The electronic structure of NiAl and NiSi

The electronic structure of NiAl and NiSi

D D Sarma†‡, W Speier†, R Zeller†, E van Leuken§‖, R A de Groot§ and J C Fuggle§

† Institut für Festkörperforschung, Kernforschungsanlage Jülich, Postfach 1913, D-5170 Jülich, Federal Republic of Germany
§ Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Abstract. A study of the electronic structures of NiSi and NiAl employing electron spectro-scopies and theoretical calculations is presented. Experimental results, obtained with x-ray photoemission and bremsstrahlung isochromat spectroscopy, are interpreted by means of density of states and matrix element calculations for the compounds in their real crystal structure. This gives a detailed picture of the electronic states over the whole bonding–anti-bonding region below and above the Fermi level. Cluster calculations based on a molecular orbital approach for NiAl provide further insight into the bonding characteristics of the states of various symmetries. We find that the simple d–p-bonding scheme used so far for the silicides, in which the metal d states are referred to as 'non-bonding', needs revision.

1. Introduction

We discuss here the electronic structure of NiAl and NiSi as prototypes for all late-transition-metal aluminides and silicides. Recent interest in p–d-bonded inter-metallics arises partly from the technological importance of the transition-metal silicides [1] and aluminides [2]. For transition-metal silicides a general picture of the electronic structure has emerged over the last few years [3–5]. As discussed in the companion paper on the 4d and 5d silicides [5], the main driving force for the bonding in these compounds is thought to originate from strong coupling of metal d with Si p states. This interaction substitutes the normal d and sp bonding of the elemental transition metals and Si, respectively. Although we shall argue that it is misleading to describe the transition-metal d states as 'non-bonding', they are normally described as non-bonding states, positioned between the bonding–anti-bonding d–p manifold [6, 7], whereas the Si s states form, in most cases, a separated band at the bottom of the valence band [6]. Metal sp states are not normally considered extensively in silicides. This scheme has apparently been supported by numerous experimental and theoretical studies (for the most recent review see [4]).

‡ Permanent address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.
‖ Present address: Natuurkundig Laboratory, Free University, PB 7161, NL-1007 MC Amsterdam, The Netherlands.

In contrast with the early-transition-metal compounds, for the late-transition-metal silicides it is believed that the majority of the transition-metal d states do not participate in the bonding because the transition-metal d band is essentially full [3]. However, the heat of formation of Ni silicides is quite similar to that of other transition-metal silicides [8] so that the bonding mechanism is unlikely to be very different. This is one of the points that we discuss in more detail here.

There are some gaps in our understanding of silicides and aluminides, and one of the most obvious concerns the role of the unoccupied states. Experimental spectroscopic studies concentrated mainly on the occupied states and even here detailed interpretation was hindered because theoretical calculations and matrix element information were made more difficult by the complex crystal structure of most of the pd compounds. In order to bridge this gap, we have investigated the electronic states employing spectro-scopies for the occupied and *unoccupied* states and interpreted the experimental data by means of density of states (DOS) and matrix element calculations for the compounds in their real crystal structure [9]. This allows assignment of the spectroscopically observed features in terms of a one-particle DOS and analysis of the spectral distribution in relation to the states of symmetry involved in the bonding.

We present here results of our x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) investigation for the late-3d transition-metal compounds, NiAl and NiSi. Numerous older investigations already exist for NiAl ([10–13] and references therein) owing to the relatively simple CsCl crystal structure whereas, for NiSi with its complicated MnP structure, only a few studies exist so far [7, 14–17]. Our purpose in the present paper is to discuss the spectroscopic results for aluminides and silicides within the same conceptual framework for the electronic structure and to use the high symmetry of the NiAl lattice to perform a molecular orbital calculation of NiAl clusters to probe the detailed character of the bonding interaction in both compounds. Accordingly our work is divided into several steps: first, we give a theoretical analysis of experimental spectra in terms of the site- and symmetry-related partial DOSS; then we discuss the results by assignment of the spectral distribution in terms of bonding states; finally, we analyse the interactions by addressing the basic questions concerning the character of the 'non-bonding' metal d states and the involve-ment of the Al (Si) s states.

