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Abstract. Several Gd compounds within the Gd–Ag, Gd–Au, Gd–In, and Gd–Si series were investigated with the use of x-ray photoelectron spectroscopy. The temperature dependence of the magnetic susceptibility was measured for some of the compounds over a large temperature range to obtain accurate values of the effective magnetic moments. The chemical shifts of the core-level photoemission lines were analysed. The shift of the Gd core levels has been found to be independent of the compound stoichiometry within a Gd–M series. The valence band structure close to the Fermi level is also characteristic for each Gd–M group of compounds and may be related to their magnetic properties.

1. Introduction

Gadolinium is a prototype rare-earth metal due to its half-filled 4f shell. The magnetism of Gd and its compounds is determined by the localized, high-spin 4f moment and the indirect interaction between the localized moments. This interaction is mediated by the conduction electrons. Their configuration is usually given as $5d6s^2$, but the very important role of the 5d electrons and the occupancy being higher than 1 is often emphasized. The 5d states are believed to be band-like; they take part in chemical bonding, and are thought to be a main source of the excess effective magnetic moment in some Gd compounds [1–3]. Angle-resolved photoemission investigation has shown a dispersion of the Gd 5d band, which appeared to be exchange split in the ferromagnetic state [4].

In the last few years, the knowledge of the electronic structure of the Gd valence band and core levels has been considerably improved due to investigation with the use of various techniques such as direct and resonant photoemission, x-ray absorption and emission, as well as Auger electron emission. Most recent results were obtained with epitaxial Gd overlayers. The electronic structure of the bulk Gd single crystal was studied earlier by Himpsel and Reihl [1]. The investigation on thin layers indicated the relationship between the surface magnetism of Gd and the electronic structure of the valence band [5, 6]. The work of Vescovo *et al* [7] clarified the situation regarding the earlier-observed features at binding energies of 10 and 6 eV, which originate from oxidation.

Only a relatively small number of Gd compounds were experimentally studied as regards their electronic structure. The variety of magnetic properties among Gd–non-magnetic metal compounds seems to be related to the electronic structure close to the Fermi level rather than simply the number of conduction electrons which is the basic parameter in the RKKY model of indirect exchange. In our previous papers we have shown that x-ray photoelectron spectroscopy (XPS) and resonant photoemission studies of Gd intermetallic compounds can give interesting results when obtained using bulk, good quality samples [8]. For the Gd–Cu

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series of compounds, we analysed the possible charge transfer and related it to the magnetic properties [9].

In this paper we present the results of a systematic XPS investigation of Gd intermetallic compounds with silver, gold, indium, and silicon. The binding-energy variation of the most prominent transitions is analysed, which allows us to study the chemical interactions (e.g. charge transfer) and the influence of alloying on the electronic structure. The valence band, especially for binding energies close to the Fermi level, is investigated, and its relation to the magnetic properties is discussed. The data relating to the crystallographic and magnetic properties obtained in this work and taken from the literature are included, to enable a comparison to be made with the results of electronic structure studies (see table 1).

Table 1. Structural and magnetic properties of the compounds investigated.

Compounds	Crystal structure	$\mu_{eff}/$Gd (μ_B)	Θ_p (K)	T_C (K)	T_N (K)	Reference
$Gd_{14}Ag_{51}$	Hexagonal $Gd_{14}Ag_{51}$	8.2	−10		22.5	[19]
$GdAg_2$	Tetragonal $MoSi_2$	8.49	−52		22.5	[20]
GdAg	Cubic CsCl	8.59	−97		136	[2]
$GdAu_2$	Tetragonal $MoSi_2$	8.38	−31		48–49.6	[19]
GdAu	Orthorhombic CrB	8.39	24		31	
$GdIn_3$	Cubic $AuCu_3$	8.20	−85		42–48	[19]
Gd_2In	Hexagonal Ni_2In	No CW behaviour		202	98	[3]
$GdSi_2$	Orthorhombic $GdSi_2$	7.7–7.81	−47 to −58		27	[19]
Gd_5Si_4	Orthorhombic Sm_5Ge_4	7.84 (CW > 700 K)	369	336		
Gd	Hexagonal A_3	7.94	310	293		

2. Experimental procedure

The XPS measurements were performed with a Physical Electronics PHI 5600 ci ESCA spectrometer, using monochromatized Al Kα radiation, under a vacuum during the measurements of about 10^{-10} Torr. The samples were mainly single crystals obtained by the Czochralski method from a levitated melt or consisted of large monocrystalline grains. Most of the samples were cleaved in the UHV chamber just before taking the spectra. To ensure that the surface was free from contaminants, some samples were sputtered with low-energy Ar-ion beams (up to 1 kV). The influence of sputtering on the chemical composition and on the shapes of the peaks was checked.

