

Electron energy loss spectra of Sc, Ti, V and their oxides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 L463

(<http://iopscience.iop.org/0953-8984/7/35/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:01

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Electron energy loss spectra of Sc, Ti, V and their oxides

Mitsunori Kurahashi, Masahiro Yamamoto and Shizuo Naito

Institute of Atomic Energy, Kyoto University, Uji, Kyoto 611, Japan

Received 4 July 1995

Abstract. Electron energy loss spectra have been investigated for Sc, Ti, V and their oxidized surfaces. The position and shape of the measured peaks associated with the 3p electron excitation are found to be consistent with $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transitions calculated for isolated Sc, Ti and V ions.

In the past decade, the excitation of 3p electrons in 3d transition metals (TM) and their compounds has attracted much interest [1] because it is closely related to resonant photoemission, which has been used for studying the electronic structure of TM compounds and their surfaces [1–8]. The details of the excitation in some 3d TMs and their compounds, however, have not been fully understood. Many authors [1–30] have reported unusual behaviour of the excitation spectra for 3p electrons of Sc, Ti, V and their compounds; the peaks associated with 3p electron excitation appear at energies 10 eV or more larger than the binding energies of the 3p electrons and their positions for the compounds almost completely coincide with those for the corresponding metals. It has been suggested that the origin of this behaviour is the quasi-atomic transitions localized at the site of the TM atoms [1–30]. The $3p^6 3d^n - 3p^5 3d^{n+1}$ transitions calculated for isolated Ti and V atoms have been shown to give a possible explanation of the excitation spectra for Ti [11] and V [11, 19, 20]. No conclusive explanation, however, has been reported on this behaviour of Sc and the compounds of Sc, Ti and V.

In the previous paper [31], we have demonstrated that the excitation spectra for 4p electrons in Zr, ZrN and ZrO₂ reflect the characteristics of the $4p^6 4d^n 5s^m - 4p^5 4d^{n+1} 5s^m$ transitions calculated for isolated Zr ions. The discussion in the previous paper is expected to apply better to the present case because the electrons involved in the 3p electron excitation in the Sc, Ti and V compounds are more localized than those in the 4p electron excitation in the Zr compounds. In the present study, we examine the electron energy loss spectra (EELS) of Sc, Ti, V and their oxidized surfaces and show that the EELS peaks associated with the 3p electron excitation are consistent with the $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transitions calculated for the isolated Sc, Ti and V ions.

We measured the EELS spectra of Ti and V and their oxides. The details of the experimental set-up and procedure for measurements have been described in the previous paper [31]. Samples used are polycrystalline titanium and vanadium foils of 99.95% purity. To obtain the oxides we heated the titanium foil to 773 K for 3 minutes under an oxygen gas pressure of 1.3×10^{-2} Pa and the vanadium foil to 673 K for 5 minutes under an oxygen gas pressure of 1.3×10^{-3} Pa. Auger spectra measured for these surfaces showed a good agreement with those reported for TiO₂ [32] and V₆O₁₃ [33].

Figures 1(a) and (b) show the EELS spectra measured for Ti, V and their oxidized surfaces at an incidence energy of 500 eV. Figure 1(c) shows the reported EELS spectra

