UV inverse photoemission from low-d-occupancy transition metals

UV inverse photoemission from low-d-occupancy transition metals

E Puppin and P Vavassori

Istituto di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Abstract. We present angle integrated isochromat spectra (11.1 eV $< h\nu <$ 22.5 eV) from six low-d-occupancy transition metals (Ti, V, Zr, Nb, Hf and Ta). In all cases the spectral shape basically reflects the energy distribution of the empty electron states: the agreement is, however, less satisfactory if compared with the same measurements for noble and near-noble metals and with x-ray inverse photoemission from the whole 3d and 4d series. The paper is focused on the observed discrepancies and on the possible role of secondary electron background, cross section and many-body effects in determining the spectral shape.

1. Introduction

Inverse photoemission spectroscopy has become, over the last decade, one of the most powerful tools for the investigation of the empty electron states in solids [1]. Simply, in an inverse photoemission experiment monoenergetic electrons are sent over a sample and the emitted radiation is detected. In the so-called 'isochromat' mode the energy of the impinging electrons is scanned whereas photons at constant energy are detected. With this technique it is possible to sample the density of states above E_F in a manner equivalent to sampling the occupied states of direct photoemission: this equivalence is a consequence of the time reversal relationship that links direct and inverse photoemission [2]. The spectra collected in this way are the empty-states equivalent of the energy distribution curves measured with direct photoemission. Isochromat spectroscopy with x-ray photons (usually called BIS (Bremsstrahlung Isochromat Spectroscopy)) has a long history which dates back to the beginning of this century. Its greatest achievements, however, have been obtained during the eighties due to the substantial improvement of vacuum techniques [3, 4]. Due to the more severe technical requirements, UV isochromat spectroscopy (usually called IPES) started only in recent years [5].

The simplest way of interpreting the isochromat spectra is to consider them a replica of the density of states (DOS) above E_F. The most convincing example of the validity of this assumption has been given by Speier *et al* [4] who measured isochromat spectra in the x-ray region ($h\nu = 1486.7$ eV) from the whole 3d and 4d transition metal (TM) series. For photon energies in the UV region the early IPES investigations allowed one to clearly relate spectra and DOS of high-d-occupancy TM [6]. In the low-d-occupancy case the agreement can be considered satisfactory only within 1–2 eV above E_F [7].

IPES also allowed progress to be made in the development of grating spectrographs which allow the collection of several isochromat spectra over a large portion of the UV range [8]. These instruments have mainly been used in angle resolved IPES investigations with the aim of determining the band structure of 2D and 3D systems [1]. Angle integrated investigations received less attention, even though, due to the strong energy dependence of the photoionization cross sections in the UV range, IPES can give very detailed information on the nature of the chemical bond. More precisely, if the total DOS contains several contributions having different orbital origins, IPES at variable $h\nu$ allows one to disentangle these contributions due to the different photon energy dependences of the corresponding photoionization cross sections. This possibility has been largely exploited in the investigation of filled electron states with direct photoemission by exploiting the tunability of synchrotron radiation. IPES at variable $h\nu$ has been employed in the investigation of the empty states of d-metal alloys [9], TM silicides [10] layered semiconductors [11] and Fe oxides [12].

The purpose of the present investigation is to present an extensive set of isochromat spectra measured in the photon energy range 11.1–22.5 eV from six low-d-occupancy TM. Our primary goal is to assess to what extent the spectra can be interpreted in terms of the available DOS calculated within the single-particle scheme. As we shall see, the spectral features can be qualitatively interpreted in terms of the ground state DOS. However, the agreement in the low-d-occupancy case is not as good as it is with noble and near-noble metals. The following discussion will point out the observed discrepancies and their physical origin.

2. Experimental details

The data have been collected with the IPES system described in more detail elsewhere [13]. Briefly, the system is based on a grating which disperses the light emitted by the sample on a flat field. The dispersed photons are detected with a multichannel plate and this allows the simultaneous collection of 12 different isochromat spectra in the photon energy range between 10 and 25 eV. The instrumental broadening, mostly determined by the optical aberrations of the grating, increases at increasing photon energy. Its value has been experimentally determined by measuring a series of isochromat spectra from a Pt reference sample and is defined as the energy range over which the sharp edge observed at E_F increases from 15% to 85% of its peak value. The instrumental broadening measured in this way is 0.35 eV for $h\nu = 10$ eV, 0.6 eV at $h\nu = 20$ eV and 1.1 eV at $h\nu = 25$ eV.

