

ANOMALOUS AUGER-ELECTRON SPECTRA OF METALLIC CALCIUM

J. VÄYRYNEN and T. T. RANTALA

Department of Physics, University of Oulu, Linnanmaa, SF-90570 Oulu 57 (Finland)

E. MINNI and E. SUONINEN

Department of Physical Sciences, University of Turku, SF-20500 Turku 50 (Finland)

(Received 22 December 1982)

ABSTRACT

Al $K\alpha$ -excited $L_{2,3}MM$ and $L_{2,3}MV$ Auger-electron spectra of Ca have been measured in ultrahigh vacuum from a metallic sample evaporated onto an Ag substrate. An interpretation of the spectra is made by applying a line-fitting procedure. The lineshape and the solid-state–free-atom kinetic-energy shift are also studied. The extrinsic loss structure in the $L_{2,3}MM$ Auger-electron emission is found to be similar to that in $2p$ photoelectron emission. Spin–density-functional (SDF) calculations for the singularity index describing the intrinsic lineshape give a value of ~ 0.35 for both processes. Thus the experimental $2p_{3/2}$ photoelectron line broadened from 1.2 to ~ 5 eV FWHM has been used as a standard line in the line fitting of the $L_{2,3}MM$ transitions. The term splitting of the $L_{2,3}M_{2,3}M_{2,3}$ transition is larger than in the corresponding free-atom spectrum. This result is also supported by the SDF calculations. The $L_{2,3}M_{2,3}V$ spectrum is anomalously sharp, probably both because of the structure of the local density of states at the site of the core-ionized atom and because of differences in the transition probabilities into the different parts of the band. The experimental solid-state shift is 20.3 eV for the $L_{2,3}M_{2,3}M_{2,3}^1D$ transition, and the binding-energy shifts are 8.3 and 6.1 eV for the $2p$ and $3p$ levels, respectively. The SDF shifts for the above transitions are 19.9 (configurational average), 9.4 and 8.0 eV, consecutively, in agreement with the experimental values. The calculations also show a localized d -type (atomic-like) structure for the screening of the initial- and final-state core hole(s). This is the origin of the large values of both the singularity index and the solid-state shift.

INTRODUCTION

Comparisons between the vapour-phase and solid-state Auger-electron spectra of metals have shown that inner-shell transitions can often be described quite accurately by an atomic model, the relative energies and intensities of the lines being the same in the spectra of both phases. Only line

broadening and extra-atomic relaxation shifts are found in the solid-state spectra of metals such as Mg, Zn and Cd [1]. The intensity ratio between the Auger groups may differ because of changes in the Coster–Kronig transition probability on going from the vapour to the solid phase, as in the case of Zn. The above metals have a closed, free-atom-like outer-shell electronic configuration, which makes theoretical interpretation of the spectra straightforward. On the other hand, small differences have been observed between the free-atom and solid-state spectra of elements having an open outer-shell configuration, e.g., Ag [2] and In [3]. The coupling of two Auger holes with an open outer shell causes a noticeable term-splitting in the free-atom spectrum, while in the solid-state spectrum the splitting effects disappear and it is more probable that the spectrum can be interpreted according to two-hole coupling.

The alkaline earths Ca, Sr and Ba form an interesting group of elements in the Periodic Table, since they have a closed outer-shell configuration also in the atomic ground state, but have the next neighbouring element with a *d*-type orbital in the ground state. In fact, atomic calculations show that the *d* character is significant and increases along the series Ca, Sr and Ba [4]. For these elements in the solid phase, the *d* admixture near the Fermi level is considerable [5]. Thus the electronic structure of the alkaline earths exhibits some features characteristic of the neighbouring series of transition elements. Various spectroscopic methods have been used widely to investigate the electronic structures of these metals, both in the vapour and the solid phase. All these studies show that the appearance of *d* character has real effects on the spectra. The photoabsorption spectrum [6] and the low-energy electron spectrum [7, 8] of Ca vapour have been studied recently. The Ca^+ auto-ionizing spectrum has also been analyzed in detail [8]. UV He (II)-excited photoelectron spectra have been measured [9], but only a few inner-shell spectra of Ca in the vapour phase have been studied: to date, the electron-excited *3p* Auger doublets [10] and the electron-excited *LMM* Auger spectra [11] have been measured. On the other hand, the photoelectron spectra of metallic Ca interpreted in some detail very recently [12] show high intrinsic loss structure as well as an extraordinarily large $3p_{1/2,3/2}$ spin–orbit splitting. The surface electronic structure of Ca metal has been studied using X-ray-induced photoemission, and the results show considerable narrowing of the bandwidth as compared to the bulk value [13].

