

Core-hole screening and plasmon satellites in calcium

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The valence bands and the outermost p core levels of Ca metal have been studied by synchrotron radiation photoemission. High-resolution studies of the $3p$ core levels reveal three peaks and anomalously strong plasmon satellites. It is shown by the $Z + 1$ approximation that empty states in Ca metal which are just above the Fermi level are pulled below E_F by the core-hole potential and the core hole is screened by a $3d$ electron. Localization of the $3d$ electron at the core-hole site is confirmed by good agreement between the observed core-level structure and the calculated $3p^5 3d^1$ multiplet. This conclusion is consistent with valence-band and core-level photoemission results for the Ca-Si interface and CaH_2 . Studies of the Ba $5p$ core levels show structures which are ascribed to the multiplet of $5d$ -screened $5p^5 5d^1$ final states. Possible effects of the poorly screened core-hole states ($3p^5 3d^0$) on the plasmon satellites are discussed.

I. INTRODUCTION

Core-level and valence-band photoemission spectra of simple metals such as Na, Be, Mg, and Al are characterized by asymmetric broadening of main lines and the appearance of plasmon satellites.^{1,2} The extent of the asymmetry and the satellite intensities has been explained quantitatively by many-body response theories of free-electron metals.³⁻⁷ On the other hand, photoemission spectra of the heavy alkaline-earth metals Ca, Sr, and Ba show anomalous features. According to x-ray photoemission (XPS) studies,⁸ core levels of these metals, particularly those of Ca, exhibit plasmon loss satellites which are much more intense than in simple metals. Furthermore, the apparent spin-orbit splitting of the Ca $3p$ core level has been reported to be considerably enhanced relative to the atomic value.⁸

This paper presents results of synchrotron radiation photoemission studies of Ca atoms in different electronic configurations with varying final-state screening. High resolution spectra for evaporated films of Ca metal reveal a $3p$ triplet associated with the Ca main-line region. We show that this triplet is due to $3p^5 3d^1$ multiplet states resulting from core-hole screening by $3d$ electrons. This screening process becomes possible in the heavy alkaline earth metals because most of the d -band states are located just above the Fermi level in these metals.⁹⁻¹³ By studying Ca at the evolving Ca-Si interface, it has been possible to vary the d -derived density of states and alter the d screening. By studying Ca in insulating CaH_2 , we have been able to observe the absence of d -screening. Finally, studies of the Ba $5p$ line shape show multiplet structures which support the interpretation for Ca metal.

We also report valence-band spectra for these materials. The valence-band changes from Ca to the Ca-Si interface to CaH_2 correspond to the changes in the $3p$ core levels. We find no evidence of surface states in the Ca valence band as reported previously,¹⁴ despite the high surface sensitivity of our measurements.

II. EXPERIMENTAL

Synchrotron radiation photoemission experiments were performed with radiation from the Tantalus 240 MeV electron storage ring at the University of Wisconsin at Madison. Photoelectron energy distribution curves (EDC's) were measured with a double pass cylindrical mirror electron energy analyzer. The total resolution of the analyzer plus monochromator was ~ 0.5 eV.

For Ca metal, thick overlayers of ultrahigh purity Ca were deposited onto oxidized Ta or Cu substrates. During evaporation, the pressure rose from operating pressures of $\sim 5 \times 10^{-11}$ Torr to 2×10^{-10} Torr—or higher if the starting metal had not been extensively degassed to remove the copious amounts of hydrogen found in even high purity Ca.¹⁵ Barium films were prepared by deposition onto Si substrates ($\Theta = 200\text{--}500$ Å).¹⁵ For CaH_2 , thin layers ($0 < \Theta \leq 40$ Å) of Ca were deposited onto substrates of YH_2 , NdH_2 , and CeH_2 which had been cleaved *in situ*. Ca silicide was prepared by direct sublimation of Ca from a W coil onto cleaved Si(111) 2×1 surfaces. The sample preparation of CaH_2 and Ca silicide has been described in detail in Refs. 16 and 17, respectively.

