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Correlation effects in valence-band spectra of nickel silicides

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We discuss the role of the electronic correlation in determining the line shapes of valence-band photoemission and Auger spectra of Ni silicides. Theoretical one-particle spectra, with correlation effects included by a perturbation approach to a degenerated Hubbard Hamiltonian, are compared with experimental energy-distribution curves. It is shown that for these compounds the electronic correlation is of crucial importance for describing valence-band photoemission. We also present the experimental line shapes of Ni L_3VV transitions and compare them with theoretical two-hole spectral densities. It is concluded that a band-theoretical approach can account for some important features of the experimental Auger spectra, but multiplet effects should be included for a more detailed description.

I. INTRODUCTION

Detailed investigations of the electronic properties of transition-metal silicides have been published in the last few years.[1-15] Several experimental studies have shown how the electronic structure evolves upon passing from the pure elements to the compounds. Theoretical work has been aimed at calculating the electron density of states, at obtaining information on the hybridization of Si valence states, the degree of interaction between Si *p* and metal *d* orbitals, and on how all these features can be extracted from the experimental data. Satisfactory agreement between theory and experiment has been obtained for the silicides of near-noble metals and some of their interfaces with Si.[9-12] An aspect which has been neglected in these papers is the role of many-body effects in the experimental spectra. Electronic correlation is often relevant in transition metals and determines the occurrence of some important features, such as satellites in photoemission or multiplet splitting in core-valence-valence Auger line shape.[16-22]

The purpose of this paper is to study the importance of many-body effects in photoemission and Auger spectra of Ni silicides. To this end we have performed theoretical calculations of one- and two-particle spectra evaluating correlation effects through a perturbative approach. Here we compare the theoretical results with experimental energy-distribution curves (EDC's) measured with x-ray and ultraviolet photons. The comparison permits to point out a number of features in the experimental spectra which are attributed to correlation effects. In order to carry out a similar study for two-particle spectra, we have measured the line shape of the Ni L_3VV transition in Ni silicides. The experimental data are presented and compared with the theoretical line shapes. This allows us to explain some of the modifications which take place in the experimental curves upon passing from pure Ni to silicides and also assess more accurately the adequacy of the theoretical approach.

Two main factors led to the choice of Ni silicides for this study. Firstly, correlation effects in pure Ni and in a number of alloys have been studied both theoretically and experimentally. It is generally agreed that their inclusion can be important for a correct description of core and valence spectra. Secondly, recent band-structure calculations for these materials[6,9,12-14] have allowed us to clarify the main aspects of the chemical bond and to determine the electronic configurations of both Ni and Si atoms in the ground state. The availability of the results of realistic single-particle calculations allow us to perform a more accurate investigation of the importance of many-body effects in the electronic properties of these compounds.

For a better presentation and understanding of the results given in this paper we have organized the work as follows. In Sec. II we discuss the main points of disagreement between the experimental photoemission spectra and theoretical single-particle calculations. This shows the necessity of introducing correlation effects in order to achieve a correct description of the data. In the same section we present the approach used to introduce these effects into the theory and display a rather complete set of theoretical one-particle spectra. We also give an accurate comparison between the theoretical results and the experimental curves. Section III is devoted to the presentation of the experimental Auger line shapes measured for Ni silicides, while in Sec. IV we present a discussion of their interpretation in terms of the theoretical model.

II. ONE-PARTICLE VALENCE-BAND SPECTRA

To make our subject more definite, in Fig. 1 we give a comparison between the theoretical density of states (DOS) of Ni_2Si calculated by two of us[6] and experimental valence-band ultraviolet-photoelectron-spectroscopy (UPS) and x-ray-photoelectron-spectroscopy (XPS) data. Together with the total DOS the figure shows the calculated contribution of Ni states. The analysis of this last curve indicates that structures in the energy region between E_F and -3.5 eV are mainly due to Ni *d* orbitals, which are not appreciably coupled with Si states, while at both lower and higher binding energies a significant interaction with Si *p* orbitals is present. It is