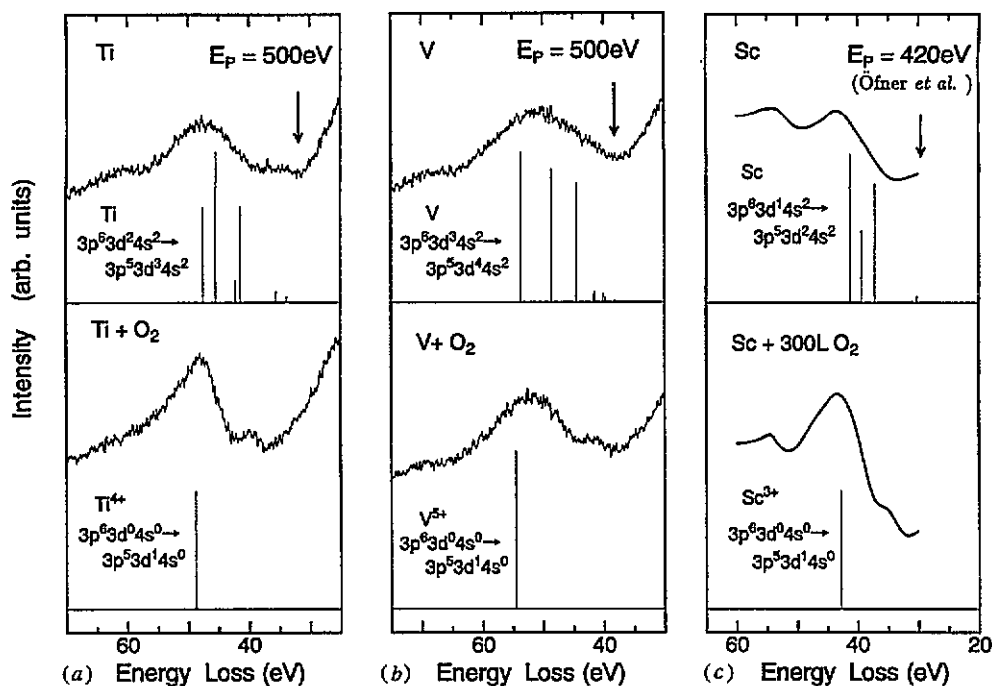


Figure 1. The electron energy loss spectra of (a) Ti, (b) V, (c) Sc (upper panel) and their oxidized surfaces (lower panel) measured with the primary electron energy shown. The thick solid lines in (c) show the spectra reported by Öfner *et al.* [34]. The energy and intensity of the $3p^6 3d^n 4s^2 - 3p^5 3d^{n+1} 4s^2$ transition calculated for Sc ($n = 1$), Ti ($n = 2$), V ($n = 3$), and the $3p^6 3d^0 4s^0 - 3p^5 3d^1 4s^0$ transition calculated for Sc^{3+} , Ti^{4+} , V^{5+} are shown by vertical bars below the measured spectra of these metals and their oxidized surfaces.

measured, with primary electron energy of 420 eV, for Sc and for its surface exposed to oxygen gas of 300 L ($1 \text{ L} \equiv 1.0 \times 10^{-6} \text{ Torr s}$) [34]. The vertical arrows in the figures indicate the 3p thresholds for Sc, Ti and V determined by x-ray photoelectron spectroscopy [35]. Each spectrum has three peaks: (I) a dominant peak at an energy ≈ 15 eV higher than the 3p threshold, (II) a small peak at an energy ≈ 10 eV lower than the dominant peak and (III) a weak peak at energy 10–20 eV higher than the dominant peak. The peak (II) for metallic Ti, V and their oxidized surfaces has been found to decay with increasing primary electron energy. This suggests that the peak (II) is due to some non-allowed transitions [31, 36]. The peak (III) is probably due to the excitation of 3s electrons and will not be discussed in this article. We note the following behaviour of the dominant peaks in the measured EELS spectra. On oxidizing Ti and V, the width of the peak tends to become narrow and its centre to shift slightly (by less than 1 eV) to a higher energy. No significant difference, however, is found in the positions and widths of the peaks for Sc and its oxide.

In order to discuss the measured EELS spectra, we have calculated, within the *LS* coupling scheme, the energies and intensities of possible $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transitions for isolated Sc, Ti and V ions. The details of the procedure of calculations have been described in the previous paper [31]. The results are shown in figures 2–4. By using these results, we discuss below the EELS spectra of Sc, Ti and V and their changes induced by oxidation.

