Synchrotron-radiation investigation of the chemical dependence
of the vacancy-satellite structure of the Ni L_3VV spectra in Ni silicides

G. Currò

Istituto di Struttura della Materia, Salita Sperone 31, Sant'Agata, 98166 Messina, Italy

R. Cosso

Interdisciplinary Research Center in Surface Science, University of Liverpool, P.O. Box 147, L69 3BX, Liverpool, United Kingdom

M. Sancrotti

Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
and Laboratorio Tecnologie Avanzate Superfici e Catalisi, Istituto Nazionale di Fisica della Materia, Padriciano 99,
34012 Trieste, Italy

L. Duó

Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

S. D'Addato

Interdisciplinary Research Center in Surface Science, Daresbury Laboratory, WA4 4AD Warrington, United Kingdom

S. Nannarone

Istituto di Fisica, Università di Modena, Via Campi 213/a, 41100 Modena, Italy

S. Iacobucci

Istituto di Metodologie Avanzate Inorganiche, Consiglio Nazionale delle Ricerche, Area della Ricerca di Roma,
Via Salaria km. 29,300, Monterotondo Scalo, 00016 Roma, Italy

G. Panaccione

Istituto di Fisica, Università degli Studi di Roma "La Sapienza," Piazzale A. Moro 2, 00185 Roma, Italy

P. Weightman

Interdisciplinary Research Center in Surface Science, University of Liverpool, P.O. Box 147, L69 3BX, Liverpool, United Kingdom
(Received 7 July 1992)

We report a synchrotron-radiation investigation of the satellite structures of the Ni $L_3M_{4,5}M_{4,5}$ Auger spectrum in the Ni compounds Ni_2Si and $NiSi_2$. The line shape of the satellites is extracted and analyzed for both compounds and compared to the corresponding structures in Ni metal as reported in the literature for a set of increasing photon energies; the procedure used to analyze the Auger data is described. The spectra analysis allows us to study the evolution in the line shape and in the energy position of the satellite structures in connection with the different chemical environment. The physical origin of these structures is discussed.

I. INTRODUCTION

The satellite structures of $L_3M_{4,5}M_{4,5}$ Auger spectra of metals such as Cu, Zn, Ni, and related compounds have been the subject of extensive investigation in the last three decades.[1-11] In particular, the dependence of such satellite structures on the chemical environment of the atom that undergoes the Auger transition has been studied for some systems.[9-11] A consideration of the physical processes involved in the generation of these satellites suggests that the composition of the material containing the atom undergoing the Auger transition may have a major influence on the spectrum. It has been shown that the satellite intensity arises from $L_3M_{4,5}M_{4,5}$ Auger transition taking place in the presence of a spectator M_{45} hole,[1] which lowers the kinetic energy of the Auger elec-

trons by a few eV's. Among the processes that have been shown to be important in the formation of an $M_{4,5}$ vacancy for metals such as Cu, Zn, and Ni, the most relevant to our discussion is the $L_2L_3M_{4,5}$ Coster-Kronig (CK) transition[3] which, when energetically allowed, may precede the $L_3M_{4,5}M_{4,5}$ Auger process, leaving a hole in the $3d$ states. As shown, for example, by McGuire,[5] the expression for the transition rate of the CK process contains the dependence on the characteristics of the electronic states and configurations involved and on the ejected electron energy. This last quantity is usually between 0 and 10 eV, i.e., the process is energetically allowed only in a few cases. Therefore, the transition rate of CK processes is expected to vary rapidly with the wavelength of the outgoing electrons, which is related to their kinetic energy (assuming for the CK electron wave function a

plane-wave expression $\chi = \exp(ikr)$, with $k = 1/\lambda$).[12] As a consequence, the transition rate is expected to change dramatically with chemistry because of the change both in the energy of the atomic levels involved in the transition and in the shape of the wave functions. One thus expects to see changes in the shape and intensity of the satellite spectrum with respect to the main Auger line on going from a pure element to its compounds. In the case of zinc, for example,[10] it has been shown that the CK probability and, therefore, the satellite intensity is greatly reduced in the oxide with respect to the case of the pure metal and that in the vapor phase the satellite structures were not observed at all.[13]

In this paper we report a study of the satellite structures of the Ni $L_3M_{4,5}M_{4,5}$ Auger spectrum in Ni silicides, namely Ni_2Si and $NiSi_2$. The study of Ni silicides is particularly interesting both in this respect and because these materials are of fundamental and technological interest in connection with the issue of Si/transition-metal interfaces. In particular, it has been shown that nearly stoichiometric compounds appear beginning at the early stage of the room temperature formation of various Si/Ni interfaces[14,15] and in this context it has been found that $NiSi_2$ can be easily grown epitaxially on the (111) face of silicon by thermally promoted interdiffusion.[16] Moreover, Ni silicides have been the subject of a large theoretical and experimental investigation of their electronic and structural properties.[9–11,17]

