that if the F(2p) peak is assumed to be angle-independent then the Mn(3d) peak changes shape (though not overall area) in the ARXPS results of Fig. 2. In particular the three \(z^-\) spectra appear very much the same, but they are different from the three comparable \(z^+\) spectra, especially the spectra for \(\theta = 38^\circ\) and \(56^\circ\) in which the Mn(3d) peak is narrower and higher than the F(2p) peak. Figure 3 shows the spectrum of the same region for a different MnF\(_2\) single crystal that has had its surface extensively scratched. To a first approximation this spectrum may be considered intermediate between the two extremes of Fig. 2.
Before proceeding it is appropriate to comment on the quality of the spectra in Fig. 2. Because of the difficulty of this experiment, the statistical accuracy is not as high as we would have desired. The statistical accuracy also worsens from right to left in the figure, as the electron take-off angle becomes more nearly grazing. Also the fits of the curves to the data are far from perfect. This last point will be discussed below. For now the curves may be regarded as simply guides for the eye. We note that the statistical accuracy, while poor on a point-by-point basis, is easily adequate to establish the main point of this paper, viz. that the Mn(3d) peak shows an angular variation. This is obvious by inspection of the spectra. Its most obvious manifestation is that the Mn(3d) peak is higher relative to the F(2p) peak in the low-\( \theta \) \( z^+ \) spectra than in the corresponding \( z^- \) spectra. Less obvious, the mean peak separation is slightly greater in the \( z^+ \) cases. This is also predicted by the model given below. We have chosen to present the raw data in Fig. 2, rather than adding channels or resorting to other smoothing techniques to give the spectra a better appearance. The above features are clear in the raw data, without the curves.

Further analysis of the spectra requires the application of a suitable model for ARXPS to the results. We have applied the angle-dependent transition-matrix model for this purpose. Using this model we may write an expression for the transition matrix element between an initial state of wavevector \( \mathbf{k} \) and energy \( E_{\mathbf{k}}(\mathbf{k}) \) and a plane wave final state of wavevector \( \mathbf{k}_f \) and energy \( E_{\mathbf{k}}(\mathbf{k}) \) as: 

\[
\text{expression for transition matrix element}
\]
for a system of octahedral symmetry, where \( \sigma(t_{2g}) \) and \( \sigma(e_g) \) are the cross-sections of the initial state wavefunctions. Here \( |t_{fi}|^2 \) is proportional to the photoemission energy distribution, and its dependence on the photoemission direction (described by the wavevector \( \mathbf{q} \) of the photoelectron) is contained in the functions \( d_i = d_i(\theta, \phi) \), which are the Fourier transforms of the angular d-orbitals \( d_i(\theta, \phi) \).

Here \( i = 1,2,3 \) corresponds to the \( t_{2g} \) functions \( d_{xy}, d_{yz}, d_{xz} \) and \( i = 4,5 \) represents the \( e_g \) functions \( d_{x^2-y^2}, d_{3z^2-r^2} \). Thus according to the angle-dependent transition-matrix model the ARXPS from the Mn(3d) part of the manganese fluoride valence band spectrum should be a linear combination of the \( e_g \) and \( t_{2g} \) projections of the density of states.

This model is approximate, as noted before, but it gave good results in XPS of noble metals.

The MnF\(_2\) crystal is made up of MnF\(_6\) octahedra, but unfortunately, unlike the cubic metal studied previously, the octahedra are not all stacked in the same direction. Manganese fluoride crystal has two types of octahedra, in equal numbers, rotated 45° to one another (Fig. 4). It is clear from Fig. 4 that a \( t_{2g} \) direction for one type of octahedron is not going to be a \( t_{2g} \) direction for the other type.

Using Equation (1) we may write the photoemission energy distribution (PED) for \( t_{2g} \) and \( e_g \) directions of a single octahedron in terms of angular d-orbitals:

\[
|t_{fi}(k)|^2 \sim 2\sigma(t_{2g}) \left( (d_1)^2 + (d_2)^2 + (d_3)^2 \right) + 3\sigma(e_g) \left( (d_4)^2 + (d_5)^2 \right) \tag{1}
\]
PED(e\(_g\)) \propto \left[ \frac{15}{4\pi} \right] \left[ \frac{1}{4} \sin^4 \theta \left( \cos^2 \phi - \sin^2 \phi \right)^2 + \frac{1}{3} \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)^2 \right] \tag{2}

PED(t\(_{2g}\)) \propto \left[ \frac{15}{4\pi} \right] \left[ \sin^4 \theta \sin^2 \phi \cos^2 \phi + \sin^2 \theta \cos^2 \theta \sin^2 \phi + \sin^2 \theta \cos^2 \theta \cos^2 \phi \right] \tag{3}

giving the expected average values (averaged over all angles of \(\theta\) and \(\phi\)) of 1/2\(\pi\) for e\(_g\) and 3/4\(\pi\) for t\(_{2g}\) directions.

