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X-Ray Photoelectron Spectroscopy of Various Core Levels of Lanthanide Ions: The Roles of Monopole Excitation and Electrostatic Coupling

A. J. Signorelli and R. G. Hayes

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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We have studied the 4*d* levels of the lanthanide ions in a number of their compounds. The 4*d* levels of the lighter lanthanides lack the satellites which appear on the 3*d* levels. This result is not unexpected if the satellites are due to shakeup of a valence-band electron to a 4*f* level as proposed previously. Limited data on the other levels having $n = 3$ and $n = 4$ are also consistent with this mechanism. We find the 4*d* levels to be affected strongly by electrostatic coupling to the unfilled 4*f* shell. Comparison of experimental spectra with predicted spectra of Ce^{+3} and Yb^{+3} reveals good agreement for Yb^{+3} and fair agreement for Ce^{+3}. Possible reasons for the disagreement between the observed and calculated spectrum for Ce^{+3} are discussed.

I. INTRODUCTION

It was shown recently[1] that the x-ray photoelectron spectra of the solid-rare-earth compounds LF_3 and L_2O_3 (where L is La, Ce, or Pr) have additional structure adjacent to the $3d_{3/2}$ and $3d_{5/2}$ core levels. The satellites were believed to be the result of the transition of a valence-band electron to an empty 4*f* orbital, occurring in parallel with the transition of a 3*d* electron to a continuum state. This process of photoionization and simultaneous outer-shell excitation is referred to as shakeup.[2]

In this paper, we report the findings of our x-ray photoelectron studies on the 4*d* levels of a number of rare-earth compounds, as well as some additional information on the 3*d* core levels of the lighter lanthanides.

We have observed that the 4*d* levels of the lanthanides also show additional structure which can best be explained, at least for the heavier lanthanides, as a result of the electrostatic interaction between a core level and the partially filled 4*f* level. This interaction gives rise to a number of energetically different final states. This phenomenon is commonly referred to as multiplet splitting.[3] For the lighter lanthanides it appears that monopole excitations, or shakeup, is also of importance in the interpretation of the 4*d* spectra. Finally, some qualitative comments are made as to the role of configuration interaction in the 4*d* spectra of the rare-earth trivalent compounds.

II. RESULTS AND DISCUSSION

A. Satellites in Photoelectron Spectra of Light Lanthanides

The satellite lines reported by Wertheim *et al.*[1] and by Jørgensen and Berthou[4] to appear on the high-binding-energy side of the 3*d* levels of LaF_3, CeF_3, and PrF_3 are not, as seen in Figs. 1 and 2, present on the 4*d* levels of the trivalent rare-earth trifluorides. These spectra were measured using a Varian IEE-15 spectrometer, an electrostatic spectrometer which uses a retarding potential.

In LaF_3 the 4*d* region contains a sharp doublet separated by 3.0 eV. This value is in agreement with the theoretically calculated $4d_{5/2}-4d_{3/2}$ spin-orbit splitting of 3.2 eV.[5] Furthermore, the intensity ratio of 1.4:1 agrees with the expected intensity rates for a simple spin-orbit doublet of 6:4 = 1.5:1. As one sees from Fig. 2, the 4*d* regions of CeF_3 and PrF_3 are rather different. In CeF_3 one still sees something of a doublet, but in PrF_3 there is only one line, 8.0 eV wide at half-maximum. The spectra of CeF_3 and PrF_3 will be discussed later in this paper. For the moment we will consider the La^{+3} spectra shown in Fig. 1.

We have examined the 3*s*, 3*p*, and 4*p* levels of La^{+3} in LaF_3, and find that the 4*s* and 4*p* levels lack satellites, whereas the 3*s* and 3*p* levels appear rather broad and skewed, so that the satellites are not resolved clearly.

