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Electron energy-loss spectra and secondary-electron emission spectra of Zr, ZrN and ZrO₂

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Abstract. Electron energy-loss spectra and secondary-electron emission spectra have been measured for Zr, ZrN and ZrO₂. The position and shape of the measured peaks associated with 4p-electron excitation are consistent with the multiplets calculated for zirconium ions possible in Zr, ZrN and ZrO₂.

1. Introduction

Much interest has recently been attracted to the process of the excitation and relaxation, such as the Auger and direct recombination processes, of outermost p electrons in transition metals. These processes are closely related to the resonance effect observed in photoemission [1]. The atomic theory has been shown to give a possible explanation of the excitation and relaxation of the outermost p electrons in some transition metals [1–5]. In a number of transition metals, especially in their compounds, however, the details of these processes have not been fully understood. The understanding of these processes is crucial for the analysis of the resonant photoemission in the compounds.

Excitation spectra for 4p electrons in zirconium compounds (ZrN [6–8], ZrO₂ [9–14]) and zirconium alloys [15] have been investigated by electron energy-loss spectroscopy (EELS) and resonant photoemission. In spite of the difference in chemical environments around zirconium atoms in these compounds and alloys, all the spectra measured have in common a dominant feature at around 40 eV, which has an energy and shape quite similar to that observed for zirconium [3–6, 9, 11–13]. No conclusive interpretation, however, has been reported on this behaviour of the spectra. Recently, Vanini *et al* applying Fano's theory to the $4p^64d^2-4p^54d^3$ atomic multiplet transition, have successfully explained the excitation spectra for 4p electrons in zirconium [4, 5]. They attributed the success in their explanation using the atomic model to the large Coulomb interaction between 4p and 4d electrons compared with the 4d-band width and to the rapid decay of the excited states. If the large Coulomb interaction and the rapid decay apply also to the case of the zirconium compounds, then the excitation spectra are expected to be determined by the multiplet structure of zirconium ions in the compounds. There have been no reports in which the excitation spectra for the zirconium compounds are compared with the multiplet structure of the zirconium ions.

In the present study, we measure EELS spectra and secondary-electron emission (SES) spectra of Zr, ZrN and ZrO₂. We show that the EELS peaks corresponding to the excitation of 4p electrons are consistent with the multiplets calculated for the zirconium ions. The physical origin of this consistency is briefly discussed.

2. Experimental details

We measured Auger electron (AES), EELS and SES spectra using a Varian single-pass cylindrical mirror analyser with a resolution (E/dE) of 200 and with its axis 30° to the normal of the specimen surface. The AES spectra were measured in derivative mode with a primary-electron beam of 3 keV. In order to obtain the accurate intensity and avoid the effect of the additional complication in the spectra resulting from the use of derivative mode, we measured the EELS and SES spectra in pulse-counting mode with primary-electron beams of 130–500 eV. All measurements were done in an ultra-high-vacuum system which had a base pressure of the order of 10^{-8} Pa.

We used a polycrystalline zirconium foil of dimensions 25 mm \times 5 mm \times 0.025 mm and 99.99% purity as a specimen. It was mechanically polished, ultrasonically degreased in acetone and spotwelded onto two tantalum support wires of 0.8 mm in diameter. The specimen was heated by passing an AC current through it. The temperature of the specimen was measured with Pt–PtRh13% thermocouple spotwelded to the specimen. The surface of the specimen was cleaned by repeating Ar^+ bombardment at 773 K and annealing at 1073 K. After this heat treatment we found no impurities on the specimen surface within the detection limit of AES.

The zirconium surface was nitrided by heating the specimen for 5 min at 1073 K under a nitrogen gas pressure of 1.3×10^{-2} Pa. The concentration of nitrogen in the surface of the specimen was estimated to be $N/Zr \approx 1.0$ from the intensity of the N(KLL) Auger peak by using the relative sensitivity factor [16]. The specimen surface was oxidized by exposing the zirconium surface to the oxygen gas ($P_{\text{O}_2} = 1.3 \times 10^{-4}$ Pa) for 100 seconds (100 L) at room temperature. In this paper, we will refer to the samples nitrided and oxidized in this way as ZrN and ZrO₂.