For the manganese fluoride crystal we may use equations (2) and (3) with the appropriate values of \(\theta\) and \(\phi\) for the two types of octahedron (\(\theta\) and \(\phi\) will generally have different values for the two cases) to work out the PED(e\(_g\)) and PED(t\(_{2g}\)) values for a given crystal orientation and photoemission direction. Various crystal orientations and photoemission directions were chosen and the PED(e\(_g\)) and PED(t\(_{2g}\)) values calculated. The experimental arrangement was picked to give the largest variation in these values over the chosen range of angle variation. Figure 5 shows how the amount of t\(_{2g}\) and e\(_g\) character varies as the experimental angle \(\theta\) (Fig. 1) is varied when the crystal is held in the z+ and z- orientation. Figure 5 assumes that the cross sections for Mn3d(t\(_{2g}\)) and Mn3d(e\(_g\)) electrons are the same, thus they show how the total Mn(3d) intensity is composed of a certain percentage of t\(_{2g}\) and e\(_g\) character using the angle-dependent transition-matrix model.

Ligand field theory predicts that the Mn3d(t\(_{2g}\)) and Mn3d(e\(_g\)) electrons will have different binding energies. Thus if the percentage of t\(_{2g}\) and e\(_g\) character varies over a set of ARXPS spectra, then according to the angle-dependent transition-matrix model, so will the shape, but not the overall area, of the Mn(3d) spectra. We have fitted the
experimental spectra shown in Fig. 2 to a spectrum calculated using this model. There is no a priori theoretical reason to use any particular simple peak shape. Various peak shapes were therefore tried in making this fit, including pure Gaussians, Gaussians with tails, Gaussian-Lorentzian mixed peak shapes, and pure Lorentzians with no tail, using a non-linear least squares fitting program. The last shape was found to give the best overall fit to the data, and we have shown these fits. The choice of peak shape will affect numerical values of the $t_{2g}$-$e_g$ separation obtained somewhat, but will not otherwise affect our interpretation. Again we emphasize that details of this fitting procedure are not essential to the main point of this paper. They simply provide a convenient framework for discussion. Other approaches would be equally justified. In Fig. 2 we show the calculated spectrum using five Lorentzians. The peak at highest binding energy is included to improve the overall fit and has little effect on the Mn(3d) region. It may arise partly due to correlation ("shake-up") states and partly due to surface contamination. The next two peaks (peaks 2 and 3) were chosen to represent the F(2p) region. In all cases the separation between peaks 2 and 3 was fixed at 1.63 eV. We are not concerned in this paper with the details of the F(2p) spectrum, and peaks 2 and 3 were chosen to represent the area of the F(2p) region. In the curve fitting procedures the total areas of both the F(2p) region and the Mn(3d) region (peaks 2 and 3, and peaks 4 and 5, respectively) were taken as being angle-independent because they represent a filled shell and a half-filled shell, respectively. Thus the ratio of the areas of these two regions should remain constant for all the ARXPS spectra of
Fig. 2. The two peaks at lowest binding energy (peaks 4 and 5) represent the $t_{2g}$ and $e_g$ components of the Mn(3d) region, respectively. The area ratio $e_g/t_{2g}$ was fixed to the values obtained from the angle-dependent transition-matrix model given in Fig. 4, and the $e_g-t_{2g}$ separation was fixed at 1.0 eV after a number of fits had shown that this value gave the best overall fit to all the spectra in Fig. 2.

The Table lists details of the fits illustrated in Fig. 2, together with the details of the fit to Fig. 3. The Table shows that the derived area ratio Mn(3d)/F(2p) is almost constant within the calculated error, which is also true of the separation of peaks 3 and 4. Further, the calculated FWHM of the $t_{2g}$ and $e_g$ peaks (assumed to be the same) varies in the same way as the FWHM of the F(ls) core peaks (vide supra). It is encouraging to find that the spectrum illustrated in Fig. 3 for a different MnF$_2$ single crystal which has had its surface extensively scratched can be fitted well to an $e_g/t_{2g}$ area ratio corresponding to an average direction. Spectra taken of this sample for other angles and also at z+ show no significant difference in appearance to the spectrum shown in Fig. 3.

