

Empty electronic states of calcium silicides: An inverse-photoemission investigation in the ultraviolet photon range

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Empty electronic states in calcium silicides (Ca_2Si , CaSi , and CaSi_2) are investigated by means of inverse photoemission. We present spectra taken in the isochromat mode in the ultraviolet photon range (10–25 eV), at different photon energies. The experimental data are discussed on the basis of theoretical results obtained by self-consistent calculations performed with the Andersen linear muffin-tin orbitals (LMTO) method in the atomic-sphere approximation (ASA). A general agreement between theory and experiment is found for all silicides. However, discrepancies in the energy positions of the observed structures suggest the importance of final-state effects in inverse photoemission. The orbital origin of the spectral features is also analyzed by exploiting the photon-energy dependence of the isochromat spectra.

I. INTRODUCTION

This paper is the second part of an extensive study on the electron states of Ca silicides. Therefore the reader is referred to the preceding paper¹ (hereafter quoted as I) for a more general introduction, including some considerations on the nature of the chemical bond and on the method of calculation.

We discuss here empty electronic states studied with inverse photoemission (IP) in the ultraviolet (uv) photon-energy range, in the isochromat mode. IP spectra taken in the x-ray regime (1486.7 eV) have been recently presented for CaSi_2 and for CaSi (Ref. 2). The purpose of the present work is twofold: (i) to present for the first time a set of inverse-photoemission data for the whole family of calcium silicides, and (ii) to give results in the uv region which have never been presented. Moreover, the energy dependence of the spectra is analyzed by comparing uv isochromat spectra taken at different energies.

The paper is organized as follows: After the experimental results presented in Sec. II, we present an overview of the experimental and theoretical results in Sec. III. In Sec. IV we compare the experimental and theoretical results and also discuss the energy dependence of the spectra. The conclusions are summarized in Sec. V. The Appendix details the results of the calculations.

II. EXPERIMENTAL

The samples were the same as in the work on the occupied states (paper I) and were cleaned by scraping in ultrahigh vacuum (UHV). The reader is referred to I for all experimental details on the sample preparation.¹

The measurements have been performed with a new inverse-photoemission apparatus³ consisting of two stainless-steel UHV chambers coupled by a gate valve. Turbomolecular and liquid-nitrogen-cooled titanium sublimation pumps were used. The sample preparation (in this case scraping) is done in the first chamber. A sketch of the measurement chamber is shown in Fig. 1. The system is equipped with a uv spherical grating which disperses photons with energy between 10 and 25 eV (blaze wavelength 775 Å). The grating is square shaped (120 mm edge) with 3600 lines/mm and is gold coated.

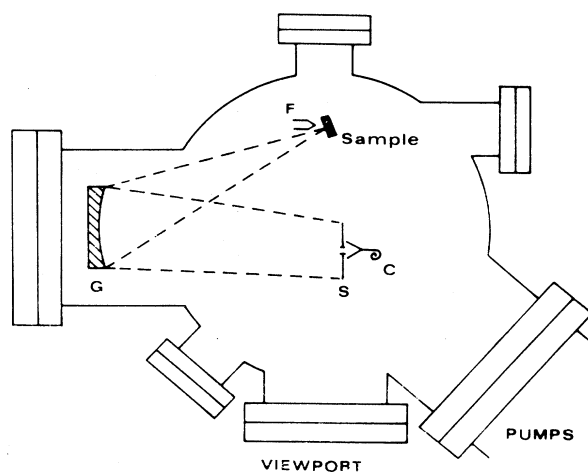


FIG. 1. Schematic view of the main chamber of the ultraviolet inverse photoemission apparatus. *F*, hairpin filament; *G*, grating (energy range 10–25 eV); *C*, movable channeltron; *S*, movable slit.

The incidence of the light is near normal. The sample is 335 mm away from the grating: a very large light-acceptance angle is thus obtained, leading to an f number equal to 2.8. In the present configuration, photons are detected by a detector assembly consisting of a channeltron behind a slit 10 mm high.

The energy of the electrons impinging on the sample is swept at a constant position of the detector assembly, so that the measurements are carried out in the isochromat mode. By moving the detector assembly, the value of the photon energy at which the isochromat spectrum is measured is changed. Three slits with different widths can be interchanged to vary the resolution.

Since the measurements are performed on polycrystalline samples, a collimated electron beam is not needed. We used electrons emitted from a hairpin filament made of thoriated tungsten activated with standard procedures.⁴ Currents through the sample of the order of 35 μA at 30 eV were used. In these conditions a typical spectrum could be measured in 90 min with a total resolution given by a full width at half maximum (FWHM) of 0.45 eV at 14.5 eV isochromat energy. At this photon energy the measuring conditions are the most favorable, since the best compromise between the channeltron efficiency and the effect of the blaze of the grating is achieved.