2. Experimental details

These are identical with those given in the companion paper [5].

3. Computations

The theoretical band-structure results have been calculated using the local form of density functional theory. The self-consistent potential for NiAl in the CsCl structure was constructed from the linear band structure using the augmented spherical-wave (ASW) method as described in [18]. Accurate bands were then calculated from the augmented plane-wave method and the Brillouin zone integration necessary to obtain symmetry- and site-projected DOSS was performed using the tetrahedron method with 756 tetrahedra in the irreducible zone. For NiSi in the B31 (MnP) structure, accurate bands were calculated by the ASW method.

The theoretical curves shown in the figures of this paper are constructed from the partial symmetry-selected DOSs of inequivalent atoms in the unit cell. In order to facilitate a closer comparison with the measurement, theoretical data are broadened by the experimental resolution function (normally 0.7 eV full width at half-maximum (FWHM) Gaussian) and an energy-dependent lifetime broadening ($0.1|E - E_F|$ FWHM Lorentzian which we have previously found to simulate experimental results quite well [19]).

The matrix element calculations have been performed within the single-site approximation in [20] as described elsewhere [21]. The only input for these calculations is the atomic potential originating from the appropriate band-structure calculation and the choice of the transition energy (1486.7 eV). Since our band-structure schemes are based on overlapping spheres, the atomic potentials had to be transformed into muffin-tin potentials for use in the matrix element calculation. The muffin-tin radius was determined as half the distance to the nearest neighbour in the different compounds.

The standard multiple-scattering X_α (MS–X_α) calculations were performed using the Norman criteria for sphere radii [22]. The various α-values were taken from the tables in [23]. l-values up to $l = 3$ within the Ni spheres, $l = 2$ in the Al spheres and $l = 4$ in the outer sphere were used for these calculations.

4. Results and interpretation

The experimental XPS–BIS spectra for NiAl and NiSi are shown in figures 1 and 2 in comparison with the DOS and spectra calculated by including the appropriate solid state matrix elements [20, 21]. The measured XPS curves for NiAl and NiSi are similar. Both spectra are dominated by a main structure situated at around -2 eV binding energy. In the case of NiSi this structure is highly asymmetric, indicating an unresolved double-peak structure (at -2.0 and -2.7 eV approximately). Around these main features we find additional structures: a shoulder right at the Fermi level and a broad tail to higher binding energies extending down to -7.5 eV for NiSi and to -6.0 eV for NiAl. Another weak broad structure is visible at even higher binding energies extending down to -14 eV in the case of NiSi and to -11 eV in the case of NiAl. The BIS spectra of the two compounds are quite distinct with a peak and step-like feature in NiAl in contrast with a rather uniform outline for NiSi.