The electron beam is generated by a current-heated thoriated tungsten filament. The outcoming electrons are accelerated by a potential applied to the sample and the angular spread of the resulting beam is large enough (around 90°) to assure sampling over a large portion of the Brillouin zone. In other words, our spectra must be regarded as k-integrated. The integration over k is *a fortiori* verified, in the present experiment, since the metallic samples were polycrystals cut from commercially available high purity rods. The cleaning procedure consisted in scraping the samples with a diamond file in vacuum (base pressure 10^{-10} Torr) immediately before the measurement.

3. Results and discussion

In order to discuss the relationship between calculated DOS and isochromat spectra

it is convenient to start by considering figure 1 where isochromat spectra ($h\nu$ = 14.5 eV) from Fe, Co and Ni (dots) are compared with the calculated DOS (solid lines) [14]. Clearly, the spectra have a shape which closely follows the density of states above E_F in accordance with the simplest model of IPES. Moreover, for noble and near-noble metals the photon energy does not affect the spectral shape and the only difference between the various isochromat spectra from a particular metal is an increasing broadening related to the variable instrumental resolution as described in the experimental section† [13].
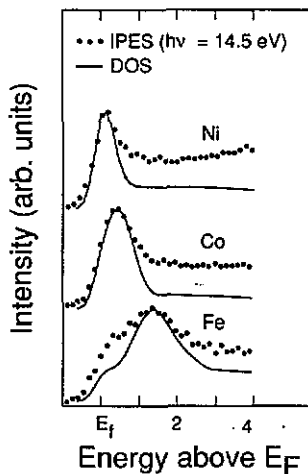

Figure 1. Isochromat spectra at the same value of the photon energy (14.5 eV) from Fe, Co and Ni (dotted lines) in comparison with the calculated DOS (solid lines, [14]).

Figure 2 shows isochromat spectra from two columns of the periodic table in the low-d-occupancy region. Each stack contains several spectra taken at different values of the photon energy. The spectra are normalized to the same height in order to compare the spectral shapes. We also include, for reference, the isochromat spectra taken by Speier *et al* at $h\nu$ = 1486.7 eV [4]. Along with the spectra we show the calculated DOS [14]. The original DOS from [14], shown in figures 1 and 2, have been broadened in order to account for instrumental and lifetime effects. First, we broadened the DOS with a Gaussian, FWHM = 0.4 eV, to simulate the instrumental broadening observed in the isochromat at 14.5 eV. The broadening introduced by lifetime effects has been taken into account with a further convolution of the DOS with a Lorentian of variable width [4]. More precisely, as in [4], the Lorentian FWHM has been chosen to increase from 0.15 at $E = E_F$ up to 1 eV for $E = 10$ eV above E_F. This corresponds to the lifetime broadening of the single-particle electron state above E_F initially occupied by the injected electron. The lifetime of this state decreases at increasing $(E - E_F)$ since the total number of final states available for its decay increases: therefore, for a generic value of E, the lifetime broadening has been assumed to be proportional to the integral of the DOS from E_F to E, i.e., to the number of states towards which the decay may occur.

---

† To economize on space we do not report data from noble and near-noble metals at variable photon energy here; see [13] for a stack of isochromat spectra from Pt.
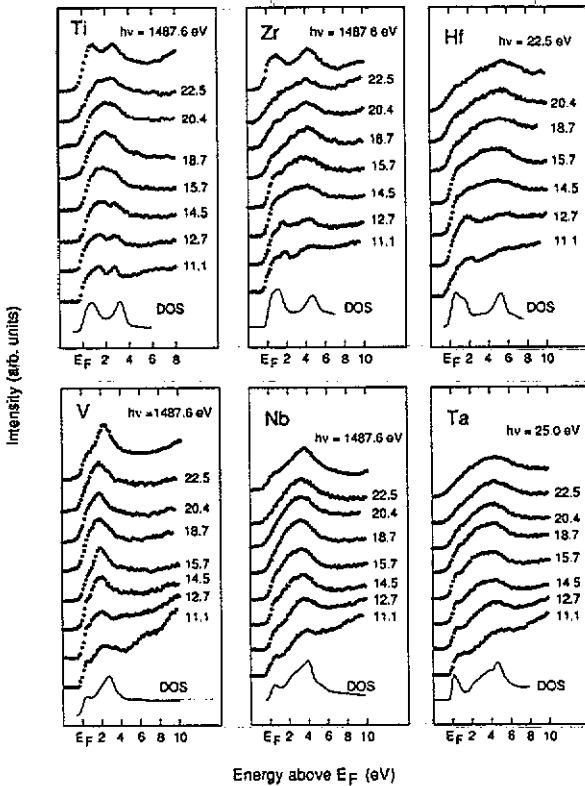
Figure 2. Isochromat spectra in the photon energy range between 11.1 and 22.5 eV from six low-d-occupancy transition metals (dotted lines) in comparison with the calculated DOS (solid lines, [14]).