The peak positions agree well with those obtained in a previous study. Thus the average positions from the top of the valence band are 2.2 eV (peak 5), 3.2 eV (peak 4), 5.95 eV (peak 3), and 7.58 eV (peak 2).
IV. CONCLUSIONS

The main point of this paper — that angular distributions exist in the Mn(3d) peak of MnF₂ which can be explained by d-orbital directed photoemission (the $t_{2g}/e_g$ effect) — is obvious by visual inspection of the data. The calculated fits to the experimental data give further support to the angular dependent transition matrix model of ARXPS in MnF₂ single crystals. While a converged non-linear least-squares fit rarely represents a unique fit in a particular case, fitting to a range of different ARXPS spectra shows not only the validity of the model, but the use of ARXPS in identifying the position of overlapping valence band peaks, improving the use of x-ray photoelectron spectroscopy as an experimental method for the testing of electronic structure calculations. Thus the $e_g-t_{2g}$ separation of 1.0 eV obtained with this study agrees well with the multiconfigurational Hartree-Fock calculations of Viinikka and Bagus on manganese fluoride clusters.¹⁶

ACKNOWLEDGEMENT

We would like to thank Mrs. Winifred Heppler for obtaining Laue back-reflection photographs of the manganese fluoride single crystals.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$</th>
<th>$z$</th>
<th>Area Ratio $e_g/t_{2g}$ (fixed)</th>
<th>Area Ratio $\frac{(4+5)}{(2+3)}$</th>
<th>Separation $t_{2g}$ (eV) 4-3</th>
<th>$t_{2g}$ &amp; $e_g$ FWHM (eV) (fitted)</th>
<th>F(1s) FWHM (eV) (expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnF$_2$(111) face, mechanically scraped</td>
<td>142°</td>
<td>-</td>
<td>0.67</td>
<td>0.87(3)</td>
<td>2.89(2)</td>
<td>1.74(4)</td>
<td>1.75</td>
</tr>
<tr>
<td>MnF$_2$(111), undamaged face</td>
<td>10°</td>
<td>+</td>
<td>1.39</td>
<td>1.04(8)</td>
<td>2.64(7)</td>
<td>1.96</td>
<td>1.93</td>
</tr>
<tr>
<td>&quot;</td>
<td>38°</td>
<td>+</td>
<td>0.45</td>
<td>0.93(4)</td>
<td>2.85(3)</td>
<td>1.57(3)</td>
<td>1.75</td>
</tr>
<tr>
<td>&quot;</td>
<td>56°</td>
<td>+</td>
<td>0.33</td>
<td>0.92(2)</td>
<td>2.74</td>
<td>1.68</td>
<td>1.75</td>
</tr>
<tr>
<td>&quot;</td>
<td>170°</td>
<td>-</td>
<td>1.63</td>
<td>0.84(19)</td>
<td>2.67(11)</td>
<td>1.97(23)</td>
<td>1.92</td>
</tr>
<tr>
<td>&quot;</td>
<td>149°</td>
<td>-</td>
<td>1.63</td>
<td>0.94(2)</td>
<td>2.71</td>
<td>2.01</td>
<td>1.92</td>
</tr>
<tr>
<td>&quot;</td>
<td>124°</td>
<td>-</td>
<td>1.63</td>
<td>0.94(5)</td>
<td>2.75(4)</td>
<td>2.10(7)</td>
<td>1.88</td>
</tr>
</tbody>
</table>

$a)$ Peaks 4 and 5 are due to $t_{2g}$ and $e_g$ levels. Peaks 2 and 3 are due to mainly fluorine non-bonding electrons. The separation between peaks 4 and 5 is fixed at 1.00 eV, and the separation between peaks 2 and 3 is fixed at 1.63 eV. The area ratio $e_g/t_{2g}$ is fixed at the values shown in all cases. The absence of error information in the table above indicates that the parameter shown has been fixed. All results were fitted with pure Lorentzian peak shapes, with no tail, and convergence with the non-linear least squares fitting method was obtained in all cases. The area ratio peak 3/peak 2 is fixed at 1.332 in all cases.
REFERENCES

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14. Hewlett-Packard Model No. 18622A flood gun was employed for these purposes.


FIGURE CAPTIONS

Fig. 1. Experimental arrangement. The manganese fluoride single crystal geometry. The crystal was held in two ways, with the (111) crystal face exposed to the x-ray beam. The crystal z direction lies in the plane of the (111) face and at right angles to the axis about which the crystal is rotated (to change the angle \( \theta \)). In the first orientation, shown here, the z direction points generally toward the electron analyzer. This is the z+ orientation. In the z- orientation the z axis is reversed.

Fig. 2. X-ray photoelectron spectra for the same MnF\(_2\) single crystal sample in the valence band region for three values of \( \theta \) in the z+ orientation and for three values in the z- orientation. The experimental spectra are compared with spectra calculated for Lorentzian curves using the theory described in the text.

Fig. 3. X-ray photoelectron spectra for a MnF\(_2\) single crystal sample in the valence band region. The (111) face of this crystal had been mechanically scraped. The sample was in the z- orientation, with \( \theta = 142^\circ \). The experimental spectrum is compared with a spectrum calculated using Lorentzian curves with a ratio \( t_{2g}/e_g = 1.5 \), the average value.

Fig. 4.* An overall view of the MnF\(_2\) lattice emphasizing the arrangement of the octahedral chains.

Fig. 5. Graph showing how the amount of \( t_{2g} \) and \( e_g \) character varies as the angle \( \theta \) is varied, according to the theory described in the text.

Fig. 2
Fig. 5
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