Synchrotron radiation (SR) was used as a source of excitation of the L_3 core hole from which the Auger transition originates. The tunability of SR allowed us to acquire a "satellite-free" spectrum by choosing a value of the energy of the photon beam just above the ionization potential of the L_3 electron. This also made it possible to scan through the L_2 threshold and acquire the L_3VV spectra for increasing values of the photon energy. By taking the differences between the spectra collected for higher values of the photon energy and the satellite-free spectrum, it was possible to identify the satellite contribution to the line shape and to follow its growth (see Sarma et al.[8] for the case of Ni metal). The first attempt to explain the origin of this satellite spectrum was that of Roberts, Weightman, and Johnson,[1] who attributed it to the presence, during the $L_3M_{4,5}M_{4,5}$ Auger process, of a spectator $M_{4,5}$ hole generated by a preceding $L_2L_3M_{4,5}$ CK transition. Support for this suggestion has been given in the case of Cu by Auger-photoelectron coincidence measurements[18] and by experiments performed using AlK_α, MgK_α, and CuK_α x-rays,[19] the latter showing a dependence of the satellite intensity relative to the main Auger line on the photon energy. Recently, this view has been disputed by the authors of Ref. 7, who performed a synchrotron-radiation investigation of Cu and Zn; they have attributed the satellite structures of the $L_{2,3}M_{4,5}M_{4,5}$ spectra mainly to Auger final-state shakeup effects generating a three-hole configuration. Moreover, they have interpreted the observed increase in the intensity of the satellite features with increasing photon energy up to far above the thresholds (≈ 200 eV) as due to a breakdown of the sudden approximation. These conclusions have been questioned by Wassdahl et al.,[20] who

showed that the strong satellites in the Cu and Zn $L_{2,3}$ x-ray emission and Auger spectra are due to M-shell vacancies produced before the decay, via CK and also by shakeup and shakeoff processes. A subsequent review of the data of Sarma et al.[7] by Fuggle and Sawatzky[21] has underlined their consistency with the original ideas, although this reinterpretation has been contested by Sarma et al.[22] In the case of the Ni $L_3M_{4,5}M_{4,5}$ Auger transition, two different contributions to the satellite line have been identified, one related to a preceding CK $L_2L_3M_{4,5}$ process and the other to a final-state shakeup effect. In this paper we will analyze the satellite behavior as a function of the chemical environment of the Ni atom that ejects the Auger electron in two different Ni silicides, in an effort to obtain insight into the mechanisms that lie at the basis of the satellite behavior.

The paper is organized as follows: in Sec. II a survey of the experimental apparatus is given; details of the data handling and the results obtained are the subjects of Sec. III, along with the discussion and conclusions.

II. EXPERIMENT

The experiments were performed on station 1.1 of the Synchroton Radiation Source of Daresbury (U.K.). A slitless entrance monochromator, based on a non-Rowland spherical grating (1800 lines/mm), was connected, without a window, to the UHV chamber. The standard deviation of the photon-energy resolution at the energies employed was $\sigma = 1.6$ eV; this means that a nonnegligible part of the photon flux lies between $E \pm 2\sigma$ and $E \pm 3\sigma$, where $3\sigma \approx 4.8$ eV. The contribution from the second-order light in the beam line is negligible (less than 5%) at the energies in use in our experiments and therefore did not affect our results. Well-prepared bulk Ni silicides[23] were cleaned in situ by scraping with a diamond-covered file. The cleanliness of the specimens was regularly checked by x-ray photoemission spectroscopy (XPS) which revealed no detectable features attributable to carbon, oxygen, or other contaminants. The Auger spectra were collected using an HA150 hemispherical analyzer manufactured by Vacuum Science Workshop, in the constant-pass energy mode with a resolution of 0.6 eV. The base pressure during the experiments was in the low 10^{-10} mbar range.

III. RESULTS AND DISCUSSION

In Figs. 1 and 2 the $L_3M_{4,5}M_{4,5}$ Auger spectra of Ni_2Si and $NiSi_2$ are shown, respectively; spectra (a) are taken with a photon-energy value below the ionization potential of the L_2 level and spectra (b) are taken with a photon energy value well above this threshold.

A large increase in intensity on the low-kinetic-energy side of the line shape occurs on going from spectrum (a) to spectrum (b), for both materials. For a nearly corresponding photon energy, the spectra of the two compounds look remarkably similar to each other and resemble the $L_3M_{4,5}M_{4,5}$ spectra reported in the literature for pure Ni,[8] in spite of the very different chemical environment of the Ni atom in the three cases. This resemblance

has been observed in a previous electron-excited study;[11] we note that for both silicides the spectra acquired with $hv = 1010$ eV [curve (b)] are very similar to the electron-excited data of Ref. 11, which are shown after a background subtraction. For both materials, by acquiring the spectra with a photon energy above the L_3 and well below the L_2 threshold ionization energy, one should obtain a satellite-free line shape.[8] The ionization energies, as determined by x-ray-absorption spectroscopy,[23] are 853 eV for the L_3 and 870.5 eV for the L_2 threshold in Ni_2Si, while for $NiSi_2$ they are found to be 2.1 eV higher in each case. In order to minimize the influence of any additional excitations accompanying the creation of a Ni L_3 hole state by photoionization, spectrum (a) in Fig. 2 was collected with a low photon energy, 852 eV, which is actually below the L_3 threshold (855 eV). This was achieved by taking advantage of the reduced resolution of the monochromator at this energy ($\sigma = 1.6$ eV). The spectrum thus corresponds to initial states excited almost exactly at threshold. We note here that the intensity of the valence-band photoelectronic signal overlapping the Auger spectrum collected with $hv = 852$ eV is negligible with respect to the intensity of the main line.