To our knowledge, Auger spectra of metallic Ca have not yet been discussed in the literature. The purpose of this paper is therefore to deal with these spectra. Although possible atomic features of the Auger spectra are masked in the metallic state, an attempt is made to analyze the components of the $L_{2,3}M_{2,3}M_{2,3}$ Auger spectrum. The conduction-electron response to Auger-electron emission and the Auger-electron kinetic-energy shift between the free atom and the metal are discussed, and the experimental results compared with calculations made using the spin–density-functional (SDF) method. Furthermore, the calculated photoelectron kinetic-energy

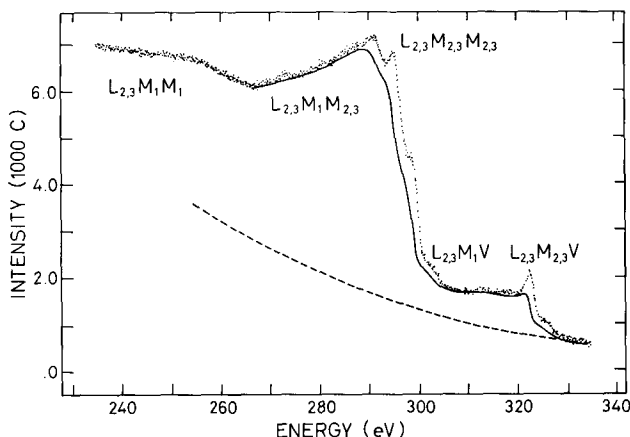


Fig. 1. Experimental $L_{2,3}MM$ and $L_{2,3}MV$ Auger spectra of Ca metal (points), together with the background intensity including solid-state effects (first method; see text) (solid curve) and the secondary-electron contribution (dashed curve).

shifts are compared to available experimental values [10]. The intrinsic lineshape of the Auger spectra is predicted successfully from the calculated structure of the screening.

EXPERIMENTAL

The measurements were made using a VG ESCA3 electron spectrometer and Al $K\alpha$ radiation to excite the Auger spectra. During the measurements the analyzer was operated with a slit width of 4 mm and with a constant pass energy of 20 eV. This implies in the XPS mode a resolution of ~ 1 eV measured at the Fermi edge for Au.

Samples were prepared by evaporating Ca films in the instrument vacuum onto Ag substrate. In order to decrease vaporization the samples were kept at a temperature of $\sim -100^\circ\text{C}$ during the measurements. The strongest photoelectron lines of oxygen and silver were monitored continuously and the evaporation was repeated when signals from oxygen or the substrate material were observed. The energy calibration of the spectra was based on a binding-energy value of 83.8 eV for the Au $4f_{7/2}$ photoelectron line. The vacuum in the spectrometer during the measurements was better than 10^{-8} Pa.

RESULTS AND DATA HANDLING

The $L_{2,3}MM$ and $L_{2,3}MV$ Auger-electron spectra (Fig. 1) show very strong solid-state effects which cause an increase in intensity with respect to the

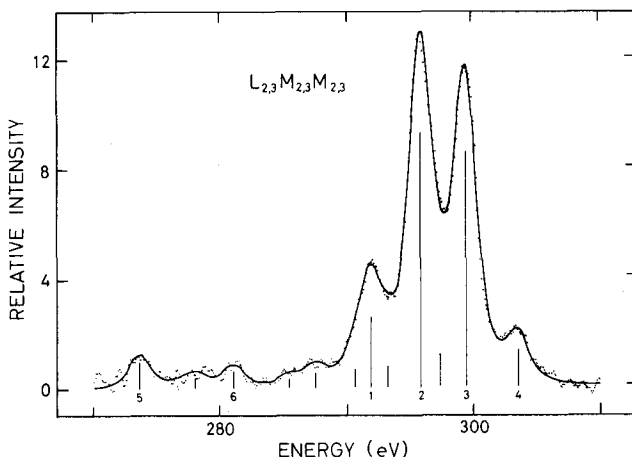


Fig. 2. Decomposition of the background-subtracted $L_{2,3}MM$ Auger spectrum into Voigt-function components with FWHM 2.3 eV. See Table 1 for identification of lines.

line intensity at the low-energy side. This makes the decomposition of the Auger spectra into individual lines ambiguous in the absence of any assumptions concerning the lineshape or background, which is commonly represented by a smoothly varying intensity superimposed on the actual line structure. In the present case we have applied two methods to treat the Auger spectra.

