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Silicon valence states in calcium silicides: A Si $L_{2,3}VV$ Auger line-shape analysis

L. Calliari and F. Marchetti
Divisione Scienza dei Materiali, Istituto per la Ricerca Scientifica e Tecnologica, I-38050 Povo (Trento), Italy

M. Sancrotti
Istituto di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, I-20133 Milano, Italy

O. Bisi
Dipartimento di Fisica, Università degli Studi di Modena, via Campi 213/A, I-41100 Modena, Italy

A. Iandelli, G. L. Olcese, and A. Palenzona
Istituto di Chimica-Fisica, Università degli Studi di Genova, corso Europa 30, I-16132 Genova, Italy

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We present a Si $L_{2,3}VV$ Auger line-shape analysis of the whole set of Ca silicides, Ca_2Si, CaSi, and $CaSi_2$. Measured spectra are compared, after data processing, to theoretical ones, computed within the framework of a one-electron picture. The overall good agreement found in this comparison allows us to understand the observed Si $L_{2,3}VV$ spectral changes in terms of the Si valence states' evolution across the whole family of Ca silicides. The narrowing of the *pp* spectral region and the appearance of a distinct *sp* shoulder observed on going from $CaSi_2$ to Ca_2Si are related, respectively, to the decreased width of the Si $3p$ band and to the narrowing of the Si $3s$ states together with their increased energy separation from the Si $3p$ states. A breakdown of the one-electron picture is observed in Ca_2Si. We find that this effect is due to the quasiatomic configuration of the Si $3s$ states in this compound. The introduction of a correlation energy between two *sp*-like–final-state holes improves the comparison between theory and experiment, but does not appear to fully account for the Si $L_{2,3}VV$ spectrum from Ca_2Si. New theoretical effort is therefore needed to understand this spectrum.

INTRODUCTION

Due to their great importance in integrated-circuit technology, metal-silicon interfaces and the related bulk metal silicides have been the subject of extensive studies devoted to the understanding of the structural and electronic properties of these systems. In this respect, a characterization of bulk systems like metal silicides is desirable in order to facilitate data interpretation from the related metal-silicon interfaces. Particular interest has been dedicated to those systems (the majority of noble and transition metals), which are known to lead to the formation of a silicidelike layer at the metal-silicon interface. Several review articles on this topic have appeared in the last few years.[1-4]

In this paper, an investigation of the Si $L_{2,3}$ Auger transition from the whole set of Ca silicides (Ca_2Si, CaSi, and $CaSi_2$) is presented. The interest in this study relies upon both fundamental and technological motivations. These systems are, in fact, interesting in view of a deeper understanding of the chemical bonding which takes place in metal-silicon compounds. Being that the bonding in transition-metal silicides is commonly described within the framework of the two-level model based on the Si p–metal d coupling, the question arises whether or not this picture can be extended to those cases in which the d occupancy of the metal is close to zero. In this respect, calcium silicides can be considered as prototypes of alkaline-earth and rare-earth silicides. Furthermore, the relevance of a detailed knowledge of the electronic and structural properties of Ca silicides should be stressed to understand Si(111)/CaF_2 and Si(111)/$CaSi_2$ interfaces. The technological importance of these systems rapidly increased due to their epitaxal growth on silicon.[5,6] CaF_2, an excellent insulator, and $CaSi_2$, a metal, result then to be ideal candidates for the construction of three-dimensional, fully epitaxial devices on silicon.

The Si-Ca system has recently been the subject of extensive studies aimed at an understanding of the chemical bond and electron states at the Si/Ca interface[7] and in Ca silicides. Concerning Ca silicides, joint theoretical and experimental work have been carried on, the latter based on photoemission to probe the occupied states[8] and on x-ray and uv bremsstrahlung isochromat spectroscopy[9,10] to probe the empty states.