Curves (a) of Figs. 1 and 2 are featureless on the low-kinetic-energy side, i.e., there are no detectable satellite structures on these line shapes. We have therefore used these spectra as a reference, to follow the growth of the satellite with increasing photon energies. In particular, we have isolated the contribution of the satellite to the main Auger line by extracting the difference spectrum of

the data obtained with increasing photon energy and the reference. In order to generate the difference spectra, each curve was normalized by aligning the high-kinetic-energy side with its respective reference spectrum, as shown in Figs. 1 and 2. This particular choice stems from the impossibility of aligning the two spectra to the $^1G_4$ main Auger peak, a satellite contribution being present in the same energy region of this peak; furthermore, it has been observed that the high-kinetic-energy side of the Auger line does not change on varying the photon energy. In Figs. 3(a) and 3(b) the difference curves obtained using the above-mentioned procedure in the case of Ni_2Si and $NiSi_2$, respectively, are displayed, for a set of photon energies ranging from a few eV's above the energy used to acquire the reference spectrum to approximately 160 eV above the L_3 threshold. In Fig. 4 the ratio between the satellite intensity and the main-line intensity is plotted versus the photon energy for the case of $NiSi_2$. The satellite intensity was deduced for each difference spectrum as the area under the curve between the kinetic energies of 832 and 853.5 eV. The same procedure and energy range were used to calculate the corresponding main-line intensity in the spectra collected at photon energies below the L_2 threshold. The observed intensity of the satellite is very low for $hv = 854.5$ eV and it increases slightly for $hv = 859.5$ eV. A pronounced increase in the intensity occurs for values of the excitation energy between approximately 867 and 876 eV; for reasons that will be clear below, we refer to this part of the curve as the CK ramp. At higher photon energies the
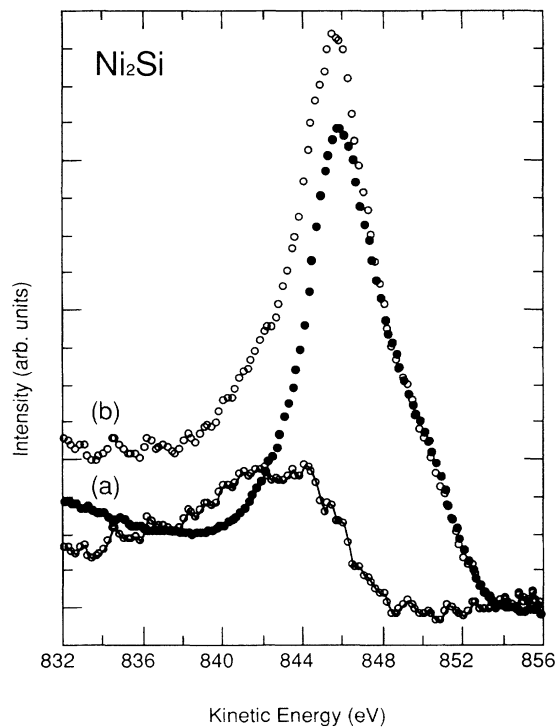

FIG. 1. Ni $L_3M_{4,5}M_{4,5}$ Auger spectra in Ni_2Si taken at two different photon energies: (a) $hv = 859.5$ eV (open circles) and (b) $hv = 1010$ eV (filled circles). The difference spectrum is also shown (see text).
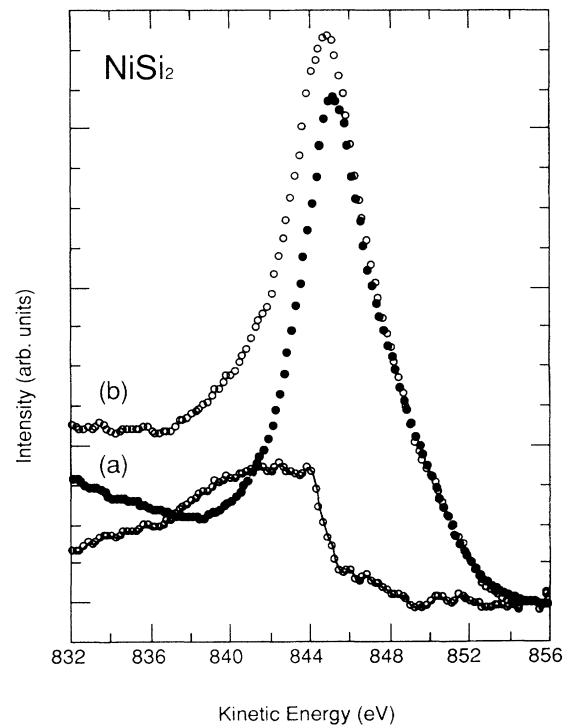
FIG. 2. Ni $L_3M_{4,5}M_{4,5}$ Auger spectra in $NiSi_2$ taken at two different photon energies: (a) $hv = 852.5$ eV (open circles) and (b) $hv = 1010$ eV (filled circles). The difference spectrum is also shown (see text).