The base pressure in the UHV chamber was below 1×10^{-10} Torr; no evidence of contamination or damaging of the samples by the electron beam has been observed over the typical duration of the experimental runs, i.e., 12 h. This point has been tested very accurately also in a separate experiment in which a similar electron source was used to irradiate the same samples. The absence of contamination was verified soon after scraping and periodically during electron bombardment by using direct photoemission.

All instrumental parameters and energy calibrations were periodically checked by means of a reference gold sample permanently installed on the manipulator close to the sample under investigation.⁵ Several samples have been prepared and investigated with reproducible results. Great care has been taken to ensure a good electrical contact between the sample and the manipulator in order to avoid minor shifts of the spectra due to charging; we could limit this effect to values less than 0.15 eV in the typical measurement conditions. This is satisfactory to the purpose of the present discussion; this uncertainty only prevents any discussion on the semimetallic nature of Ca_2Si with inverse photoemission (this point is treated on the basis of direct photoemission in I).

In order to reduce the background, the sample and the filament have been enclosed within a cage of thin grid. Both the sample and the filament have been positively biased (10 V) with respect to the vacuum chamber. The electron-accelerating potential is superimposed to this bias. In this way no electron can escape from the sample region and be picked up by the detector. We note also that, as mentioned above, the system is pumped by Ti sublimation and turbomolecular pumps, thus avoiding any possible background coming from ion pumps. As a result we reduced the background virtually to zero; actu-

ally, it amounted to less than 0.2 counts per second to be added to the noise of the channeltron and the electronics.

III. RESULTS

An overview of the behavior of the whole Ca silicide family is presented in Fig. 2, where spectra taken at 14.5 eV isochromat energy are shown. The spectra are normalized to the same height in order to compare their shape easily. The general features of the spectra are similar for the three silicides. In all cases a structure around 6–7 eV above the Fermi level E_F is seen (labeled *A* in Fig. 2). Moreover, a shoulder (labeled *B*) is found at about 2 eV which is quite visible in the two extreme stoichiometries, while in the case of CaSi it barely emerges from noise.

Isochromat spectra were also taken at different photon energies to investigate their energy dependence. The interesting results are shown in Figs. 3, 4, and 5 for the three silicides CaSi_2 , CaSi , and Ca_2Si , respectively. In order to extend the energy range, we have also reported IP spectra from Ref. 2 taken in the x-ray regime, when available. There is basically evidence of substantial stability of the positions of the spectral features against a drastic change of the isochromat energy. However, deformations of the spectra are also observed, at least in some cases. Both these aspects will be discussed below.

We note that the alignment of the IP spectra measured in the inverse uv and x-ray regimes is somehow questionable due to the different resolution of the two apparatus and to different lifetime effects, together with the possible, but minor, charging effects as discussed above. This implies that the comparison between the energy values of the features seen in the two experiments could be subject to some uncertainty (typically up to about 0.5 eV).

The knowledge of the empty density of states is a

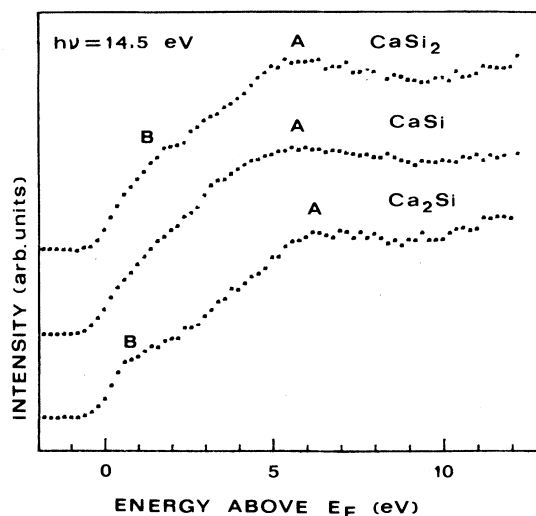


FIG. 2. Inverse-photoemission spectra, normalized to the same height, for the three calcium silicides. The spectra have been taken in the isochromat mode at a fixed photon energy equal to 14.5 eV.