The EELS spectra of Sc, Ti and V are now compared with the transitions calculated

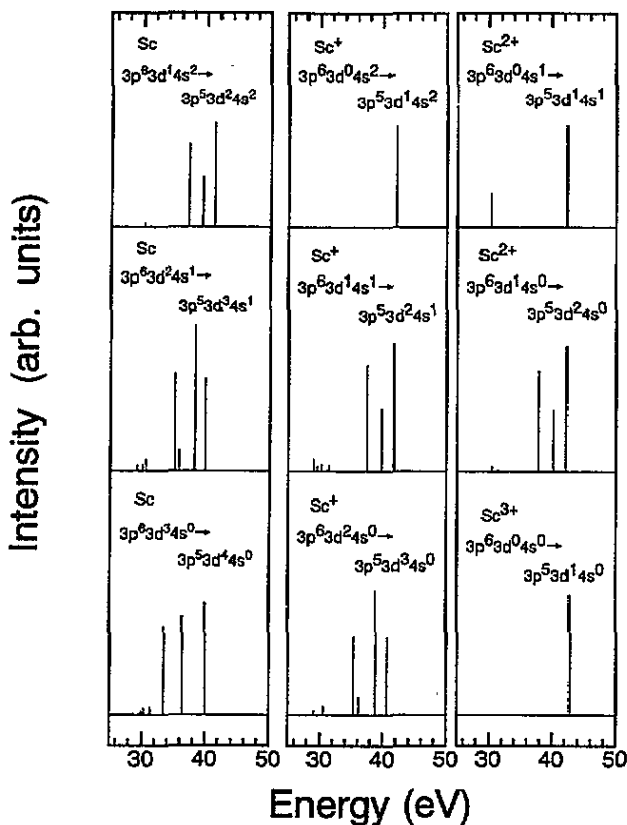


Figure 2. The energy and intensity of the $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transition calculated for Sc ions.

for isolated, neutral Sc, Ti and V atoms. We discuss three electronic configurations (i.e. $3p^6 3d^n 4s^2$, $3p^6 3d^{n+1} 4s^1$ and $3p^6 3d^{n+2} 4s^0$) for Sc ($n = 1$), Ti ($n = 2$) and V ($n = 3$) atoms in the metallic state. For the isolated Sc, Ti and V atoms, the energy of the ground state term calculated for the $3p^6 3d^n 4s^2$ configuration is found to be lower than for the other two configurations. We first consider the case where Sc, Ti and V atoms take the $3p^6 3d^n 4s^2$ configurations in the metallic state as well. Figure 1 shows the energies and intensities of the $3p^6 3d^n 4s^2 - 3p^5 3d^{n+1} 4s^2$ transitions calculated for these atoms. We can see that intense transitions lie at energies 10–15 eV larger than the 3p thresholds and the most intense transitions agree well with the measured EELS peaks. This is consistent with the behaviour of the EELS peaks for these metals. We next consider the case where Sc, Ti and V atoms take the $3p^6 3d^{n+1} 4s^1$ configurations in the metallic state. The intensity distribution of the $3p^6 3d^{n+1} 4s^1 - 3p^5 3d^{n+2} 4s^1$ transitions calculated for Sc and Ti are also consistent with the behaviour of the EELS peaks for Sc and Ti (figures 2 and 3). For V, however, the intensity distribution of the calculated $3p^6 3d^4 4s^1 - 3p^5 3d^5 4s^1$ transition does not reflect the EELS spectra of V (figure 4). This is possibly because of a small contribution of the $3p^6 3d^4 4s^1$ configuration of the V atom to the spectra. In this article, we will not consider the $3p^6 3d^{n+2} 4s^0$ configuration of Sc, Ti and V atoms in the metallic state because the energy calculated for this configuration of the isolated Sc, Ti and V atoms is much larger than for the other two configurations.