III. RESULTS

In Fig. 1 we show valence-band and $3p$ core-level emission of Ca in EDC's taken at $h\nu = 40$ eV and $h\nu = 70$ eV. These photon energies exhibit the $h\nu$ dependence of the plasmon loss features and avoid overlap of the strong $M_{2,3}VV$ Auger features with the $3p$ and valence bands. Loss features are indicated by shaded areas. The Ca $3p$ level exhibits unusually high loss intensities, as reported in a previous XPS investigation.⁸ Our $h\nu$ -dependent studies show that these loss features become weaker as the electron kinetic energies become lower, consistent with the electron-kinetic-energy dependence of the plasmon loss intensities in Al and Si.^{18,19} The valence band exhibits satellites up to two plasmon losses, but their intensities are much weaker than those of the Ca $3p$ core level. Three

peaks are resolved in the $3p$ main lines. The valence band of Ca metal shows a full width at half maximum (FWHM) of ~ 1 eV, consistent with earlier ultraviolet photoemission results.^{20,21} This narrow band emphasizes the d -like part of the occupied density of states (DOS) because the Ca $3d$ cross section dominates the spectra for these photon energies. The valence band shows no surface states.¹⁴

An EDC for Ba metal is shown in Fig. 2. Emission at ~ 5 eV binding energy is due to oxygen contamination.¹⁵ Studies of oxygen exposure of Ca metal showed a growing feature at 5.5 eV below E_F with FWHM equal to 1.3 eV, as reported previously.²¹ From these studies, the amount of oxygen on Ba is estimated to be much less than a monolayer, so that the core-level spectra would be almost unaffected by the contamination. Each spin-orbit component of the Ba $5p$ outermost core level shows previously unresolved structures. The apparent spin-orbit splitting is larger than the atomic one (2.0 eV) by $\sim 10\%$. Plasmon loss intensities are weaker than in Ca metal.

Figure 3 shows EDC's for the Ca-Si(111) interface. Detailed studies of the evolution of the interface can be found elsewhere.¹⁶ The overlayer spectrum at 8.5 Å Ca coverage shown in the figure is representative of a silicide-like interface phase.¹⁶ The important point here is that the Ca $3p$ core level is a simple asymmetric unresolved spin-orbit doublet without appreciable plasmon satellites. The DOS at E_F is so small that no Fermi edge is identified.

EDC's for CaH₂ are shown in Fig. 4, where one can see the very low DOS within ~ 2 eV of E_F , consistent with the insulating character of CaH₂. Emission centered at ~ 5 eV is due to Ca-H bonding states and has been compared with a band calculation in Ref. 17. The Ca $3p$ level is again a simple unresolved spin-orbit doublet, but is symmetric.

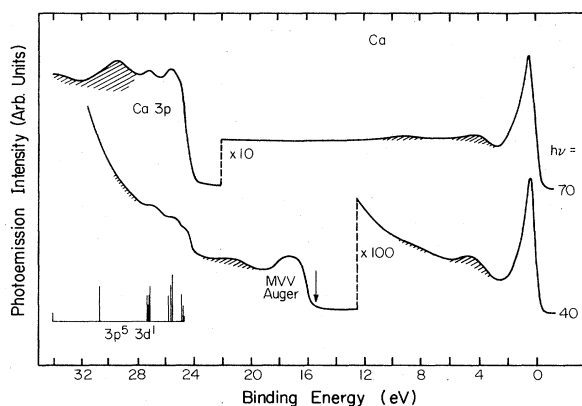


FIG. 1. Photoemission energy distribution curves for Ca metal. The shaded areas represent plasmon loss satellites associated with the valence band, the $M_{2,3}VV$ Auger, and the Ca $3p$ level. The vertical bars at the bottom show calculated multiplet lines of the $3d$ -screened $3p^3 3d^1$ configuration. Note that the height of the bar gives the multiplicity of the line and not the spectral intensity exactly. The arrow indicates an Auger electron kinetic energy originating from the lowest binding energy $3p$ hole and two electrons at E_F calculated using one-electron energy levels.