3. Method of calculating multiplets

We calculated for Zr, Zr⁺, Zr²⁺, Zr³⁺ and Zr⁴⁺ the energy of transition between the multiplets of electronic configurations ($4p^6 4d^n 5s^2 - 4p^5 4d^{n+1} 5s^2$, $4p^6 4d^{n+1} 5s - 4p^5 4d^{n+2} 5s$, $4p^6 4d^{n+2} 5s^0 - 4p^5 4d^{n+3} 5s^0$) within the *LS*-coupling scheme following the method described in [17]. In this method, the radial wave functions, which are required in calculating radial integrals ($I(nl)$, F^k , G^k), were obtained by solving self-consistently the non-relativistic Hartree–Fock equation for each electronic configuration. We have solved the radial wave functions within the local density approximation (LDA) [18], using the Perdew and Zunger form of the exchange and correlation energy and potential. In order to make correction for the many-body effects, Hartree–Fock values of F^k and G^k were scaled down to 80% of their original values when calculating those parts of energy matrix elements other than the average energy of a configuration [20, 21]. We have assumed the ground state of a configuration to be a multiplet term with the minimum energy. The transition energy was calculated as the difference in energy between the terms in the ground state and excited state. The transition probability between the terms was calculated within the dipole approximation by using the values in the table reported by Shore *et al* [22].

4. Results

4.1. EELS and SES spectra

Figure 1, (a)–(c), shows the EELS spectra measured for Zr, ZrN and ZrO₂ at incidence energies 130, 200 and 500 eV. Each spectrum has a dominant and broad peak at around 40 eV, a small peak at 30–35 eV and a weak and broad peak at around 55 eV. Judging from the positions of these three peaks, we assign the first and second peaks to the excitation of 4p electrons of the zirconium atom. The broad peak at around 55 eV is probably due to the excitation of the 4s electron of the zirconium atom and will not be discussed in this paper.

We notice the following with respect to the dominant peak at around 40 eV: (i) on nitriding or oxidation, the position of this peak shifts 2–3 eV to high energy and its width becomes narrow; and (ii) the width of this peak is narrower in ZrO₂ than in ZrN and its position is almost the same in these two samples. The weak peak observed at 30–35 eV tends to decay with increasing primary-electron energy. Vanini *et al* examined this behaviour in the EELS spectra of zirconium, and they assigned this peak to a non-dipole transition [5]. The peak observed at 30–35 eV in ZrN and ZrO₂ is expected to be due also to the non-dipole transition.

Figure 2 shows the SES spectra of Zr, ZrN and ZrO₂. We have added the work function of the spectrometer 5 eV to the measured kinetic energy, and the kinetic energy is shown relative to the Fermi energy E_F of each sample. Three features can be seen in figure 2. According to the interpretation proposed for these three peaks in the SES spectra of Zr and ZrO₂ [11–13, 23], we make assignment of them as follows. The feature below 15 eV corresponds to the emission of the true secondary electron and the peak at 20–30 eV corresponds to the N₂₃VV Auger emission. The broad feature above the N₂₃VV Auger peak would be due to the emission of a valence electron through direct recombination of an excited 4p electron with a 4p hole left behind it. We notice that the intensity of this emission relative to that of the N₂₃VV Auger emission increases in order of Zr, ZrN and ZrO₂. A similar enhancement caused by oxidation of 3d transition metals [24] and zirconium [12] has been reported and attributed to the decrease in the d electrons in them. The observed increase in the relative intensity implies the similar decrease in 4d electrons in the order of Zr, ZrN and ZrO₂.

4.2. Multiplet structures calculated for zirconium ions

Figure 3, (a)–(e), shows the energy and intensity calculated for $4p^6 4d^n 5s^2 - 4p^5 4d^{n+1} 5s^2$, $4p^6 4d^{n+1} 5s - 4p^5 4d^{n+2} 5s$ and $4p^6 4d^{n+2} 5s^0 - 4p^5 4d^{n+3} 5s^0$ transitions in zirconium ions. Here, $n = 2 \sim n = -2$ corresponds to the case of (a) Zr ~ (e) Zr⁴⁺. The overall shape of the intensity distribution calculated for the $4p^6 4d^2 5s^2 - 4p^5 4d^3 5s^2$ transition well agrees with the reported calculation in which the spin-orbit interaction was considered [4, 5]. This suggests that the overall shape of the intensity distributions calculated for those other than the $4p^6 4d^2 5s^2 - 4p^5 4d^3 5s^2$ transition also remains unchanged if the spin-orbit interaction is included in the present calculation.