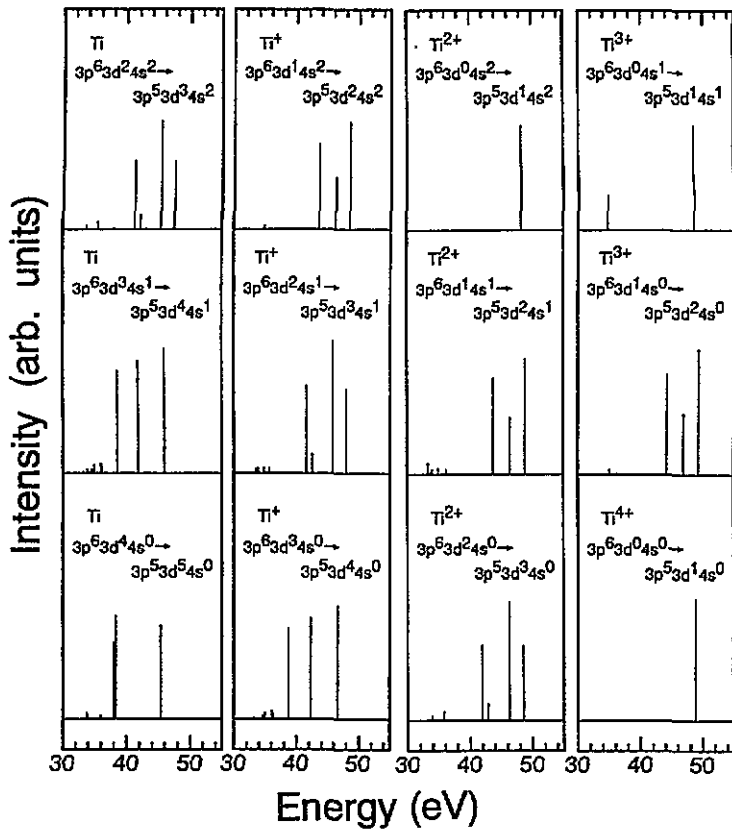


Figure 3. The energy and intensity of the $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transition calculated for Ti ions.

On oxidation of Sc, Ti and V, the density of 3d and 4s electrons in the site of these metal atoms is expected to decrease. We therefore compare the change in the EELS spectra of these metals induced by oxidation with the change in the calculated $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transitions with the decrease in the number of the 3d and 4s electrons. According to the above discussion, the EELS spectra of Sc, Ti and V are expected to be dominated by the $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transitions in which the number of 3d electrons (n) is less than three. These transitions calculated for isolated Sc, Ti and V ions (figures 2–4) include the following changes with the decrease in the number of 3d or 4s electrons: (i) the intensity distribution is almost independent of the number of 4s electrons, (ii) the distribution tends to become narrower and the average energy to shift to a higher energy as the number of 3d electrons decreases and (iii) the most intense transition shifts only slightly (by less than 2 eV) as the numbers of 3d and 4s electrons decrease. To show an example of a comparison between the experimental and calculated results, we present in figure 1 the energies and intensities of $3p^6 3d^0 4s^0 - 3p^5 3d^1 4s^0$ transitions below the spectra measured for oxidized Sc, Ti and V. From figure 1, we can see that the position of the EELS peak of Sc, Ti and V only slightly changes (within 1 eV) on oxidation. This is consistent with the change (iii). On oxidizing Ti and V, the decrease in the width of the EELS peak and the shift in its centre to a high energy have been observed. This is consistent with the change (ii). However, similar changes in the EELS peak have not been found in the oxidation of Sc. The reason