In the first method, all solid-state effects associated with the lineshape are included in the background and subtracted out under the assumption that the background at a certain energy increases with decreasing energy proportionally to the intensity and that each increment attenuates exponentially to lower energies. This method has been applied previously to the Auger spectrum of Cd, for example [1]. Line fitting of Voigt functions (FWHM 2.3 eV) to the spectrum corrected by this method is presented in Fig. 2. The line-fitting procedure is based on a linearized method of least squares [14] also used previously as a standard method [2, 3]. The relative energies and intensities of the line components are shown in Table 1.

The second method is based on finding the lineshape for the Auger-electron emission including all solid-state effects. These solid-state effects are usually divided into intrinsic and extrinsic parts, the former describing the conduction-electron response to the core hole and the latter including the loss processes experienced by the emitted electrons during transport to the surface. The extrinsic-loss structure can be expected to be quite similar in both photoelectron and Auger-electron emission. The intrinsic contributions in these processes are included within the Doniach-Šunjić (DS) lineshape [15], and according to our SDF calculations these lineshapes should be the same for both processes (see next Section). Thus, as a first approximation, the experimental $2p_{1/2, 3/2}$ photoelectron line measured using

TABLE 1

EXPERIMENTAL ABSOLUTE ENERGIES (eV), RELATIVE ENERGIES (eV) AND INTENSITIES (ARBITRARY UNITS) OF $L_{2,3}$ MM TRANSITIONS

Line		Absolute energy (± 0.4 eV)	Relative energy		Relative Intensity Exp. ($\pm$ 0.5)
			Exp. ($\pm$ 0.2 eV)	Theor.	
$L_{2,3}M_{2,3}M_{2,3}$					
1	$L_3 : ^1S$	291.8	- 4.0	- 3.5	3.3
2	$L_2 : ^1S + L_3 : ^1D$	295.8	0.0	0.0	11.8
3	$L_2 : ^1D + L_3 : ^3P$	299.4	3.6	2.4	10.9
4	$L_2 : ^3P$	303.4	7.6	6.1	1.7
$L_{2,3}M_1M_{2,3}$					
5	$L_3 : ^1P$	273.6			
6	$L_3 : ^3P$	280			

the same instrument, after subtracting (stripping) the contribution due to the $2p_{1/2}$ component using an intensity ratio of 1:2, is a reasonably good standard line for the $L_{2,3}M_{2,3}M_{2,3}$ Auger-electron spectrum. Because the $2p$ photoelectron and Auger-electron spectra are within different kinetic-energy regions, they have different secondary-electron backgrounds. The shape of the background obeys approximately $1/E^2$ law, since fast electrons produce secondaries mainly by small-angle Coulomb scattering [16]. The secondaries can be separated from the above-mentioned extrinsic processes and their contribution is presented in Fig. 1. Taking this correction into account, the curve in Fig. 3 was fitted to the experimental spectrum with four components within the $L_{2,3}M_{2,3}M_{2,3}$ region, using the stripped photoelectron line broadened from 1.2 to ~ 5 eV FWHM. The relative energies and intensities obtained for the components are within the same limits of accuracy as in the first method (Table 1).

The $L_{2,3}M_1M_{2,3}$ transition was also treated by this curve-fitting procedure and the absolute energies obtained for the components are also presented in Table 1. The $L_{2,3}M_1M_1$ transition has a very low intensity [17] and seems to overlap other spectral structures in the region of 250 eV. The $L_{2,3}M_{2,3}V$ transition creates the second hole in the valence band; hence its decomposition into line components is not straightforward.