In spite of this extensive experimental and theoretical work, a Si $L_{2,3}VV$ Auger investigation of Ca silicides appears to be attractive in view of the unique characteristic of this electron spectroscopy. Whenever transitions involving valence holes in the final state are considered, the Auger process provides information about a local valence density of states, as opposed to all-sites density of states probed, for example, in conventional photoemission.[11] It has to be stressed that photoemission methods which could be, in principle, angular momentum and/or Si-site selective are not effective for the specific case of Ca silicides because (i) Ca 3*d* photoionization cross sections do not exhibit any Cooper minimum effect and (ii) resonant photoemission at any Si core level would be hindered by the very strong contribution of Ca 3*d* states at the pertinent photon energies.

In Auger spectroscopy, on the other hand, the Si valence states can be directly investigated by the Si $L_{2,3}VV$ transition. The use of a core-valence-valence (CVV) Auger transition to gain information on the valence states relies upon the assumption that many-body effects, in particular, hole-hole correlation in the final state, are not too important. This requirement has been shown to be generally met by the Si $L_{2,3}VV$ transition, not only in elemental silicon,[12-15] but also in silicon compounds.[16-19] This transition is therefore commonly interpreted within the framework of a pure bandlike picture, as opposed to the atomiclike picture holding in cases in which many-body effects are important. Provision only has to be made for matrix element variations across the valence band,[13] which greatly favors final states with 2*p* holes with respect to final states with one *s* and one *p* hole or with 2*s* holes.

Previous Auger work on Ca silicides has been devoted to draw attention to the presence of correlation effects in the Si $L_{2,3}VV$ Auger spectrum from Ca_2Si (Ref. 20) and to assess the relevance of a knowledge of Ca silicide electron states to rare-earth–silicon systems like the Yb/Si interface[21] and Gd silicides.[22]

In this paper, the Si $L_{2,3}VV$ Auger transition from the whole set of Ca silicides is investigated and interpreted on the basis of theoretical valence-band density of states (VBDOS) calculations. A discussion of the Si $L_{2,3}VV$ transition from the intermediate monosilicide is presented here for the first time. A close relationship is found between calculated valence electron states and measured Si $L_{2,3}VV$ spectra. In particular, on going from $CaSi_2$ to Ca_2Si, the observed narrowing of the *pp* spectral region is related to the decreasing width of the Si 3*p* band and the formation of a distinct *sp* shoulder reflects the narrowing of the Si 3*s* states together with their increasing energy separation from the Si 3*p* states. Moreover, the appearance of atomic effects in the *sp* part of the Ca_2Si spectrum is consistently related to the valence-band configuration of this system, that is to the quasiatomic character of the Si 3*s* states. The introduction of a correlation energy between two *sp* final-state holes within the framework of the Cini-Sawatzky theory is shown here to improve the agreement with the experiment. Nevertheless this approach is not completely adequate to give a detailed description of the Ca_2Si spectrum. New theoretical work is therefore stimulated in order to undersand the *sp* part of the Si $L_{2,3}VV$ spectrum from Ca_2Si.

EXPERIMENTAL AND THEORETICAL TECHNIQUES

Experimental procedure

The samples have been prepared by melting stoichiometric amounts of Ca and Si in tantalum crucibles in an inert gas atmosphere. The structure of the Ca silicides has been checked with x-ray diffraction. The extra phases resulted to be confined below 3%.

The Auger measurements have been performed in an ultra-high-vacuum (UHV) system (base pressure $\approx 1\times10^{-10}$ mbar), on which a PHI model 590 Single Pass cylindrical mirror analyzer (CMA) with internal coaxial electron gun is mounted. The sample surfaces have been cleaned by scraping with a diamond file in the same UHV apparatus. The Auger spectra have been excited by an electron beam with 1 keV primary energy and have been acquired in the derivative mode (2 eV peak-to-peak modulation voltage) via a lock-in amplifier. The CMA intrinsic resolution has been fixed to 0.6%. Electron-energy-loss spectra, excited by a primary beam at the energy of the main peak in the Si $L_{2,3}VV$ transition, have been acquired for each Ca silicide with the same experimental conditions.