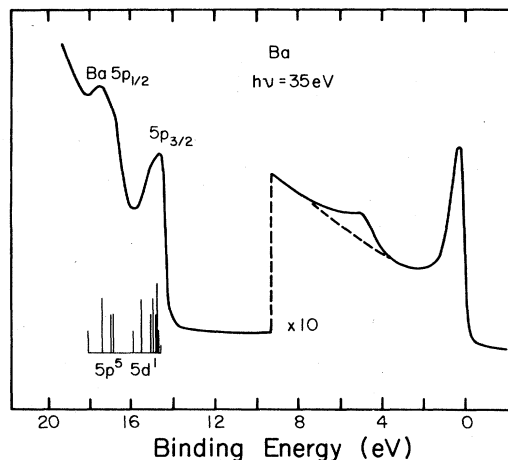


FIG. 2. Photoemission energy distribution curve for Ba. The dashed line shows estimated oxygen contamination. The $5p^5 5d^1$ multiplet lines are shown by vertical bars.

IV. DISCUSSION

The high resolution photoemission results shown in Figs. 1 and 2 for Ca and Ba demonstrate complex lineshapes for the outermost p core levels and strong plasmon losses. We also show that the $3p$ line shape for Ca on Si(111) is asymmetric and that for Ca in insulating CaH₂ is symmetric, both showing an unresolved spin-orbit doublet. The plasmon intensity is low or unobservable for the Ca-Si interface and CaH₂. On the other hand, light alkaline earth metals Be and Mg have shown simple (asymmetric) main lines, normal spin-orbit splitting, and moderate plasmon satellite intensities.^{1,2}

A most significant point that distinguishes the heavy alkaline earth metals from the light alkaline earth metals is the presence of fairly narrow and mostly unoccupied d -band states near E_F , as has been revealed by crystal structure studies,^{12,13} band structure calculations,⁹⁻¹² and the present valence-band spectra. It is therefore necessary to consider the role that these d states play in the core level anomalies. We suggest that in the presence of a np core hole, nd states could be pulled down below E_F , become

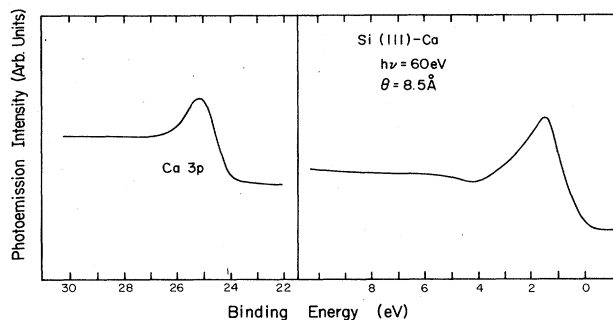


FIG. 3. Photoemission energy distribution curves for the Ca-Si interface prepared by depositing Ca metal on cleaved Si(111) surfaces. The overlayer thickness of Ca is 8.5 Å.

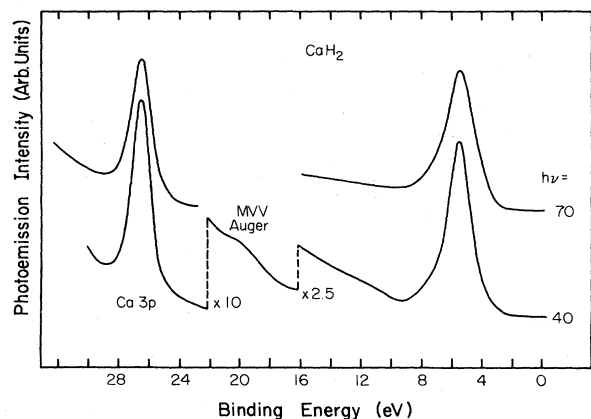


FIG. 4. Photoemission energy distribution curves for CaH_2 . The valence band centered at ~ 5 eV below E_F is the Ca-H bonding band.

occupied, and screen the core hole according to the mechanism of Kotani and Toyozawa.²² One of the main points of this paper is to prove that this suspicion is indeed the case.