Figure 3 indicates that the transitions between the multiplets have large intensities in the energy range 3–40 eV for all the electronic configurations assumed for the zirconium ions except for the $4p^6 4d^4 5s^0 - 4p^5 4d^5 5s^0$ transition, which has large intensities in the range 30–35 eV. The contribution of the $4p^6 4d^4 5s^0 - 4p^5 4d^5 5s^0$ transition has been excluded because the energy of the ground-state term of the $4p^6 4d^4 5s^0$ configuration is much larger ($\Delta E \simeq 2$ eV) than those of the $4p^6 4d^2 5s^2$ and $4p^6 4d^3 5s$ configurations and their difference is small

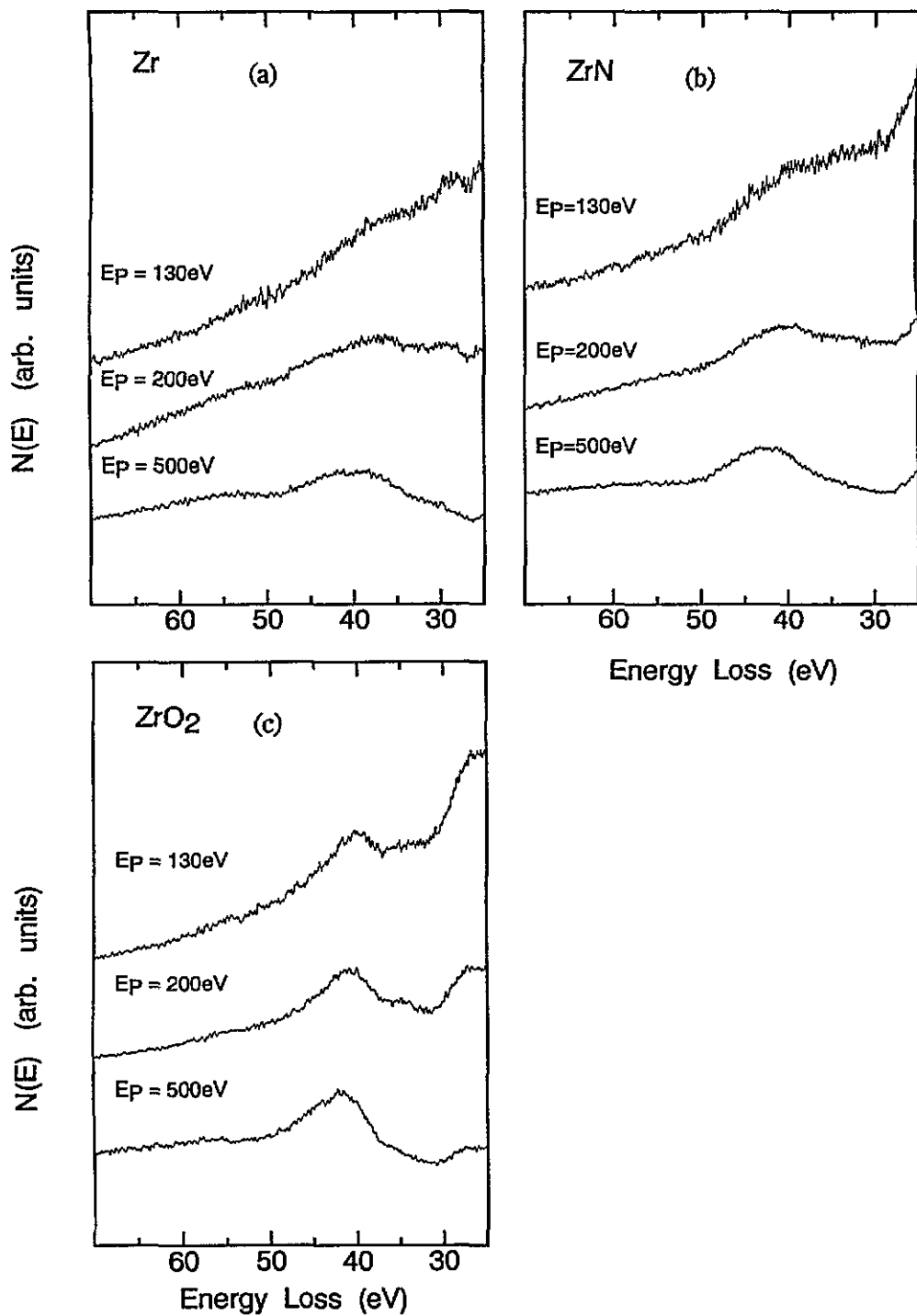


Figure 1. The electron energy-loss spectra of (a) Zr, (b) ZrN and (c) ZrO_2 measured with the primary-electron energy shown.