SPIN-DENSITY-FUNCTIONAL CALCULATIONS

The density-functional formalism in spin-polarized form was applied for self-consistent-field ab initio calculations of the electron structure of a Ca

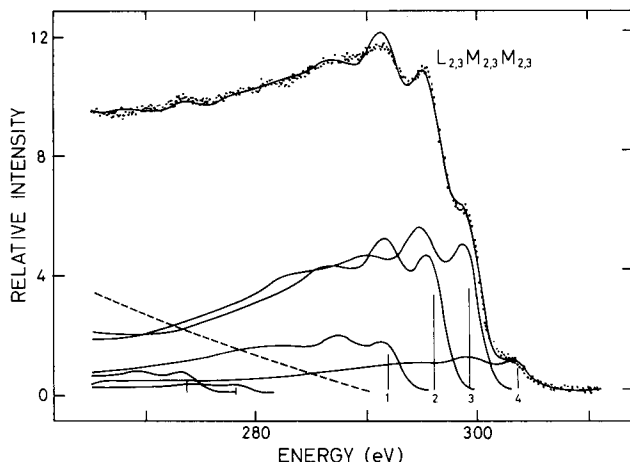


Fig. 3. Decomposition of the $L_{2,3}MM$ Auger spectrum into line components with FWHM 5 eV (solid-state effects included). The secondary-electron scattering intensity is represented by the dashed line.

atom and the conduction electrons around it. Results for other elements and a description of the calculations have been given elsewhere [18]. The program code we have employed here is essentially the same as that used previously by Nieminen and Puska [19] in kinetic-energy shift calculations for several elements. A detailed description may be found in their paper. Therefore only the application and the results for Ca are given here.

The atom-in-jellium vacancy model [19] is adopted for a metal atom. The conduction electrons are regarded as a free-electron gas modified by scattering in the screened potential of the nucleus, in the approximation of spherical symmetry of both the core and the conduction-electron states. Both of these states are worked out in the same spin-dependent one-electron effective potential, where the exchange and correlation contribution is estimated by means of the local-density interpolation formulae given in ref. 20. In addition to the solid-state calculations, the corresponding free-atom results are needed to evaluate the shift values. The kinetic-energy shift of a photoelectron or Auger electron is obtained simply as the difference between the metallic and free-atom transition energies, which are both differences between the corresponding final and initial states [18, 19]. Thus a single shift value requires four separate SCF calculations: two for a free atom, and two for an atom in jellium.

Because the Ca atom has closed electron shells both as a free atom and as an ion in a metallic lattice, there are only two possible spin-hole combinations for the double-hole final state of the Auger transition: either spins parallel or spins opposite. These combinations can be interpreted in the LS

TABLE 2

EXPERIMENTAL AND CALCULATED FREE-ATOM—METAL KINETIC-ENERGY SHIFTS (eV) AND SINGULARITY INDICES α

	Exp. $L_{2,3}M_{2,3}M_{2,3} : ^1D$	Calc. $L_{2,3}M_{2,3}M_{2,3}$			Exp. ^a		Calc.	
		$3p^{-2}(\uparrow\uparrow)$	$3p^{-2}(\uparrow\downarrow)$	Con- figur- ational average	2p	3p	2p	3p
$\Delta E = E_{\text{kin}}^{\text{F}} - E_{\text{kin}}^{\text{V}}$	20.3	20.9	19.2	19.9	8.3	6.1	9.4	8.0
α	0.3–0.4	0.40	0.31	0.35			0.34	0.36

^a From refs. 10 and 37.

coupling scheme, and the configurational average can be defined [18]. An Auger-electron kinetic-energy shift of 19.9 eV is obtained for the configurational average. The photoelectron kinetic-energy shifts are 9.4 eV for the 2p and 8.0 eV for the 3p level. The kinetic energies of electrons emitted from a metallic sample are referred to the Fermi level, whereas the corresponding free-atom values refer to the vacuum level. To correct for this difference, we have used 2.87 eV [21] for the work function of Ca metal. The corrected shift values are shown with the corresponding experimental values in Table 2.

In order to demonstrate the screening response to the Auger transition, the total change in the radial charge density and its screening-charge contribution are presented in Fig. 4. The change in density of states for the Auger transition, shown in Fig. 5, consists purely of *d*-type conduction electrons, which are seen to be localized in energy. The screening is also totally spin-polarized, being of only one spin: opposite to the hole spin. Hence the screening charge mimics an occupied atomic 3*d* orbital. Therefore the excited-atom model should also be valid for the energy-shift evaluation. Atomic Hartree–Fock and corresponding SDF excited-atom calculations yield 18.1 and 24.5 eV, respectively, supporting the idea of localized *d*-electron screening. A similar spin-polarized *d*-type screening is localized during the formation of the initial-state 2p hole [18].