In order to determine the character of the screening charges, we applied the $Z+1$ approximation.²³ There the core hole is assumed to be screened by a unit electronic charge on the same atomic site (complete screening²³). Binding energies of core holes with zero, one, and two d electrons can be obtained by considering the energies of corresponding free atom configurations and cohesive energies, as in Fig. 5. The $3d$ -screened Ca $3p$ binding energy relative to that of sp screening was calculated by assuming that $3d$ electrons become localized at the core-hole site and do not participate in the metallic bonding. The energy difference between a free atom with a core hole $3p^5 3d^1 4s^2$ and a core hole in the metal $3p^5 3d^1 [4s^2]$,

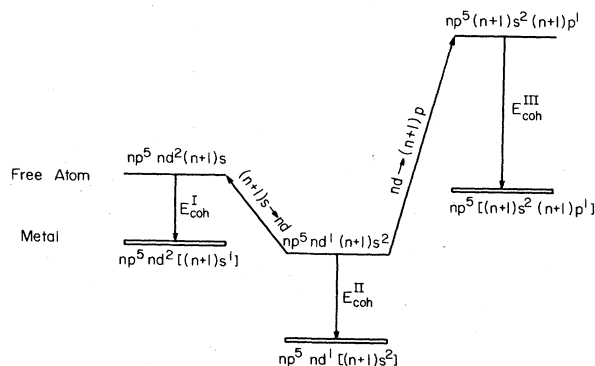


FIG. 5. Energy-level diagram for calculation of the relative binding energies of differently screened outermost p core levels in heavy alkaline earth metals. E_{coh}^I , $E_{\text{coh}}^{\text{II}}$, and $E_{\text{coh}}^{\text{III}}$ represent the cohesive energies of monovalent, divalent, and trivalent sp metals.

where $[]$ represents electrons forming metallic bonds, is approximated by the cohesive energy of a divalent sp metal, Mg (Ref. 24). Similarly, the cohesive energy of Al (Ref. 24) can be used to estimate the energy difference between $3p^5 4s^2 4p^1$ and $3p^5 [4s^2 4p^1]$. The difference between the two atomic configurations $3p^5 3d^1 4s^2$ and $3p^5 4s^2 4p^1$ can be estimated within the $Z+1$ approximation by the $3d \rightarrow 4p$ excitation energy²⁵ ($3d^1 4s^2 \rightarrow 4s^2 4p^1$) of Sc. In addition to screening by one d electron, there is also the possibility of screening by two d electrons, although it may not be important, particularly for Ba where the ground state d -electron number is larger ($n_d \sim 0.85$ as compared to $n_d \sim 0.55$ of Ca).¹² The binding energies of two d -electron final states are estimated similarly using the cohesive energy²⁴ of Na metal. Relative binding energies of the variously screened final states thus estimated are listed in Table I. One finds that in all the heavy alka-

TABLE I. Relative binding energies of the outermost p core levels in Ca, Sr, and Ba in variously screened final states calculated by the $Z+1$ approximation assuming complete screening. Three screening charge configurations d^0 , d^1 , and d^2 have been considered.

	Ca ($n=3$)	Sr ($n=4$)	Ba ($n=5$)
Free-atom energy levels ^a			
$E(np^5(n+1)s^2(n+1)p^1) - E(np^5 nd^1(n+1)s^2)^b$	4.8	2.9	3.7
$E(np^5 nd^2(n+1)s^1) - E(np^5 nd^1(n+1)s^2)^c$	1.4	1.9	0.3
Core-level binding energies in metal			
$E(np^5[(n+1)s^2(n+1)p^1]) - E(np^5 nd^1[(n+1)s^2])^d$	3.0	1.1	1.9
$E(np^5 nd^2[(n+1)s^1]) - E(np^5 nd^1[(n+1)s^2])^e$	1.8	2.3	0.7

^aThe lowest multiplet term of each configuration is taken from Ref. 25.