growth becomes slower and tends asymptotically to a saturation value. It should be noted that a very similar trend in the growth is observed in the case of Ni_2Si, as shown in Fig. 4. The observed shape of the satellite is very similar in the two compounds for corresponding $(h\nu\text{-}L_3)$ energy differences in spite of the different stoichiometry.

We suggest that the pronounced increase in the intensity of the satellite observed in the case of $NiSi_2$ for values of the excitation energy around 867 eV and for Ni_2Si around 865 eV is mainly a consequence of the excitation of the L_2 threshold, which opens the possibility of $L_2L_3M_{4,5}$ CK decay, leading to a two-hole $L_3M_{4,5}$
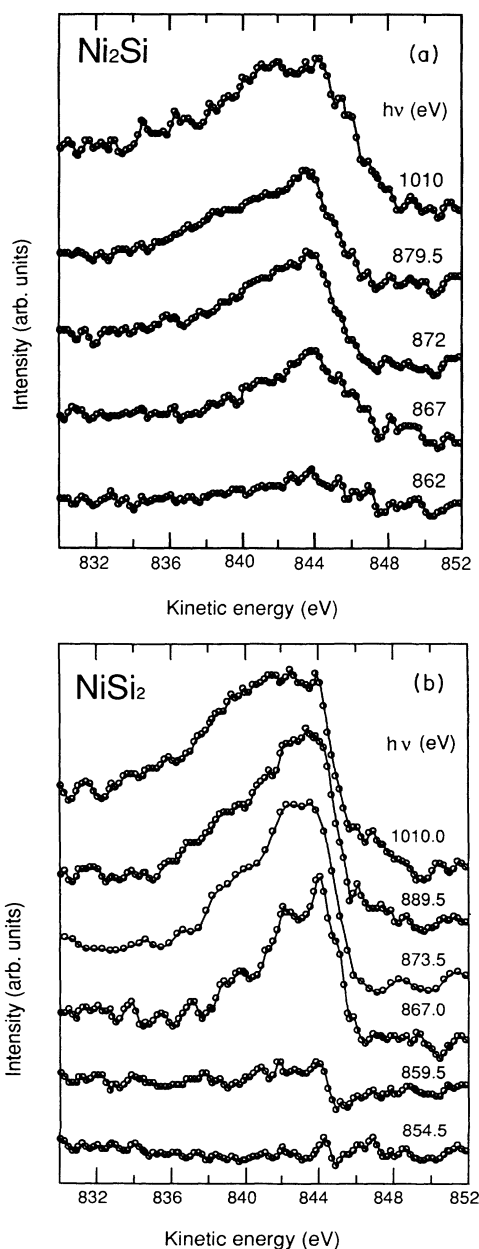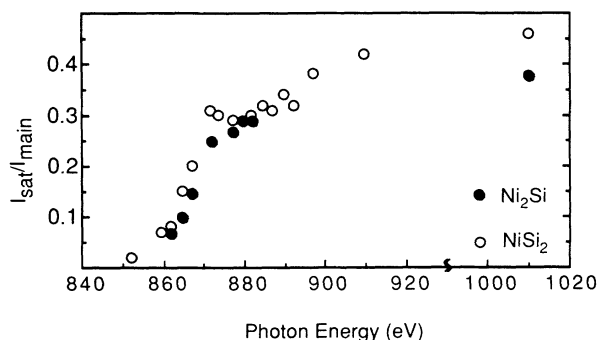

FIG. 4. Intensity of the satellite structures relative to the main $L_3M_{4,5}M_{4,5}$ Auger line as a function of $h\nu$ in Ni_2Si (filled circles) and in $NiSi_2$ (open circles).

FIG. 3. (a) Evolution of the satellite line shape vs the photon energy for Ni_2Si. (b) Same as (a) but for $NiSi_2$.

configuration in the initial state of the Auger process. The intensity observed before this pronounced increase could be due to shakeup processes in the photoemission of the L_3 electron leading, again, to the two-hole $L_3M_{4,5}$ Auger initial state.

This latter state will decay via an $L_3M_{4,5}\text{-}M_{4,5}M_{4,5}$ $M_{4,5}$ transition, giving rise to the satellite structure located at a lower kinetic energy with respect to the main line. This interpretation is consistent energetically if we consider the aforementioned arguments concerning our experimental resolution. In fact, our data show the steep increase in the satellite intensity for a value of the photon energy which is approximately 5 eV below the ionization energy of the L_2 threshold, which is consistent with our previous observations regarding the excitation of the L_3 threshold.

