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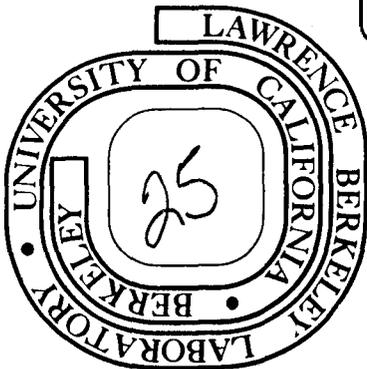
S. P. Kowalczyk, F. R. McFeely, L. Ley, and D. A. Shirley

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MULTIPLY SPLITTING OF X-RAY PHOTOEMISSION
SPECTRA CORE LEVELS IN MAGNETIC METALS*

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ABSTRACT

The results of high resolution x-ray photoemission studies of the multiplet splitting of the 3s core levels in the 3d transition metals and the 4s, 5s, and 4d core-levels in the lanthanide metals are reported.

INTRODUCTION

Measurements of core-level binding energies and valence band density-of-states by x-ray photoemission spectroscopy (XPS), has proved very valuable to the understanding of the electronic structure of solids. For systems with unpaired spin, information about the initial state spin S can in principle be obtained by correlation with the measured splitting of a core level caused by the phenomenon of multiplet splitting.¹ The basis of obtaining S is the use of Van Vleck's Theorem,²

$$\Delta E_{nl} = \frac{2S+1}{2M} G^{nl}(nl, n'l'), \quad (1)$$

where ΔE_{nl} is the splitting of the nl level, G^{nl} is the appropriate atomic exchange integral, and n and n' are the principle quantum numbers of the level measured and the level with the unpaired spin respectively. Unfortunately the situation is not so straightforward. Using (1) overestimates ΔE_{nl} by a factor of ~2 when $n=n'$. It is now understood that this discrepancy is due to intra-shell electron correlations.^{3,4} It will be shown in this paper that by using systems where the correlation effects are nearly the same, measured ΔE_{ns} can still be used to obtain S.

EXPERIMENTAL

High resolution XPS spectra were obtained from the 3d metals Sc through Zn and the rare earth metals La through Lu (excluding Pm). The samples were prepared *in situ* under ultra high vacuum conditions ($<5 \times 10^{-10}$ torr) by either vapor or sputter deposition.⁵

RESULTS AND DISCUSSION

The 3d metals can be divided into 3 classes according to their magnetic properties: paramagnetic (Sc, Ti, V), antiferromagnetic (Cr, Mn), and ferromagnetic (Fe, Co, Ni). Figure 1 shows a typical 3s spectrum of a metal from each of these classes. The Sc spectrum shows a single peak as expected from a band theory explanation of Pauli paramagnetism. Paramagnetic Ti and V exhibit 3s spectra similar to Sc (i.e. no splitting). Antiferromagnetic Cr and α -Mn show sizeable 3s splittings (2.8 and 4.1 eV, respectively). Likewise ferromagnetic Fe, Co and Ni show multiplet structure. Unfortunately the structure can not

be resolved in the cases of Co and Ni due to correlation effects (see Ref. 5 for detailed discussion). Cu and Zn with filled 3d-shells exhibit no multiplet structure in their 3s spectra.

Figure 2 demonstrates how S can be obtained from measured ΔE_{ns} despite large correlation effects. The integral in (1) should be dominated by the atomic core region and be relatively insensitive to bonding effects outside the atomic core. Thus for an atom in various environments, ΔE_{ns} should still be proportional to $2S+1$. By plotting measured ΔE_{ns} vs $2S+1$ of ionic systems, where S is well defined, one obtains an effect a "calibration curve" on which one can place an observed ΔE_{ns} of a metal or an atom in an alloy or a compound and get a value for $2S+1$ or the localized moment. Using this calibration procedure for Fe with an observed $\Delta E_{3s} = 4.5$ eV yields a magnetic moment $\mu = 2.2 \mu_B$ which agrees quite well with the generally accepted value of $2.22 \mu_B$.⁶ This agreement suggests the correlation factor is roughly constant for Fe atoms in different surroundings. Our α -Mn measurements were obtained at room temperature and from the above procedure implied a localized moment with an average value of $\sim 2.5 \mu_B$. This is at odds with neutron diffraction measurements above $100^\circ K$, which set an upper limit of $0.5 \mu_B$ per atom.⁷ This is due to the fact the XPS time scale (10^{-15} sec) is several orders of magnitude faster than neutron diffraction.⁵ The XPS observation of two well defined peaks indicates that all the Mn atoms have a moment close to the average value.