A detailed discussion of the data shown in figure 2 would take too much space for a single paper. Furthermore, this is the first systematic presentation of isochromat at variable photon energies in the UV region and many aspects of this kind of spectrum are still under investigation. In the following, therefore, we will discuss the general features of the spectra shown in figure 2 by pointing out the most relevant considerations and problems.

(i) A more detailed comparison between DOS and spectra is shown in figures 3 and 4; the filled dots refer to the isochromat at $h\nu = 14.5$ eV and the solid lines to the calculated DOS. A common feature observed in all DOS is the presence of a double structure: this is a consequence of the crystal structure (HCP for Ti, Zr and Hf; BCC for V, Nb and Ta) which determines the gross features of the DOS [15]. Generally speaking, a correspondence exists between the structures observed in the DOS and the spectral features: however, it is not as good as occurs in IPES from noble and near-noble metals (figure 1) and in BIS (figure 2). Furthermore, as shown in figure 2, the spectral shape undergoes a significant evolution for $h\nu$ below 15 eV: in this energy region it is possible to distinguish two structures both in the spectra and in the DOS. At higher photon energies (above 15 eV) the peaks merge in a single structure which has its maximum in correspondence with the high-energy peak observed in the DOS; the low-energy peaks lose their individuality but still appear in the spectra as well-defined shoulders. It is important to observe that, above a photon
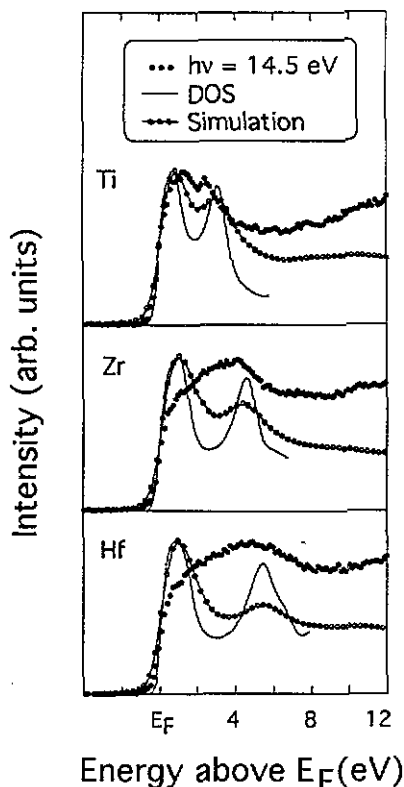
Figure 3. Comparison between isochromat spectra ($h\nu$ = 14.5 eV), theoretical DOS (from [14]) and simulations for Ti, Zr and Hf. The role of background has been taken into account in the Monte Carlo simulations according to the model described in [7].

energy of 15 eV, the spectral shape of each metal is quite stable, and the strongest variations are observed in the low-energy range.

(ii) In order to discuss our spectra it is important to assess the possible role of instrumental effects, in particular of resolution. In our apparatus, the experimental broadening increases at increasing photon energy, as discussed in the experimental section. This fact, in principle, might be invoked in order to explain the merging of the spectral features at increasing photon energy. However, a quantitative consideration of the problem excludes this possibility. For instance, if we consider the Ti spectra, it would be necessary to broaden the isochromat at $h\nu$ = 11.1 eV with a Gaussian of FWHM = 1.5 eV in order to simulate the isochromat at 15.7 eV. This broadening is however absurd since the experimental linewidth of our apparatus is almost the same at these two photon energies: 0.35 eV for $h\nu$ = 11.1 eV and 0.5 eV for $h\nu$ = 15.7. Also, for V, Nb and Ta the simple increase of the instrumental broadening is not sufficient to explain the observed evolution of the spectra at increasing $h\nu$ and, in particular, the washing out of the peak closer to E_F.