We now discuss the high and low kinetic-energy regions of the Auger spectrum separately.

A. High-kinetic-energy region

The underlying multiplet structure of the d^8 states created by $L_3M_{4,5}M_{4,5}$ processes, which appear at high kinetic energy in the spectra reported here, is known to be composed of $^1S_0$, $^1G_4$, $^1D_2$, ^3P, and ^3F components. Bisi et al.[11] have noted that the U value of the least-bound ^3F component, which corresponds to the high-kinetic-energy edge of the Auger spectrum, is very small and, consequently, in light of the Cini-Sawatzky theory, we expect this region of the spectrum to have some contribution from the self-convolution of the local density of states of the valence band. In Ni alloys this region of the spectrum is sensitive to the changes in the local electronic structure induced by alloying.[4,9] Alloying with the narrow band metal La causes the spectrum to sharpen and suggests the presence of a quasiatomic ^3F component, whereas alloying with Al causes a reduction in intensity in this region. Figure 5 shows the high-kinetic-energy region of the spectrum in detail for Ni metal and its two silicides and it is notable that the spectra are almost identical. Given the large differences in the valence-band density of states between metallic Ni and its silicides, we would expect that any bandlike contribution would be
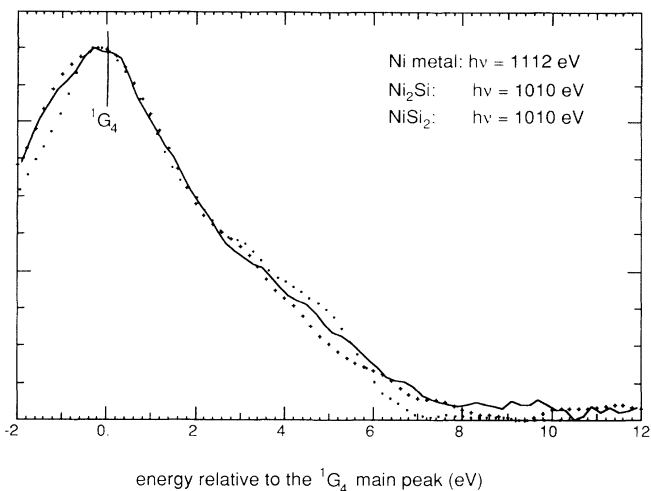
Ni metal: hv = 1112 eV
Ni$_2$Si: hv = 1010 eV
NiSi$_2$:   hv = 1010 eV

energy relative to the $^1G_4$ main peak (eV)

FIG. 5. Comparison of the high-kinetic-energy part of the $L_3M_{4,5}M_{4,5}$ Auger spectra of Ni metal (dotted curve), Ni$_2$Si (solid line), and NiSi$_2$ (crosses) after alignment of the $^1G_4$ peaks.

different in the spectrum obtained from each material. Consequently, the identical spectral profiles of Fig. 5 imply that the total bandlike contribution to the spectrum is small. The dominant contribution to the spectrum arises from the more bound $^1G_4$ component, identified with the main peak in the spectrum, which is expected to be largely atomiclike. The relative intensity of bandlike and atomiclike contributions to the valence-band Auger spectra change very rapidly with the ratio U/W and the line shape arising from the atomic components is expected to be independent of the shape of the local valence-band density of states. We conclude that, with the possible exception of the ^3F component, the d^8 final states created by the $L_3M_{4,5}M_{4,5}$ transitions in all the three materials are predominantly atomiclike. The Auger profiles of these materials suggest that the changes in the local electronic structure on a Ni site that arise from forming Ni silicides are, in some sense, intermediate between those produced by alloying with La, which causes a sharpening of the ^3F component, and those resulting from alloying with Al, which reduces its intensity. This is an interesting result in light of a recent comparison of the electronic structures of NiSi and NiAl, which concluded that the simple d-p bonding scheme usually used to explain the electronic structure of silicides needs revision.[24]

B. Satellite region

First of all, on increasing the photon energy the total area of the three-hole satellite line in terms of its ratio to the main line area appears to grow with nearly the same rate for all the stoichiometries analyzed (silicides and Ni metal as reported in Ref. 8). This seems to suggest that the Auger satellite structures in the two silicides originate from the same physical processes that give rise to the homologous structures in the pure Ni: the $L_2L_3M_{4,5}$ CK decay of the initially created L_2 hole seems to be the process leading to the most striking effects in the satellite line-shape evolution vs photon energy, and this would be

in partial agreement with that proposed by Sarma *et al.*[8]

An expression for the kinetic energy of the CK electron is given by the Shirley's formula,[25] which is, in the case of the $L_2L_3M_{4,5}$ transition,

$$E_k(L_2L_3M_{4,5}) = E_b(L_2) - E_b(L_3) - E_b(M_{4,5})$$
$$- \mathscr{F}(L_3M_{4,5}) + \mathscr{R}(L_3M_{4,5}),$$

where $\mathscr{F}(L_3M_{4,5})$ is the Coulomb energy of the L_3-$M_{4,5}$ hole pair and $\mathscr{R}(L_3M_{4,5})$ is the relaxation total energy, which is the relaxation energy of the two-hole system that must be added to the relaxation energy of the single-hole system already contained in the XPS-derived binding-energy terms E_b.