^b $E((n+1)s^1(n+1)p^1) - E(nd^1(n+1)s^1)$ of the $Z+1$ element (Ref. 25) was used. $E((n+1)s^2(n+1)p^1) - E(nd^1(n+1)s^2)$ is a more appropriate $Z+1$ estimate, but could not be found in the literature.

^c $E(nd^2(n+1)s^1) - E(nd^1(n+1)s^2)$ of the $Z+1$ free atom (Ref. 25) was used.

^dCohesive energy difference between Al and Mg (1.8 eV, Ref. 24), was used for that between the trivalent and divalent configurations.

^eCohesive energy difference between Mg and Na (0.4 eV, Ref. 24), was used for that between the divalent and monovalent configurations.

line earth metals, final states with one localized d electron have the lowest binding energies and are expected to give the main lines.

The Ca $3p$ spectrum is compared to the calculated $3p^5 3d^1$ multiplet in Fig. 1. The multiplet lines have been calculated using the atomic spin-orbit splitting^{8,26} of 0.35 eV and Slater integrals between $3p$ and $3d$ orbitals²⁷ [$F_2=0.17$ eV, $G_1=0.495$ eV, and $G_3=0.055$ eV (Ref. 27)]. The heights of the lines have been assumed to be proportional to the multiplicity since no accurate intensity calculation could be performed for those lines produced by the screening process. Allowing for this, agreement between the experiment and calculated Ca $3p$ spectra is excellent: The experimentally observed three peak features correspond well to the calculated three groups of lines. Thus we conclude that the Ca $3p$ core hole is screened by one d electron and the $3p^5 3d^1$ configuration is localized.²⁸

In Fig. 2 we compare the experimental Ba $5p$ line shape with the calculated $5p^5 5d^1$ multiplet. In this case smaller Slater integrals ($F_2=0.025$ eV, $G_1=0.073$ eV, and $G_3=0.008$ eV) have been used, corresponding to the large radii of the $n=5$ orbitals with atomic spin-orbit splitting 2.0 eV.²⁶ The calculated lines are in reasonable agreement with the experiment: The apparent splitting of ~ 2.2 eV can be attributed to the multiplet structure.

According to Ley *et al.*⁸ the Sr $4p$ level also exhibits at least two components with a splitting of ~ 1.3 eV as compared to the atomic spin-orbit splitting of 0.96 eV.²⁶ Considering the present observation of the multiplet structures in the Ca $3p$ and Ba $5p$ lines, we would expect the Sr $4p$ level to exhibit a multiplet splitting with a magnitude intermediate between Ca and Ba. In order to estimate the contributions of the Sr $4p$ - $4d$ multiplet coupling to the Sr $4p$ line shape, we calculated the multiplet structure for the Sr $4p$ level by using the free atom spin-orbit splitting²⁶ and Slater integrals intermediate between those for Ca and Ba. In Fig. 6, we show how the multiplet effects modify the $4p$ line shape for different sets of Slater integrals. Thus our high resolution results, combined with the calculated multiplet structures, demonstrate that the splitting of the outermost p core lines for the heavy alkaline earth metals is due to multiplet coupling with screening d electrons in the final state.