The many-body response of the conduction electrons to the core hole created is known to be responsible for the asymmetry of photoelectron lines from metal samples [15, 22, 23]. Theoretically, the asymmetry has been explained by Mahan [24a] and by Nozières and De Dominicis [24b] as arising from electron-hole excitations near the Fermi level. In the approximation of spherical symmetry, the latter authors described this effect on the lineshape by a singularity index α , which is obtained from the conduction-electron scattering phase shifts in the core-hole potential. The D $\check{S}$ line [15]

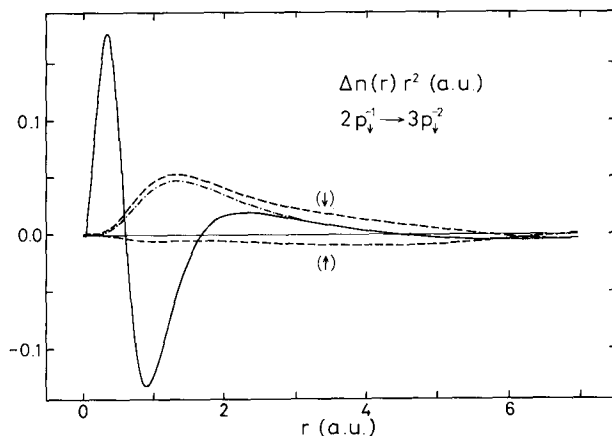


Fig. 4. Calculated total change in radial charge density (nr^2) for Auger transition with double-hole final-state spins parallel (solid curve), together with the spin components of the conduction-electron contribution (dashed curves) and their sum (dot-dashed curve).

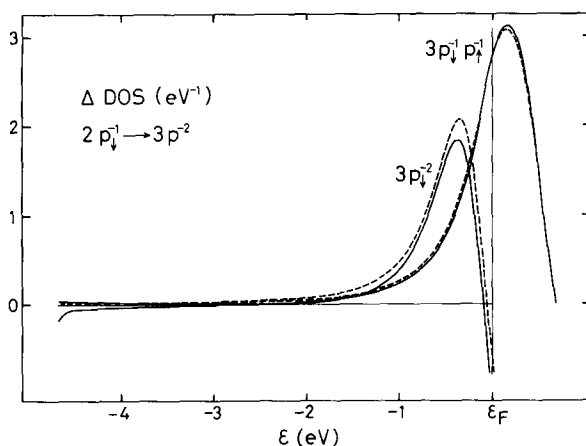


Fig. 5. Calculated change in local density of states for the $L_{2,3}M_{2,3}M_{2,3}$ Auger transition (solid curve) (also essentially the $d_{\uparrow} + d_{\downarrow}$ contribution), together with the majority-spin d -component for both final states (dashed curve).

is a Lorentzian line incorporating the singular electron-hole energy distribution by convolution. Density-functional calculations for the photoelectron lineshapes of simple metals have been presented previously [25]. However, the screening of a core hole in Ca requires a spin-polarized treatment [18]. The observed asymmetric lineshapes of the $KL_2L_3: {}^1D$ Auger lines from Mg and Na [26] have also been calculated in terms of the singularity index [18]. Our calculated values for the Ca photoelectron and Auger lines are

given in Table 2. The large values obtained for α result from the spin polarization of the screening: our spin-symmetric estimates, comparable to those of ref. 25, are only of the order of 0.1, and are clearly incompatible with the experimental measurements. The spin-symmetric value of α can be regarded as a lower limit to the spin-polarized value (see ref. 18 for more details).

DISCUSSION

The background-subtraction method gives highly symmetric lines, as can be seen in Fig. 2. The reason is the exponential attenuation factor in the subtraction procedure, which removes most of the line asymmetry. The loss-peak structure, however, remains in the spectrum. The optimal linewidth (2.3 eV) found by line fitting using the first method has a clear connection with the linewidth in the second method, in which the proper total width is ~ 5 eV. If the singularity index (0.35) calculated in the previous Section is used, the Lorentzian contribution in the proper DS line turns out to be ~ 2.5 eV, which is in good agreement with the above value of 2.3 eV. The latter value includes an instrumental contribution of ~ 1 eV. The experimental $2p$ photoelectron linewidth is ~ 0.7 eV [27]. Thus the observed width of the $L_{2,3}M_{2,3}M_{2,3}$ Auger lines indicates large final-state broadening. A level width greater than 1 eV has been reported for the $3p$ photoelectron line of Ca metal, but the value was disturbed by sample-preparation effects [27]. On the other hand, the Auger spectrum may consist of many overlapping lines impossible to separate by line fitting. Therefore, the width values have to be considered with caution, and should not be taken too literally. However, the intensity distribution within the spectrum can be considered on the basis of the selected number of lines.

