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Calculation of multiplet structure of core p-vacancy levels. II

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The multiplet structure of core $2p$-vacancy levels for 36 ions belonging to $3d$ transition metals have been calculated and their plots presented. Only the ground-state configuration $2p^5 3d^n$ ($n = 1,...,9$) is considered for each ion. The spin-orbit interaction has been incorporated exactly, but the crystal-field effect is ignored. While there is general agreement with the available experimental works, higher-energy resolution in x-ray-photoelectron measurements is necessary for detailed comparison of the spectra presented here. On the theoretical side inclusion of crystal field appears to be important. One should go beyond single-configuration approximation to have the observed satellite structure in $2p$-x-ray-photoelectron spectra appear in the calculations.

I. INTRODUCTION

Application of x-ray-photoelectron spectroscopy to the exploration of the inner-shell structure of atoms has acquired a very important usefulness in recent years.[1-12] A wealth of information is now available on the multiplet structure in the x-ray-photoelectron spectra. The structure arises when upon photoionization of a core electron, the angular momenta of the resulting partially filled core shell couple with the angular momenta of various states of the atom before photoionization. In many cases the number of states formed in the photoionization process is so large that a completely generalized treatment of the photovacancy multiplet structure becomes prohibitively computer intensive and so complicated as to be devoid of all physical and chemical understanding of the phenomenon. In a previous paper[13] (hereafter referred as I) the p^5d^5 configuration for the ions Mn^{3+} and Fe^{4+} was considered and their multiplet structure calculated assuming them to be free ions, having spin-orbit interactions, in the crystal field. Recent measurements by Kowalczyk *et al.*[2] are in good agreement with the predictions of I.

The purpose of this communication is to report the calculations for p^5d^n ($n=1,\cdots,9$) configurations, thereby extending the calculations of I to most of the $3d$-transition-metal ions. The effect of spin-orbit interaction has been rigorously considered, but the crystal-field effect was found too cumbersome to include following the procedure of I. It is found that the application of Löwdin's projection-operator technique[14] is more direct and manageable for the calculation of crystal-field states of p^5d^n configuration from the knowledge of the crystal-field states of the parent configuration d^n than the one used in I. McWeeny's theory[15] also appears to be of value for such calculations. Application of the projection-operator method to the calculation of the multiplet structure of core vacancy levels of atoms in a crystal field will be reported elsewhere.

Free-ion multiplet structure arising due to $2p$ photoejection from 36 transition-metal ions has been calculated in this paper. While there is general agreement of the calculated spectra with the available experimental studies, higher-energy resolution in the x-ray-photoelectron measurements is required for detailed comparison of the results obtained in the present investigation. On the other hand, the crystal field appears to play a significant role.[16] The effect of the crystal field is expected to be trivial on the *splitting* of the eigenstates calculated for free ions. However, the ground state of an ion in a crystal field may be different from that of the free ion, and could be split. This would lead to significant *redistribution* of the intensity of certain spectral lines. Since the ground state of free ions is generally a high-spin state, the spectra calculated in the present study are expected to resemble more closely those observed in high-spin complexes. In addition to the crystal-field effect, one needs to consider configurations other than the ground-state configuration in order to have the observed satellite structure[4,7,9] in $2p$-x-ray-photoelectron spectra appear in the calculations.

II. CALCULATIONS

Essential algebra required to do the calculations for p^5d^n ($n=1,\cdots,9$) is very similar to that given in I and will not be repeated here. Four cases, p^5d^1 and p^5d^9, p^5d^2 and p^5d^8, p^5d^3 and p^5d^7, and p^5d^4 and p^5d^6, will be considered separately. The configuration p^5d^5 has already been considered in I.

A. Configurations p^5d^1 and p^5d^9

The parent configurations d^1 and d^9 have only one state ^2D possible. p^5d^1 and p^5d^9 can have ^3F, ^3D, ^3P, ^1F, ^1D, and ^1P states. The spin-orbit coupled angular momenta for them are, respectively, 4, 3, 2; 3, 2, 1; 1, 0; 3; 2; and 1. There are thus 12 J states in all. The representative ions considered are Sc^{2+}, Ti^{3+}, V^{4+}, and Cr^{5+} having the prephotoionized configuration d^1; and Ni$^+$, Cu^{2+}, and Zn^{3+}, having the configuration d^9.