The calculated spectra, broadened for the lifetime and the experimental resolution, describe the overall intensity distribution of the measured curves. The energy positions show deviations of the order of 0.5 eV, most clearly observable for the main peak. We also find an appreciable narrowing of the main structure in NiSi and additional intensity on the high-binding-energy side of the main peak in comparison with the calculation. These effects probably indicate the need for self-energy corrections to the calculated DOS for description of the photoemission process (for a discussion see [13, 14, 19]). However, comparison of the experimental data with the calculated intensity distribution still shows that, apart from the possible slight redistribution of states [14], almost all experimentally observed structures can be related to DOS effects. This allows assignment of the observed features in terms of the different contributions from states of different symmetry. Both XPS and BIS are dominated by the states of metal d symmetry, owing to the large number of d states and large cross section (see, e.g., [9, 21]). At a high binding energy we find contributions of Al and Si s states, which are clearly observable for NiSi and less obvious for NiAl. For both cases we can hardly distinguish special features of
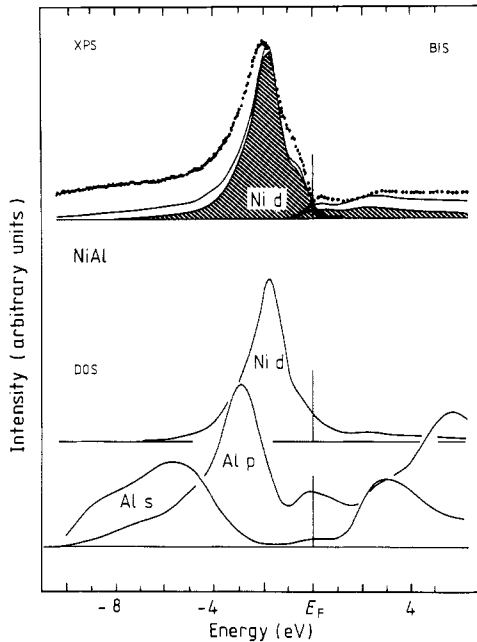
Figure 1. XPS and BIS of NiAl (·····) in comparison with the calculated spectral distribution (——) and the DOS. The partial DOS for the metal d and Si s and p states without the Fermi level cutoff are also shown with arbitrary scaling to allow the s- and p-band features to be seen. The metal d contribution (▨▨▨) to the XPS-BIS intensity is included.
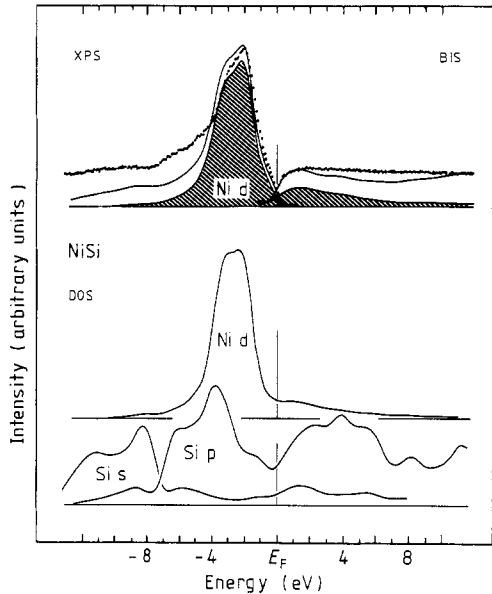
Figure 2. Comparison of XPS and BIS for NiSi with theory. Symbols as in figure 1.

Al or Si p symmetry in the overall intensity distribution and we also find the Al and Si d-state contributions totally suppressed as an effect of the centrifugal barrier [21].

The dominant contribution to the overall intensity distribution of the XPS and BIS spectra arises from the metal d states. It can be seen that the metal d states extend appreciably to both sides of the main structure, to high binding energies as well as far up into the unoccupied states. This is an important result since the main metal d part is narrower than for the pure element [17] and is situated well below the Fermi level as an effect of the band filling on the formation of the compound [6, 13].

From comparison of the XPS-BIS spectra with the calculations we find mixing of Ni d states over the entire energy range inspected but do not obtain experimental information on the Al or Si p contributions which are the most likely origin of the interaction, causing the spread. Experimental results for the occupied Al and Si p states in NiAl and NiSi do, however, exist in form of x-ray emission spectra [15, 24]. X-ray emission is a local process, probing a site-selective DOS because of the small size of the initial core hole. In addition, dipole selection rules apply so that the spectra probe a symmetry-selected DOS (see, e.g., [25]). Thus, for instance, decay of an Al 1s hole in NiAl gives an intensity distribution related to the distribution of valence states of Al p symmetry. The x-ray emission results are shown in figure 3 together with the corresponding partial DOS and the XPS results which provide the necessary information about the Ni d states. The most
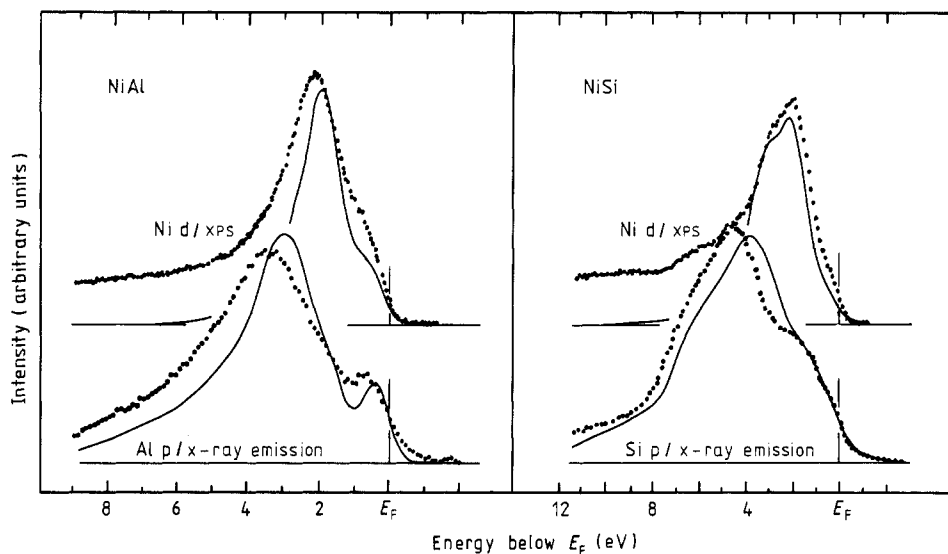
Figure 3. Composite picture of the partial DOS for the Ni d and Al (Si) p symmetry in NiAl and NiSi taken from experiments and theory. For the valence band we used the XPS spectra to give the occupied Ni d states and x-ray emission data for the Al p states. The x-ray emission data are taken from [15, 24].