Method of calculation

The structure of Ca-silicides is quite complex: $CaSi_2$ and CaSi present two molecules per unit cell with two nonequivalent Si atoms in $CaSi_2$, while Ca_2Si has four molecules per unit cell with two nonequivalent Ca atoms.[23] For this reason, the calculation of their electronic properties has been performed only recently.[8-10] The present study of the Auger line shape of Ca silicides is based on these recent papers.

Details of the VBDOS calculation are out of the scope of the present work and presented in Ref. 8. We are simply reminded that the electronic structure of Ca silicides has been investigated through a first-principle approach by using the efficient computational scheme offered by the Andersen's linear muffin-tin orbitals method in the atomic-sphere approximation.[24,25] Exchange and correlation contributions to both atomic and crystalline potential have been included through the Hohenberg-Kohn density-functional description in the Kohn-Sham local-density approximation[26-28] and the **k**-integrated functions have been evaluated by the Jepsen-Andersen-Lehmann-Tart tetrahedron method[29] on a grid of 140 (Ca_2Si) and 147 ($CaSi,CaSi_2$) **k** points in an irreducible portion of the first Brillouin zone.

RESULTS AND DISCUSSION

Theoretical results

A comprehensive presentation of the calculated VBDOS for the three Ca silicides can be found in Ref. 8. Here, we just recall the main conclusions which can be drawn from a joint analysis of total and partial density of states concerning the chemical bond in Ca silicides.

(i) The Si-Ca interaction presents both covalent and ionic contributions. Interatomic transitions[11] associated with this partial ionicity of the bond cannot in any case affect the picture of a local density of states probed by the Si $L_{2,3}VV$ transition, because silicon is the most electronegative element in this compound.

(ii) Ca *s,p*, and *d* states participate in the covalent interaction with Si states, this situation being different from the commonly accepted picture of the bonding in transition-metal silicides, where this interaction involves primarily the metal-d states.

(iii) The participation of the Si states in the bonding interaction is strongly dependent on the stoichiometry. Whereas in the Si-rich compound both s and p states interact with Ca states, the s states participation in the bonding gradually decreases with increasing Ca content. In the Ca-rich compound, the s states are completely dehybridized from the other valence states and the Si configuration is closer to the atomic s^2p^2 rather than to the sp^3 one typical of solid-state silicon.

Total densities of states have been compared in Ref. 8 to photoemission results showing a good agreement for each silicide. This makes us quite confident in using these calculations to interpret the Auger spectra. To this end, Si site s and p projected densities of states have to be considered and compared to the Si $L_{2,3}VV$ measured spectra. This comparison looks interesting, the Si states being more stoichiometry dependent than the Ca ones. In view of this comparison and to better describe the features present in the DOS, Si site, and angular momentum projected densities of states are shown in Fig. 1 for the three Ca silicides [for $CaSi_2$, the results relative to the two inequivalent Si sites, Si(1) and Si(2), are shown]. The most striking feature in these curves is the Si 3s states' evolution on passing from $CaSi_2$ to Ca_2Si. In fact, whereas in $CaSi_2$ and in CaSi these form a broad band of states partially hybridized with the Si 3p ones, in Ca_2Si the s-p hybridization is almost completely absent. The 3s states are in this case separated by a ≈ 4 eV energy gap from the upper 3p states: they are located at ≈ 7 eV below the Fermi level and their bandwidth is of the order of 1 eV so that they are really in a quasiatomic configuration. Concerning the Si 3p states, the trend shown in Fig. 1 corresponds to a decrease in their energy bandwidth on going from $CaSi_2$ to Ca_2Si, this reflecting a reduced Ca-Si interaction in the Ca-rich compound.

