Resonance Auger and autoionization processes in solid lanthanum after 4d to 4f resonant excitation by synchrotron radiation

1991 J. Phys.: Condens. Matter 3 8707

(http://iopscience.iop.org/0953-8984/3/44/015)

J. Phys.: Condens. Matter 3 (1991) 8707–8714. Printed in the UK

Resonance Auger and autoionization processes in solid lanthanum after 4d → 4f resonant excitation by synchrotron radiation

O-P Sairanen, S Aksela and A Kivimäki
Department of Physics, University of Oulu, SF-90570 Oulu, Finland

Received 13 June 1991

Abstract. The decay processes of metallic lanthanum after resonant 4d → 4f excitation by synchrotron radiation have been studied by means of electron spectroscopy. Excitation to the $4d^9 4f^1(^3D_1)$ state, which is below the 4d ionization threshold, was found to decay predominantly through $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ spectator resonance processes. The energy shift relative to the corresponding normal Auger energies was 1.6 ± 0.3 eV in the case of NOO resonance Auger decay, whereas no energy shift was found for the NOV resonance Auger electrons. The excitation to the main 4d → 4f giant resonance was found to decay through autoionization leading to a one-hole final state $5s^{-1}$ or $5p^{-1}$, or through normal Auger processes. Autoionization processes are strong on the low energy side of the resonance, but when the excitation energy increases, normal Auger processes become more and more dominant, indicating a change in the nature of the giant resonance.

1. Introduction

The absorption spectra of rare-earth elements are characterized by a group of weak narrow absorption peaks below the one-electron 4d ionization threshold and by a broad strong maximum close to the threshold [1–3]. This maximum is called a giant resonance and it is interpreted as a multiplet of the discrete 4d → 4f excitation that is raised into the ϵf continuum by exchange interaction. The large overlap between the occupied 4d and unoccupied 4f wavefunctions results in a strong coupling of the 4d core-excited [$4d^{10}4f^n \rightarrow 4d^9\,(4f, \epsilon f)^{n+1}$] states with the 4f ionization ($4f^n \rightarrow 4f^{n-1}$, ϵl) continua and is held responsible for the broadening of these multiplet lines and the asymmetric profiles of the resonance [4–10].

The 4d → (4f, ϵf) resonance excitation can decay through three principal channels:

(i) the excited electron tunnels through the potential barrier leading to an excited ionic $4d^{-1}$ state which predominantly decays via the normal Auger process,

(ii) the excited electron takes directly part in the decay process via autoionization (direct recombination) leading to the emission of an electron from one of the 5s, 5p, 4f core levels or the valence band, or

(iii) the excited electron remains as a spectator during the recombination process which is called a resonance Auger process.

In the autoionization process the energy of the ejected (5s, 5p, 4f or valence) electron is the same as if it had been produced by direct photoionization so in the

0953-8984/91/448707+08$03.50

photoelectron spectrum these processes should be seen as enhanced intensity of the corresponding photopeaks [11, 12]. The resonance Auger structure should appear in the spectrum like the corresponding normal Auger structure with slightly shifted kinetic energies [11, 12].

Different decay channels are related to the nature of the resonance. A tunneling process (followed by normal Auger ejection) is typical for a shape resonance, whereas an autoionization and a resonance Auger process are connected to a discrete resonance. Therefore the change in the relative strength of different channels also gives information about the change in the nature of the excitation in different parts of the giant resonance region.

The purpose of this work is to study the decay channels of 4d → 4f resonantly excited metallic lanthanum. In particular we like to show that the resonance Auger decay process found earlier e.g. in rare gases [13–16] and some molecules [11, 12, 17, 18] can be an important decay channel also in solid state elements. Among the rare-earths lanthanum [$Xe(5d6s)^3$] is of particular interest because it has an empty 4f orbital in the ground state. The interaction between the excited electron and other electrons is thus weaker than in the other rare-earth elements. The resonance Auger effect is therefore expected to be stronger and easier to observe in the experimental spectra. The decay channels of solid La (in LaB_6) after 4d → 4f resonant excitations have earlier been discussed by Aono *et al* [19, 20]. We shall study the decay processes in more detail and arrive at somewhat different results. Different partial cross sections of atomic La have been recently studied both experimentally (Richter *et al* [21]) and theoretically (Amusia *et al* [22]). Dzionk *et al* [23] have also recently studied the decay channels of atomic La by photo-ion spectroscopy.