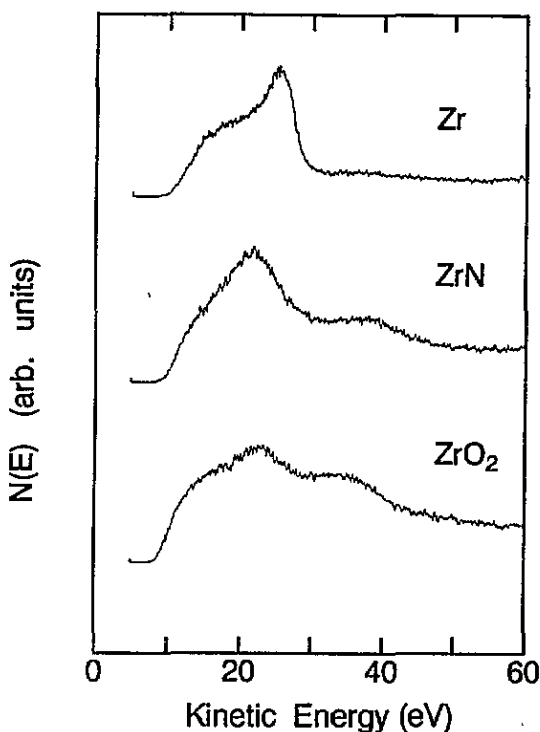


Figure 2. The secondary-electron emission spectra of Zr, ZrN and ZrO₂ measured with the primary-electron beams at 500 eV. The kinetic energy is relative to E_F of each sample.

($\Delta E \approx 0.3$ eV).

The intensity distributions, except for the $4p^6 4d^4 5s^0 - 4p^5 4d^5 5s^0$ transition, have the following characteristics: (i) for the electronic configurations with the same number of 4d electrons, the distributions are quite similar to each other and their positions shift to higher energy as the number of 5s electrons decreases; (ii) for the electronic configurations with the same number of 5s electrons, they shift to higher energy as the number of 4d electrons decreases; (iii) Their width tends to decrease as the number of 4d electrons decreases and is almost independent of the number of 5s electrons.

4.3. Comparison between the EELS spectra and the multiplet structures

The position and shape of the EELS peaks associated with 4p-electron excitation observed for Zr, ZrN and ZrO₂ are discussed on the basis of the multiplet structures of the zirconium ions in these samples. Figure 3 shows that the zirconium ions in Zr, ZrN and ZrO₂ are capable of intense transitions in the energy range 35–40 eV. To show an example of a comparison of experiments with calculations, we present in figure 4 the EELS spectra of Zr, ZrN and ZrO₂ measured with the primary-electron energy of 500 eV and, below each spectrum, the multiplet transitions calculated for Zr ($4p^6 4d^2 5s^2 - 4p^5 4d^3 5s^2$), Zr³⁺ ($4p^6 4d^1 5s^0 - 4p^5 4d^2 5s^0$) and Zr⁴⁺ ($4p^6 4d^0 5s^0 - 4p^5 4d^1 5s^0$). The energies of the EELS peaks are a few eV higher than those of intense transitions and the peaks are broad. These behaviours can be interpreted as resulting from the shift of energies and broadening of peaks corresponding to these transitions owing to the auto-ionization [25]. This interpretation is