(iii) The photoionization cross section σ, which determines the signal intensity in direct and inverse photoemission, strongly depends both on the photon energy and on the orbital character of the final (initial in direct photoemission) electron state. For this reason the spectral shape cannot be simply considered as a replica of the
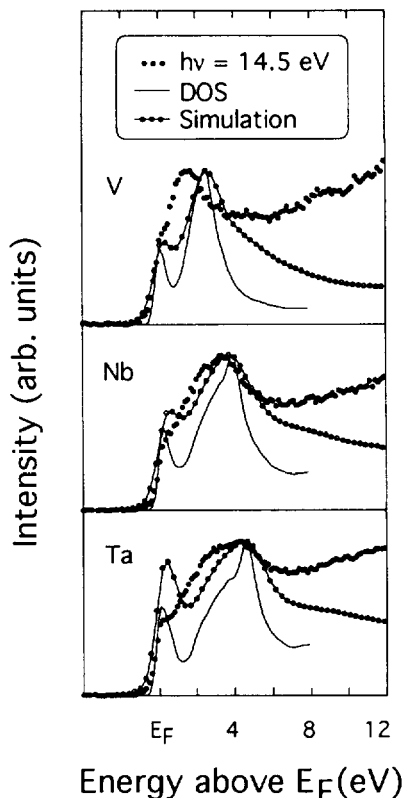
Figure 4. Comparison between isochromat spectra ($h\nu$ = 14.5 eV), theoretical DOS (from [14]) and simulations for V, Nb and Ta. The role of background has been taken into account in the Monte Carlo simulations according to the model described in [7].

DOS. In fact, each partial component of the DOS (i.e., each projection of the DOS on a particular angular momentum component) contributes to the spectrum with a different weight. If the energy dependence of σ for each orbital symmetry is different, the spectral shape will be $h\nu$ dependent. In this connection, working in the UV offers a substantial advantage since in this photon energy region σ undergoes its strongest variations [16] and therefore the spectral shape is more sensitive to $h\nu$ if compared to the x-ray regime [17].

In our case the electron states which contribute to the DOS are the sp- and d-bands. In order to evaluate the relative weight of these components in the isochromat spectra of figure 2 we measured, in strictly comparable conditions, two series of isochromat spectra from Pt and Au. These two metals have approximately the same electronic structure, with the only major difference being that Pt has a partially unfilled d-shell, at variance with gold whose d-states are completely occupied. For this reason, a comparison of Pt and Au isochromat spectra gives an indication of the relevance of the sp-signal with respect to the d-signal. The data are shown in figure 5 for two different photon energies. Clearly, the role of the sp-states is stronger at lower $h\nu$ and this is in quantitative agreement with the estimates obtained with direct photoemission [18]. This is also in qualitative agreement with the calculated values of σ [16] for the isolated atoms.
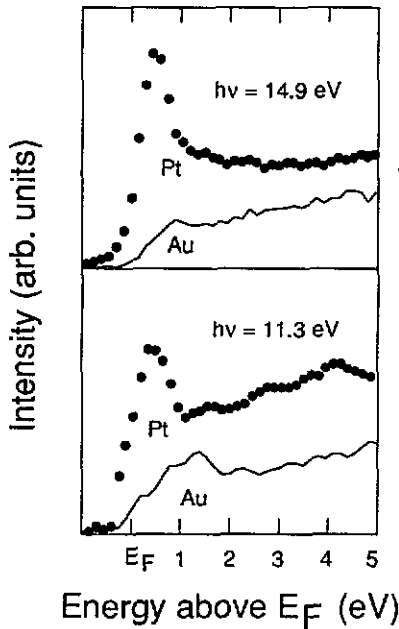
Figure 5. Comparison of isochromat spectra from Pt and Au at two different photon energies. The Au spectra give an indication of the relative weight of sp-derived states in the Pt spectra (see text). At increasing photon energy the role of this contribution clearly decreases and the dominant contribution is from d-states.