B. Configurations p^5d^2 and p^5d^8

The parent configurations d^2 and d^8 have ^3F as the ground state. The ^3F state, when coupled with a p vacancy, could give rise to ^4G, ^4F, ^4D, ^2G, ^2F, and ^2D states, which could also be obtained by coupling ^3P, ^1G, and ^1D states of the parent configuration[17] with the p vacancy. In the self-explanatory notation,[17] one could write all relevant states for p^5d^2 and p^5d^8 configurations as

$$^4G(^3F,\,p),\quad ^4F(^3F,\,p),\quad ^4D(^3F,\,p;\,^3P,\,p),$$

$$^2G(^3F,\,p;\,^1G,\,p),\quad ^2F(^3F,\,p;\,^1G,\,p;\,^1D,\,p),$$

$$^2D(^3F,\,p;\,^3P,\,p;\,^1D,\,p)\,.$$

These 12 terms have 32 J states in all. The representative ions considered are Sc$^+$, Ti^{2+}, V^{3+}, and Cr^{4+} having prephotoionized configuration d^2; and Co$^+$, Ni^{2+}, Cu^{3+}, and Zn^{4+} having the configuration d^8.

C. Configurations p^5d^3 and p^5d^7

The parent configurations d^3 and d^7 have ^4F as the ground state. The ^4F state, when coupled with a p vacancy, could give rise to ^5G, ^5F, ^5D, ^3G, ^3F, and ^3D states. The states are also obtainable by coupling ^4P, ^2H, ^2G, ^2F, $^2D_1$, $^2D_2$, and ^2P states of the parent configurations[17] with the p vacancy:

$$^5G(^4F,\,p),\quad ^5F(^4F,\,p),\quad ^5D(^4F,\,p;\,^4P,\,p),$$

$$^3G(^4F,\,p;\,^2H,\,p;\,^2G,\,p;\,^2F,\,p),$$

$$^3F(^4F,\,p;\,^2G,\,p;\,^2F,\,p;\,^2D_1,\,p;\,^2D_2,\,p),$$

$$^3D(^4F,\,p;\,^4P,\,p;\,^2F,\,p;\,^2D_1,\,p;\,^2D_2,\,p;\,^2P,\,p)\,.$$

The 19 terms have 65 J states in all. Representative ions considered are Ti$^+$, V^{2+}, Cr^{3+}, Mn^{4+}, and Fe^{5+} for prephotoionized configuration d^3; and Fe$^+$, Co^{2+}, Ni^{3+}, and Cu^{4+} for the configuration d^7.

D. Configurations p^5d^4 and p^5d^6

The d^4 and d^6 configurations have ^5D term as the free-ion ground state. The ^5D state coupled with a p vacancy gives rise to ^6F, ^6D, ^6P, ^4F, ^4D, and ^4P terms. These terms could also be obtained by coupling ^3G, $^3F_1$, $^3F_2$, ^3D, $^3P_1$, and $^3P_2$ terms of the parent configuration[17] with the p vacancy:

$$^6F(^5D,\,p),\quad ^6D(^5D,\,p),\quad ^6P(^5D,\,p),$$

$$^4F(^5D,\,p;\,^3G,\,p;\,^3F_1,\,p;\,^3F_2,\,p;\,^3D,\,p),$$

$$^4D(^5D,\,p;\,^3F_1,\,p;\,^3F_2,\,p;\,^3D,\,p;\,^3P_1,\,p;\,^3P_2,\,p),$$

$$^4P(^5D,\,p;\,^3D,\,p;\,^3P_1,\,p;\,^3P_2,\,p)\,.$$

These 18 terms have 70 J states. The representative ions considered in this work are V$^+$, Cr^{2+}, Mn^{3+}, and Fe^{4+} for d^4 configuration; and Mn$^+$, Fe^{2+}, Co^{3+}, and Ni^{4+} for d^6 configuration before photoionization.

In addition, the calculations are reported for Cr$^+$ and Co^{4+} as well as for Mn^{2+} and Fe^{3+} having prephotoionized configuration d^5. For Mn^{2+} and Fe^{3+} the results were published earlier,[13] but these are included here for completeness and to facilitate comparison with other ions.

The electrostatic interaction[13] $(\sum_d 1/r_{pd})$ matrix elements for d^np configuration have been tabulated by Slater.[17] For d^5d^n configuration the change could be very easily incorporated with the rule: For p^5d^n configuration, use the matrix elements corresponding to the pd^{10-n} configuration.

The spin-orbit matrix elements were calculated using Eq. (4) of I, which was derived for pd^n configuration. The p^5d^n configuration could easily be accommodated by changing the sign of the first term in the equation. Further, one could use the matrix elements of V[11] for p^5d^n $(n \leq 5)$ configurations and change their signs while considering p^5d^{10-n} configurations. Clementi's wave functions[18] for the ions before photoionization were used in the computations.