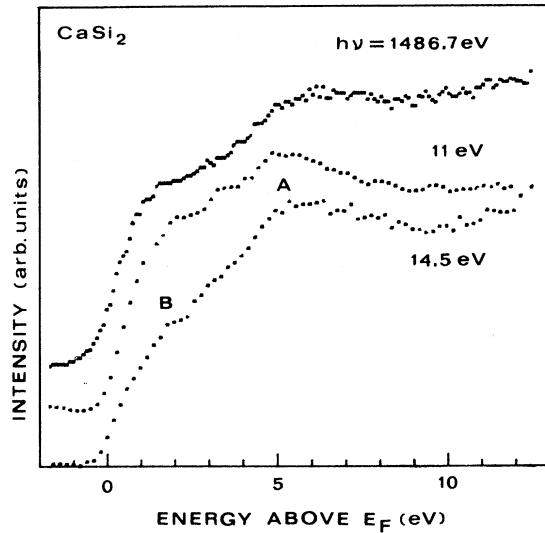


FIG. 3. Comparison of inverse-photoemission spectra for CaSi_2 at different isochromat energies: 1486.7, 11, and 14.5 eV. The data referring to 1486.7 eV photon energy have been taken from Ref. 2.

prerequisite for the comparison between experimental and theoretical data. It is then necessary to perform calculations in an energy range wider than the one given in the figures of paper I on occupied states. The calculations have been extended up to 12 eV above E_F by using the Andersen linear muffin-tin orbitals (LMTO) method in the atomic-sphere approximation (ASA), as described in I. The LMTO eigenvalue E has errors of fourth and higher order in $E - E_v$ with respect to the fixed but arbitrary energy E_v . Care has been taken to minimize the inaccuracies of the calculations in the empty-state region by a proper choice of E_v .

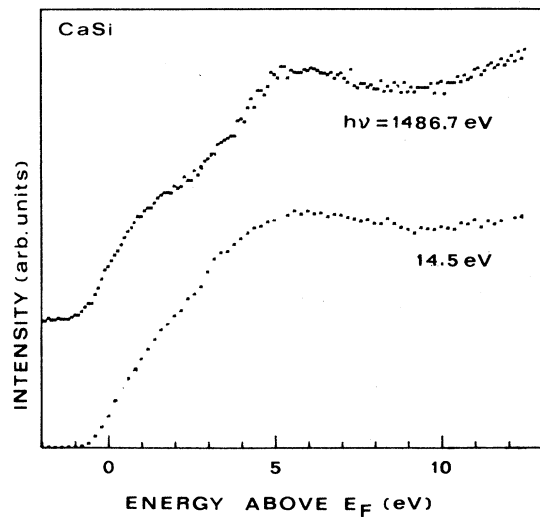


FIG. 4. Comparison of inverse-photoemission spectra for CaSi at different isochromat energies: 1486.7 and 14.5 eV. The data referring to 1486.7 eV photon energy have been taken from Ref. 2.

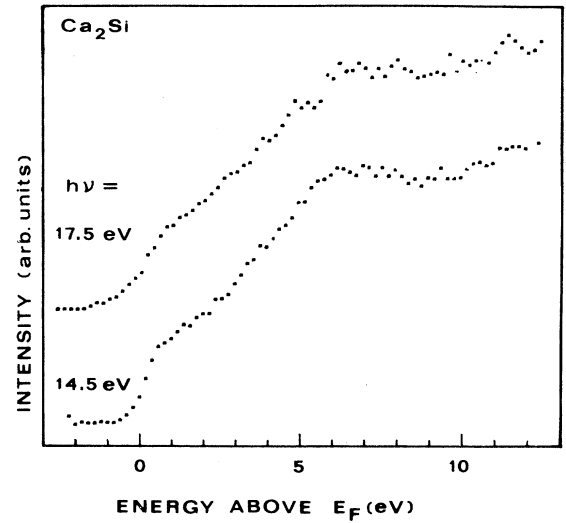


FIG. 5. Inverse-photoemission spectra for Ca_2Si taken at 17.5 and 14.5 eV isochromat energies.

The results for the total density of states (DOS) in the three compounds are given in Fig. 6. The partial DOS's projected onto the different angular momenta on the different atomic sites are summarized in the Appendix.

IV. DISCUSSION

The discussion is done within a single-particle picture and by disregarding the electron-addition effects involved in IP.