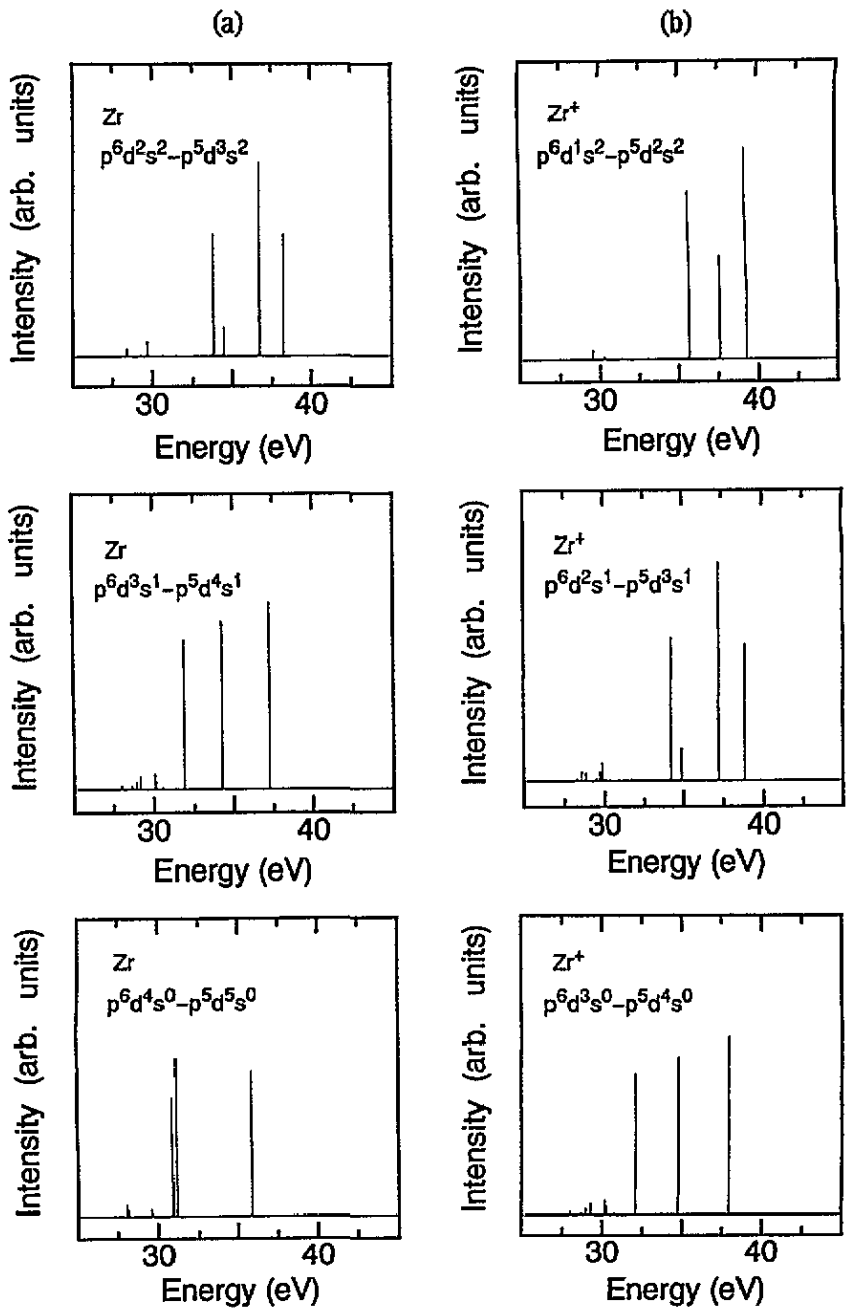


Figure 3. The energy and intensity between $4p^64d^n5s^2-4p^54d^{n+1}5s^2$, $4p^64d^{n+1}5s-4p^54d^{n+2}5s$, $4p^64d^{n+2}5s^0-4p^54d^{n+3}5s^0$ transitions calculated for (a) Zr, (b) Zr⁺, (c) Zr²⁺, (d) Zr³⁺ and (e) Zr⁴⁺.