2. Experimental procedure

The measurements were carried out at MAX synchrotron radiation laboratory in Lund, Sweden, using the 4.7 m toroidal grating monochromator with a 1200 l/mm laminar grating. The bandwidth of the monochromatized light was less than 0.5 eV. The spectra were recorded with a commercial double pass cylindrical mirror analyser applying a constant 20 eV pass energy which gives a spectrometer resolution of about 0.3 eV.

The lanthanum sample was evaporated on a tantalum substrate *in situ* from a tungsten wire. The background pressure during the measurements was $4–8\times10^{-10}$ mbar and the purity of the sample was controlled regularly by recording the photoelectron spectrum. A small oxygen 2p signal was detected but it remained constant during the course of the measurements and gave us a good reference for intensity comparison. In order to study the decay channels we measured the electron spectra of La using photon energies below, at, and above the main giant resonance. To determine the 4d → 4f resonant energies we also recorded an electron yield spectrum with a constant-final-state method i.e. by scanning the photon energy through the range of the giant resonance and by measuring the intensity of (in this case) 10 eV secondary electrons. Electron yield spectra have been shown to be analogous to photoabsorption spectra [24] so they also reveal the sharp absorption fine structure below the main resonance.

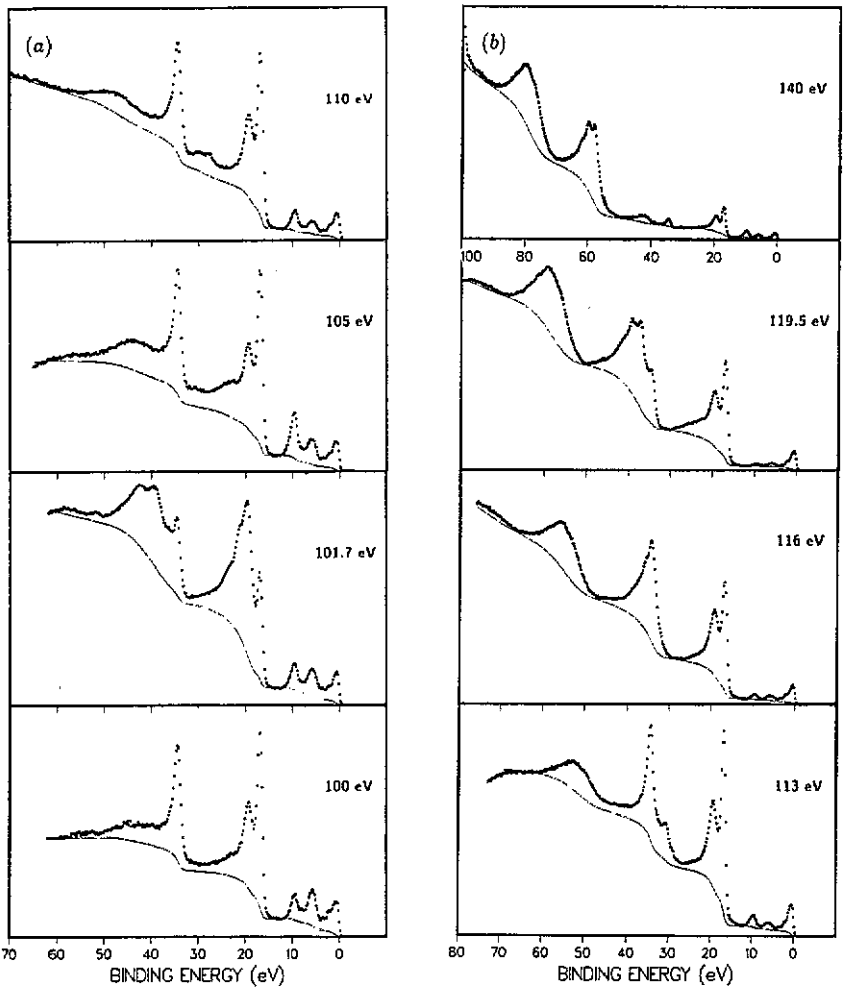

Figure 1. The original electron spectra of La measured with 100 eV, 101.7 eV, 105 eV, 110 eV, 113 eV, 116 eV, 119.5 eV and 140 eV photons. Full curve corresponds to the estimated background.