The inclusion of the crystal-field effect has not been attempted in this work. However, it is easy to see that it could not be omitted for p^5d^n configurations, in general, on the grounds that the effect was found trivial for p^5d^5 configuration.[13] The crystal field is effective in two ways. One is in the energy-eigenstates calculation by including the crystal-field operator in the Hamiltonian of the ion, as was done in I. The other is in the redistribution of the intensity due to the fact that the ground term in the crystal field before photoionization is constituted by the states which are nondegenerate except when the ground term is S state. One then needs to consider the crystal-field symmetry-adapted eigenstates for the parent configuration d^n to construct the states for the photoionized-ion configuration p^5d^n. Splitting and rearrangement of various terms of the parent configuration due to the crystal field makes it necessary to reformulate the intensity distribution by including the probability distribution of the relevant crystal-field states of the lowest energy. Löwdin's projection-operator technique[14] appears to be very convenient for such calculations. The results utilizing the technique will be reported elsewhere.

III. RESULTS AND DISCUSSION

The results obtained in this study are presented in Figs. 1–4 in such a format as to provide an easy comparison of the spectra for all ions with the same atomic number, as well as with the spectra of other ions. These are arbitrarily grouped for the convenience of presentation and economy of space. It is difficult to assign a particular ionic charge to a transition-metal ion in a complex, due to the covalency effect. The observed multiplet structure in photoelectron spectra could then be expected to correspond to something between the spectrum for the conventionally ascribed ionic state and those having the charges one lower or one higher. However, this point should not be given too much emphasis since there are various other atomic and solid-state factors which could significantly change the multiplet structure. As argued above, a strong crystal field (and possibly the covalency and overlap effects) could lead to the redistribution of intensity of various eigenstates in a spectrum. The zero energy of each spectrum in a group is arbitrary.

There have been some measurements reported on $2p$-photoelectron spectra of certain transition-metal ions. These are difficult to reproduce accurately from the original publications and, therefore, are not drawn in the figures. The full width at half-maximum (Γ) for all the lines theoretically calculated was taken as 1 eV and the intensities fitted to the Gaussian shape. The $\Gamma = 1$ eV value was chosen in order to be consistent with the claimed resolution of many x-ray-photoelectron spectra (XPS). However, the intrinsic line broadening has not been estimated or fitted to the Lorentzian distribution.

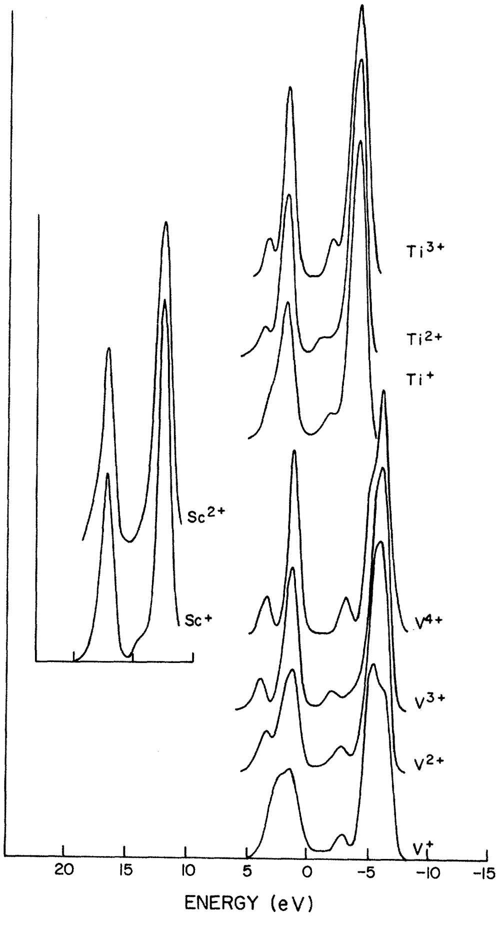

FIG. 1. Multiplet structure of $2p$ vacancies created in the ions as labeled. The zero energy is arbitrary and the intensity normalization is same for all spectra shown.

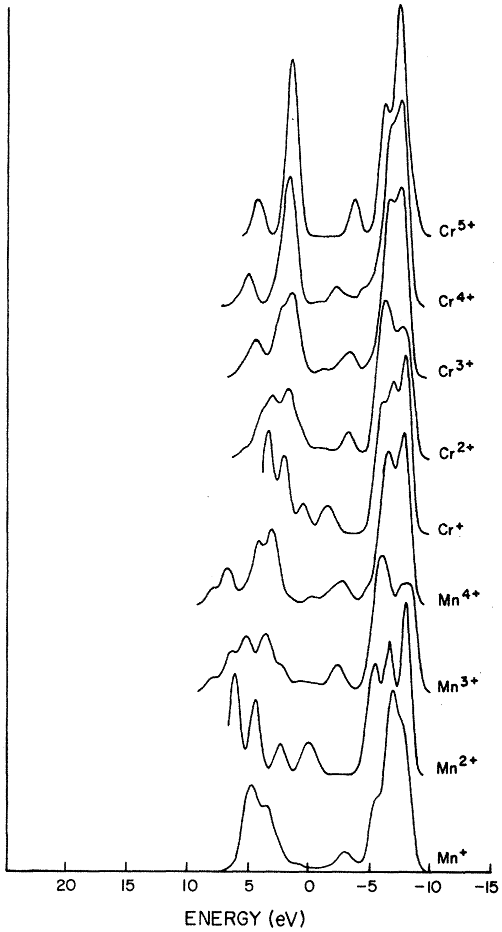

FIG. 2. Description is same as for Fig. 1.