One sees from Fig. 1 that as the electronegativity of the anions composing the ligand cluster surrounding the La^{+3} decreases, the intensity of the satellites adjacent to the $3d_{3/2}$ and $3d_{5/2}$ core levels increases until, as in $LaBr_3$, the satellites are far more intense than the parent peaks. As previously mentioned, the 4*d* level of LaF_3 is devoid of satellites. In La_2O_3, however, the apparent $4d_{3/2}$ and $4d_{5/2}$ spin-orbit splitting is reduced to 2.7 eV and the intensity ratio is altered from 1.4:1 to 1:1. Finally, in $LaBr_3$ the simple spin-orbit doublet completely disappears and one can see the satellite of $4d_{3/2}$ at the high-energy side of the spectrum. These effects are the result of increased monopole excitation.

The satellites appearing on the 3*d* levels have been assigned to population of an excited state[1] in which an electron is removed from the fluoride 2*p* band and placed in the lanthanide 4*f* level. Our observations support this assignment. The satellites

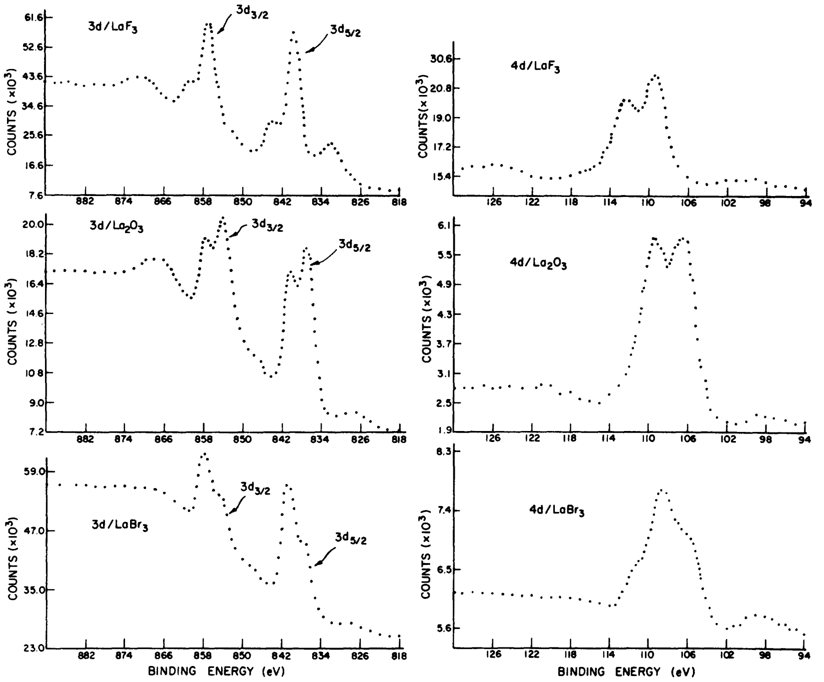

FIG. 1. Comparison of the x-ray photoelectron spectra of the $3d$ and $4d$ regions of three lanthanum compounds. Note that only in LaF_3 is the simple $4d$ spin-orbit doublet observed.

are due to monopole excitation arising from a sudden change in the screening of the valence electrons on removal of a core electron. The outer levels with $n=4$, which have a radial dependence similar to that of $4f$, screen the valence levels much less, so that their removal causes less monopole excitation. In general, the difference between the amount of excitation associated with the $3d$ and $4d$ photoholes is not unexpected. The change in the effective nuclear charge on removal of a $3d$ electron must be near 1.00, whereas that arising from removal of a $4d$ electron should be nearer to 0.35, using Slater's rules.[6]

Furthermore, one can explain the variation in satellite intensity in chemical terms, if one considers La^{+3} with a core hole to be like Ce^{+4} and the excited state of La^{+3} with a core hole plus a ligand electron in an empty $4f$ orbital to be like Ce^{+3}. The probability of going from the ground state La^{+3} to a ground state of La^{+4} by ejection of a core electron decreases in going from F^- to O^{-2} to Br^- with a concomitant increase in the probability of populating the Ce(III)-like excited state. For the tetrapositive cerium the only binary solid compounds known to exist are CeO_2 and CeF_4. We feel that the existence of these two compounds and the nonexistence of the compound Ce(IV)Br_4[7] is borne out by the probability of monopole excitation.

The remarks of the preceding paragraph may be expressed more quantitatively by using a simple molecular-orbital model.