Since we are dealing with angle-integrated measure-

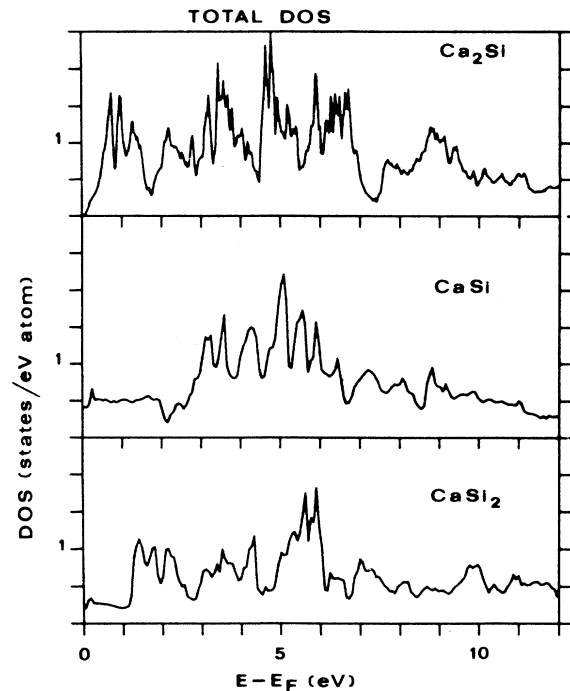


FIG. 6. Total density of empty states for the three calcium silicides.

ments on polycrystalline samples, information averaged over the whole Brillouin zone is obtained. Thus all transitions corresponding to the same photon energy contribute to the isochromat spectra. In the constant-matrix-element approximation, they reflect the joint density of states (JDOS). Moreover, if the initial states of the transition (some 10–40 eV above E_F) are structureless, only the final-state DOS just above E_F has to be considered.

In our calculations the range of final states of the experiment is very well covered. On the other hand, calculations at higher energies are necessary in order to deal with the initial states. Since the accuracy of the LMTO ASA method is limited in this energy range, we cannot perform a detailed discussion of the JDOS effects. However, the stability of the energy of the spectral features against drastic changes of the isochromat energy (cf. Figs. 3–5), shows that these effects, if any, are weak, so that such limitation is not too relevant.

On the other hand, matrix-element effects have to be considered. In fact, dipole-allowed optical transitions sample, with quite different weights, different angular-momentum components projected onto the different atomic sites. Theoretical spectra can thus be obtained by a superposition of contributions having different orbital character, weighted by the appropriate matrix element. It is then important to choose values for these weights and to assess the uncertainties coming from this choice.

A. Matrix-element effects

A first guess of the relative weights comes from the atomic cross section for direct photoemission,⁶ which is related to IP by time reversal. These show clearly that our uv data refer to a situation in which the sensitivity to the d states is much higher than in the x-ray regime of

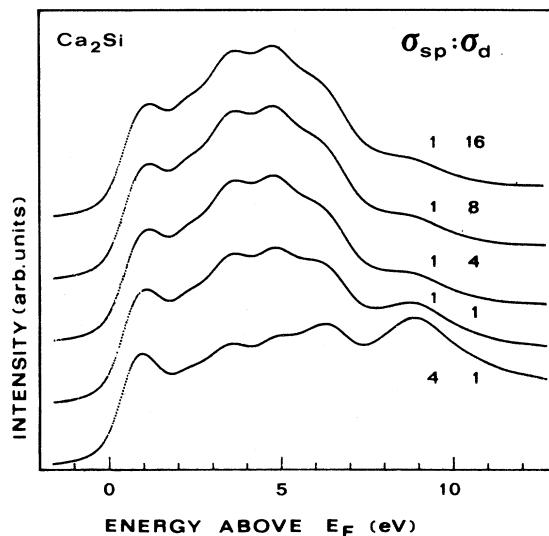


FIG. 7. Calculated inverse-photoemission spectra for different values of the relative (sp) to (d) cross sections around the atomic one (1:4). Broadening effects due to instrumental resolution and finite lifetime of the states have been considered (see text).

Ref. 2. In the calculated DOS the d contribution basically comes from Ca (see the Appendix) in the region up to about 10 eV above E_F . The cross sections of Ref. 6 would give a relative weight of the d to the sp contribution equal to 4:1 at $h\nu=14.5$ eV. However, solid-state effects may drastically change the cross-section values based on atomic calculations.⁷

The sensitivity of the calculated spectra to the variations of the relative (d):(sp) cross section in a wide interval around the atomic value is shown in Fig. 7 for Ca_2Si . Note also that the extreme case in which the sp weight is dominant (bottom curve in Fig. 7) is considered, in order to allow comparison with the x-ray regime. Broadening effects due to instrumental resolution and finite lifetime of the states have been taken into account by means of a Gaussian and a Lorentzian with FWHM's equal to 0.45 eV and $0.6 + 0.1(E - E_F)$ eV, respectively.