By writing

$$\Delta E = E_b(L_2) - E_b(L_3) - E_b(M_{4,5})$$

and

$$W^* = \mathscr{F}(L_3M_{4,5}) - \mathscr{R}(L_3M_{4,5}),$$

we can conclude that the CK decay is energetically allowed when $\Delta E > W^*$ and its probability grows upon increasing this energy difference. This is why Antonides and Sawatzky[10] noted that on going from Zn metal to ZnO the $L_2L_3M_{4,5}$ intensity decreases. In the case of Ni metals, Matthew, Nuttal, and Gallon[26] found that $\Delta E \gg W^*$, that is, the $L_2L_3M_{4,5}$ is highly allowed. Furthermore, in metals the CK probability increases slowly with the electron energy above the Fermi level, due to the efficient core-hole screening given by the conduction electrons. In the case of Ni$_2$Si and NiSi$_2$, the L_2-L_3 spin-orbit splitting remains the same as in pure Ni and a good core-hole screening is granted by Silicon sp electrons; this allows us to expect that $\Delta E \gg W^*$ for these compounds as well.

The final $[2p_{3/2}3d]$ hole states for the CK transitions consist of several multiplet-structure components, with different values of the L, S, and J quantum numbers, spread over ~ 7 eV. The CK transition rate to each of these two-hole multiplet components is expected to be very sensitive to the details of the wave functions and to the precise energy of the transitions. One might expect the difference in chemical environment between the Ni silicides and the Ni metal to result in an LSJ dependence of the transition rate which gives rise to a different population of components of the multiplet structure in the metal and in the silicides. This would then give rise to the differences in the $L_3M_{4,5}$ (LSJ)-$M_{4,5}M_{4,5}M_{4,5}$ profile. The difference in core-hole screening in the two environments, which is expected to involve local metal d-like states in Ni and less localized Si sp states in the silicides, may also influence the LSJ dependence of the $L_2L_3M_{4,5}$ CK rate. In support of this view, we note that small changes in chemistry are known to significantly change the transition rate of $L_2L_3M_{4,5}$ CK processes in this region of the periodic table.[3,10,12]

A comparison of the satellite lines of the two silicides taken at similar photon energy (at the same hv-L_2 energy difference) just above the end of the steep intensity ramp characteristic of the intensity evolution curves [see Figs.
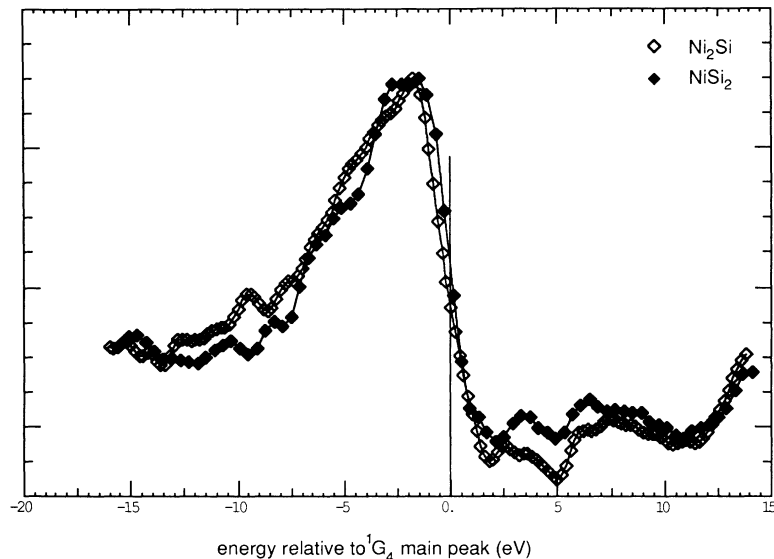
FIG. 6. Comparison of the Auger satellite structures of Ni_2Si (open squares) and $NiSi_2$ (filled squares) collected at nearly the same photon energy (872 eV for Ni_2Si and 873.5 eV for $NiSi_2$) taken just above the steep CK-intensity ramp. Both spectra have been normalized to have the same maximum height; the energy is referred to the respective $^1G_4$ positions.

3(a) and 3(b)], is reported in Fig. 6; it shows that even the relative intensities of each multiplet term of the d^7 final-state configuration are almost the same, within the accuracy of the measurements and data handling, between the two silicides. In particular, the influence of the final-state-term splitting and the position of the centroid of the satellite structures are remarkably similar in the two compounds. The width of the spectrum which is largely determined by the multiplet splittings appears to be comparable to the results of McGuire's calculations[5] for Cu metal and to the measurements of Roberts, Weightman, and Johnson[1] for Cu.