In summary, for low values of $h\nu$ the sp-states have a non-negligible weight in the spectra. This is also true in the case of low-d-occupancy metals even though, due to the higher number of empty d-states compared with that in noble and near-noble metals, the d-signal is expected to be much stronger than the sp-signal. This last component does in fact remain essentially the same and independent of the d-occupancy, since the number of empty states having sp-character does not change significantly. This can explain the observed evolution of the spectra for low values of $h\nu$. At higher energies, on the other hand, the d-contribution becomes dominant and this fact, in turn, explains the observed stability of the spectra for higher values of $h\nu$.

(iv) Up to this point it has been assumed that the spectral shape can be interpreted simply in terms of the energy distribution of the final state of the excitation process. This assumption, however, needs to be better justified, since the spectral shape is actually determined by the energy distribution both of the initial and the final states involved in the excitation process. In direct photoemission the effects on the spectra determined by the energy distribution of the joint density of states (EDJDOS) generally show up in the UV region for $h\nu \simeq 10$ eV [19]. In IPES, due to the complementarity with direct photoemission, EDJDOS effects can legitimately be expected to show up. However, looking at the spectra of figure 2 no clear indication of such effects is observed. In fact, the stability of the spectra for $h\nu > 15$ eV rules out this possibility in this range. Below 15 eV the observed evolution of the spectra can be explained in terms of the $h\nu$ dependence of σ, the photoionization cross section, as discussed in (iii). This explanation appears to be more likely since EDJDOS effects generally produce extra features in the spectra which disappear by changing the value of $h\nu$. In

our spectra no extra features are observed and the evolution with $h\nu$ mostly involves the merging, above 15 eV, of the two features better resolved at low $h\nu$. An exception might be represented by the isochromat at 11.1 and 12.7 eV from Zr and Hf. In particular, the Zr isochromat at 11.1 eV shows the presence of a third feature around 2 eV above E_F. In order to explain this feature in terms of the EDJDOS effect would require a detailed theoretical analysis which is beyond our purposes.

A good argument which can explain a lowest weight of EDJDOS effects in IPES if compared with direct photoemission is the following. The radiative transitions in IPES occur between states located higher in the energy scale than those of direct photoemission; in particular, in an isochromat at $h\nu = 10$ eV the initial state occupied by the injected electron is located between 10 and 20 eV above E_F (for E scanned between 0 and 10 eV above E_F). Since the most significant structures in the DOS show up within 8 eV above E_F at the most, it is reasonable to assess that EDJDOS effects are less likely to occur in IPES. In contrast, in a direct photoemission EDC taken at the same photon energy, the final states occupied by the outcoming electron fall within the first 10 eV above E_F, i.e., in a region where the most significant structures of the DOS fall.

(v) The secondary-electron background strongly affects the spectral shape. In particular, Dose and Reusing showed that Hf, Nb and Ta give rise to isochromat spectra ($h\nu = 9.7$ eV) in which the valley in the calculated DOS is almost completely filled [7]. Our data confirm the presence of this effect in a variety of different samples for photon energies up to 25 eV. (It is interesting to note that in BIS, for a photon energy of 1487.6 eV, the peaks are clearly visible and well separated [4].) In order to take into account the role of background in our spectra we implemented a Monte Carlo simulation (whose details will be given elsewhere) of the model described in [7]. The simulated spectra are shown in figures 3 and 4 with open circles. The comparison with the DOS shows that the main effect on background consists in filling the valley between the structures in the DOS. However, the valley is still visible in the simulations whereas the experimental spectra show a complete filling and the simulation can be considered satisfactory only in the case of V and Nb. Since this filling represents a strong deviation of the spectral shape from the DOS, it would be desirable to develop a satisfactory model of this effect. If this effect is related to the background the inadequacy of the existing models is probably related to the fact that inelastic scattering of low-energy electrons (10–20 eV) is poorly understood and that the electron–hole creation probability is not simply related to the DOS as assumed in [7] and in our simulation.

(vi) As already observed above, even though all the structures observed in the DOS have a counterpart in the spectra, their positions on the energy scale do not always match. The effect is particularly evident in the lightest elements, Ti and V. This discrepancy between experiment and theory is also observed in the isochromat spectra measured by Speier *et al* [4] for a photon energy of 1487.6 eV. On the basis of the available data it is difficult to give a clear explanation of this difference and the following discussion must be regarded as conjecture which, hopefully, will stimulate further investigations.