3. Results and discussion

Solid state spectra are typically characterized by a relatively high background which increases towards lower kinetic energies and is caused by inelastically scattered electrons. The lineshape of Auger and photoelectron lines is a Doniac–Šunjić shape [25] instead of a symmetrical (Lorenzian) lineshape. To eliminate the inconvenience of the asymmetry in the lines when comparing the intensities of different peaks it was taken into account in the background estimation. The background was assumed to increase proportionally to the integrated intensity on going from higher to lower kinetic energies in the spectrum. Furthermore, each increment was supposed to decrease exponentially. This 'continuous' background [26, 27] was subtracted from the electron spectra. In this kind of treatment it is assumed that the background is constant for all energy losses and the constructed background is set to match the experimental spectrum at some point on the low kinetic energy side of every peak group. It does not

take any material-specific differences (shakeup, intrinsic excitations, mean free path) into account. A better background estimation could be achieved by determining the electron energy loss spectrum and using a deconvolution procedure [28] or using a 'universal' cross section [29] to determine the shape of the inelastically scattered background following a peak. However, a simpler treatment described above seemed to be good enough for our purposes. The energy calibration of the spectra was based on the binding energies taken from the study of Riviere *et al* [30].

The original electron spectra of La measured with photon energies 100 eV, 101.7 eV, 105 eV, 110 eV, 113 eV, 116 eV, 119.5 eV and 140 eV are displayed in figure 1. The shape of the estimated background is also included as a full curve.

In order to visualize the changes in the intensities of different decay channels the pure photoelectron spectrum was measured with 100 eV photons (well below all resonance energies) and subtracted from the resonance spectra. Intensities were normalized relative to the small O 2p line (at about 6 eV binding energy) whose intensity should not vary in this photon energy region.

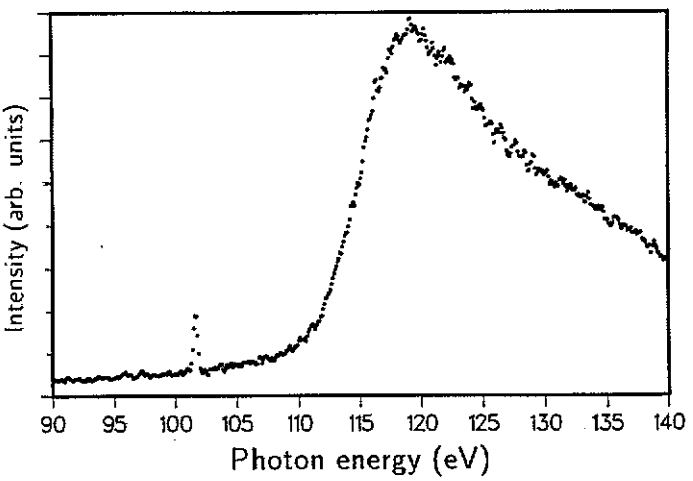

Figure 2. The electron yield spectrum of La.

In the electron yield spectrum of La (figure 2) we can see a broad strong maximum at the photon energy of about 119 eV and a weak sharp peak at the photon energy of 101.7 eV. The broad maximum is identified as a resonance excitation from the ground state to the excited state $4d^9\,4f^1(^1P_1)$ (giant resonance) and the sharp peak as an excitation to the excited state $4d^9\,4f^1(^3D_1)$ [5,31]. The binding energies of La 4d core level are 102.5 eV ($4d_{5/2}$) and 105.3 eV ($4d_{3/2}$) [30]. The $4d^9\,4f^1(^3D_1)$ resonance state is thus below the first 4d threshold energy, whereas the main giant resonance is clearly above the 4d ionization energies.