A molecular-orbital model, including the lantha-

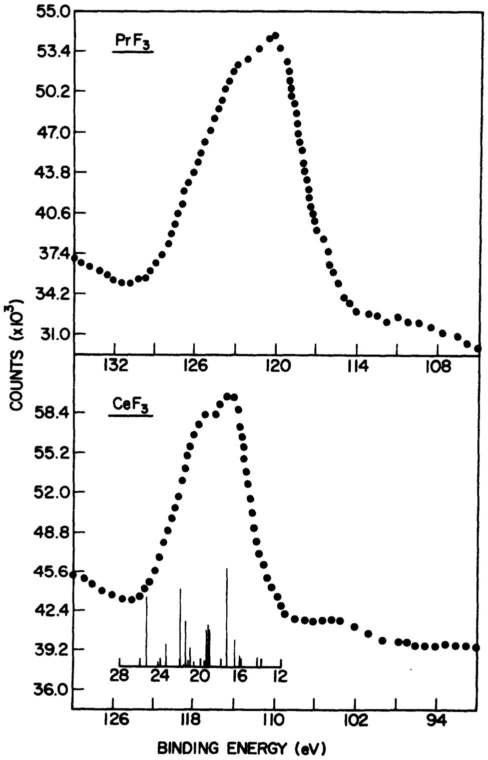

FIG. 2. Spectrum of PrF_3, characteristic of the photon-electron spectra of the $4d$ regions of the ions from Sm^{+3} to Dy^{+3}. Calculated final-state intensities and energy distribution of the $4d^9\,4f^1$ final states for Ce^{+3} are presented.

nide ion and its surrounding cluster, provides a useful approximate description of the system, since the $2p$ band is narrow. In such a model the molecular orbitals of the initial state of the system are the set of f orbitals of the lanthanide ion and a set of symmetry orbitals made up of anion orbitals, which we shall call $\{\chi_j\}$. This choice of initial molecular orbitals reflects the facts that f-orbital covalency in the lanthanides is negligible and that overlap between f orbitals and ligand orbitals is very small.

The final state of the system, in which we have removed a core electron, contains a much more electronegative lanthanide ion, so that one can expect some withdrawal of charge from the anions. We may write a set of bonding molecular orbitals $\{(1-\lambda^2)^{1/2}\chi_j + \lambda f_j\}$ and corresponding antibonding orbitals $\{\lambda\chi_j - (1-\lambda^2)^{1/2} f_i\}$, abbreviated $\{\phi_j\}$ and $\{\psi_j\}$. These are oversimplified, since there may be at least three different λ, but they will serve our purpose. Using these, we find that the ratio of intensity in the satellites (corresponding to occupation of one of the $\{\psi_j\}$ in the final state) to the main line (corresponding to occupation of $\{\phi_j\}$ only) is $7\lambda^2/(1-\lambda^2)$. The factor of 7 accounts for the fact that there are several excited final states.

Examination of the expression for the intensity of the satellite relative to the intensity of the main line reveals that the two lines have equal intensity when λ^2 equals 0.125. This value of λ corresponds to the donation of essentially one electron by the ligands to the metal ion in the ground final state. This is expected to be the case in those compounds of La^{+3} having ligands which do not form stable Ce(IV) compounds, if one is studying $3d$ levels or similar corelike levels. As we have mentioned already, we find that in the case of $LaBr_3$ the satellite is stronger than the main line, and that $CeBr_4$, indeed, does not exist.

The values of λ^2 appropriate to the $3d$ core hole states of LaF_3, La_2O_3, and $LaBr_3$, deduced from the satellite intensities, are 0.05, 0.10, and 0.18, respectively. As we have said, these values are of relevance in describing Ce(IV) compounds. We are unable to estimate values of λ^2 for the $4d$ core hole state because the satellites are not well resolved, but λ^2 is clearly much smaller in each case.

The satellites on the $3d$ hole state fall at different energies in the compounds studied. They are separated from the main lines by 3.2, 2.8, and 2.4 eV in LaF_3, La_2O_3, and $LaBr_3$, respectively. Both the values of λ and the energy separations of the satellites from the main lines may be estimated from a molecular-orbital calculation if one chooses a model Hamiltonian, but we have not attempted such calculations.