Concerning the relative energies and intensities of the main line components, the two methods applied in the decomposition of the $L_{2,3}M_{2,3}M_{2,3}$ spectrum show surprisingly good agreement. This supports the assumption that the conduction-electron responses in photoelectron and Auger-electron emission are similar. With respect to the secondary-electron background, the two processes differ because of the different kinetic energies, but the difference in the shape can be estimated and taken into account as a correction (see Fig. 3). Separation of the spectrum into the individual lines is very tedious, because the L_2-L_3 splitting is only 3.7 eV, and thus the L_2 and L_3 Auger groups overlap. However, the most prominent lines can be interpreted as the ^1D and ^3P terms of the L_3 group of the $3p$ double-hole final state. In order to compare the observed term splitting with the corresponding atomic values, an evaluation was performed for the $3p^{-2}$ final state in LS coupling. Splittings $^1S-^1D$ of ~ 3.5 eV and $^1D-^3P$ of ~ 2.4 eV are obtained using Slater integrals from Mann's tables [28]. These values differ markedly from the present experimental values for Ca metal, which are ~ 4.0 and

3.6 eV, respectively. A similar difference between the calculated splitting and the measured spectral structure has been observed for Zn metal [29]. In the latter case, McGuire [30] explained this difference by invoking configurational interaction, which may change both the relative energies and intensities between transitions described by the one-configurational model. Considerable increase of the splitting in the metal spectrum as compared to that in the atomic spectrum is predicted by the SDF double-hole final-state results. The energy difference between the two possible spin combinations is twice as large for the metal as for the free atom. This may arise from the overlap of the final-state holes and the spin-polarized screening seen in Fig. 4. The transition $L_{2,3}M_1V$ (~ 302 eV) is quite close in energy to $L_{2,3}M_{2,3}-M_{2,3}$ (~ 297 eV), supporting possible configurational interaction. Furthermore, the valence shell provides a localized d -type screening. Therefore an interaction between $(3p^{-2})^1D$ and $3s^{-1}V^{-1}$ of the same symmetry might be possible. This interaction should decrease the intensity of the $L_{2,3}M_{2,3}-M_{2,3}:^1D$ component with respect to the others, but the effect is difficult to distinguish because of the multiple overlapping of the lines. If the $L_{2,3}M_1V$ transition is present, its intensity may add to the higher-energy components of the $L_{2,3}M_{2,3}M_{2,3}$ transition, distorting the spectral structure. Because there is not clear evidence for a significant intensity of the $L_{2,3}M_1V$ as compared to the $L_{2,3}M_{2,3}M_{2,3}$ transition, we have ignored it.

The Auger spectrum of metallic Ca does not exhibit the anomalous intensity ratio $I(L_3M_{2,3}M_{2,3})/I(L_2M_{2,3}M_{2,3}) \simeq 1$ reported for the free-atom Auger spectrum [31]. On the contrary, for Ca metal the intensity ratio is probably greater than the statistical ratio of 2. This estimate is supported by the experimental ratio $I(L_3:^1D + L_2:~^1S)/I(L_3:~^1S) \simeq 3.6$ from Table 1. This is very close to the theoretical free-atom $I(L_3:~^1D)/I(L_3:~^1S)$ value [31]. Furthermore, the component identified as the $L_2:~^3P$ line has lower intensity than the $L_3:~^1S$ line. One process which could decrease the L_2 Auger group intensity is the L_2L_3V -type Coster—Kronig transition. However, the L_2-L_3 splitting is only 3.7 eV; hence the Coster—Kronig transition becomes energetically possible only with the assistance of the strong d -screening of the core hole. The valence electrons may take part at the same time in this transition and screen the core hole, which results in difficulties when applying only simple models. In order to estimate the effect of screening on the binding energies with and without the core hole, SDF calculations of the $3p$ binding energy in the ground state and of the $3p^{-1}$ state were performed. Whatever the choice of the spin of the electron to be ionized with respect to the spin of the $3p^{-1}$ hole, the $3p$ -electron binding energy deviates only slightly from that in the ground state. Thus it can be concluded that the L_2L_3V Coster—Kronig transition may be possible in Ca metal.