It is clear that in the uv energy range the position of the spectral features is quite insensitive to the choice of the relative weights. For instance, they occur at almost the same position in the 4:1 case as in the 1:1 case. This indicates that matrix-element effects are irrelevant at 14.5 eV. Therefore the spectra of Fig. 2 can be interpreted on the basis of the total DOS. On the other hand, in an x-ray experiment with high sp sensitivity, the spectrum is distorted with respect to the total DOS, and a shift of the features towards higher energy may be expected. Indeed, in the case of CaSi_2 of Fig. 3 a small shift of this kind is seen between the data at 14.5 eV and at 1486.7 eV.

B. Comparison between measured and calculated spectra

Theoretical spectra have been calculated by using the total DOS with the broadening given above. The broadening parameters have been empirically found in

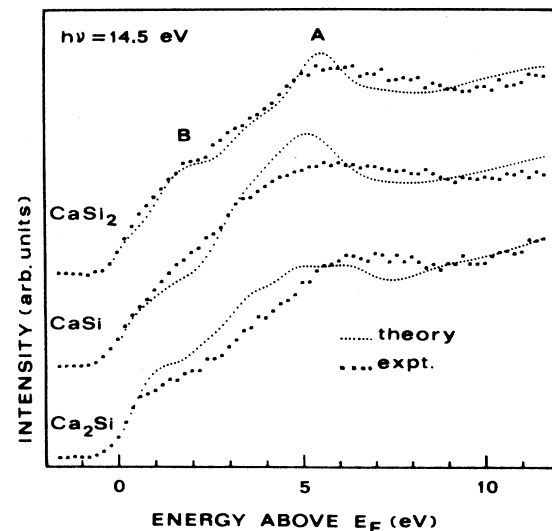


FIG. 8. Comparison between experimental and theoretical inverse-photoemission spectra for the three silicides at 14.5-eV isochromat energy. The calculated spectra have been obtained by using the same weight for the (sp) and (d) contributions (total DOS), considering the broadening effects and adding a linear background (see text).

order to give the best agreement with the experimental data. As in paper I, the choice of the broadening parameters turned out to not be critical for the purpose of the present discussion. A continuous linear background due to multiple processes, which is analogous to the secondary electron distribution in direct photoemission, has also been considered. These effects are very important in measurements on scraped samples, since the amount of secondary electrons is much higher than in other experiments. Such a background, however, does not affect the positions of the spectral features at all.

The comparison between theoretical and experimental spectra is presented in Fig. 8. A good qualitative agreement is obtained, though some differences in the position of peak *A* are visible. The occurrence of both peak *A* and shoulder *B* in the theoretical spectra is confirmed by the measurements. Moreover, in the calculated spectra shoulder *B* is weaker in the monosilicide than in the other two compounds. This is indeed seen in the experimental spectra of CaSi, where feature *B* is almost lost within the noise.

For a quantitative comparison, a more detailed discussion is necessary. In particular, the main feature *A* is systematically found in the experimental data at higher energies with respect to the theory. The difference increases with the Ca content, being of the order of 2–2.5 eV in Ca₂Si. In consideration of the much better agreement found in occupied states and the satisfactory results for the heat of formation of these silicides (see paper I), we do not attribute this quantitative discrepancy to an inadequacy of the calculations. Consistently, with the evaluations given in I, an upper limit of this inaccuracy

should be put around 1 eV.

In principle, the discrepancy could originate from JDOS effects, but we have already seen that this is a minor effect. A closer examination calls for the existence of Si *d* levels in the initial-state region of our measurements (typically around 20 eV). In fact, empty *d* states have been observed at these energies in electron-energy-loss spectroscopy from Si.⁸ This effect must be maximum in the Si-rich system. Figure 3, on CaSi₂, indeed shows a minor displacement of peak *A* in the comparison between the isochromat spectra at 14.5 eV and at 11 eV. At present, we cannot state that this is a JDOS effect, but we can establish that such effects, if any, are quite small and cannot account for the discrepancy in the most unfavorable case, i.e., in Ca₂Si.

Therefore, we attribute part (about 1 eV) of the discrepancy to the effects of the electron addition in-