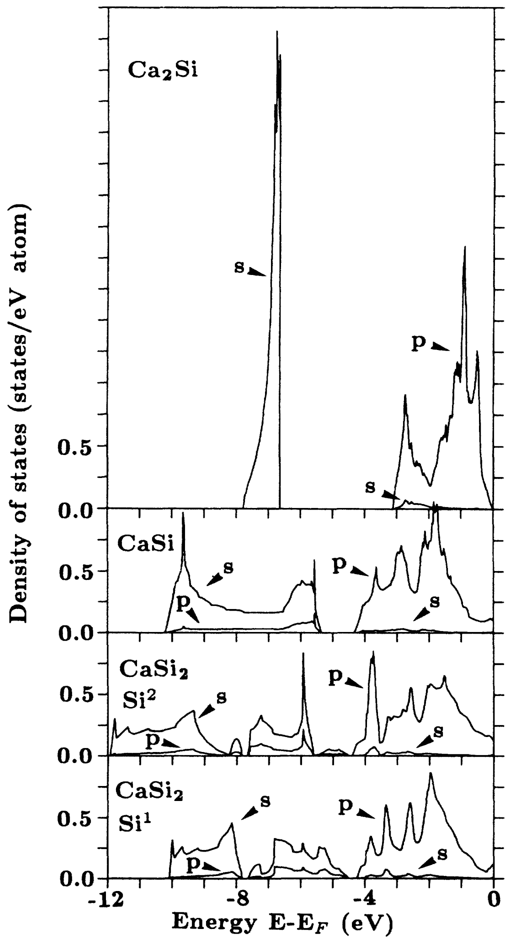

FIG. 1. Density of states of the three Ca-silicides projected onto the Si s and p orbitals.

Experimental results

The as-acquired derivative spectra relative to the Si $L_{2,3}VV$ Auger transition from the three Ca silicides are presented in Fig. 2. The trends observed on going from $CaSi_2$ to Ca_2Si are the following: (i) the main peak becomes narrower and more symmetric in shape; (ii) around 85 eV a feature, absent in $CaSi_2$, becomes visible in CaSi and grows to a well-defined peak in Ca_2Si. The same spectra are shown in Fig. 3 after computer integration, linear background subtraction, and deconvolution of instrumental broadening and energy-loss structures. The subtracted background has been determined by a straight line extrapolating the almost linear background at the high-energy side of the integral spectrum. Concerning the deconvolution, the acquired electron-energy-loss spectra have been integrated and the background subtracted in the same way as the Auger spectra. They have then been used as an approximation of the instrument-loss function for the Si $L_{2,3}VV$ Auger transition in the deconvolution procedure, which has been performed by using the well-known Van Cittert iterative method.[30] It should be reminded here that a rescaling of the loss struc-

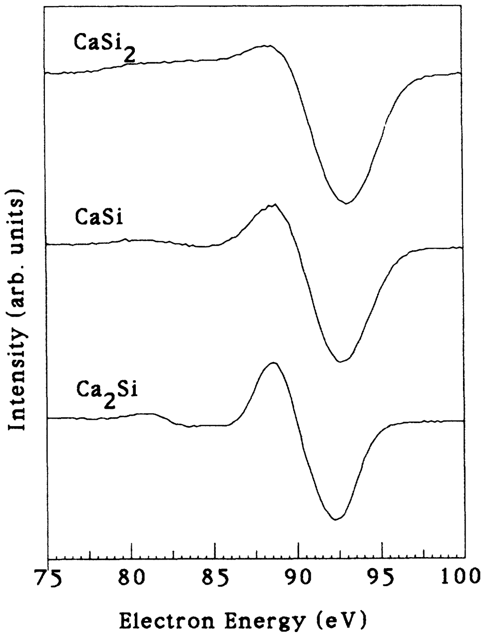

FIG. 2. As-acquired, derivative spectra of the Si $L_{2,3}VV$ transition from the whole set of Ca silicides.