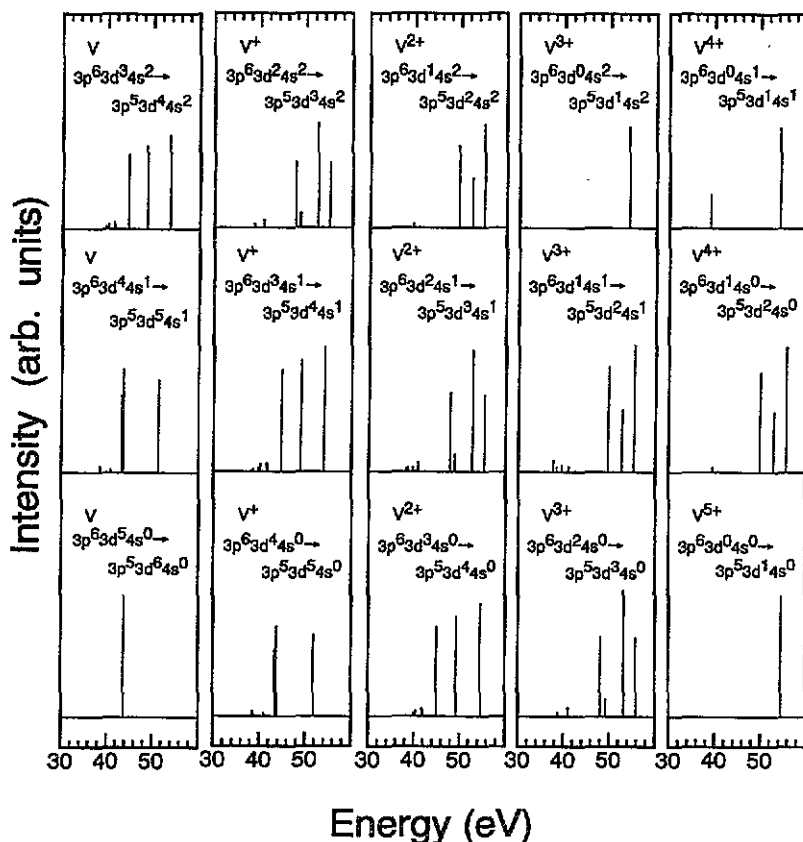


Figure 4. The energy and intensity of the $3p^6 3d^n 4s^m - 3p^5 3d^{n+1} 4s^m$ transition calculated for V ions.

for this observation may be that the spread of the transitions calculated for isolated Sc ions and its change with the decrease in the number of 3d electrons are smaller than those for Ti and V ions.

We briefly discuss the origin of the consistency between the EELS peaks associated with the 3p electron excitation and the transitions calculated for the isolated Sc, Ti and V ions. The factors that are likely to affect the behaviour of the 3p electron excitation are Coulomb interaction between 3p and 3d electrons, spin-orbit interaction, crystal field parameter ($10Dq$) and dispersion of 3d band. In the present calculation, only the Coulomb interaction between 3p and 3d electrons has been considered. As can be seen from figures 1-4, the splitting of the transition energies caused by the Coulomb interaction is more than 15 eV. This value is much larger than the splitting of the 3p level due to the spin-orbit interaction (less than 1 eV for these metals [35]), the value of $10Dq$ (less than 3 eV for Sc_2O_3 , TiO_2 and VF_3 [37, 38]) and the dispersion of 3d bands (less than 5 eV for these metals [39, 40], their oxides [41] and TiO_2 [42]). This is thus the origin of the consistency between the EELS spectra and the present calculation.

We mention that it has been known that the position of the peak in the excitation spectrum for 3p electrons in Sc, Ti and V compounds other than their oxides also agrees well with that in Sc, Ti and V [1-3, 24-30]. This is consistent with the result of the present

calculation that the position of the most intense transition remains within 2 eV with the change in the number of 3d or 4s electrons.

In summary, we have examined the electron energy loss spectra of Sc, Ti, V and their oxidized surfaces and shown that the position and shape of the EELS peak associated with the 3p electron excitation in these samples are consistent with the $3p^6 3d^n 4s^m \rightarrow 3p^5 3d^{n+1} 4s^m$ transitions calculated for the isolated Sc, Ti and V ions.