Figure 3 displays the electron spectrum of La measured with 140 eV photon energy. Strong peaks can be seen around 55–65 eV and 75–84 eV kinetic energies, their maxima being at 61.0 eV and 82.1 eV. These structures originate from Auger transitions $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$, respectively [30,32]. The smaller broad structure around 98 eV results also from an Auger process ($N_{4,5}VV$), but the rest of the peaks are caused by direct photoemission from the outer orbitals (5s, 5p, and valence).

Figure 4 shows the electron spectra of La measured with photon energies 101.7 eV, 105 eV, 110 eV, 113 eV, 116 eV and 119.5 eV together with the normalized pure pho-

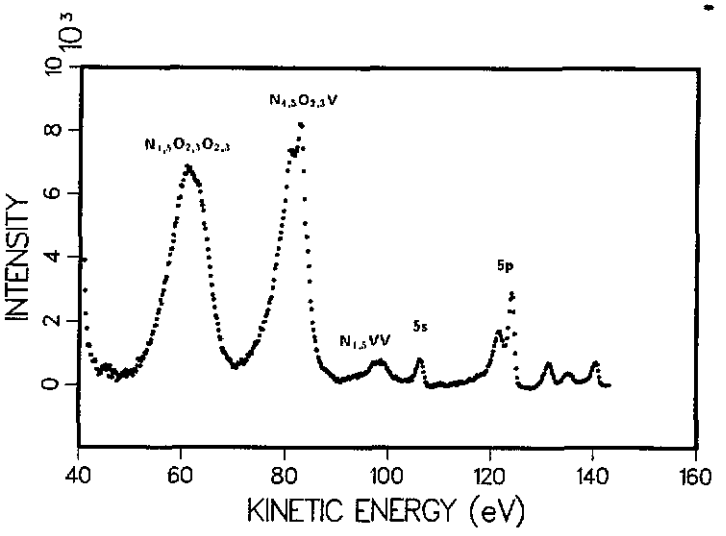

Figure 3. The normal Auger spectrum of La measured with 140 eV photons.

toelectron spectrum. The corresponding 'difference' spectra are shown in figure 5. In the pure photoelectron spectrum there are three different line groups: 5s photoemission structure around 35 eV binding energy, $5p_{1/2}$ and $5p_{3/2}$ photoemission structure around 20 eV and 17 eV binding energies, and valence photoemission line at about 1 eV binding energy. In the spectrum taken at 101.7 eV photon energy strong enhancement can be seen around 46–36 eV and 25–15 eV binding energies, the maxima of these stuctures being at 39.1 eV and 19.5 eV binding energies (62.6 eV and 82.2 eV kinetic energies, respectively). These new structures correspond to the main Auger peaks, but because the excitation energy is now below the 4d ionization limit, the excited electron is expected to remain as a spectator during the decay process. The Coulomb interaction involving the spectator electron leads to a slight energy shift of 1.6 ± 0.3 eV towards higher kinetic energies in the case of $N_{4,5}O_{2,3}O_{2,3}$ resonance transition. The effect is similar to the one found earlier in the case of rare gases and some molecules and in contradiction with the results of Aono *et al* [19] who found the shift to be towards *lower* kinetic energies. On the other hand no energy shift can be observed between the resonance and the normal $N_{4,5}O_{2,3}V$ transition. This seems to indicate that the interaction between the valence band hole and the excited 4f electron in the final state cancels the change in the Coulomb interaction.