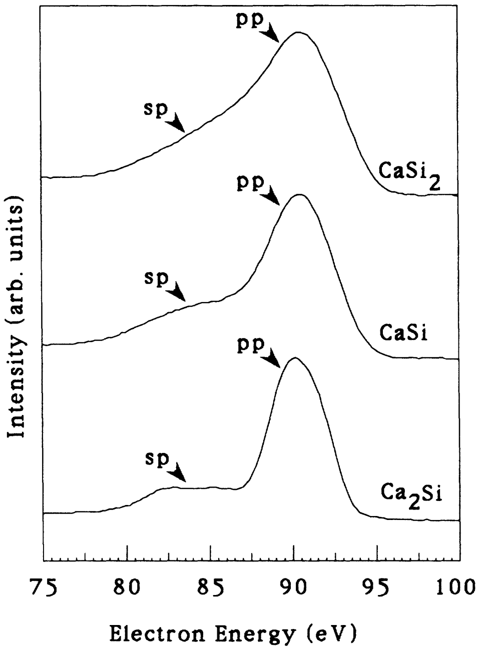

FIG. 3. Si $L_{2,3}VV$ line shape from the whole series of Ca silicides after data processing showing the spectroscopic assignments of the different structures.

tures' intensity with respect to that of the elastic peak would, in principle, be required. This is due to the fact that the use of the elastic peak spectrum as the instrument-loss function generally underestimates the inelastic structure of the Auger emission spectrum.[31,32] Though this kind of rescaling has not been shown in the data presented here, we checked that this procedure would essentially depress the region lying at the low-energy side of the main peak without affecting peak shapes and peak positions.

The evolution of the spectra shown in Fig. 3 is similar to that found in the as-acquired derivative spectra, that is (i) the main peak, located at about 90 eV, becomes more symmetric and its width decreases with increasing Ca content; (ii) a shoulder at the low-energy side of the main peak grows up to a well-defined structure in Ca$_2$Si.

Within the bandlike picture, a *CVV* Auger transition is given by the self-convolution of the VBDOS projected onto the atomic site where the initial core hole has been created. As mentioned above, the Si $L_{2,3}VV$ spectrum is dominated by *pp* transitions. In elemental silicon, the $I(pp){:}I(sp){:}I(ss)$ ratio, computed from atomic wave functions, is 1.0:0.9:0.1, but a comparison to measured spectra suggests the ratio 1.0:0.6:0.1 as a more realistic one for solid-state silicon.[13] This reduction of the *s*-states contribution has been interpreted,[14] keeping in mind the local nature of the Auger process, as due to the high radial extent of these states associated with their bonding character.

Taking into account the different relative weight of the *pp*, *sp*, and *ss* transitions in the Si $L_{2,3}VV$ spectrum, an assignment of the experimentally observed features shown in Fig. 3 can be done. The main peak is associated with transitions leaving 2*p* holes in the final state, while the shoulder at the low-energy side of this peak is due to transitions leaving one *s* and one *p* hole in the final state; *ss*-like contributions cannot be observed. The evolution of the spectra with increasing Ca content can be understood on the basis of the single-particle VBDOS presented in Fig. 1. In particular, the narrowing of the main peak and its more symmetric shape are due to the decreased width of the Si 3*p* band and to the formation of the energy gap between 3*s* and 3*p* states. In the same way, the fact that the *sp* part of the spectrum becomes more and more resolved on going from CaSi$_2$ to Ca$_2$-Si is related to the narrowing of the Si 3*s* states and to their increased energy separation from the Si 3*p* states.

Comparison between measured spectra and theoretical calculations

Having checked that the major features in the experimental spectra can be interpreted on the basis of the calculated VBDOS, we now present a more detailed comparison between calculated and measured spectra. To take into account the different weights of the *pp*, *sp*, and *ss* transitions, the Auger current is computed as the self-convolution of the "transition density of states."