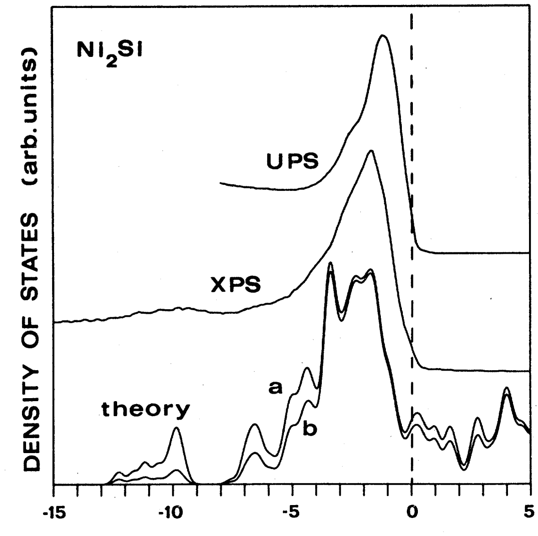

FIG. 1. Comparison between the calculated DOS of Ni_2Si and experimental UPS ($h\nu=50$ eV) and XPS energy-distribution curves. Total DOS (curve *a*) and Ni projected DOS (curve *b*) from Ref. 6. Experimental results from Refs. 15 (UPS) and 7 (XPS).

the nonbonding portion of the *d* band which determines the main structures seen in the photoemission spectra. Indeed, a significant correlation has been found between experimental EDC's and the behavior of the theoretically calculated nonbonding portion of the *d* band in many transition-metal silicides.[9–15]

There are two main points of disagreement between the theoretical results and the experimental spectra. The first concerns the width of the *d* band. In both XPS and UPS data the *d* band is narrower than in the theoretical DOS. The full width at half maximum is, in fact, 2.42 eV in the spectrum at $h\nu=50$ eV, and 2.9 eV in the XPS spectrum, to be compared with a value of 3.5 eV found in the theory. A second point of disagreement is the shape of the *d* band. The theoretical *d* DOS is approximately constant over a 3-eV region between -1 and -4 eV, while both EDC's have an almost triangular shape and are more asymmetrical on the high-binding-energy side.

Similar difficulties arise if one tries to compare the XPS spectrum of pure Ni with the results of theoretical calculations of the density of states: The *d* band appears narrower in the experiments than in the theory, and has a characteristic triangular shape.[16,22] An additional important feature of the pure-Ni spectrum is the presence of a satellite at about 6 eV below E_F. A similar feature appears around -6.3 eV in Ni_2Si, but with less intensity. In the pure element the presence of this structure helps in the interpretation of the EDC's. Satellites can occur only if the intra-atomic Coulomb interaction between valence-band holes, *U*, is sufficiently large to cause a separation in binding energy between different atomic configurations contributing to the ground state of the solid.[16] For the case of pure Ni the ground state is known to be a mixture of d^9s and d^{10} atomic configurations. After photoionization the valence states are superpositions of d^8s and d^9 configurations, which are separated in energy by *U*. They determine two different structures in the spectrum; the main maximum is assigned to the d^9 configuration, while the d^8s configuration is responsible for the satellite peak around -6 eV.

It is clear from the shape of the EDC's for Ni_2Si that similar effects are present in this compound as well: The main peak of the spectrum still has a shape rather similar to the Ni EDC and is considerably narrower than the theoretical bandwidth, while the satellite peak gives rise to a structure around -6.3 eV. However, this structure is less resolved than in pure Ni, partly because the center of gravity of the *d* band shifts by nearly 0.6 eV toward higher binding energy, partly due to the presence of an additional broad structure at lower energies, probably determined by a band of Si *s* states lying in this energy range.[6]

Upon passing from Ni_2Si to NiSi the line shape of the main structure in the EDC spectrum becomes more symmetrical and the satellite is seen less clearly. This is evident from Fig. 2, where the experimental EDC's are reported. In the same figure we show the results of the DOS calculation. Even if the agreement with the experiments is better than in Ni_2Si, the theoretical DOS still does not accurately reproduce the line shape of the experimental EDC; in particular the *d* band is wider than in the experiments. We can conclude that a theoretical description of single-particle spectra in Ni silicides must take into account correlation effects.

A theoretical approach, which allows the inclusion of these effects by perturbation theory, has been proposed by Treglia *et al.*[20] who have used it to study correlation in Ni band structure. This approach has two attractive features: (i) It is not limited to situations where the number of holes in the *d* band is small, and (ii) it is relatively