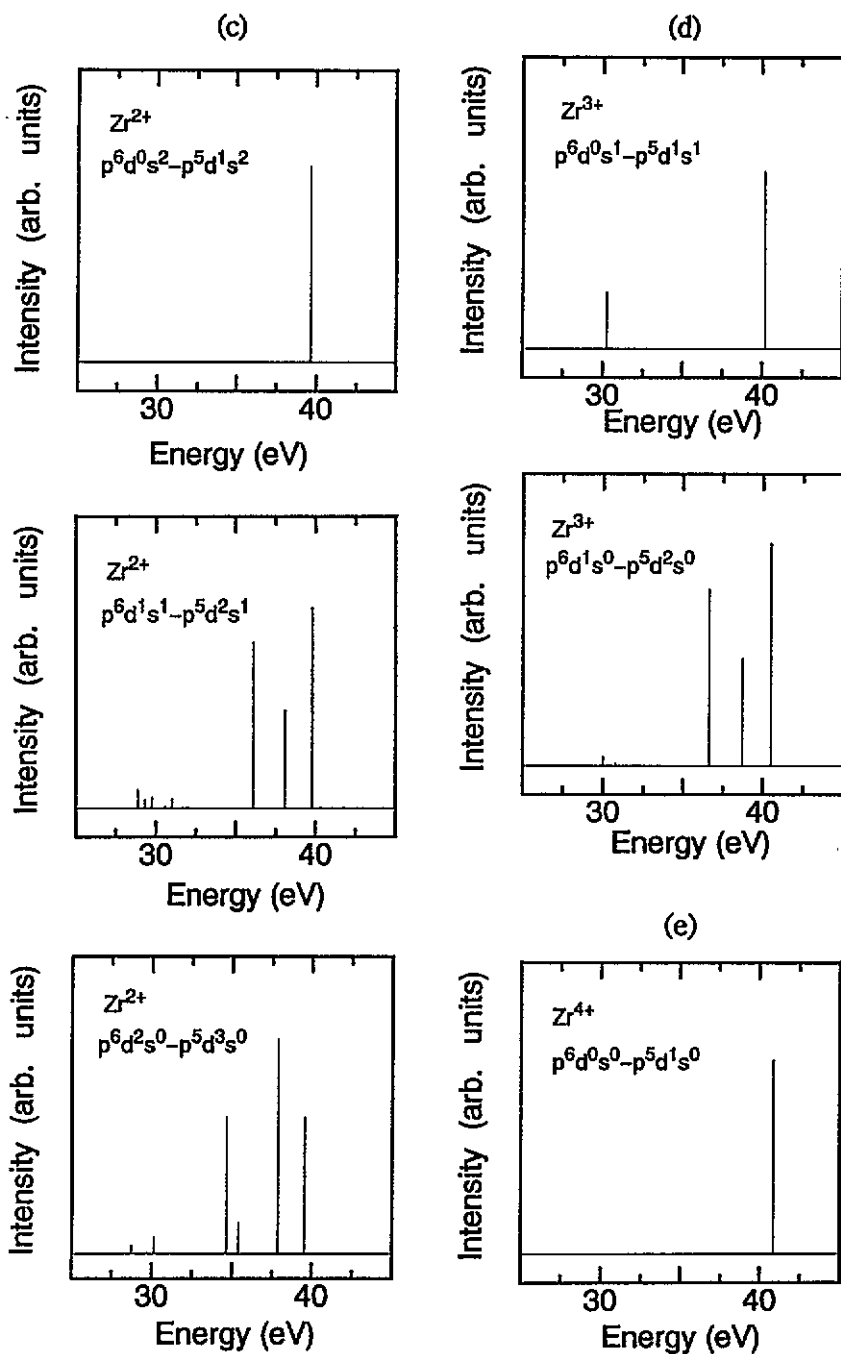


Figure 3. (Continued)

supported by the fact that the peaks due to the auto-ionization, such as in the $N_{23}VV$ Auger and direct recombination processes, are actually observed in the SES spectra of these three samples.