Standard x-ray diffraction and Berg–Barrett methods were used to check the quality of the samples. The level of oxygen and carbon contamination was controlled during the measurements by monitoring the C 1s and O 1s photoemission levels. The compositions of the samples obtained from the intensities of the photoelectron lines were in agreement with the nominal stoichiometries.

The magnetic susceptibility measurements were performed using the Faraday method, over the temperature range 77–800 K, under an atmosphere of helium.

3. Results and discussion

The XPS spectra of the valence band are presented for the binding-energy range up to 12 or 35 eV for the Gd–M (M = Ag, Au, In, and Si) series of compounds (figures 1–4). The spectra of the pure metals (and Si) are added for comparison. Additionally the EDC (energy distribution curve) spectra, for the binding-energy range near the Fermi energy, are collected for the Gd–noble-metal (figure 5), Gd–In (figure 6), and Gd–Si (figure 7) series. In the vicinity of the Fermi level the observed XPS intensity is related mainly to the d electrons, as the photoexcitation sensitivity factor for these electrons is much larger than those for s and p ones.
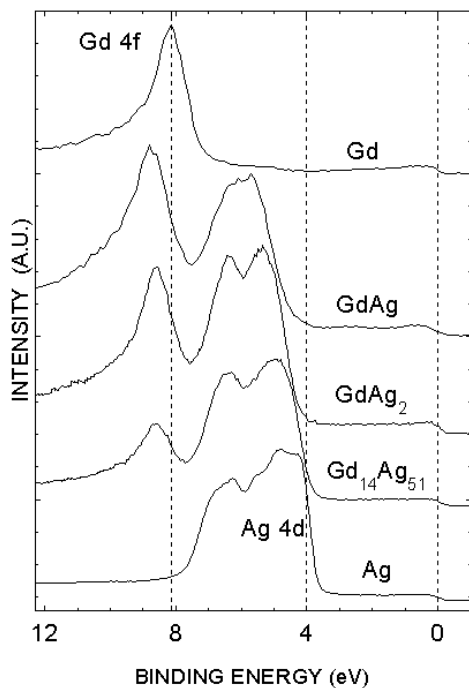

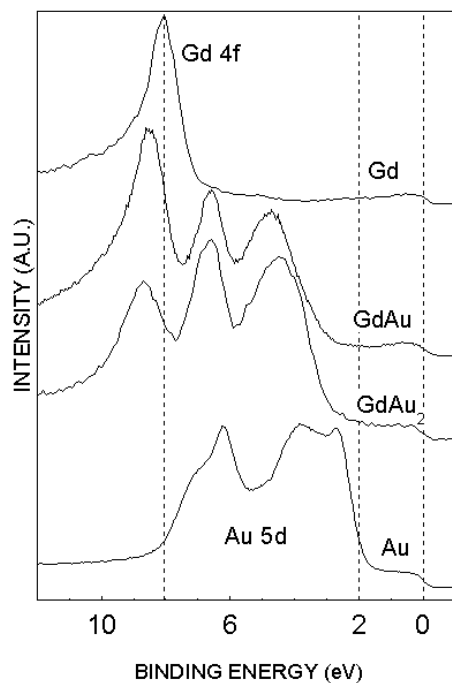**Figure 1.** XPS spectra of Gd–Ag compounds. Gd and Ag metal spectra are added.

Figure 2. XPS spectra of Gd–Au compounds. Gd and Au metal spectra are added.

The valence band spectrum of Gd metal, used here for reference, was obtained for a single crystal cleaved in the UHV chamber. Two spectral structures, visible at the Fermi level and 2 eV below, may be attributed to the exchange-split 5d band.

All Gd core-level spectra are influenced by the interaction of a photoelectron hole with a half-filled 4f level and its large spin momentum, and form multiplets that are particularly complex for the 4d photoemission. The analysis of the Gd 4d photoelectron spectra for Gd metal and some its intermetallic compounds was published earlier [10]. However, some features of these spectra need explanation, for example the existence or shape of a broad feature at a binding energy of about 155 eV. It is not visible in the spectra obtained from Gd–Au and Gd–Ag compounds and is more pronounced in Gd–In spectra. The electron energy-loss measurements revealed that the energy losses are not responsible for this behaviour. According to the calculation by van der Laan *et al* [11] the broad peak consists of many small lines which are the result of a $4d^9$–$4f^7$ interaction with non-S states of the 4f level. We think that the details of the valence band structure obtained within this work may help in explaining the

above-mentioned features. The analysis of the Gd 3d, 4p, 4s, and 5s core-level spectra will be presented in a separate paper.