The d screening of the core holes in Ca metal is consistent with the core levels of the Ca-Si interface (Fig. 3) and CaH₂ (Fig. 4). The Ca-Si interface is metallic with a low DOS at E_F . Experimental core-level shifts of Ca $3p$ and Si $2p$ show that the Ca-Si bonding has a substantial ionic component.¹⁶ Thus the nonbonding Ca $3d$ states are expected to be higher than in Ca metal and there would be smaller probability of core-hole screening by $3d$ electrons localized at the same core-hole site. In fact, band structure calculations²⁹ have shown that in Ca silicides most of the nonbonding Ca $3d$ states are 3–10 eV above E_F while some $3d$ states form bonding states with Si p states extending well below E_F . The core line shapes shown in Fig. 3 reveal a simple unresolved asymmetric $3p$ spin-orbit doublet, consistent with the atomic splitting. The asymmetry suggests that the Ca $3d$ or $4sp$ partial DOS is finite at E_F , although emission at E_F is too weak to establish the metallic character. In the case of insulating

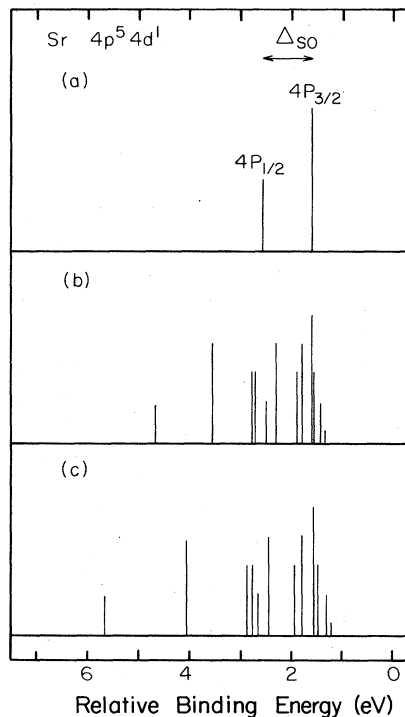


FIG. 6. Calculated multiplet structure of the Sr $4p$ core level. (a) $F_2=G_1=G_3=0.0$ eV, (b) $F_2=0.05$ eV, $G_1=0.145$ eV, $G_3=0.016$ eV, (c) $F_2=0.07$ eV, $G_1=0.204$ eV, $G_3=0.023$ eV. The free-atom spin-orbit splitting 0.96 eV has been used for the three cases.

CaH₂, the Ca $3p$ core level (Fig. 4) is again an unresolved spin-orbit doublet, and the line shape is symmetric since no localized or metallic screening is expected for this wide gap insulator.

It is worth noting that the atomic character of the core-level photoemission spectra, as revealed in the alkaline earth metals, is suppressed or disappears for most of the elemental transition metals but is again seen in satellites of Ni and Pd. This means that d electrons are most likely to be localized in the heavy alkaline earth metals (d^{0-1}) and Ni- and Pd-like metals ($d^{\sim 9}$). This is consistent with the d -band widths of the $3d$ and $4d$ transition metals calculated by the renormalized-atom method,³⁰ which showed a band width maximum around the half-filled d shells but a small bandwidth for the near noble metals and the alkaline earth metals.

Finally, we would like to discuss the anomalous plasmon satellite intensity of Ca core levels. Our results show that the plasmon intensity is significantly higher for the Ca $3p$ level than for the valence band and the MVV Auger emission. In the case of valence-hole final states, including the MVV Auger final states, the holes are not localized [the itinerant character of Auger final states can be seen from their kinetic energies, which are lower than those predicted by one electron energy levels by less than 1 eV (Ref. 31)] while core holes are localized, as is shown above. Thus the anomalous satellite intensity seems to be correlated with the formation of localized holes. As the

localized core holes screened by d electrons give the main lines, we propose that the poorly-screened (sp -screened) core-hole states contribute to the intense satellites.²² According to this mechanism, the more localized the screening d orbitals are, the more intense the satellites become relative to the main lines.^{22,32} The alkaline earth metals Ca, Sr, and Ba do in fact follow this tendency. The position of poorly screened core levels are given by Table I to be 1–3 eV above the main lines. We note that in Ca the enhancement of the loss features are more significant for energies where the poorly screened final states should be located. On the other hand, the line shapes of the enhanced satellites are close to those of the loss functions,⁸ and the $h\nu$ dependence of the intensity is consistent with plasmon losses.^{6,18,19} It might therefore be possible that the poorly screened states and the plasmon are coupled to each other and are modified, but so far mechanisms for such a coupling have not been described.