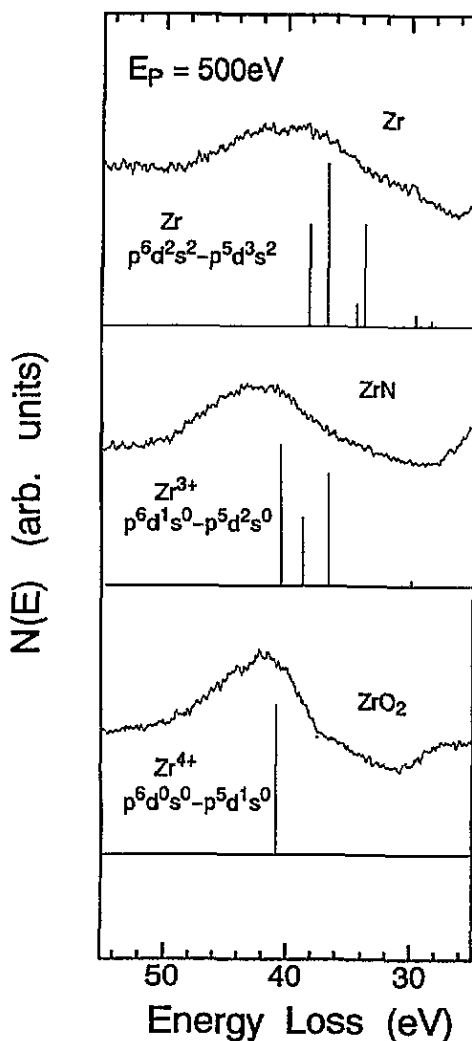


Figure 4. The electron energy-loss spectra of Zr, ZrN and ZrO₂ measured with the primary-electron energy of 500 eV. The energy and intensity of the multiplet transitions calculated for Zr ($4p^64d^25s^2-4p^54d^35s^2$), Zr³⁺ ($4p^64d^15s^0-4p^54d^25s^0$) and Zr⁴⁺ ($4p^64d^05s^0-4p^54d^15s^0$) are shown by vertical bars below the spectra of Zr, ZrN and ZrO₂, respectively.

We now compare the change in the EELS peak caused by nitriding and oxidation with the change in the multiplet structures caused by the decrease in 4d and 5s electrons. The number of 4d and 5s electrons is expected to decrease in the order Zr, ZrN, and ZrO₂ because the energy-band calculation for Zr [26], ZrN [27] and ZrO₂ [28, 29] shows that the partial charge of s and d electrons inside the muffin-tin sphere around a zirconium atom decreases in this order. The expectation is also consistent with the change in the relative intensity of the emission due to the direct recombination. (See figure 2.) In addition, the result of the multiplet structure calculation in the preceding section indicates that the

intensity distribution for the transition between the multiplets of the zirconium ions in solid Zr, ZrN and ZrO₂ becomes narrow in this order. This is consistent with the decrease in the width of the EELS peaks observed for these solids (figure 1). Furthermore, the peak of the distribution is expected to shift to higher energy in the same order. This expectation is consistent with the EELS peaks observed for Zr and ZrN. However, the fact that the positions of the observed EELS peaks in the spectra of ZrN and ZrO₂ almost coincide cannot be explained solely by the change in the multiplet structure with the number of 4d and 5s electrons. For a further discussion about this, we need to discuss details of the line shape [30] using the multiplet structure calculated with the effect of the crystal field included.

5. Discussion

We will briefly discuss the origin of the fact that the multiplet structure of the zirconium ions can give an explanation of the overall shape of the EELS peaks observed for Zr, ZrN and ZrO₂. For Zr, Vanini *et al* suggested that the success of the use of the atomic model in explaining the spectra was due to the Coulomb interaction between 4p and 4d electrons being large compared with the 4d-band width [4, 5]. This condition applies also to the case of ZrN and ZrO₂ for the following reasons. First, there is no significant change in the magnitude of the dispersion of 4d bands. (They are less than 0.3 Ryd for Zr [26, 31, 32], 0.4 Ryd for ZrN [27] and 0.3 Ryd for ZrO₂ [33, 34].) Secondly, the magnitude of the calculated Coulomb and exchange integrals, i.e. $F^2(4p, 4d)$, $G^1(4p, 4d)$, $G^3(4p, 4d)$, which determine the multiplet structure, tends to increase with the decrease in the number of 4d or 5s electrons. This indicates that the Coulomb interaction between 4p and 4d electrons increases in the order Zr, ZrN, ZrO₂ because the number of 4d and 5s electrons decreases in this order. The atomic model can thus give a reasonable explanation of the EELS spectra of Zr, ZrN and ZrO₂.

The multiplet calculation in which the effects of the crystal field are included has been successfully applied to the explanation of the excitation spectra of core electrons of some transition metal compounds [1]. In the present case, however, the crystal field can have minor effects on the excitation spectra because the magnitude of the multiplet splittings due to the Coulomb interaction is expected to be much larger than that due to the crystal field. In fact, we can estimate the latter from the crystal-field parameter ($10Dq$). Its value for ZrN and ZrO₂ would not be very different from that of TiO₂, i.e. 1.8 eV [21]. This value is much smaller than the magnitude of the multiplet splittings. (See figure 3.) The overall shape of the multiplet structures shown in figure 3 therefore is not much altered by the effect of the crystal field.

6. Conclusion

We have measured the electron energy-loss and secondary-electron emission spectra for Zr, ZrN and ZrO₂. The position and width of the EELS peaks associated with 4p-electron excitation in these samples have been found to be consistent with the multiplet structure of the zirconium ions. This indicates that the consideration of the intra-atomic interaction is crucial for discussing the excitation spectra of 4p electrons of Zr, ZrN and ZrO₂.

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