In the spectrum taken at 105 eV photon energy the resonance Auger structure has almost completely vanished appearing only as low, broad structures on the low kinetic energy sides of the 5s and 5p photolines. In the next spectra (110 eV, 113 eV) the 5s and 5p photolines as well as valence emission increase compared to the spectrum taken at 100 eV photon energy. Some growing Auger structure can also be seen. There still seems to be a slight shift ($\sim$ 0.6 eV at 113 eV photons) in the energy of the NOO Auger electrons. Thus even though the excitation energy is above the 4d threshold energy, the excited electron remains bound and affects the outgoing Auger electron. When the excitation energy approaches the top of the main giant resonance—photon energies 116 eV and 119.5 eV—the Auger transitions begin to dominate though autoionization channels (5s, 5p, and valence emission) are still quite strong. No energy shift relative to the Auger electrons can be observed. This

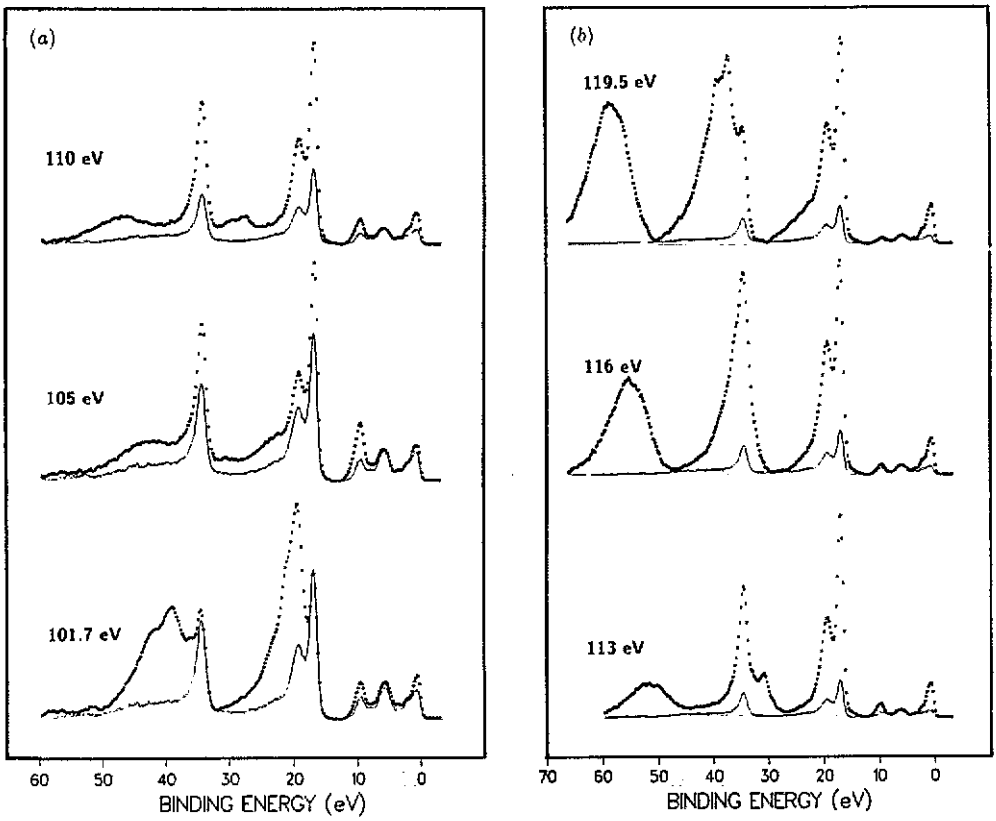

Figure 4. The electron spectra of La measured with 101.7 eV, 105 eV, 110 eV, 113 eV, 116 eV and 119.5 eV photons. The full curve corresponds to the reference spectrum measured with 100 eV photons.

indicates that near and at the main resonance energy the excited 4f electron becomes less localized and interacts with the continuum so strongly that it can lead to ionization and the excited state decays also through a normal Auger process.

4. Conclusions

We have studied the decay channels of solid lanthanum after excitation with different photon energies covering the the 4d $\rightarrow$ (4f, ϵf) giant resonance region. The results indicate that in the excitation to the $4d^9\,4f^1$ state ($^3D_1$) (101.7 eV) the excited electron remains as a spectator and the state decays almost entirely through $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ resonance Auger processes. The kinetic energy shift relative to the normal Auger energies was found to be 1.6 eV for NOO processes whereas no shift was observed for NOV processes.