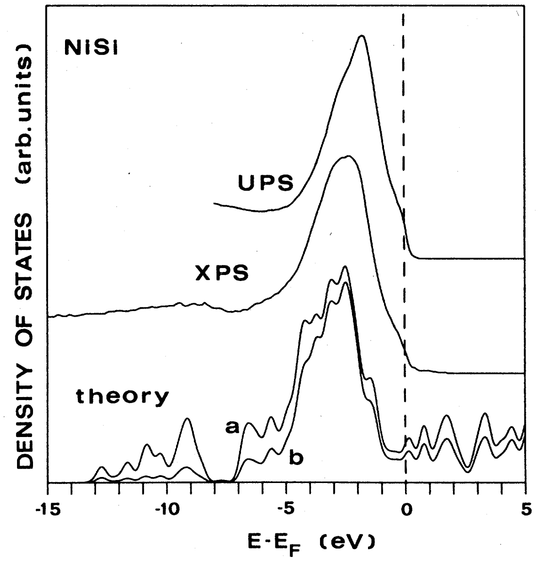

FIG. 2. Comparison between the calculated DOS of NiSi and experimental UPS ($h\nu=50$ eV) and XPS energy-distribution curves. Total DOS (curve *a*) and Ni projected DOS (curve *b*) from Ref. 6. Experimental results from Ref. 15 (UPS) and private communication by Dr. P. Grunthaner (XPS).

simple from a computational point of view. Both features are important for the purpose of carrying out calculations in Ni silicides, which have complicated structures and do not show a small hole concentration. In this section we present the basic ideas underlying the method and we refer to the original literature for an extensive discussion.

In order to interpret the photoemission spectra it is assumed that the experimental EDC's can be represented by the spectral function of the created hole,

$$\tilde{n}(E)=-\frac{1}{\pi}\operatorname{Im}\int_{-\infty}^{\infty}dE'\frac{n(E')}{E-\Sigma(E)-E'}\ , \tag{1}$$

where $n(E)$ is the one-particle DOS and $\Sigma(E)$ is the self-energy. In our calculations we took the DOS from Ref. 6. The self-energy can be calculated using a degenerate Hubbard model with a Hamiltonian

$$\hat{H}=\hat{H}_0+\tfrac{1}{2}U\sum_{\nu,\sigma}\sum_{\nu',\sigma'}\sum_{l}(1-\delta_{\nu\nu'}\delta_{\sigma\sigma'})\hat{n}_{l\nu\sigma}\hat{n}_{l\nu'\sigma'}\ . \tag{2}$$

Here, $\hat{H}_0$ is the band Hamiltonian, U is the average Coulomb potential between electrons sitting on the same atom l in different atomic orbitals ν, σ is a spin index, and $\hat{n}_{l\nu\sigma}$ is the particle-number operator.

To second order in U the self-energy can be written as

$$\Sigma(E)=9U^2\int dE_1\int dE_2\int dE_3\{f(E_1)[1-f(E_2)][1-f(E_3)]+[1-f(E_1)]f(E_2)f(E_3)\}\frac{n(E_1)n(E_2)n(E_3)}{E+E_1-E_2-E_3}\ , \tag{3}$$

where $f(E)$ is the Fermi-Dirac function,

$$f(E)=[1+\exp(E/k_BT)]^{-1}\ .$$

In deriving Eq. (3) it has been assumed that the linear term in U can be included in the initial-energy bands and that the self-energy can be evaluated in the so-called "local approximation."[20] Treglia and co-workers[20] calculated the single-particle spectrum of pure Ni, taking a value of 2.25 eV for U, and found a significant agreement with experimental XPS data. A value of U equal to 2.5 eV has been used by Liebsch[21] in his study of the band self-energy. Such values are in close agreement with what found by Davis and Feldkamp[23] by solving numerically the Hubbard model for a finite number of atoms. An estimate of U from a comparison between Auger spectra and the self-fold of the d density of states leads to a similar value. For this reason we have performed our calculations assuming $U=2.5$ eV for all the silicides. This may seem to be a rather drastic approximation in view of the fact that the d-band shape changes considerably upon passing from Ni- to Si-rich silicides and modifications in the screening of the Coulomb potential could take place. Since a first-principles determination of U is not possible, the only alternative would be to evaluate this parameter through a fit of the single-particle spectrum to the experimental EDC's. This procedure is not necessary, since, as will be shown in the following, the value $U=2.5$ eV gives an excellent description of the experiments for all the silicides.

The results of the application of this theory to the calculation of the electronic structure of Ni silicides are given in Fig. 3, which shows the single-particle spectra of Ni_2Si, NiSi, and $NiSi_2$. The contribution of the Ni states to this spectrum is also reported. Three aspects of these results are particularly relevant. First, we note that the d part of the spectrum is dominated by a peak with a nearly triangular shape and is considerably asymmetrical on the high-binding-energy side for Ni-rich materials. The width of the peak and its location depend upon the Si content. In Ni_2Si it extends from E_F to -5 eV and the maximum is located at -1.4 eV. In NiSi the maximum is shifted at -2.1 eV, while the peak extends from about -1 to -5 eV. In $NiSi_2$ it becomes very narrow and occupies an energy region about 3 eV wide near -2.5 eV. The asymmetry of the peak decreases with Ni content. The total single-particle spectrum in this energy region essentially coincides with the d part, the contribution of sp states being mainly concentrated around -5 eV.