A structure presumably due to $L_{2,3}M_1M_{2,3}$ transitions with ^1P and ^3P components can just barely be distinguished above the background and

statistical variations of the spectrum (Fig. 1). The experimental term splitting is $\sim 7\text{--}8\text{ eV}$ (Table 1), whereas atomic calculations give a value of 9 eV in LS coupling, slightly overestimating the experimental splitting. This tendency has generally been found [32] in connection with the Slater integrals from Mann's tables [28].

The region of the $L_{2,3}M_1M_1$ transition (Fig. 1) shows a distinct hump, which is, however, probably due mostly to a loss structure associated with the $L_{2,3}M_{2,3}M_{2,3}$ transition. A similar broad structure has been observed in the photoelectron spectrum of Ca metal at a distance of $\sim 35\text{ eV}$ from the main line toward lower energies [12]. Furthermore, a broad maximum appears in the electron energy-loss spectra of metals which have a d or f shell near the Fermi surface [33, 34].

The $L_{2,3}M_{2,3}V$ lines appear at a kinetic energy which corresponds directly to the $L_{2,3}-M_{2,3}$ energy difference. The structure is extraordinarily sharp, in spite of the fact that the second hole is in the valence band. Furthermore, this transition seems to have significant intensity. There is no simple relation between the shape of this spectrum and the valence-electron structure of Ca metal, since the bandwidth for bulk Ca is $\sim 3.6\text{ eV}$ [13]. If surface effects are excluded, only few explanations exist for this narrow shape. The transition-matrix element may differ for different parts of the band. Furthermore, the density of states is modified around the core-ionized Ca atom, as discussed in the preceding Section. The SDF calculations show a narrow d -type screening peak in the initial single-hole state localized below the Fermi level. This has been discussed in detail in ref. 18. Similarly to the L_2L_3V transition discussed above, the valence electrons also may be considered to take part simultaneously in the transition and to screen the core hole. The change in the density of states of core-ionized Ca metal is much more drastic than for, e.g., Na, Mg and Al [18], whose KLV spectra have more band-like features [35]. Concerning the intensity ratio between the L_3 and L_2 groups, the $L_{2,3}M_{2,3}V$ transition also indicates a ratio larger than 2, because of the low background intensity toward higher energies from the main line.

The solid-state—free-atom kinetic-energy shift is exceptionally large: 20.3 eV for the $L_{2,3}M_{2,3}M_{2,3}:^1D$ transition referred to the free-atom ^1D -line experimental value (272.7 eV) [11], which is very close to the Hartree—Fock value. Although accurate determination of the shift is disturbed by the change in term splitting, the calculated shift values agree well with the experimental values (Table 2). Because of the localized character of the d -type screening, the excited-atom model [36] calculations for the shift are also in good agreement with experiment, i.e., the screening charge can be considered with reasonable accuracy to occupy the first empty atomic orbital.

The experimental photoelectron kinetic-energy shifts can be obtained from ref. 37 and data for the Ca atom [10]. The energy shifts turn out to be

8.3 eV for $2p$ and 6.1 eV for $3p$ photoelectrons. The calculated shift values are in satisfactory agreement with experiment (Table 2). Also the thermochemical model [38] gives a good estimate of 6.7 eV for the core-level binding-energy shift.

In conclusion, we have shown that the broadened photoelectron lineshape can be used as a standard line in curve fitting of the inner-shell Auger spectrum of Ca, since the intrinsic-loss structure described by the Doniach—Šunjić lineshape according to SDF calculations is the same for both processes and the extrinsic losses can be expected to be similar. Decomposition of the $L_{2,3}M_{2,3}M_{2,3}$ Auger-electron spectrum exhibits term splittings larger than the calculated free-atom values. The kinetic Auger and photoelectron shifts are large compared to those for the simple metals. Most of the features of the spectra are directly related to strong localization of d -type screening around core-ionized Ca. The spin—density-functional calculations support all of the experimental results.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. S. Aksela for useful discussions and his interest in their work. They thank Prof. R. Nieminen and Mr. M. Puska for providing their program code. The authors also thank Miss H. Pulkkinen for her help in data handling. This work was partly supported by the National Research Council for Sciences (Finland).