$$N'(E)=N_p(E)+\alpha_s N_s(E)\ .$$

Here $N_p(E)$ and $N_s(E)$ are partial (angular-momentum– and Si-site–projected) densities of states, with angular momentum *p* and *s* respectively; α_s is a number that is fixed to 0.3 and that gives a measure of the *s*-electron participation in the transition, thus simulating nonconstant matrix elements. By self-folding $N'(E)$, one obtain a linear superposition of self-folds and crossfolds of the *s* and *p* partial densities of states, with the $I(pp){:}I(sp){:}I(ss)$ ratio equal to 1.0:0.6:0.09, nearly equal to that found by Feibelman and McGuire in elemental silicon.[13] Different values of α_s, considered as a fitting parameter, can be found in the literature for different silicon compounds.[17,18,33]

The computed self-folds of Ca silicides are presented in Fig. 4. As one can see, they actually show the same trends observed in the experimental spectra. In particular, they show a narrowing of the main peak and a better resolution of the *sp* spectral region on going from CaSi$_2$ to Ca$_2$Si. A direct comparison between theory and experiment is presented in Fig. 5, where the self-fold of the transition density of states of each Ca silicide is superimposed to the corresponding experimental spectrum. To simulate effects such as lifetime broadening, the theoretical curves have been Gaussian broadened ($\sigma=1$ eV). Furthermore, they have been shifted in energy by the binding energy of the $L_{2,3}$ core level, with the work function of our analyzer subtracted, so that the experimental energy scale of the Auger measurements can be retained. The core-level binding energies have been derived, for each silicide, from photoemission measurements.[34] The theoretical curves have been vertically scaled in order to get, at the curve maximum, the same height of the measured curves. Within the present experimental accuracy, the energy position of the main peak (that is the *pp* part of the spectrum) in the measured curve is in close agree-

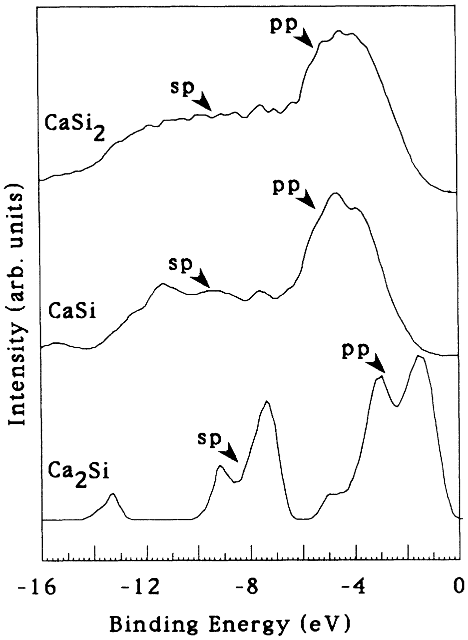

FIG. 4. Self-fold of the transition density of states for the whole set of Ca silicides.

ment with that of the same peak in the calculated curve for each Ca silicide. The shape of the main structure in the computed curve is also in fairly good agreement with that of the measured curve. All these observations lead us to conclude that, as far as the main structure is concerned, a one-electron picture appears to be satisfactory.

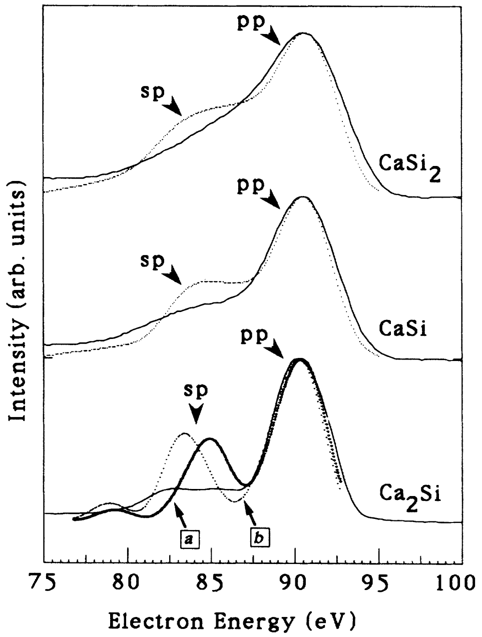

FIG. 5. Comparison, for the three Ca-silicides, between the measured Si $L_{2,3}VV$ line shape (solid line) and the Gaussian broadened self-fold of the transition density of states. For Ca$_2$Si, together with the uncorrelated spectrum (*a*), a correlated spectrum (*b*) is also shown computed with $U_{sp}=U_{ss}=3$ eV and $U_{pp}=0$ eV.