Comparisons of the satellite line shapes performed at several photon energies allow us to conclude that, despite the different atomic coordination of the Ni atoms in the two silicides and the difference in the valence-band structures, the Auger satellite lines (and the main lines, as well) evolve exactly in the same way for Ni_2Si and $NiSi_2$. This suggests that the final-state d^7 configuration is atomiclike in the Auger process, in the sense that the three localized d holes in the final state break the translational symmetry in the Ni-site neighborhood. We also remark that the site-projecting character of the Auger matrix element selects mainly the Ni d charge that is localized onto a Ni site and is not directly involved in the bonding with the Si atoms.

Figure 7 contains a comparison between the satellite line of Ni_2Si and that of Ni metal at comparable $h\nu$ taken above the CK growth ramp. In this comparison the energy difference between $h\nu$ and the L_2 threshold is nearly the same for each material. The first observation regards the satellite centroid position referred to the $^1G_4$ peak of the Auger main line; this energy position represents the F_0 Slater integral which already contains all the screening and relaxation effects: on going from Ni metal to the Ni silicides, the centroid distance from the $^1G_4$ peak

remains the same. Moreover, it can be seen that the line shapes are similar, although the relative intensities of the multiplet terms change a little.

We conclude that the different Ni-Ni coordination and the different core-hole screening character between Ni and Ni silicides does not affect the position of the overall satellite contribution. However, it can be concluded that the satellite behavior is mainly atomiclike for both the silicide stoichiometries and for the pure Ni.

The most notable difference between Ni and Ni silicides satellite line shapes involves the region between 5 and 10 eV away from the $^1G_4$ peak, which typically contains the contribution coming from the presence of the spectator $M_{4,5}$ holes created in the L_3 photoemission final-state shakeup and shakeoff. Our results suggest that either the rate of production of $M_{4,5}$ holes by this process is different for Ni metal and the Ni silicides, or that the d-electrons reservoir for hole excitation changes with the chemistry; the first conclusion seems the more appropriate, since the d occupancy is almost unchanged on going from pure Ni to Ni_2Si and to $NiSi_2$.[27]

It is more difficult to compare the Auger satellite of Ni and its silicides at photon energies falling in the CK-ramp region, due to the strong dependence of the line shapes on $h\nu$. We tentatively suggest that the different stoichiometry reflects a different distribution of intensity among the d^7 multiplet terms as a consequence of the different initial $L_3M_{4,5}$ population and CK matrix element effects even at the same $h\nu$. However, we have found that also in this case the ΔF_0 value between pure Ni and Ni silicides is about zero, which seems to suggest that this quantity is not affected by the CK transition rate.

In conclusion, we suggest that the Auger satellite formation involves only localized d charge even in the d^7 final-state configuration and, moreover, the correspond-
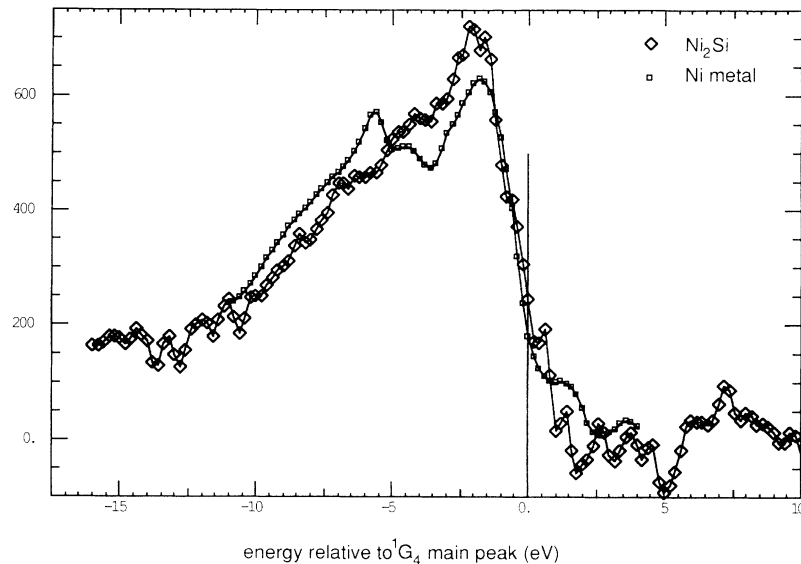
FIG. 7. Comparison of the Auger satellite structure of Ni_2Si (large open squares) and that of Ni metal (small open squares) as taken from Ref. 8; the photon energy employed is the same for both spectra and falls into the asymptotic flat region of the intensity growth curves ($h\nu = 879.5$ eV for Ni_2Si and $h\nu = 879$ eV for Ni metal). The energy is referred to the respective $^1G_4$ peaks.

ing spectrum is mostly atomiclike both in Ni metal and in the silicides. The difference in the screening behavior at different Ni-Ni coordination is not strongly evidenced in our measurements and the change in the satellite line shape with the chemical environment of Ni atoms is not as striking as expected on the basis of atomic CK transition rates intuitive predictions, thus confirming previously reported results.[5,11]

IV. CONCLUSIONS

In summary, the vacancy satellite structures of the Ni $L_3M_{4,5}M_{4,5}$ Auger spectrum in Ni_2Si and $NiSi_2$ have been investigated employing tunable synchrotron radiation as the source of excitation of the initial-state core hole. A remarkable similarity in the line shape of the two series of satellite spectra is found in spite of the different stoichiometry, that is, Ni-Ni coordination and chemical bonding. The measured satellite-intensity dependence on photon energy is found to be almost the same in the Ni compounds, and it strongly resembles previous observa-

tions concerning Ni metal: this suggests a common origin for these spectral features.