It is interesting to note that for those metallic compounds which show strong core-level satellites, there are low-energy plasmons whose energies are nearly the same as the main-to-satellite separations [ReO_3 , Na_xWO_3 (Ref. 33), ScH_2 , YH_2 (Refs. 34 and 35), etc.] These satellites have been attributed to plasmon losses in some cases³³ and to “shake-up” satellites due to poorly-screened final states in other cases.^{33,35} They are more intense for transition metal core levels than for the other core levels and the valence bands, thus excluding simple plasmon identification. Trends in changes of the relative intensities of the main and satellite lines with the localization of screening orbitals are qualitatively consistent with the theoretical prediction for the poorly screened satellites.^{22,32} For example, in the outermost p core levels of the series ScH_2 - YH_2 - LuH_2 ,³⁴ where the screening orbitals become

less localized in that order, the satellite intensity decreases correspondingly. These compounds are different from the alkaline earth metals in that there is a valence band derived from nonmetal elements below the conduction d bands and that free-electron-like sp bands do not overlap the d bands but are similar to them in having a small number of d electrons ($n_d \leq 1$). It has been pointed out in the case of Na_xWO_3 that neither poorly screened states nor plasmons can fully explain the satellite behavior and that processes intermediate between localized screening and collective plasmon excitations should be considered.³³ Further theoretical studies including both local core-hole screening and plasmon excitations would be necessary to understand the satellite features in these narrow-band metals.

V. CONCLUSION

We have shown that the complex features of the $3p$ core level of Ca metal are derived from multiplet coupling between the core hole and a screening d electron. This screening and the multiplet coupling are also shown to be present in Ba metal. The anomalously intense plasmon satellites are proposed to be related to poorly screened core-hole states.

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¹L. Ley, F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, *Phys. Rev. B* **11**, 600 (1975).

²P. Steiner, H. Höchst, and S. Hüfner, *Z. Phys. B* **30**, 129 (1978); in *Photoemission in Solids*, edited by L. Ley and M. Cardona (Springer, Berlin, 1979), Vol. 2, p. 349.

³S. Doniach and M. Sunjić, *J. Phys. C* **3**, 285 (1970).

⁴P. Minnhagen, *Phys. Lett.* **56A**, 327 (1967).

⁵G. D. Mahan, *Phys. Rev.* **163**, 612 (1967).

⁶J. E. Inglesfield, *Solid State Commun.* **40**, 467 (1981); *J. Phys. C* **16**, 403 (1983).

⁷D. R. Penn, *Phys. Rev. Lett.* **38**, 1429 (1977).

⁸L. Ley, N. Mårtensson, and J. Azoulay, *Phys. Rev. Lett.* **45**, 1516 (1980).

⁹J. M. McCaffrey, J. R. Anderson, and D. Papaconstantopoulos, *Phys. Rev. B* **7**, 674 (1973).

¹⁰V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

¹¹J.-P. Jan and H. L. Skriver, *J. Phys. F* **11**, 805 (1981).

¹²H. L. Skriver, *Phys. Rev. Lett.* **49**, 1768 (1982).

¹³H. Olijnyk and W. B. Holzapfel, *Phys. Lett.* **100A**, 191 (1984), and references therein.

¹⁴L. Ley, G. P. Kerker, and N. Mårtensson, *Phys. Rev. B* **23**, 2710 (1981).

¹⁵Ca metal was purified by fractional sublimation under partial pressure of He to remove Mg, Ba, and Sr. It was then sealed in a Ta container and H was removed by heating for 5 d at 950°C. The resulting Ca pieces were handled in an Ar-filled glove box and sealed in quartz capsules until they were loaded into the spectrometer. Prior to deposition, the Ca evaporator was degassed *in situ* to ensure deposition of clean Ca in the 10^{-10} -Torr range. Ba was handled in a similar manner, but, since it is more reactive, it developed an oxide skin. Contamination as judged from the 4.8-eV feature in the photoemission spectrum could be minimized by prolonged evaporation, but could not be eliminated.