A second important feature of these spectra is the presence of a d structure around -6 eV in all the compounds. It derives from joint contributions of the d^8 satellite and of d states interacting with Si p orbitals. Compared with the main peak this structure has a much lower intensity and becomes weaker upon increasing the Si content. This is not a consequence of a decreased weight of the d^8 configuration in the ground state compared to the pure nickel, since the number of empty d states does not change appreciably upon passing from Ni to $NiSi_2$. It comes mainly from the modification in the distribution of the d states below the nonbonding d band; in $NiSi_2$ these states occu-

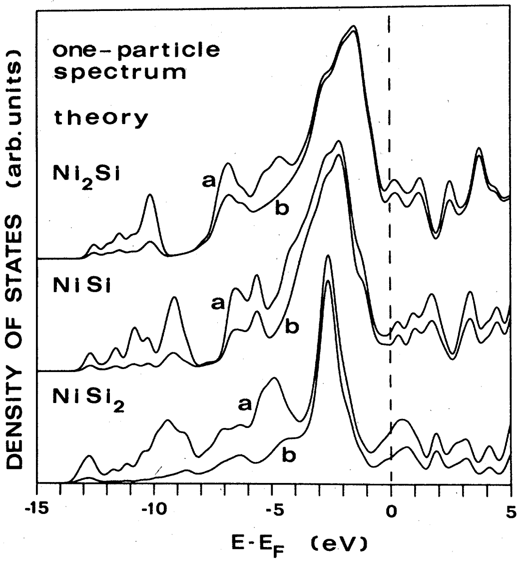

FIG. 3. Theoretical one-particle spectra for Ni silicides. Total DOS (curve a) and Ni projected DOS (curve b) have been computed with $U=2.5$ eV.

py a wider region than in the other compounds and have a smaller density of states with respect to the main peak. It therefore appears that, as an effect of the interaction with Si *p* orbitals, the d^8 structure becomes smeared over a larger energy region, when more Si is present in the compound. The total spectrum in the same energy range shows an increasing contribution of Si *sp* states.

A third point worth emphasizing is the presence of two main Si structures. The lowest one, separated from the rest of the spectrum in Ni_2Si and NiSi, is of *s* character and lies at around -9.5 eV, being at higher binding energies in Ni-rich compounds. The second one is found between -7 and -5 eV and has to be associated with Si *p* states.

The comparison between the curves of Fig. 3 and the experimental data of Figs. 1 and 2 shows that the inclusion of intra-atomic correlation significantly improves the agreement between theory and experiment. In particular, we notice that in Ni_2Si the main maximum is now located at -1.4 eV, while the UPS spectrum gives a value of -1.3 eV and the XPS EDC gives -1.6 eV. The additional feature seen in the XPS spectrum at about -4.15 eV corresponds to the broad structure located between -4 and -5 eV in the theoretical curve of the total DOS. The peaks at -6.4 and -9.45 eV in the experiments correspond to the structures around -6.5 and -10 eV in the theoretical spectrum. A similar correspondence between theory and experiment is found for NiSi and $NiSi_2$.

In conclusion, all the main structures seen in the photoemission spectra are reproduced in our theoretical results both in shape and, within a few tenths of an eV, in energy location. Such an agreement provides direct evidence of the importance of correlation effects in Ni silicides and supports the theoretical model we have adopted in the calculations.

III. EXPERIMENTAL AUGER L_3VV SPECTRA

Thin nickel silicide films (Ni_2Si, NiSi, and $NiSi_2$) were prepared by evaporating Si and Ni films onto a SiO_2 substrate. The thickness of the films ranged between 600 and 3000 Å for Si and 800 and 1300 Å for Ni. The system was then heated in a vacuum furnace (10^{-8} Torr) at temperatures ranging from 200 to 500 °C for 180 min. The stoichiometry of all the samples was checked by Rutherford backscattering. Deviations from the nominal stoichiometry were less than 1%. The x-ray-diffraction data showed the correct crystal structures.