striking feature of the spectra in figure 3 is the similarity of the p–d bonding interactions in NiAl and NiSi. In both cases, the Al and Si p DOSs peak around the higher-binding-energy side of the main Ni d band and decrease in the region of the d band itself. It should be noted that much of the intensity in the region of the experimental x-ray emission spectra overlapping the Ni d band is due to lifetime and instrumental broadening of the peak at about 4 eV binding energy. The Al and Si p-state densities have a minimum on the higher-energy side of the Ni d bands. The ligand p states again contribute features close to E_F in both compounds.

Unfortunately the unoccupied Al and Si sp states cannot be easily studied experimentally because the inverse technique of x-ray emission, namely x-ray absorption, shows a distortion of the DOS due to the presence of the core hole in the final state [24]. From our DOS calculation in figures 1 and 2 and the BIS results, we conclude that a strong mixing of the Ni d with Al or Si p states takes place. Ni d character is distributed over a range of more than 10 eV, although the main d band is only about 4 eV wide and is filled. The existence of Ni d character in the unoccupied states demonstrates that the band filling of the Ni d band should not be described as a simple charge transfer, in which case Ni d-state character amounting to 10 states/atom would be found below E_F. Clearly hybridisation effects [6, 13] lead to some Al or Si sp character in the 10 states/unit cell of the so-called Ni d band and to some d character in the Al or Si sp bands. The presence of Ni d character in the unoccupied anti-bonding states implies that the net effect of the occupied Ni d states is bonding.

With these results for the spectral distribution of the different symmetry states, we can now make an assignment of structures within the bonding scheme put forward for the d–p inter-metallics [3–7, 26]. At high binding energies, one finds the broad Al or Si s-band positioned at the bottom of the valence band. Above this s-band region we find in NiAl and NiSi a continuous change from states of nearly pure Al and Si p character

to states of nearly pure metal d character. The bonding metal d–Al (Si) p states are observed in the range from -2 to -7 eV binding energy. Much of the main d-band structure, near -2 eV, is situated in a region of low Al (Si) sp-state density and is normally referred to as 'non-bonding'. Anti-bonding metal d–Al (Si) p states constitute the main part of the unoccupied states and are thought to contribute also to the occupied states right at E_F. Note that we also find some unoccupied Al (Si) s-state character above the Fermi level, implying that these states also have a net bonding effect and contribute to the cohesion energy of the compounds.

Comparing NiAl and NiSi, we are also able to relate some of the differences directly to the different effective atomic energy levels of s and p states for Al and Si. The p DOS in the case of NiAl peaks at around -3 eV and extends all the way down to -11 eV. In the case of NiSi the Si p partial DOS shows peaks between -3 and -7 eV and extends altogether down to -12 eV. The p state DOS peaks again in the anti-bonding region above the Fermi level at about 4 eV in NiSi and at about 6 eV in NiAl.