It is noteworthy that the molecular-orbital description we have outlined corresponds to the qualitative description of the satellites in terms of excitation of an electron from the anion valence band into the metal f band only in compounds of electronegative anions. In compounds of anions having a smaller electronegativity, the ground final state actually corresponds to transfer of electrons to the metal, and the excited state to the more ionic configuration. If one chose to call the less intense feature the satellite, irrespective of its position, one could say that the satellite moves through the main line, which now always corresponds to the more ionic final state, as the electronegativity of the anion decreases. This is to be expected, of course, because as the $4f$ binding energy in the core hole state becomes greater than the anion valence binding energy, the state involving charge transfer to the metal becomes more stable than the more ionic state.

B. Multiplet Splitting of Lanthanide 4*d* Levels

For the $4d$ regions of the lanthanides, other than La^{+3}, the x-ray photoelectron spectra are complex. Hagström, Hedén, and Löfgren[8] measured the binding energies of the $4d_{3/2}$ and $4d_{5/2}$ core levels in ytterbium metal, which, on the basis of magnetic properties, is doubly charged. They found that the spin-orbit splitting was 8.8 eV. The x-ray photoelectron spectra of several compounds of the ytterbic ion are shown in Fig. 3. The binding energies have been corrected for charging effects by referring all binding energies to the N_{VI} level of a thin gold film deposited over the sample. The binding energy of the N_{VI} level was taken to be 87.0 eV.

The ytterbic-ion spectra do not show a simple spin-orbit doublet, but exhibit a very complex pattern. There may be several explanations for the presence of this structure. The possibility of Auger electrons may be ruled out since the kinetic energy of the outgoing d electron is approximately 1280 eV, so this would require a primary ionization in excess of the photon energy of the Al$K\alpha$ x rays (1486.6 eV). Two other possibilities are chemical decomposition or quantized energy losses suffered by the photoelectron in inelastic collisions in leaving the solid. The latter was suggested by Hagström *et al.*[8] as a possible explanation for the complex spectrum which resulted from oxidized films of ytterbium metal. This energy-loss mechanism should give rise to similar structure in all core levels with similar binding energies.[9] Chemical changes would involve a change in the valence state and since all core levels shift similarly with chemical changes, multiple signals should also be observed in all the core levels. We have investigated the $4s$ and $4p$ levels of the various ytterbic compounds and have found no such structure. We thus rule out chemical decomposition and quantized energy losses as the source of the structure. The absence of structure in the other $n=4$ core levels indicates that the structure in the $4d$ region is not the result of shakeup processes.

The structure is best explained by the electrostatic coupling of a $4d$ photohole to the unfilled valence shell of $Yb^{+3}(4f^{13})$. The possible final states for $4d^9\,4f^{13}$ are $^3(HGFDP)$ and $^1(HGFDP)$ in Russell-Saunders coupling. The final states are quite mixed, however, and prove to be closer to j-j states than to L-S states. We have calculated the energies of the final states using the $4d$-$4f$ Slater-Condon parameters calculated for Yb^0 by Mann[10] and spin-orbit parameters ξ_{4d} and ξ_{4f} published in Ref. 8. The relative positions, in eV, for the various final states are indicated on the inserted scale beneath the ytterbic ion spectra in Fig. 3. The vertical lines on the scale represent the calculated relative intensities of the final states of $4d^9 4f^{13}$.