Afterwards, the samples were transferred to a UHV chamber for the surface analysis. The surfaces were cleaned by using a differential Ar^+ ion gun. In this way surface contaminants were reduced below 0.5 at. %. By using appropriate ion-beam energies in the range between 0.5 and 1 keV, it was possible to produce samples with the correct bulk stoichiometry in the surface region after the sputtering.[24] The final relative concentration was checked by analyzing the low-energy Si and Ni Auger lines with the elemental-standard method. The measurements of the Ni L_3VV line were carried out at 2×10^{-10} Torr by a double-pass cylindrical mirror analyzer (CMA) in the retarding-field mode with a resolution of nearly 1 eV. The coaxial electron gun was used to excite the samples with a beam of 4 keV, 1μA.

Figure 4 shows the measured L_3VV Auger spectra of pure Ni and its silicides. A glance at these curves shows clearly that, in spite of the great difference in the chemical environment of the Ni atom, the general shape of the Auger line is similar in all the compounds: It has a pronounced maximum flanked by other structures of minor intensity and is stretched on the high-energy side. The curve of pure Ni appears more clearly structured, showing a bulge in the high-energy side of the maximum and a wide structure in the low-energy side. A more detailed comparison between the curve of the metal and those of the compounds points out the following modifications:

(i) The width of the curve decreases by nearly 0.6 eV upon passing from Ni to Ni_2Si, and by nearly 1 eV upon going to $NiSi_2$; such a change is mainly a consequence of the reduction in the emission on the two sides of the maximum, since the width of the maximum calculated at two-thirds of its height is not appreciably modified.

(ii) The position of the maximum shifts by nearly 1 eV toward lower kinetic energies upon going from Ni to $NiSi_2$.

(iii) The wide structure to the left of the main peak decreases in intensity and changes its shape upon passing from the pure elements to the silicides. In nickel it appears as the result of different contributions lying in an energy range of approximately 4 eV around 839 eV. One of the reasons of the complexity of the spectrum in this energy region is the occurrence of vacancy-satellite structures caused by a Coster-Kronig L_2L_3V decay of a L_2 hole preceding the L_3VV transition.[25] In copper, where this effect is seen most clearly, two distinct satellites appear a few eV below the main maximum, in correspondence with the main structures of the Auger spectrum itself.[26] The difference in energy between the Coster-Kronig—preceded transition and the common L_3VV pro-

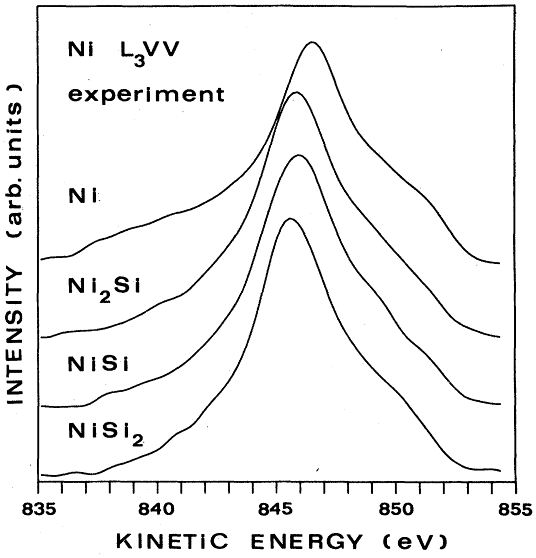

FIG. 4. Experimental Ni L_3VV integrated Auger line for Ni silicides. Electron energies are referred to the Fermi level.

cess is thought to be due to the Coulomb repulsion between the extra hole created by the L_2L_3V process and the holes in the final state of the L_3VV transition. Having a d^7 final configuration, this curve should be displaced from the main Auger line by approximately $2U$. This is only a qualitative estimate since a change in relaxation may take place due to the presence of the spectator valence hole. Upon going toward Si-rich compounds this part of the spectrum becomes less intense, although structures can still be distinguished. In $NiSi_2$ we find two distinct features at 841 and 842.1 eV and a smaller structure at 836.5 eV. Similar features are identified in the Ni_2Si spectrum at 843, 841.9, 839, and 836.5 eV.

(iv) The evolution of the high-energy structure is particularly interesting; the pronounced bulge at 851.3 eV in Ni is smoothed upon going to Ni_2Si, but its intensity increases in the other compounds, until in $NiSi_2$ it appears again as a well-resolved peak at 850 eV.