It is seen from the figures that there is significant structure present in most spectra. The inclusion of the crystal field has been made in an approximate way by Asada *et al.*[16] for Ni^{2+} in its complexes and has been shown to be significant. However, it may need further investigation to see if the structure in the spectra reduce in general with the inclusion of a crystal field. Comparison of the spectra presented here with the various experimental investigations[1–8, 11] appears to establish that the multiplet splitting and the shake-up processes are both important in the $2p$-vacancy spectra of $3d$-transition-metal ions. While the presence of the shake-up effect has been emphasized in most papers, the importance of the multiplet structure has been unambiguously proved by Kowalczyk *et al.*[2] in

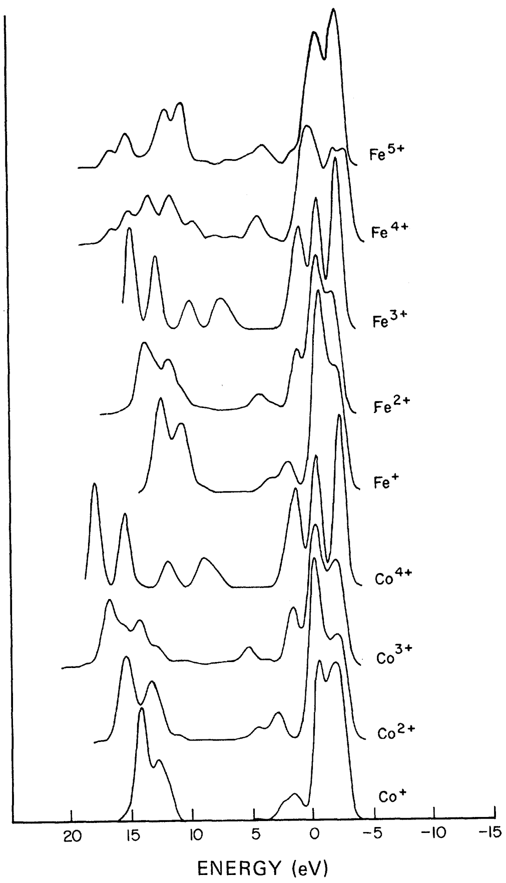

FIG. 3. Description is same as for Fig. 1.

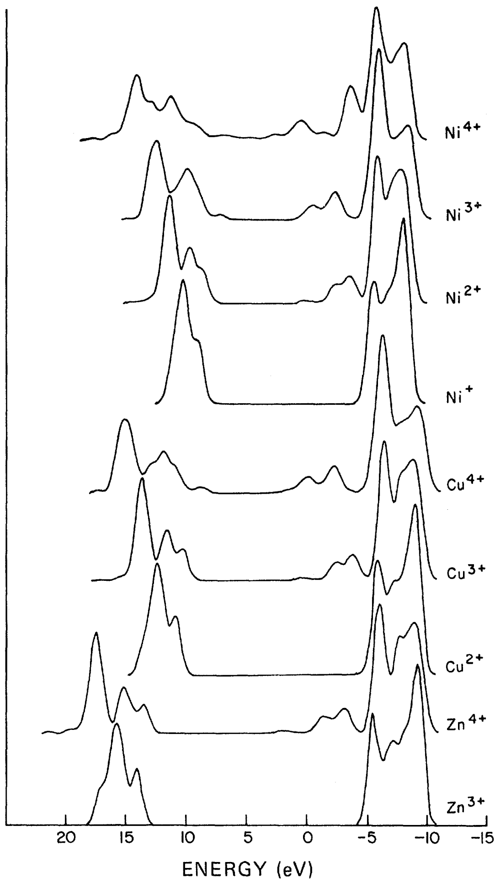

FIG. 4. Description is same as for Fig. 1.

their recent XPS measurement on the manganese $2p$ levels in MnF_2.

It may be noted that the calculations presented here may be extended to include ionic configurations other than the ground-state configuration considered in this work. Such multiconfiguration multiplet-structure calculations will automatically and naturally also predict the so-called shake-up satellites.

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