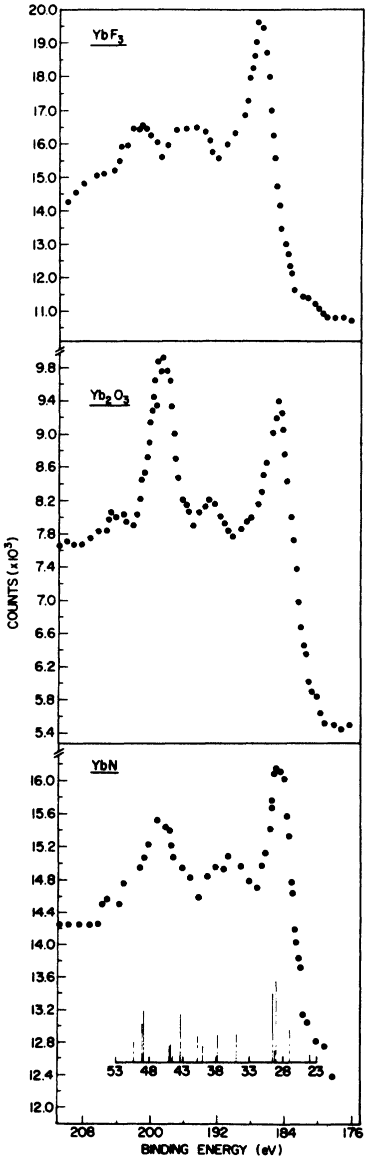

FIG. 3. Spectra of several ytterbic compounds. Calculated relative intensities and energy distribution for the possible $4d^9 4f^{13}$ states are presented.

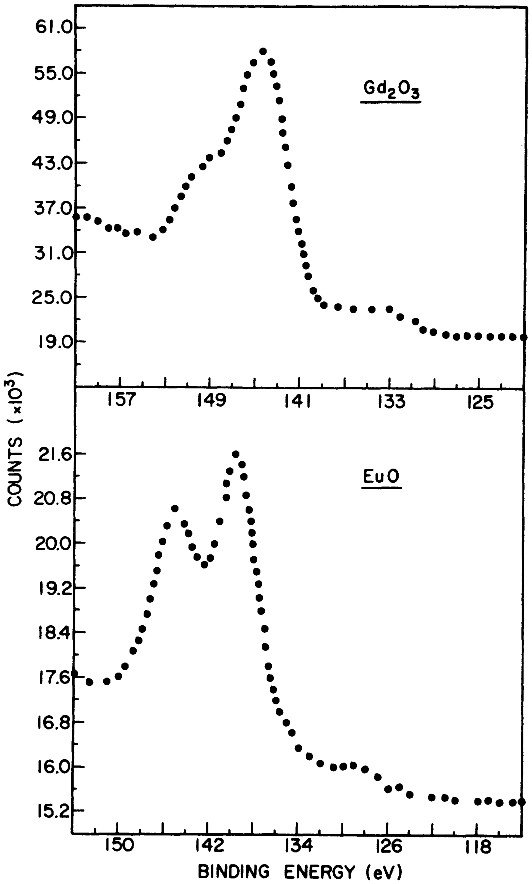

FIG. 4. $4d$ regions of Gd_2O_3 and EuO. The separation between the peaks for Eu^{+2} agrees well with the expected splitting for a spin-orbit doublet.

The intensities may be obtained by expanding the various final states $|J, \alpha\rangle$, where α distinguishes various states having the same J, in j-j coupling. If one writes

$$|J, \alpha\rangle = \sum_{j_1, j_2} \langle J\alpha|j_1 j_2\rangle |j_1 j_2\rangle, \tag{1}$$

where j_1 refers to the d^9 configuration and j_2 to the f^{13} configuration, one may show that

$$I_{J\alpha} \propto (2J+1) \sum_{j_1} |\langle J\alpha|j_1 j_2\rangle|^2, \tag{2}$$

where $I_{J\alpha}$ is the probability of obtaining the final state $|J, \alpha\rangle$. Since the calculation is essentially one involving two electrons only, formula (2) may be obtained by elementary methods.

All intensities represented in Fig. 3 are relative to the most "stretched" final state, $J=6$. We note that the spread in energy, as well as the intensity distribution, reproduces the observed spectrum quite well. We conclude that the complex spectrum of Yb^{+3} is a consequence of $4d$-$4f$ electrostatic interaction.

We have observed similar structures in the x-ray photoelectron spectra of $Er^{+3}(4f^{11})$ in Er_2O_3 and in $Tm^{+3}(4f^{12})$ in Tm_2O_3. We believe that the complex spectra of these ions are also linked to $4f$ electrostatic interaction with the $4d$ photohole. The spectra of these two ions are, however, much more complex, presumably because of the larger number of final states.