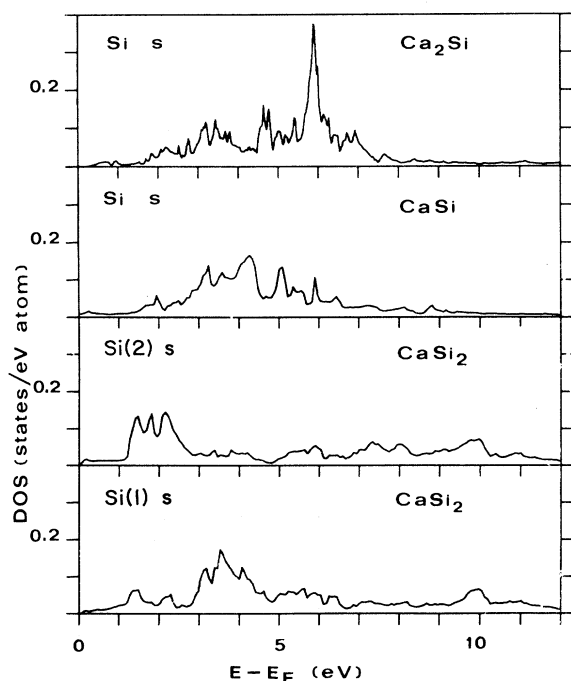


FIG. 9. Density of empty states of Ca silicides projected on the Si *s* orbital.

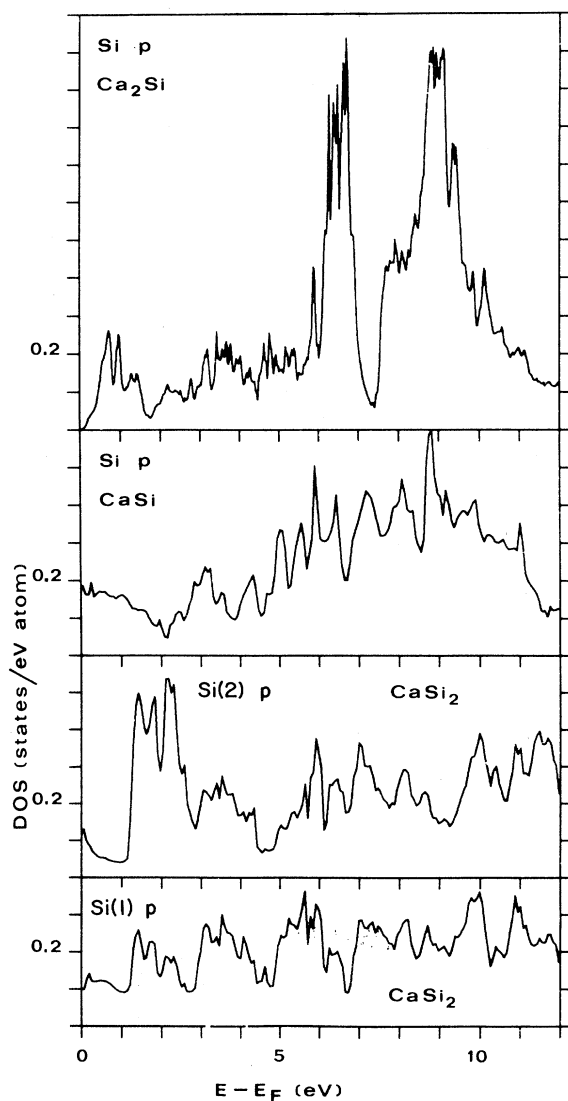


FIG. 10. Density of empty states of Ca silicides projected on the Si *p* orbital.

volved in the IP measurements. As is well known, this can originate a shift of the spectral features towards higher energies. The magnitude of this self-energy contribution is consistent with the trend seen in Ti and Sc,⁹ considering that here we are investigating systems with lower screening efficiency.

We remark that in direct photoemission no evidence of such effects has been observed (see paper I). We note that in these low-*d*-occupancy silicides the occupied states are essentially of bonding type, the antibonding states being above the Fermi level. Therefore the degree of localization is expected to be higher in electron-addition than in electron-subtraction experiments. This, in turn, could justify the stronger final-state effects in empty-state spectroscopy. This argument, however, cannot be put forward quantitatively in the absence of a theoretical investigation, which is beyond the purpose of the present work.

C. Photon-energy dependence of the spectra

The energy dependence of the isochromat spectra adds relevant support to the electronic-state calculations. For this purpose, the most interesting compound is the disilicide, in which the partial DOS's show the greatest differences in the shape of the *sp* and *d* contributions (see the Appendix). Thus the disilicide is the best candidate to show significant distortions of the spectra when the relative *d* to *sp* sensitivity is changed.