The DOS shown in this paper have been calculated by Papaconstantopoulos within a single-particle scheme. Deviations from single-particle calculations are expected to occur in narrow band systems due to the stronger role of correlation there. Among early TM the band width is around 7 eV in Ti and V, 8 eV in Zr and Nb and 9 and 10 eV, respectively, in Hf and Ta [14]: this trend is related to the nature

of the d-wavefunctions which are more localized in 3d elements than in 4d and 5d elements [20]. For this reason the possible deviation from a single-particle description is expected to be stronger in 3d metals than in 4d and 5d metals. The discrepancy between spectra and DOS is, in fact, more pronounced in the lightest elements (as far as the peak position is concerned) and this suggests that true many body calculations of the quasi-particle energies are necessary in order to fit the Ti and V spectra.

4. Conclusions

Isochromat spectra measured in the photon energy range 11.1–22.5 eV from low-d-occupancy TM allows one to assess that the gross features of the spectra can be directly explained in terms of the ground state DOS calculated within a single-particle scheme. The agreement between spectra and DOS however is not as good as occurs in BIS over the whole 3d and 4d series and in IPES from noble and near-noble metals. The major cause of the observed discrepancies is the presence of a strong secondary-electron background, whose role is not yet fully understood. Other discrepancies are related to cross section effects. A better understanding of these discrepancies, which will be the subject of further investigations, will put the use of IPES in the investigation of the electron states of solids on a firmer basis. A remarkable observation is that IPES and BIS point out a possible inadequacy of a single-particle picture of the valence states in the low-d-occupancy region of the periodic table.

References

[1] Himpsel F J 1990 *Phys. Scr.* **T31** 171
Johnson P D and Hulbert S L 1990 *Rev. Sci. Instrum.* **61** 2277
Smith N V 1988 *Rep. Prog. Phys.* **51** 1227
Andrews P T and Collins I R 1989 *Phys. Scr.* **T29** 116
[2] Pendry J B 1980 *Phys. Rev. Lett.* **45** 1356; 1981 *J. Phys. C: Solid State Phys.* **14** 1381
[3] Lang J K and Baer Y 1979 *Rev. Sci. Instrum.* **50** 221
[4] Speier W, Fuggle J C, Zeller R, Ackermann B, Szot K, Hillebrecht F U and Campagna M 1984 *Phys. Rev.* B **30** 6921
[5] Dose V 1977 *Appl. Phys.* **14** 117
[6] Dose V, Fauster T and Scheidt H 1981 *J. Phys. F: Met. Phys.* **11** 1801
[7] Dose V and Reusing G 1980 *Appl. Phys.* **23** 131
[8] Chauvet G and Baptist R 1981 *J. Electron Spectrosc. Relat. Phenom.* **24** 255
[9] Braicovich L, Ciccacci F, Puppin E, Sancrotti M, Vescovo E and Bertuccio G 1991 *Solid State Commun.* **79** 379
[10] Chemelli C, Luridiana S, Sancrotti M, Braicovich L, Ciccacci F, Iandelli A, Olcese G L and Palenzona A 1990 *Phys. Rev.* B **42** 1829
[11] Puppin E, Chemelli C and Scagliotti M 1991 *Solid State Commun.* **78** 905
[12] Ciccacci F, Braicovich L, Puppin E and Vescovo E 1991 *Phys. Rev.* B **44** 10444
[13] Sancrotti M, Braicovich L, Chemelli C, Ciccacci F, Puppin E, Trezzi G and Vescovo E 1991 *Rev. Sci. Instrum.* **62** 639

[14] Papaconstantopoulos D A 1986 *Handbook of the Band Structure of Elemental Solids* (New York: Plenum)

[15] Andersen O K and Jepsen O 1977 *Physica* B and C **91B** 317

[16] Yeh J J and Lindau I 1985 *At. Data Nucl. Data Tables* **32** 1

[17] Speier W 1988 *J. Phys. C: Solid State Phys.* **21** L1183

[18] Eastman D E and Cashion J K 1970 *Phys. Rev. Lett.* **24** 310

[19] Smith N V 1971 *Crit. Rev. Solid State Sci.* **2** 45

[20] van der Marel D and Sawatzky G A 1988 *Phys. Rev.* B **37** 10674