There is clear evidence for the role of electrostatic coupling in the photoelectron spectra of the $4d$ regions of the lighter lanthanides also. Of course, such effects are to be expected, since the electrostatic coupling between $4d$ and $4f$ does not change dramatically across the series. We have had less success in accounting for the spectra of the lighter lanthanides quantitatively, however.

The salient features of our data appear in Figs. 2 and 4. As one sees, the $4d$ photoelectron spectra of CeF_3 and PrF_3 are much broader than is that of LaF_3, and the spin-orbit doublet splitting is not observed. The spectra of Sm^{+3}, Nd^{+3}, and Dy^{+3} are similar to that of Pr^{+3}. As Fig. 4 shows, however, the spectra of Gd^{+3} and Eu^{+2} are relatively simple again, and the splitting observed for Eu^{+2} agrees well with the theoretically predicted spin-orbit splitting.[5]

It is clear that one must attribute the peculiar spectra of the $4d$ regions of the lanthanide ions between Ce^{+3} and Dy^{+3} to electrostatic coupling, with its concomitant production of many final states with different energies. The only alternative explanation for the broad spectra due to these ions is that the $4d$ hole state has a very short lifetime in these ions. Such an explanation does not, however, account for the narrowing of the lines again in Eu^{+2} and Gd^{+3}. The lifetime of the $4d$ hole state depends on the rates of the Coster-Kronig processes $N_{IV}N_{VI,VII}N_{VI,VII}$ and $N_VN_{VI,VII}N_{VI,VII}$, which should, on the whole, increase with the number of f electrons.

We have calculated the spectrum to be expected of Ce^{+3}, using Mann's Slater-Condon parameters again, and taking ζ_{4d} from Herman and Skillman's tabulation.[5] The results appear in Fig. 2. As one sees, the results are somewhat less satisfactory than the results of the similar calculation on Yb^{+3}. The spectrum is rather narrower than the predicted spectrum. Reduction of the Slater-Condon parameters cannot improve the fit,[11] because the $4d$ spin-orbit constant is some 3.0 eV, whereas the observed splitting is only some 1.7 eV. We have examined the $4d$ photoelectron spectrum of CeF_4 and have seen that ζ_{4d} is, indeed, some 3.0 eV. The photoelectron spectra of both the $3d$ and $4d$ regions of CeF_4 appear in Fig. 5, which, aside from demonstrating our point, shows that the satellites on both the $3d$ and $4d$ levels are rather stronger in CeF_4 than in LaF_3, as expected.

We can only speculate on the reasons why our calculations fit the spectrum of Yb^{+3} better than that of Ce^{+3}. In general, one might expect correlation effects to be important in $4d$-$4f$ electrostatic splittings, because of the similar radial dependence of $4d$ and $4f$ orbitals. In the similar case of $3s$-$3d$ couplings in the iron series, correlation effects reduce the electrostatic splittings to about half those predicted from theoretical Slater-Condon parameters and make some qualitative changes in the spectrum.[12] The effects of correlation on the $3s$-$3d$ interaction in Mn^{+2} has been accounted for quantitatively. Similarly, the $4s$ exchange splittings in the lanthanides are only about half the values predicted from theoretical Slater-Condon parameters, where-