It is of some interest to compare our experimental data with those of Bennet *et al.* on the Ni-Al alloys.[22] The trend in the line shape is rather similar: Upon increasing the Ni dilution the curves show a decreased emission on the two sides of the maximum. The wide bulge of pure Ni is first smoothed and then, for high aluminum concentrations as in Al_3Ni, a well-resolved structure appears in the same energy range. Unlike our results, those for Ni-Al alloys show a narrowing of the maximum upon increasing the Al content. This and other minor differences may be due to the different resolutions of the experimental apparatuses used in the measure of the line shapes.

It is customary to compare photoemission and Auger line shapes in order to obtain an estimate of the effective Coulomb interaction between the holes. If we indicate the kinetic energy corresponding to the main peak in the Auger curve by E_{kin}, and the binding energy of the core level by E_c, the Auger parameter U_{eff} is given by

$$U_{\text{eff}}=E_c-E_{\text{kin}}-2E_d \ . \tag{4}$$

Here, E_d is taken as the d-band centroid, evaluated from XPS, as indicated in Ref. 22. U_{eff} cannot be identified with the same intra-atomic Coulomb parameter U used in the preceding section since it includes intra-atomic as well as extra-atomic relaxation effects, the contribution of which to the kinetic energy of the Auger electrons is not negligible.[27] However, Eq. (4) may provide an estimate about the way in which U changes as a function of the Si content. To evaluate U_{eff} we have measured the binding energy of the $2p_{3/2}$ core level in Ni silicides; the experimental values are presented in Table I together with the other quantities entering Eq. (4). In the table we also give the estimated value for U_{eff}. It is seen that this value does not change appreciably upon passing from Ni to its silicides. These results may be taken as evidence that the intra-atomic Coulomb parameter is nearly the same in all the compounds.

TABLE I. Estimated value of U_{eff} from Eq. (4). E_{kin}, energy of the main peak; E_d, d-band centroid; and E_c, core-level binding energy. Units are eV.

	E_c	E_{kin}	$2E_d$	U_{eff}
Ni	852.28	846.5	2.8	3.0
Ni_2Si	852.65	845.9	3.6	3.2
NiSi	852.85	846.0	3.9	3.0
$NiSi_2$	852.99	845.6	4.5	2.9

IV. THEORETICAL TWO-PARTICLE SPECTRA

The perturbation method which has been used in discussing valence-band spectra can be adopted for the interpretation of the Auger data also. Neglecting nonlocal contributions, the two-hole spectrum is given by[18–20]

$$D(E)=\frac{D^0(E)}{[1-F(E)U]^2+U^2D^0(E)} \ , \tag{5}$$

where

$$D^0(E)=\int_{-\infty}^{E_F} dE'\tilde{n}(E')\tilde{n}(E-E') \tag{6}$$

is the self-fold of the one-particle spectrum, and $F(E)$ is the Hilbert transform of $D^0(E)$ given by

$$F(E)=\mathrm{P}\int_{-\infty}^{+\infty} dE'\frac{D^0(E)}{E-E'} \ . \tag{7}$$

In applying this theory to the calculation of the Auger spectrum one is faced with the problem of choosing the correct function $\tilde{n}(E)$ to be inserted into the preceding equations. If one neglects the hole-hole interaction, $D(E)$ is simply the self-convolution of the density of states. For the case of pure Ni this gives the two-particle spectrum shown by curve a in Fig. 5. This curve does not in any way resemble the experimental line shape. The maximum is at about 848 eV, nearly 2 eV higher than the main peak

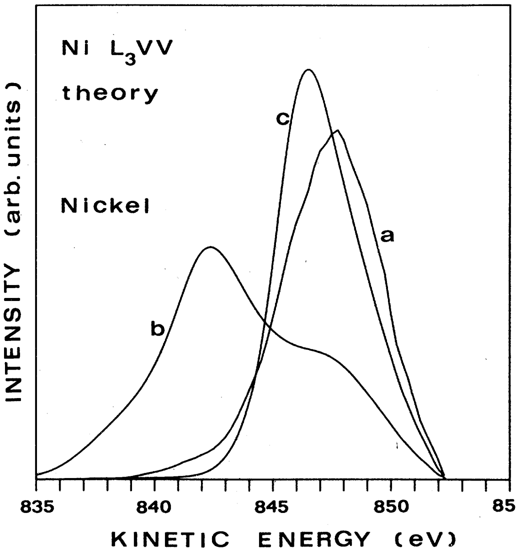

FIG. 5. Theoretical Ni L_3VV Auger line shape for pure nickel, evaluated using Eq. (5) with $\tilde{n}(E)$, from the Ni d DOS (curve a); $\tilde{n}(E)$ from Eq. (1) with $U=2.5$ eV (curve b); and $\tilde{n}(E)$ from Eq. (1) with only $3d^9$ contributions and $U=2.5$ eV (curve c). Electron energies are referred to the Fermi level.