The common position of the centroids of the satellite double-hole structures of pure Ni and Ni silicides suggests that the global effect of relaxation and screening of the $L_3M_{4,5}$ double-ionized atom is almost the same for all the involved stoichiometries. Our measurements lead directly to the conclusion that both the d^8 final state of the L_3VV transition and the d^7 final state of the $L_{2,3}M_{4,5}\text{-}M_{4,5}M_{4,5}M_{4,5}$ Auger decay are mainly atomiclike.

[1] E. D. Roberts, P. Weightman, and C. E. Johnson, J. Phys. C **8**, L301 (1975).

[2] J. F. McGilp and P. Weightman, J. Phys. C **11**, 643 (1978).

[3] P. Weightman, J. F. McGilp, and C. E. Johnson, J. Phys. C **9**, L585 (1976).

[4] P. T. Andrews, T. Collins, and P. Weightman, J. Phys. C **14**, L957 (1981).

[5] E. J. McGuire, Phys. Rev. A **17**, 182 (1978).

[6] N. Mårtensson, R. Nyholm, and B. Johansson, Phys. Rev. B **30**, 2245 (1984).

[7] D. D. Sarma, C. Carbone, P. Sen, R. Cimino, and W. Gudat,

Phys. Rev. Lett. **63**, 656 (1989).

[8] D. D. Sarma, C. Carbone, P. Sen, and W. Gudat, Phys. Rev. B **40**, 12 542 (1989), and references therein.

[9] P. A. Bennett, J. C. Fuggle, F. Ulrich Hillebrecht, A. Lenselink, and G. A. Sawatzky, Phys. Rev. B **27**, 2194 (1983).

[10] E. Antonides and G. A. Sawatzky, J. Phys. C **9**, L547 (1976).

[11] O. Bisi, C. Calandra, U. del Pennino, P. Sassaroli, and S. Valeri, Phys. Rev. B **30**, 5696 (1984).

[12] P. Weightman, Rep. Prog. Phys. **45**, 753 (1982).

[13] S. Aksela, J. Väyrynen, and H. Aksela, Phys. Rev. Lett. **33**, 999 (1974).

[14]F. Comin, J. Rowe, and P. H. Citrin, Phys. Rev. Lett. **51**, 2402 (1984); F. Comin, J. Vac. Sci. Technol. A **3**, 930 (1985).

[15]J. van Loenen, J. W. M. Frenken, and J. F. Van der Veen, Appl. Phys. Lett. **45**, 41 (1984).

[16]K. C. R. Chiu *et al.*, Appl. Phys. Lett. **38**, 988 (1981).

[17]C. Calandra and F. Manghi, Phys. Rev. B **45**, 5819 (1992).

[18]H. W. Haak, G. A. Sawatzky, and T. D. Thomas, Phys. Rev. Lett. **41**, 1825 (1978).

[19]P. Weightman and P. T. Andrews, J. Phys. C **12**, 943 (1979).

[20]N. Wassdahl, J. E. Rubensson, G. Bray, P. Glans, P. Bleckert, R. Nyholm, S. Cramm, N. Mårtensson, and J. Nordgren, Phys. Rev. Lett. **64**, 2807 (1990).

[21]J. C. Fuggle and G. A. Sawatzky, Phys. Rev. Lett. **66**, 966 (1991).

[22]D. D. Sarma, C. Carbone, P. Sen, R. Cimino, and W. Gudat, Phys. Rev. Lett. **66**, 967 (1991).

[23]M. Sancrotti, L. Duo, R. Cosso, S. D'Addato, S. Iacobucci, G. Panaccione, A. Ruocco, S. Nannarone, M. Surman, P. Unsworth, and P. Weightman, Solid State Commun. **78**, 641 (1991), and references therein.

[24]D. D. Sarma, W. Speier, R. Zeller, E. van Leuken, R. A. de Groot, and J. C. Fuggle, J. Phys. Condens. Matter **1**, 9131 (1989).

[25]D. A. Shirley, Phys. Rev. A **7**, 1520 (1973).

[26]J. A. D. Matthew, J. D. Nuttal, and T. E. Gallon, J. Phys. C **9**, 883 (1976).

[27]A. Franciosi, J. H. Weaver, and F. A. Schmidt, Phys. Rev. B **26**, 546 (1982).