Correlation effects between 2*p*-like–final-state holes in the Si $L_{2,3}VV$ transition from Ca-silicides are therefore weak. Having established this result for the *pp* part of the spectrum, we turn our attention to the *sp* one. We should first notice that the *sp* shoulder intensity is always higher in the theoretical curves than in the experimental ones. This can hardly be ascribed to uncertainties connected to data processing. In fact, both a rescaling of the inelastic structure with respect to the elastic one in the backscattering spectrum and a different background subtraction among those commonly quoted in the literature[11] would depress the *sp* structure with respect to the *pp* one. The observed disagreement can be due to an overestimation of the *s*-electrons contribution to the Si $L_{2,3}VV$ transition that we fixed by keeping $\alpha_s=0.3$. For CaSi$_2$ and CaSi, a better agreement between theory and experiment can be achieved by properly adjusting this parameter. However, this does not appear to be true for Ca$_2$Si. In this case part of the measured *sp* feature lies outside the low-energy end of the calculated one and a reduction of the *sp* structure as a result of a smaller α_s value would increase the observed disagreement. Furthermore, a smaller α_s value would be inconsistent with the degree of Si 3*s* states localization, which is maximum in Ca$_2$Si. In fact, on the basis of the strong localization of the Si 3*s* states in this system, one should expect a value of α_s greater than that of the other two Ca silicides. A better agreement with the experimental data cannot, therefore, be achieved by adjusting α_s. One should question at this point the validity of the picture used to describe the Si $L_{2,3}VV$ transition from Ca$_2$Si. As we have already concluded in Ref. 20, a pure bandlike picture cannot properly describe the *sp* part of the Si $L_{2,3}VV$ transition of Ca$_2$Si. In fact, atomiclike effects have been found in Ca$_2$Si and have been consistently related to the VBDOS configuration of this system.

From the analysis of the whole set of Ca silicides, we can point out a clear relationship between calculated VBDOS and the appearance or not of atomiclike effects in the measured Auger spectra. A pure bandlike picture results, in fact, to be adequate in the case of CaSi and CaSi$_2$, whose theoretical VBDOS calculations show that the Si 3*s* states are spread over a wide energy range, in a bandlike configuration. On the contrary, a failure of this picture is observed in Ca$_2$Si, that is in the case for which the calculations show the Si 3*s* states to be in a quasicore configuration. The absence of many-body effects in the main peak of the Si $L_{2,3}VV$ Auger spectrum from Ca silicides, well described by the self-fold of the Si *p* partial density of states, provides support to the theoretical results on the Si 3*p* states and on their evolution through the Ca silicides. Such a check of the theory would not have been possible with photoemission data alone. Concerning the Si 3*s* states, even though the calculated distribution well describes the measured spectrum of CaSi$_2$ and CaSi, a check of the evolution of these states across the whole family of Ca silicides is prevented from the breakdown of the bandlike picture in the *sp* region of the Ca-rich compound.

The breakdown of the bandlike picture in the case of

CVV Auger transitions can be treated within the framework of the theory proposed by Cini[35] and, independently, by Sawatzky[36] in the case of initially filled valence bands. For nondegenerate bands, the correlation energy U between the two final-state valence holes enters the theory through the expression

$$D(E)=\frac{D^0(E)}{[1-UF(E)]^2+\pi^2U^2[D^0(E)]^2},$$

where $D^0(E)$ is the self-fold of the one-particle density of states and $F(E)$ is the Hilbert transform of $D^0(E)$.