found in the experiments, and the curve does not show the skewness on the high-energy side typical of the measured spectrum. Attempts to improve on the aforementioned theory by taking $\tilde{n}(E)$ from Eq. (1) are not successful. As shown by Fig. 5, curve *b*, the maximum shifts to lower energy by 5 eV (twice the Coulomb energy *U*), while a wide and less intense structure is found in the energy range where the maximum falls in the experiments. The shift of the main peak in the theoretical curve is due to the fact that $\tilde{n}(E)$ contains a mixture of $3d^8$ and $3d^9$ states, the former being responsible for the satellite feature seen in photoemission EDC's. As a consequence, the calculated two-particle spectrum contains both three-hole and two-hole final states. However, three-hole final states, such as those arising from vacancy satellites, lie at lower kinetic energies than the main Auger peak, which should be ascribed to transitions leading to a final d^8 configuration. This is clearly shown by the fact that the energy of the $3d^8$ satellite found in XPS is identical to the two-electron binding energy of the *VV* final state derived from the Auger transition.[16,22] Therefore to find the correct $\tilde{n}(E)$ to be inserted into the preceding expression, we have to use the one-particle spectrum corresponding to the initial $3d^9$ configuration only. This can be extracted from either the calculated one-particle spectra or from the measured photoemission curves, as is done in Ref. 16. Since one of the purposes of the present paper was to see how correlation effects can be treated within a simple theoretical model, we have opted for the first choice and have calculated the two-particle spectra starting from our theoretical $\tilde{n}(E)$, but including d^9 states only. Curve *c* in Fig. 5 shows the calculated line shape for pure Ni. It is seen that, in agreement with the experimental data, the maximum is now located at 846.7 eV and the curve is more asymmetric on the high-energy side. This result is remarkable and indicates that, provided the right initial states are considered, a band theory can account for some important features of the experimental line shapes.

Using the same approach we have calculated the two-particle spectrum for the silicides with the same *U* value. The theoretical curves are shown in Fig. 6. As expected, the general shape of these curves is similar to that of pure Ni. In agreement with the experiments we find that the maximum moves at lower energies upon increasing the Si content. The shift is larger in $NiSi_2$ and NiSi, having maximums at 845.2 and 845.8 eV, respectively, than in Ni_2Si, whose maximum is at 846.5 eV. The shift in the experimental spectra is very close to these values, the peak being at 845 eV in $NiSi_2$. The theoretical model accounts for the observed narrowing of the curve: Upon passing from Ni to $NiSi_2$ the width decreases by approximately 1 eV, in fair agreement with the data.

It is interesting to discuss the behavior of the vacancy-satellite structure in terms of our simplified model. As indicated in Fig. 5 three-hole final states are likely to be located below 842 eV in pure Ni. This is precisely the energy region where the satellite structures appear in the experiments. Unlike what happens in copper, where these satellites are very well resolved, the partial bandlike character of the L_3VV transition in Ni causes them to give rise to a broad band which extends over an energy region nearly equal to the *d*-band width. The decrease in the intensity of this structure upon going to Si-rich compounds is a consequence of the smearing of the d^8 structure in the silicide DOS, caused by the strong coupling between metal *d* and Si *p* orbitals. The fact that the main satellite structures shift at lower energies upon increasing the Si content seems to be a consequence of the displacement of the main peaks of the L_3VV curve.

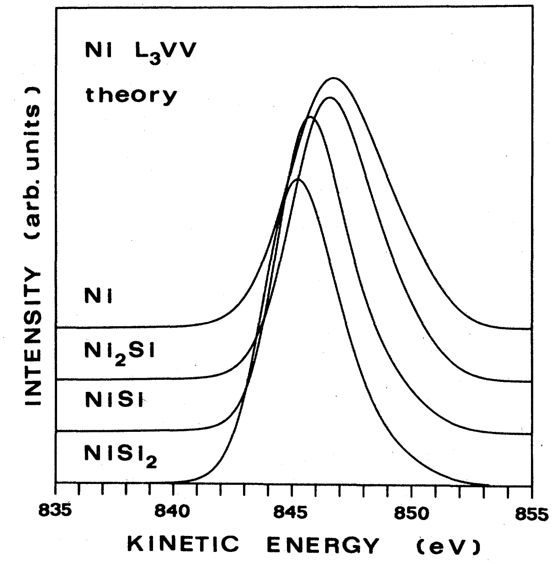

FIG. 6. Theoretical Ni L_3VV Auger line shape for Ni silicides calculated with $U=2.5$ eV and retaining $3d^9$ contributions only.