References

- [1] Davis L C 1986 *J. Appl. Phys.* **59** R25
- [2] Brookes N B, Law D S-L, Padmore T S, Warburton D R and Thornton G 1986 *Solid State Commun.* **57** 473
- [3] Courths R, Cord B and Saalfeld H 1989 *Solid State Commun.* **70** 1047
- [4] Smith K E and Henrich V E 1988 *Solid State Commun.* **68** 29
- [5] Smith K E and Henrich V E 1988 *Phys. Rev. B* **38** 9571
- [6] Zhang Z, Jeng S P and Henrich V E 1991 *Phys. Rev. B* **43** 12004
- [7] Heise R, Courths R and Witzel S 1992 *Solid State Commun.* **84** 599
- [8] Diebold U, Tao H, Shinn N D and Madey T 1994 *Phys. Rev. B* **50** 14 474
- [9] Zajac G, Bader S D, Arko A J and Zak J 1984 *Phys. Rev. B* **29** 5491
- [10] McKay J M, Mohamed M H and Henrich V E 1987 *Phys. Rev. B* **35** 4304
- [11] Farnoux F C and Lamoureux M 1974 *Proc. 4th Int. Conf. on Vacuum Ultraviolet Radiation Physics* ed E E Koch *et al* (Hamburg: Pergamon) pp 89-91
- [12] Wehenkel C and Gauthé B 1974 *Phys. Lett.* **47A** 253
- [13] Bertel E, Stockbauer R and Madey T E 1983 *Phys. Rev. B* **27** 1939
- [14] Bertel E, Stockbauer R, Kurtz R L, Madey T E and Ramaker D E 1985 *Surf. Sci.* **152/153** 776
- [15] Barth J, Gerken F and Kunz C 1985 *Phys. Rev. B* **31** 2022
- [16] Smith K E and Henrich V E 1988 *Phys. Rev. B* **38** 5965
- [17] Goodman K W and Henrich V E 1994 *Phys. Rev. B* **50** 10 450
- [18] Bader S D, Zajac G and Zak J 1983 *Phys. Rev. Lett.* **50** 1211
- [19] Bader S D, Zagac G, Arko A J, Brodsky M B, Morrison T I, Zaluzec N, Zak J, Benbow R L and Hurteh Z 1986 *Phys. Rev. B* **33** 3636
- [20] Cornaz A, Erbudak M, Aebi P, Stucki F and Vanini F 1987 *Phys. Rev. B* **35** 3062
- [21] Hu Y, Wagener T J, Gao Y and Weaver J H 1988 *Phys. Rev. B* **38** 12 708
- [22] Hu Y, Wagener T J, Gao Y and Weaver J H 1989 *Phys. Rev. B* **39** 8162
- [23] Säisä L, Kaurila T and Väyrynen J 1992 *Solid State Commun.* **83** 407
- [24] Biwer B M and Bernasek S L 1986 *Surf. Sci.* **167** 207
- [25] Shin S, Suga S, Taniguchi M, Kanzaki H, Shibata S and Yamaguchi T 1982 *J. Phys. Soc. Japan* **51** 906
- [26] Bringans R D and Höchst H 1984 *Phys. Rev. B* **30** 5416
- [27] Ueda Y, Negishi H, Koyano M, Inoue M, Soda K, Sakamoto H and Suga S 1986 *Solid State Commun.* **57** 839
- [28] Lindberg P A P, Johansson L I, Lindström J B and Law D S L 1987 *Phys. Rev. B* **36** 939
- [29] Lindström J B, Lindberg P A P, Johansson L I, Law D S L and Cristensen A N 1987 *Phys. Rev. B* **36** 9514
- [30] Shin S, Tezuka Y, Ishii T and Ueda Y 1993 *Solid State Commun.* **87** 1051
- [31] Kurahashi M, Yamamoto M, Mabuchi M and Naito S 1995 *J. Phys.: Condens. Matter* **7** 4763
- [32] Solomon J S and Baum W 1975 *Surf. Sci.* **51** 228
- [33] Tompkins H G, Cureleru J M and Din K S 1985 *Appl. Surf. Sci.* **21** 280
- [34] Öfner H, Ramsey M G, Netzer F P, Matthew J A D and Yousif F N 1994 *J. Phys.: Condens. Matter* **6** 34
- [35] Weast R C, Astle M J and Beyer W H 1986 *Handbook of Chemistry and Physics* 67th edn (Boca Raton, Chemical Rubber Company)
- [36] Vanini F, Erbudak M, Aebi P and Kostortz G 1990 *Phys. Rev. B* **42** 5984
- [37] Yamaguchi T, Shibuya S and Sugano S 1982 *J. Phys. C: Solid State Phys.* **15** 2625
- [38] De Groot F M F, Fuggle J C, Thole B T and Sawatzky G A 1990 *Phys. Rev. B* **41** 928
- [39] Blaha P, Schwarz K and Dederichs P H 1988 *Phys. Rev. B* **38** 9368
- [40] Moruzzi V L and Sommers C B 1995 *Calculated Electronic Properties of Ordered Alloys*: (Singapore: World Scientific)
- [41] Neckel A, Rastl P, Eiber R, Weinberger P and Schwarz K 1976 *J. Phys. C: Solid State Phys.* **9** 579
- [42] Mo S and Ching W Y 1995 *Phys. Rev. B* **51** 13 023