The principal decay channels at photon energies corresponding to the low energy side of the main giant resonance are $4d^9\,4f^1\,5s^2 \rightarrow 4d^{10}\,5s^1$, $4d^9\,4f^1\,5p^6 \rightarrow 4d^{10}\,5p^5$, and $4d^9\,4f^1\,V^3 \rightarrow 4d^{10}\,V^2$ appearing in the experimental spectra as enhanced intensities of 5s, 5p, and valence structure. But when the excitation energy increases Auger

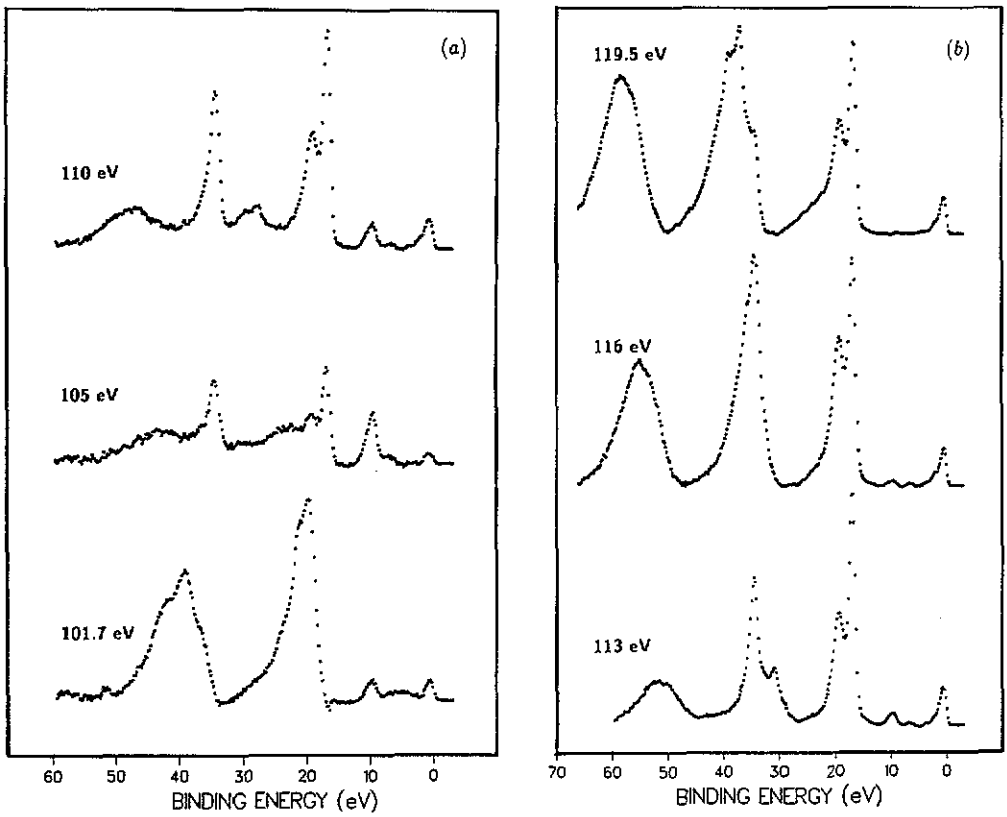

Figure 5. The 'difference' spectra of La.

processes begin to dominate. The NOO Auger electrons have a slight energy shift which together with the strenght of the autoionization processes indicates that the resonance has a very discrete character at the onset of the main resonance.

Acknowledgments

The authors wish to thank Mr Terho Kaikuranta and the staff of MAX-LAB for their assistance in the measurements. The financial support of the Academy of Finland is gratefully acknowledged.