¹⁶A. Franciosi, J. H. Weaver, and D. T. Peterson, *Phys. Rev. B* (to be published).

¹⁷J. H. Weaver, M. Gupta, and D. T. Peterson, *Solid State Commun.* (to be published).

¹⁸S. A. Flodstrom, R. Z. Bachrach, R. S. Bauer, J. C. McMena-min, and S. B. M. Hagström, *J. Vac. Sci. Technol.* **14**, 303

- (1977).
- ¹⁹L. I. Johansson and I. Lindau, *Solid State Commun.* **29**, 379 (1979).
- ²⁰L. Armand, J. L. Bouillot, and L. Gaudart, *Surf. Sci.* **86**, 75 (1979).
- ²¹J. Kress and G. J. Lapeyre, *Solid State Commun.* **9**, 827 (1971); *Phys. Rev. Lett.* **28**, 1639 (1972).
- ²²A. Kotani and Y. Toyozawa, *J. Phys. Soc. Jpn.* **37**, 912 (1974).
- ²³B. Johansson and N. Mårtensson, *Phys. Rev. B* **21**, 4427 (1980).
- ²⁴K. A. Gschneidner, *Solid State Phys.* **16**, 275 (1964).
- ²⁵C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1957), Vols. 1–3.
- ²⁶W. Schmitz, B. B. Brenckman, and W. Mehlhorn, *J. Phys. B* **9**, L493 (1976).
- ²⁷These Slater integrals can be roughly estimated by extrapolating those of $3d$ transition metal ions [T. Yamaguchi, S. Shibuya, and S. Sugano, *J. Phys. C* **15**, 2625 (1982); R. E. Watson, Massachusetts Institute of Technology Technical Report No. 12, 1959 (unpublished)], but they were actually obtained by adjusting them around the roughly estimated ones. F_2 was regarded as a free parameter, and G_1 and G_3 were derived by $G_1 = 2.91F_2$ and $G_3 = 0.325F_2$, which holds quite well for the $3d$ transition metal ions.
- ²⁸Recent $2p$ core absorption and emission studies on Ca metal have also suggested that an occupied localized d level is formed near E_F in the core-hole state [H. Nakamura, K. Ichikawa, T. Watanabe, and K. Tsutsumi, *J. Phys. Soc. Jpn.* **52**, 4014 (1983)] and that excitations of $2p^5 3d^1$ multiplet states should be considered [J. Barth, F. Gerken, and C. Kunz, *Phys. Rev. B* **28**, 3608 (1983)].
- ²⁹J. H. Weaver, A. Franciosi, and V. L. Moruzzi, *Phys. Rev. B* **29**, 3293 (1984).
- ³⁰L. Hodges, R. E. Watson, and H. Ehrenreich, *Phys. Rev. B* **5**, 3953 (1972).
- ³¹G. A. Sawatzky and A. Leselink, *Phys. Rev. B* **21**, 1979 (1980).
- ³²K. Schönhammer and O. Gunnarsson, *Solid State Commun.* **23**, 691 (1977); **26**, 399 (1978).
- ³³G. K. Wertheim, L. F. Mattheiss, M. Campagna, and T. P. Pearsall, *Phys. Rev. Lett.* **32**, 997 (1974); J.-N. Chazalviel, M. Campagna, G. K. Wertheim, and H. R. Shanks, *Phys. Rev. B* **16**, 697 (1977).
- ³⁴J. H. Weaver, D. T. Peterson, and R. L. Benbow, *Phys. Rev. B* **20**, 5301 (1979); D. J. Peterman, J. H. Weaver, and D. T. Peterson, *ibid.* **23**, 3903 (1981).
- ³⁵A. Fujimori and L. Schlapbach, *J. Phys. C* **17**, 341 (1984).