The details in the forms of the s and p DOSs in NiAl and NiSi are quite different. This is mainly a crystal structure effect. Similarly we attribute the differences in spectral shape within the d band and above the Fermi level to the different coordination spheres. Interestingly enough the energy position of the main Ni d structure and also the extent below and above E_F are similar in both cases.

The interpretation of the electronic structure of NiAl and NiSi in terms of a common sequence of levels (light elements s, p–d bonding, d non-bonding and p–d non-bonding) relied on the fact that similar structures in the different partial DOS reflect orbital overlap [27]. However, this analysis does not provide any information on the detailed character of interaction nor its energy dependence. Since band-structure calculations are not immediately transparent to these questions, we decided to study the bonding interaction by a molecular orbital approach. Cluster calculations within a multiple-scattering approach have been applied to the problem of aluminides [28] and silicides [29]. We extend these works for NiAl to follow the development of orbital interaction from the basic microscopic unit and subsequent addition of neighbour interaction in order to proceed from the atomic levels via the cluster to the actual solid state.

Our results for clusters of $NiAl_8$ and $NiAl_8Ni_6$ by the multiple-scattering scheme together with the final full band-structure calculation for the CsCl lattice are summarised in figure 4. The results illustrate the change in electronic structure as we go from simple nearest-neighbour interaction of Ni with eight surrounding Al atoms to additional second-nearest-neighbour metal–metal interaction to, finally, the infinite compound. On the level of the simple $NiAl_8$ cluster we recognise that all orbitals are mixed and form a wide spectrum of Ni d–Al sp bonding–anti-bonding states. By closer inspection we can observe the characteristic distribution of weight for the molecular orbital interaction expected from the energy positions of the elemental atomic orbitals. We find strong Al s-state character at the bottom of the valence band, then metal d with contribution from Al p and some Al s character and finally the Al p character dominating in the range of anti-bonding states. Note that there are no non-bonding states for a Ni atom with eight nearest-neighbour Al atoms and there is evidence for significant inter-mixing of Al and Ni d states at all energies. This clearly establishes that the presence of the so-called 'non-bonding' d states in NiAl solid cannot be attributed to local symmetry or to weak orbital overlap, as is normally the case for a true non-bonding state. If they had been important, both symmetry constraints, or very weak overlap, would have been reflected in the results from this small cluster.

Addition of extra Ni atoms at the centre of the neighbouring cubes causes a major redistribution of states. At the bottom of the valence band we still find the Al s states
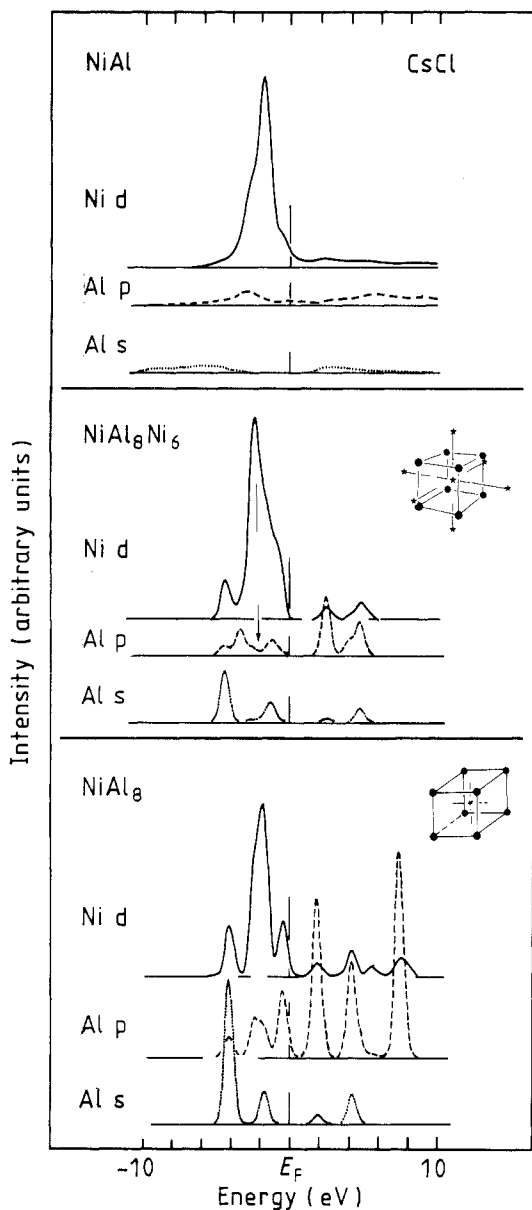
Figure 4. The multiple-scattering calculation for two different NiAl clusters ($NiAl_8$ and $NiAl_8Ni_6$) are compared with the full band-structure result for the solid CsCl-type crystal. The Ni d, Al s and Al p symmetries are shown. Gaussian broadening has been introduced to facilitate comparison of the intensity and energy distributions of the calculated molecular eigenvalues in the cluster with the DOS of the infinite solid state.