References

[1] Zimkina T M, Formichev V A, Gribovskii S A and Zhukova I I 1967 *Sov. Phys.–Solid State* **9** 1128
[2] Formichev V A, Zimkina T M, Gribovskii S A and Zhukova I I 1967 *Sov. Phys.–Solid State* **9** 1163
[3] Haensel R, Rabe P and Sonntag B 1970 *Solid State Commun.* **8** 1845
[4] Connerade J P 1987 *Controlled Collapse and the Profiles of 'Giant Resonance' (Giant Resonances at Atoms, Molecules, and Solids)* ed J P Connerade *et al* (New York: Plenum)
[5] Dehmer J L, Starace A F, Fano U, Sugar J and Cooper J W 1971 *Phys. Rev. Lett.* **26** 1521
[6] Starace A F 1972 *Phys. Rev.* B **5** 1773
[7] Mansfield M W D and Connerade J P 1976 *Proc. R. Soc.* A **352** 125

[8] Wendin G and Starace A F 1978 *J. Phys. B: At. Mol. Phys.* **11** 4119
[9] Meyer M, Prescher Th, Raven E von, M Richter, Schmidt E, Sonntag B and Wetzel H-E 1986 *Z. Phys.* D **2** 347
[10] Becker U, Kerkhoff H G, Lindle D W, Kobrin P H, Ferrett T A, Heimann P A, Truesdale C M and Shirley D A 1986 *Phys. Rev.* A **34** 2858
[11] Aksela S, Sairanen O-P, Aksela H, Bancroft G M and Tan K H 1988 *Phys. Rev.* A **37** 2934
[12] Bancroft G M, Tan K H, Sairanen O-P, Aksela S and Aksela H 1990 *Phys. Rev.* A **41** 3717
[13] Aksela H, Aksela S, Bancroft G M, Tan K H and Pulkkinen H 1986 *Phys. Rev.* A **33** 3867
[14] Aksela H, Aksela S, Pulkkinen H, Bancroft G M and Tan K H 1986 *Phys. Rev.* A **33** 3876
[15] Aksela H, Aksela S, Pulkkinen H, Bancroft G M and Tan K H 1988 *Phys. Rev.* A **37** 1798
[16] Aksela H, Aksela S, Tulkki J, Åberg T, Bancroft G M and Tan K H 1989 *Phys. Rev.* A **39** 3041
[17] Aksela H, Aksela S, Ala-Korpela M, Sairanen O-P, Hotokka M, Bancroft G M, Tan K H and Tulkki J 1990 *Phys. Rev.* A **41** 6000
[18] Aksela S, Tan K H, Aksela H and Bancroft G M *1986 Phys. Rev.* A **33** 258
[19] Aono M, Chiang T-C, Knapp J A, Tanaka T and Eastman D E 1980 *Phys. Rev.* B **21** 2661
[20] Aono M, Chiang T-C, Himpsel F J and Eastman D E 1981 *Solid State Commun.* **37** 471
[21] Richter M, Meyer M, Pahler M, Prescher Th, Raven E von, Sonntag B and Wetzel H E 1989 *Phys. Rev.* A **39** 5666
[22] Amusia M Ya, Chernysheva L V, Ivanov V K and Kupchenko V A 1989 *Z. Phys.* D **14** 215
[23] Dzionk Ch, Fiedler W, Lucke M van and Zimmermann P 1989 *Phys. Rev. Lett.* **62** 878
[24] Gudat W and Kunz C 1972 *Phys. Rev. Lett.* **29** 169
[25] Doniach S and Šunjić M 1970 *J. Phys. C: Solid State Phys.* **3** 285
[26] Aksela H, Väyrynen J and Aksela S 1979 *J. Electron Spectrosc. Relat. Phenom.* **16** 339
[27] Chorkendorff Ib, Onsgaard J, Aksela H and Aksela S 1983 *Phys. Rev.* B **27** 945
[28] Powell C P and Seah M P 1990 *J. Vac. Sci. Technol.* A **8** 735
[29] Tougaard S 1990 *J. Electron Spectrosc. Relat. Phenom.* **52** 243
[30] Riviere J C, Netzer F P, Rosina G, Strasser G and Matthew J A D 1985 *J. Electron Spectrosc. Relat. Phenom.* **36** 331
[31] Sugar J 1972 *Phys. Rev.* B **5** 1785
Dehmer J L and Starace A F 1972 *Phys. Rev.* B **5** 1792
[32] Richter M, Prescher Th, Meyer M, Raven E von, Sonntag B and Aksela S 1988 *Phys. Rev.* B **38** 1763