While these results are encouraging, it is clear that a detailed explanation of the additional structures appearing in the experimental line shapes on both sides of the main peak cannot be provided by the model. This is not surprising, since in pure Ni it has been shown that they are due to multiplet effects. Such effects could be included in our theory by allowing different Coulomb parameters for different multiplet terms, as indicated by Liebsch.[21] Fuggle and co-workers[28,22] have shown that in pure Ni the main peak corresponds to the ^1G term, which from standard multiplet theory is expected to be the most intense; the bulge at high kinetic energy is associated mainly with the ^3F term, while the ^1D and ^3P terms lie in the same energy region as the ^1G, but having a very small intensity, cannot be resolved in the experiments.

Previous work on multiplet effects in a large number of alloys[28] indicates that these integrals are rather insensitive to alloying and are essentially the Hartree-Fock values[29] reduced by 20% for solid-state screening effects. To show the sort of agreement which can be obtained using standard multiplet theory, in Fig. 7 we give the Auger line shapes for Ni and $NiSi_2$ calculated using the $F^{(2)}$ and $F^{(4)}$ values given in Ref. 28, and combining the various terms with the constraint that the intensity ratios of the terms are given by the theoretically calculated transition probabilities.[29] The widths and shapes of the curves for every term were evaluated following the procedure indicated by

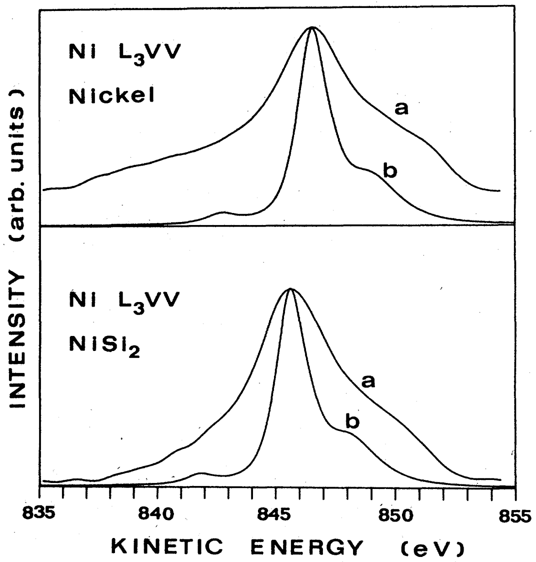

FIG. 7. Comparison between experimental L_3VV integrated Auger lines of Ni and $NiSi_2$ (curve *a*) and the spectrum calculated with standard multiplet theory with $F^{(2)}=9.6$ and $F^{(4)}=6.4$ eV (curve *b*).

Antonides *et al.*[17] The experimental curves are reported for sake of comparison.

The theoretical curves show a main peak, corresponding to the ^1G term, straddled by two structures, which are associated to ^1S (at lower energy) and ^3F, respectively. There is a qualitative correspondence between the experimental line shape and the calculated multiplet. In particular, the location of the ^1S term seems in good correspondence with the structure found to the left of the main peak. The structure at high energies is reproduced with less accuracy since the ^3F term is located at lower energies then the experimental peak. Since the high-energy region is more sensitive to the chemical environment of the Ni atom, the discrepancy may be due to the difficulty of reproducing such effects with a simple atomic theory. A calculation with higher values of the Slater integrals does not significantly improve this situation. Perhaps the most interesting conclusion to be drawn from Fig. 7 is that the trend in the behavior of the Auger line shapes previously found in Ni alloys[22,28] seems to be true even in metallic Ni compounds. However, we believe it is important to stress that the atomic multiplet theory does not allow a quantitative and detailed explanation of the Auger line shape.

V. CONCLUSIONS

We have provided clear evidence that electronic correlation is of crucial importance in the interpretation of the valence photoemission and Auger spectra of Ni silicides. We have also shown that a simple band model corrected by a perturbative inclusion of the intra-atomic correlation may explain many important features seen in the experimental EDC's and Auger line shapes.

It would be interesting to verify the relevance of these effects in core-level spectroscopies. It is well known that as a consequence of intra-atomic correlation, satellites can arise in core-level photoemission. Their location with respect to the main peak is expected to be of the order of the Coulomb repulsion *U*. A study of this sort could provide additional information on the electronic correlation in these materials.

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