mixed with Al p and Ni d states and then the bonding Ni d–Al p states, but this is now followed by a range dominated by metal d character, with little admixture of any other symmetries. Finally the anti-bonding Ni d–Al p states are found above E_F. The results summarised in figure 4 also clearly show that there is substantial contribution of Al s character in the unoccupied states. This supports our earlier conclusion that the Al s states make a significant contribution to the bonding interactions in these compounds.

Note in the $NiAl_8Ni_6$ cluster the characteristic splitting of Al p states around the metal d peak which must be related to the introduction of direct transition-metal d–transition-metal d interaction. It clearly demonstrates that, even for late transition metals, this d–d coupling causes a redistribution by 'pushing out' bonding–anti-bonding

d–sp states, with the formation of a dip in the position of the main density of transition-metal d states and giving rise to the so-called non-bonding features. In the final solid state this dip becomes part of the 'quasi-gap' of minimal density of Al s and p states. Note also that the position of the Ni d band does not change appreciably on increase in the cluster size and thus is mainly determined by the original nearest-neighbour Ni d–Al sp interaction.

These results of the cluster calculation clearly show that the main metal d band cannot be simply viewed as a 'non-bonding' state, that is not involved in the bonding, but rather plays a crucial role in the general distribution of states. We believe that this viewpoint has not been extensively stressed until now.

The conclusions reached here for the case of NiAl can be transferred to the case of NiSi. Of course the different positions in energy of the original atomic orbitals influence the weight and splitting of the various states and clearly the different crystal structure determines the details of the spectral distribution. For example we find less s character in the unoccupied states in the case of the silicide (figure 2) than in the case of the aluminide (figure 1), which is related to higher binding energy of the s level in Si compared with Al. However, the general bonding characteristics and the type of inter-action found for NiAl is expected to be very similar for NiSi. In fact, these results provide a detailed analysis and extend the more general description for the electronic structure of the Ni silicides given by the pioneering work in [6].

5. Conclusions

By means of spectroscopic data and the detailed theoretical analysis we have been able to describe the observed spectral distribution and contributions of the states of different symmetries in XPS–BIS spectra of NiAl and NiSi. This analysis provided the material for discussing the electronic structure of late-transition-metal aluminides and silicides within the same conceptual framework of bonding interaction. Some of our conclusions are common to those in our study of 4d and 5d silicides [5]. Thus we find the following.

(i) The Ni d band splits the Al and Si p bands into a bonding region, mostly below the Ni d band, and an anti-bonding region, mostly above E_F. This splitting is similar to that found in other transition-metal silicides and is clearly important for the cohesion of the solid.

(ii) There is Al and Si s-state character in the anti-bonding states above E_F, from which we conclude that these states contribute to the bonding of the solid.

(iii) We also deduce from cluster calculations that direct metal d–metal d interaction plays a crucial role in the general distribution of states of late-transition-metal aluminides and silicides. The Ni d orbitals are not 'non-bonding' in the conventional sense of states which are forbidden by symmetry considerations from overlap with states on neighbouring atoms. Neither do the Ni d orbitals have such small dimensions that they cannot overlap. In particular the term 'non-bonding' for the main d band is misleading since these states are obviously important for determining the precise form and position of the bonding–anti-bonding metal d–Al (Si) p states in the region of the metal d resonance and contribute in this way to the bonding energy, apart from the direct d–d bonding. We believe that this may be the single most important conclusion of our paper.

In addition we reach the following conclusion specific to late-transition-metal compounds.