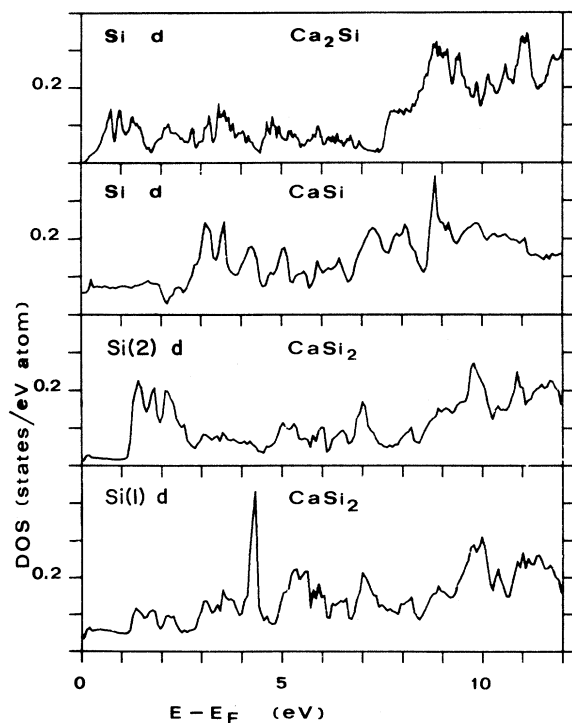


FIG. 11. Density of empty states of Ca silicides projected on the Si *d* orbital.

In the uv range the decrease of the photon energy causes a rapid increase of the *sp* cross section.⁶ On the other hand, the *sp* sensitivity is also increased in the x-ray regime. We refer here to the CaSi₂ data of Fig. 3, where the isochromat spectra at 14.5, 11, and 1486.7 eV (from Ref. 2) are compared. As far as shoulder *B* is concerned, the modification of the spectrum at 14.5 eV with respect to the other two is qualitatively the same. This indicates very clearly that feature *B* contains a substantial amount of *sp* contribution.

On the other hand, the calculations give the following fractional *sp* contributions integrated in the region between 1 and 3 eV above E_F : 62%, 40%, and 27% for CaSi₂, CaSi, and Ca₂Si, respectively. In the region of peak *A* (4–7 eV above E_F), the following values are obtained: 43%, 34%, and 25% for CaSi₂, CaSi, and Ca₂Si, respectively. Thus only for the disilicide is a fractional (*sp*):(*d*) composition markedly different for features *A* and *B* present, so that only in this case is a distortion of the spectra at different isochromat energies to be expected.

The behavior of Fig. 3 is thus strong support for the calculations. Further support comes from the rather poor sensitivity to variations of the isochromat energy in the case of the other two silicides, as shown in Figs. 4 and 5.

We can then conclude that the photon-energy dependence of the spectra is well explained by the present theoretical analysis: in empty-state spectroscopy of Ca silicides this fact is probably the strongest support for the calculations.

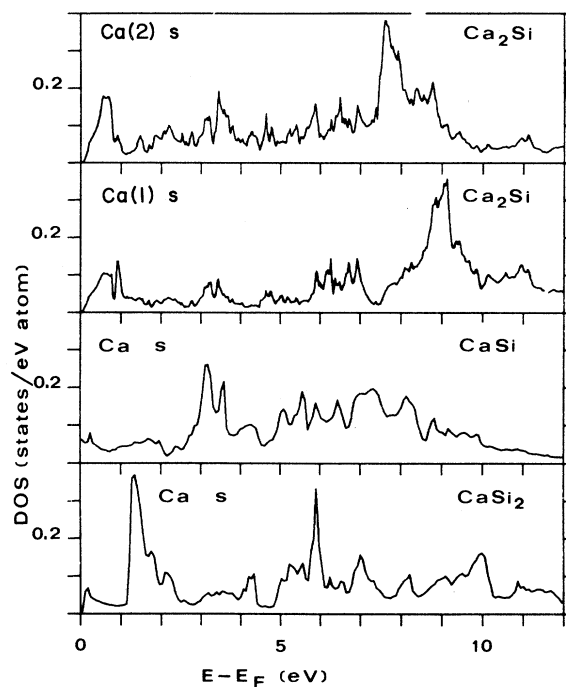


FIG. 12. Density of empty states of Ca silicides projected on the Ca *s* orbital.

V. CONCLUSIONS

We have given for the first time the inverse photoemission spectra of all calcium silicides in the ultraviolet region; the measurements were done in the isochromat mode. We have discussed the results of a calculation of the empty electron states carried out with use of the LMTO ASA method. A general agreement between theory and experiment, as far as the main structures are concerned, and an excellent agreement with the identification of the orbital origin of all spectral features, has been found. In this sense the present experimental results support the theoretical method presented in paper I. A systematic shift towards high energy of the prominent feature in the experimental spectra with respect to the calculations is, at least in part, attributed to final-state interaction due to the electron addition involved in inverse photoemission.