Figure 3 summarizes the results for the 4s and 5s measured splittings for the rare earth metals. The solid lines are Van Vleck's theorem estimates for the metals in their trivalent state. The estimates for ΔE_{4s} have been scaled by 0.55 to account for correlations. The observed values follow the theoretical curve quite well which supports the idea of the near constancy of correlation. Only Eu and Yb significantly deviate and this is due to their divalent character. This suggests that ΔE_{ns} measurements could be applied to the problem of determining valency ratios in mixed valency rare earth compounds. Levels with nonvanishing orbital angular momentum often possess very complicated multiplet structures.^{4b, 8} This structure can be useful as a valency fingerprint. The 4d spectra of La($4f^0$) and γ -Ce($4f^1$) metals are displayed in Fig. 4. One could for instance determine if Ce was tetravalent ($4f^0$) or trivalent ($4f^1$) in a particular compound or alloy. A trivalent Ce 4d spectrum would resemble that of γ -Ce, while tetravalent Ce would exhibit a 4d spectrum similar to La metal which just shows spin-orbit splitting.

FOOTNOTES AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

†IBM Fellow.

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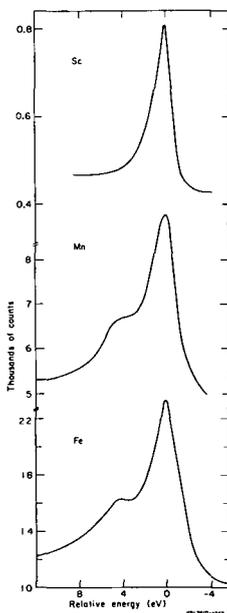
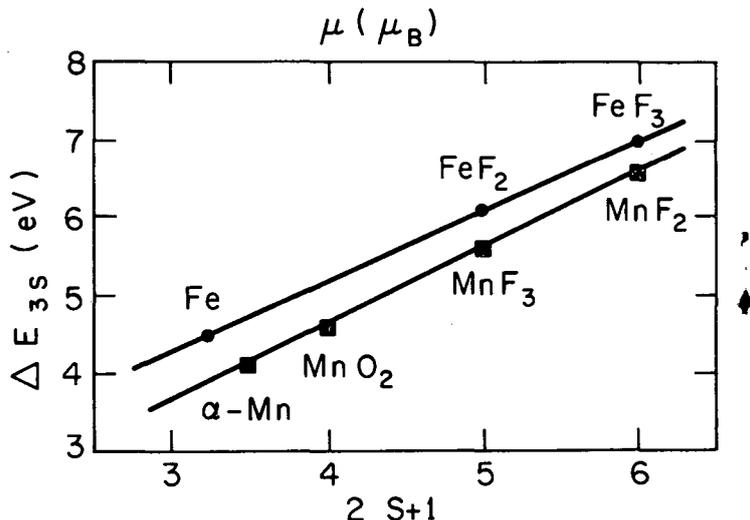


Fig. 1.

XPS 3s spectra of Sc, Mn, and Fe.



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Fig. 2.

Calibration curves for Fe and Mn. Fe, α -Mn, FeF₂ and MnF₂ from data of the authors. FeF₃ and MnF₃ are taken from J.C. Carver, G.K. Schweitzer, and T.A. Carlson, J. Chem. Phys. 57, 973-982 (1972).

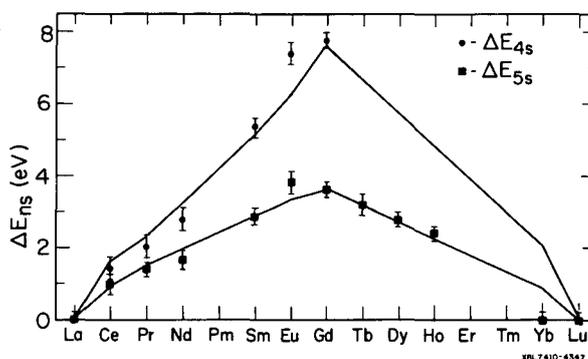


Fig. 3.

Observed 4s (●) and 5s (■) multiplet splitting in the rare earth metals. The solid curves are estimates based on Eq. 1. The 4s estimates have been reduced by a factor 0.55

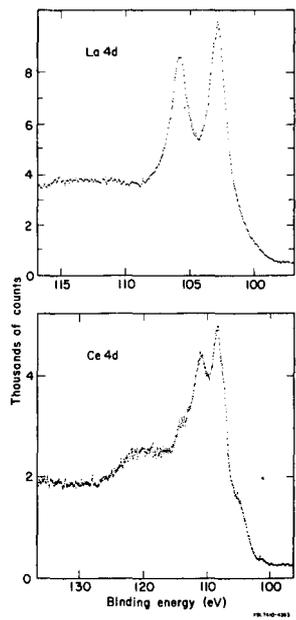


Fig. 4.

La and Ce 4d spectra.

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