(iv) Ni d character is found in the anti-bonding states above E_F. The d band of the silicide is filled and has 10 electrons per metal atom because it contains contributions from states centred on Si or Al atoms. However, there is still d character above E_F, just as for the transition metals themselves, and the net effect of the d bands is bonding, again just as for the pure transition metals.

Acknowledgments

References

[1] Mohammadi F 1981 *Solid State Technol.* **24** 65
    Murarka S P 1986 *J. Vac. Sci. Technol.* B **4** 1325
[2] Pettifor D G 1986 *J. Phys. C: Solid State Phys.* **19** 285
[3] Rubloff G W 1983 *Surf. Sci.* **132** 268
[4] Calandra C, Bisi O and Ottaviani G 1985 *Surf. Sci. Rep.* **4** 271
[5] Speier W, Kumar L, Sarma D D, de Groot R A and Fuggle J C 1989 *J. Phys.: Condens. Matter* **1** 9117–29
[6] Bisi O and Calandra C 1981 *J. Phys. C: Solid State Phys.* **14** 5479
[7] Franciosi A, Weaver J H and Schmidt F A 1982 *Phys. Rev.* B **26** 546
[8] Schumm R H, Wagman D D, Bailey S, Evans W H and Parker V B 1965–73 *Selected Values of Chemical Thermodynamic Properties* NBS Publication 270
[9] Speier W, van Leuken E, Fuggle J C, Sarma D D, Kumar L and Dauth B 1989 *Phys. Rev.* B at press
[10] Kowalczyk S P, Apai G, Kaindl G, McFeely F R, Ley L and Shirley D A 1978 *Solid State Commun.* **25** 847
[11] Müller Ch, Wonn H, Blau W, Ziesche P and Krivitskii V P 1979 *Phys. Status Solidi* b **95** 215
[12] Eibler R and Neckel A 1980 *J. Phys. F: Met. Phys.* **10** 2179
[13] Fuggle J C, Hillebrecht F U, Zeller R, Zolnierek Z and Bennett P A 1982 *Phys. Rev.* B **27** 2145
[14] Bisi O, Calandra C, del Pennino U, Sassaroli P and Valeri S 1984 *Phys. Rev.* B **30** 5696
[15] Tanaka K, Saito T, Suzuki K and Hasegawa R 1985 *Phys. Rev.* B **32** 6853
[16] Azizan M, Baptist R, Chauvet G and Nguyen Tan T A 1986 *Solid State Commun.* **57** 1
[17] Moruzzi V L, Williams A R and Janak J F 1974 *Phys. Rev.* B **10** 4856
[18] Williams A R, Kübler J and Gellatt C D 1979 *Phys. Rev.* B **19** 6094
[19] Speier W, Zeller R and Fuggle J C 1985 *Phys. Rev.* B **32** 3597
[20] Winter H, Durham P J and Stocks G M 1984 *J. Phys. F: Met. Phys.* **14** 1047
[21] Speier W, Fuggle J C, Durham P, Zeller R, Blake R J and Sterne P 1988 *J. Phys. C: Solid State Phys.* **21** 2621
[22] Norman J G 1974 *J. Chem. Phys.* **61** 4630
[23] Schwarz K 1972 *Phys. Rev.* B **5** 2466; 1974 *Theor. Chim. Acta* **34** 225
[24] Kortboyer S, Grioni M, Speier W, Fuggle J C, Gibson M, Watson L M and Schäfer F 1989 *J. Phys.: Condens. Matter* **1** 5981
[25] Fabian D J, Watson L M and Marshall C A W 1971 *Rep. Prog. Phys.* **34** 601
[26] Pettifor D G and Podloucky R 1986 *J. Phys. C: Solid State Phys.* **19** 315
[27] Williams A R, Gelatt C D, Connolly J W D and Moruzzi V L 1982 *Alloy Phase Diagrams* ed. L H Bennett, J Massalski and M Griesse (Amsterdam: North-Holland) p 17
[28] Weinberger P 1977 *J. Phys. C: Solid State Phys.* **10** L347
[29] Collins A, O'Handley R C and Johnson K H 1988 *Phys. Rev.* B **38** 365