For an unfilled band, different treatments have been proposed. According to Tréglia *et al.*,[37] this equation is still valid, but now $D^0(E)$ is the self-fold of the single-particle spectrum, with self-energy effects included. In this light, various Auger spectra have been investigated by computing $D^0(E)$ from the measured photoemission spectrum.[38] More recently, Cini and Verdozzi[39] suggested that $D^0(E)$ should be computed from the undressed particle hole, without self-energy effects, as in the filled band case. The two holes tend to interact as bare holes essentially because the size of their screening clouds is larger than the range of hole-hole repulsion. This bare-ladder approximation is correct when the number of the holes in the valence band is low.

The method has been extended to the case of degenerate bands,[40] showing that, if the spherical symmetry of the atom is not too much distorted by the solid, the equations for different total angular momenta decouple giving rise to a set of equations, each being identical to the one valid for nondegenerate bands and having its own value of the correlation energy U.

The low-hole density condition is not fulfilled by the Ca silicides, thus making the Cini-Sawatzky approach not strictly applicable in this case. However, due to the lack of a more general theory, we may use it to investigate, at least in an approximate way, the presence of atomic effects in the Si $L_{2,3}VV$ transition from Ca_2Si. It has already been shown that the best agreement between theory and measured spectrum can be obtained by assuming a correlation energy U_{sp} of the order of 3 eV between two *sp* final-state valence holes, while leaving equal to zero the correlation energy U_{pp} between two *p*-like holes.[20] The correlated Auger spectrum of Ca_2Si, computed with $U_{sp}=U_{ss}=3$ eV and $U_{pp}=0$ eV, is also shown in Fig. 5. The calculation leads to a shift of the *sp* peak to lower kinetic energies in such a way that the low-energy tail of the calculated and measured spectra coincide. However, the shape of the *sp* structure is different from the measured one. In particular, the shift of the *sp* peak to lower kinetic energies causes a depletion of Auger current at 85–86 eV. This is in contrast to the experimental result, which shows a well distinct emission at that energy. We believe that this disagreement is not due to some broadening or matrix element effects, but gives evidence of the occurrence of phenomena not described in our treatment of two-holes interaction. It follows that our inclusion of correlation effects in a bandlike Auger calculation cannot definitely remove all the observed discrepancies. Theoretical work is in progress to better understand the Si $L_{2,3}VV$ transition from Ca_2Si.

CONCLUSIONS

A joint experimental and theoretical investigation of the Si $L_{2,3}VV$ Auger transition from the whole set of Ca silicides has been carried out. By comparing the measured spectra to the self-convolution of calculated transition densities of states, it is found that this transition can be fairly well accounted for in a pure bandlike picture for $CaSi_2$, CaSi, and for the *pp* spectral region of Ca_2Si. On the contrary, a breakdown of this picture is observed for the *sp* part of the Ca_2Si spectrum, where evidence is found of a correlation between the two final-state *sp* valence holes. The overall result provides complementary support to the theoretical calculations with respect to that provided by photoemission experiments. Whereas, in fact, in photoemission the evolution of the total density of states across the whole family of Ca silicides can be investigated, the Si $L_{2,3}VV$ Auger analysis allows the evolution of just the Si states to be followed. The good agreement found here between theory and measured spectra concerning the *pp* spectral region supports the theoretical picture of the Si *p* partial density of states evolution in Ca silicides, that is the narrowing of the Si 3*p* band with increasing Ca content. The failure of the bandlike picture in the *sp* region of the Ca_2Si spectrum is also directly related to the computed Si *s* partial density of states, which shows a quasicore configuration of the Si 3*s* states in Ca_2Si. On the other hand, the absence of this effect in the other two compounds is due to the bandlike configuration of their *s* states. The introduction of a correlation energy restricted to the *sp* region of the spectrum of Ca_2Si within the Cini-Sawatzky theory improves the comparison with the experimental data, but is not able to fully account for the measured Si $L_{2,3}VV$ Auger transition from this compound. A detailed understanding of it is therefore still an open problem and new theoretical effort is needed.

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