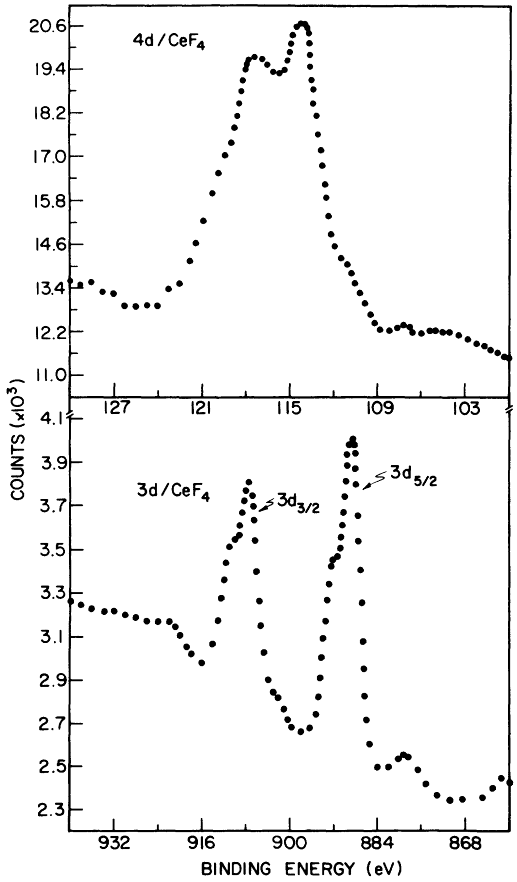

FIG. 5. The simple spin-orbit doublet is present for the $4d$ core level of CeF_4. Note the intensities of the satellites adjacent to the $3d$ levels.

as the 5*s* splittings are predicted well by theoretical Slater-Condon parameters.[13]

The difficulty with the results we have obtained is that, in the other known cases, correlation effects are more or less constant across the series, whereas we find different effects in Ce^{+3} and Yb^{+3}. The only obvious explanation we have for the difference is that there are relatively low-lying excited states, coupled strongly to the ground state by electrostatic interactions, which are available in Ce^{+3} but not in Yb^{+3}. These are states of the type $4d^7 4f^{n+2}$, coupled to a nominal ground state $4d^9 4f^n$. We have not, however, attempted to calculate the effects on the spectrum of the inclusion of such configurations.

III. CONCLUSIONS

Studies of the photoelectron spectra of various levels of the lanthanide ions in several compounds have confirmed the suggestion made previously that an excited final state involving charge transfer between the anions and the metal 4*f* levels is populated in the earlier members of the lanthanide series. It is possible to relate the probability of population of the various final states to parameters describing the interaction between anion valence levels and the metal 4*f* levels in the final core hole state of the system.

Electrostatic coupling between the 4*d* and 4*f* levels, which is predicted to be significant across the series, produces observable, albeit qualitatively distinct, effects in the spectra of both light and heavy lanthanides. Comparison of experimental spectra with predicted spectra of Ce^{+3} and Yb^{+3} reveals good agreement for Yb^{+3} and fair agreement for Ce^{+3}.

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Energy Loss of ^{20}Ne Ions in Aluminum*

K. C. Shane and G. G. Seaman

Department of Physics, Kansas State University, Manhattan, Kansas 66506

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The energy losses of 19.8- and 18.5-MeV ^{20}Ne ions in aluminum have been measured by a new technique. The Doppler-shifted energies of γ rays from the first excited state of ^{20}Ne, produced in the $^{12}C(^{12}C,\alpha)^{20}$Ne reaction, were used to determine the Ne-ion velocities before and after passing through an aluminum foil. The results are in good agreement with expected energy losses, thus removing a discrepancy in earlier work.

I. INTRODUCTION

We present a new method for measuring the energy loss of ions in solids, and apply this technique to measure the energy loss of Ne ions in aluminum at energies of 19.8 and 18.5 MeV. The velocities of Ne ions before and after passing through an aluminum foil are determined by measuring the Doppler shift of γ rays from the 1.633-MeV first excited state of ^{20}Ne.

Measurements of the energy loss of Ne ions in aluminum by Northcliffe[1] from energies of 200 down to 20 MeV are in good agreement with universal curves obtained for C, N, O, and F ions in the

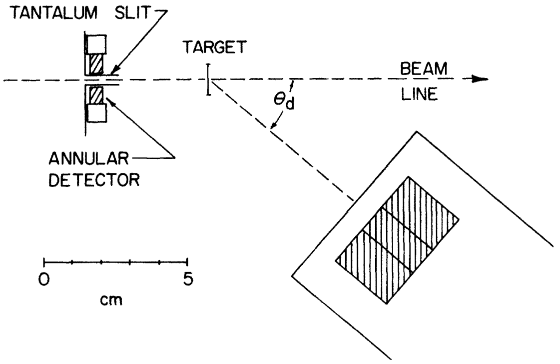

FIG. 1. Physical geometry of the experiment.