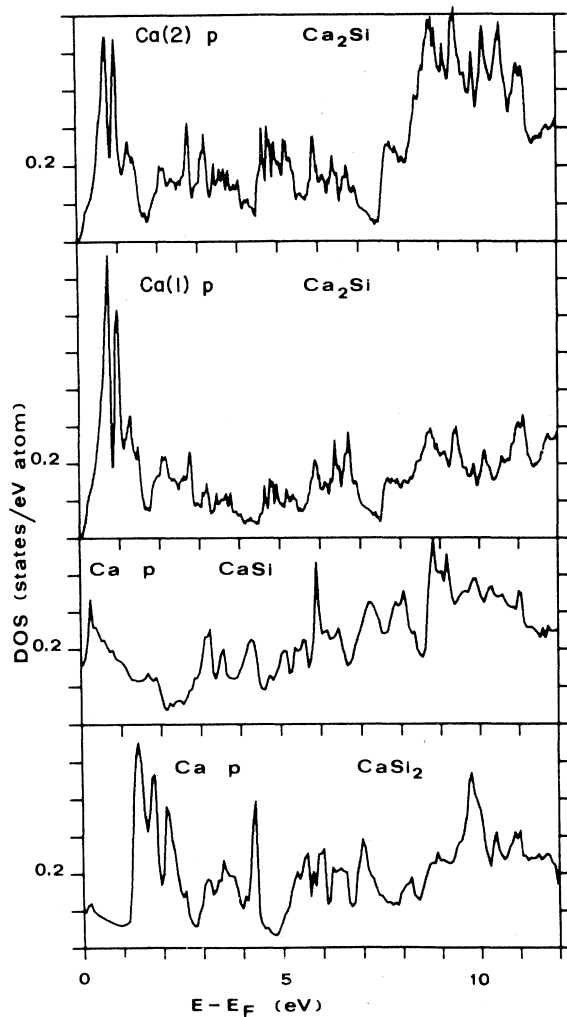


FIG. 13. Density of empty states of Ca silicides projected on the Ca *p* orbital.

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APPENDIX

In our discussion on the matrix-element effects, we have used the outcome of the DOS's projected onto the different angular momenta on the different atomic sites.

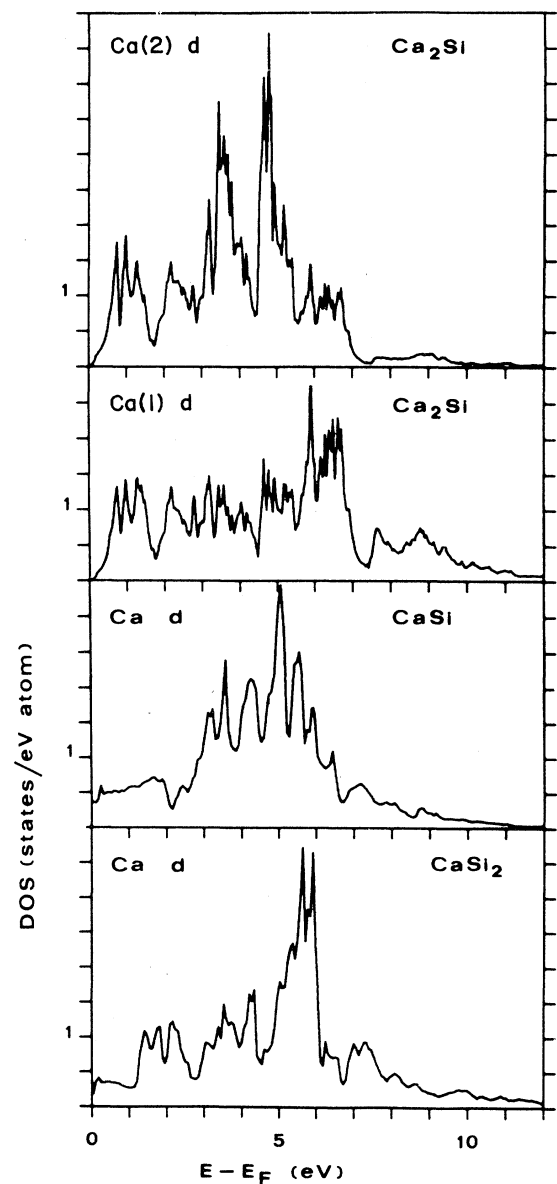


FIG. 14. Density of empty states of Ca silicides projected on the Ca *d* orbital.

These results may be very useful for future investigations. For the sake of completeness, such partial DOS's are presented here. The results for the three silicides are summarized in Figs. 9–11 (Si *s*, *p*, and *d* states) and Figs.

12–14 (Ca *s*, *p*, and *d* states). The curves are normalized to units of states/eV atom, so that they can be directly compared, in spite of the different number of atoms per unit cell.

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