REFERENCES

- 1 J. Väyrynen, S. Aksela and H. Aksela, *Phys. Scr.*, **16** (1977) 452.
- 2 J. Väyrynen, S. Aksela, M. Kellokumpu and H. Aksela, *Phys. Rev. A*, **22** (1980) 1610.
- 3 S. Aksela, J. Väyrynen, H. Aksela and S. Pennanen, *J. Phys. B*, **13** (1980) 3745.
- 4 Y. -K. Kim and P. S. Bagus, *Phys. Rev. A*, **8** (1973) 1739.
- 5 B. Vasvari, A. O. E. Animalu and V. Heine, *Phys. Rev.*, **154** (1967) 535.
- 6 M. W. D. Mansfield and G. H. Newsom, *Proc. R. Soc. (London)*, *Ser. A*, **357** (1977) 77.
- 7 W. Smits, B. Breuckmann and W. Mehlhorn, *J. Phys. B*, **9** (1976) L 493.
- 8 V. Pejcev, T. W. Ottley, D. Rassi and K. J. Ross, *J. Phys. B*, **11** (1978) 531.
- 9 E. P. F. Lee and A. W. Potts, *J. Phys. B*, **14** (1981) L 61.
- 10 W. Mehlhorn, B. Breuckmann and D. Hausmann, *Phys. Scr.*, **16** (1977) 177.
- 11 H. Aksela, S. Aksela and J. Väyrynen, to be published.
- 12 L. Ley, N. Mårtensson and J. Azoulay, *Phys. Rev. Lett.*, **45** (1980) 1516.
- 13 L. Ley, G. P. Kerker and N. Mårtensson, *Phys. Rev. B*, **23** (1981) 2710.
- 14 T. T. Rantala, Rep. No. 75, Department of Physics, University of Oulu, Finland, (1980).
- 15 S. Doniach and M. Šunjić, *J. Phys. C*, **3** (1970) 285.
- 16 P. A. Wolff, *Phys. Rev.*, **95** (1954) 56.

- 17 E. J. McGuire, Sandia Labs., Rep. SC-RR-710075, 1971 (unpublished).
- 18 T. T. Rantala, Phys. Rev. B, in press.
- 19 R. M. Nieminen and M. J. Puska, Phys. Rev. B, 25 (1982) 67.
- 20 O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B, 13 (1976) 4274.
- 21 J. Hölzl and F. K. Schulte, Springer Tracts in Modern Physics, Vol. 85, Springer, Heidelberg, 1979.
- 22 S. Hüfner and G. K. Wertheim, Phys. Rev. B, 11 (1975) 5197.
- 23 P. Steiner, H. Höchst and S. Hüfner, Z. Phys. B, 30 (1978) 129.
- 24 (a) G. D. Mahan, Phys. Rev., 163 (1967) 612; (b) P. Nozières and C. T. De Dominicis, Phys. Rev., 178 (1969) 1097.
- 25 C. -O. Almbladh and U. von Barth, Phys. Rev. B, 13 (1976) 3307; G. W. Bryant and G. D. Mahan, Phys. Rev. B, 17 (1978) 1744.
- 26 P. Steiner, F. J. Reiter, H. Höchst, S. Hüfner and J. C. Fuggle, Phys. Lett., 66A (1978) 229.
- 27 J. C. Fuggle and S. F. Alvarado, Phys. Rev. A, 22 (1980) 1615.
- 28 J. B. Mann, Atomic Structure Calculations. I, Hartree—Fock Energy Results for the Elements Hydrogen to Lawrencium, Los Alamos Scientific Laboratory, Rep. LASL-3690, 1967.
- 29 J. M. Mariot and G. Dufour, J. Phys. C, 10 (1977) L213.
- 30 E. J. McGuire, Phys. Rev. A, 16 (1977) 2365.
- 31 H. Aksela, J. Electron Spectrosc. Relat. Phenom., 19 (1980) 371.
- 32 S. Aksela, J. Väyrynen and H. Aksela, Phys. Rev. Lett., 33 (1974) 999.
- 33 M. J. Lynch and J. B. Swan, Aust. J. Phys., 20 (1967) 345.
- 34 J. Langkowski, J. Phys. D., 8 (1975) 2058.
- 35 R. Lässer and J. C. Fuggle, Phys. Rev. B, 22 (1980) 2637.
- 36 L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak and D. A. Shirley, Phys. Rev. B, 8 (1973) 2392.
- 37 H. Van Doveren and J. A. Th. Verhoven, J. Electron Spectrosc. Relat. Phenom., 21 (1980) 265.
- 38 B. Johansson and N. Mårtensson, Phys. Rev. B, 21 (1980) 4427.