In the following we discuss the details of the electronic structure of various groups of compounds. The shifts of binding energy of the most prominent transitions are collected in table 2.

Table 2. Binding-energy shifts of core levels with respect to those of pure elements (eV). The experimental error bar may be estimated for most XPS lines as ± 0.1 eV.

Gd–Ag				
	Gd 4f 8.1 eV	Gd 4d 140.3 eV (first line of the multiplet)	Ag $3d_{5/2}$ 368.3 eV	Ag $4p_{3/2}$ 573.3 eV
GdAg	+ 0.6	+ 0.5	+ 0.1	+ 0.1
GdAg$_2$	+ 0.6	+ 0.7	0.0	0.0
Gd$_{14}$Ag$_{51}$	+ 0.7	+ 0.5	+ 0.1	0.0
Gd–Au				
	Gd 4f 8.1 eV	Gd 4d 140.3 eV	Au $4f_{7/2}$ 84.0 eV	Au $4d_{5/2}$ 335 eV
GdAu	+ 0.5	+ 0.6	+ 0.8	+ 1.0
GdAu$_2$	+ 0.6	+ 0.7	+ 0.6	+ 0.6
Gd–In				
	Gd 4f 8.1 eV	Gd 4d 140.3 eV	In $4d_{5/2}$ 16.9 eV	In $3d_{5/2}$ 443.9 eV
Gd$_2$In	+ 0.3	+ 0.3	−0.7	−0.4
GdIn$_3$	+ 0.3	+ 0.3	−0.2	−0.4
Gd–Si				
	Gd 4f 8.1 eV	Gd 4d 140.3 eV	Si 2p 99.3 eV	Si 2s 150.2 eV
Gd$_5$Si$_4$	0.0	0.0	−0.5	−0.3
GdSi$_2$	+ 0.1	+ 0.1	−0.3	0.0

3.1. Gd–noble-metal compounds

All of the Gd–noble-metal (Cu [9], Ag, Au) compounds, measured with XPS (figures 1, 2), exhibit similar features in the valence band region. The Gd 4f peak is always shifted, in relation to that for the Gd metal, to higher binding energy. The value of the shift is about 0.6 eV for all compounds with silver and gold (table 2). The shift observed in the copper compounds was slightly smaller but also composition independent. Only if the samples are free of contamination is it found that the shape and width of the 4f peak are not influenced by alloying with other metals. Screening by the conduction electrons ensures the stability of this atomic level for all compounds investigated.

When analysing the shift of the Gd 4d peak, we took into account the first line that could be fitted to the 4d multiplet. The shift obtained for this level is close to the one for the 4f peak.

The origin of the energy shift of the Gd levels (observed also in Gd–In compounds) is the increase of the environmental potential, which is the result of a charge transfer from Gd to a neighbouring 'unlike' atom. We assume that this effect is related mainly to 6s electrons, and additionally this may lead to the increase of the d character of the conduction electrons
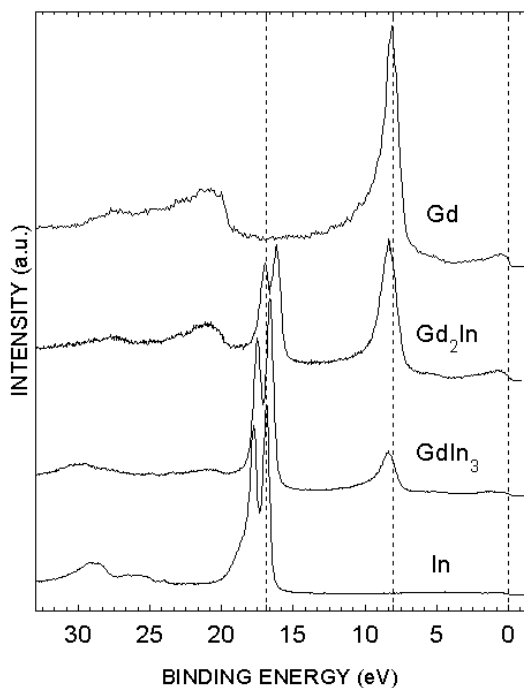
Figure 3. XPS spectra of Gd–In compounds. Gd and In metal spectra are added.
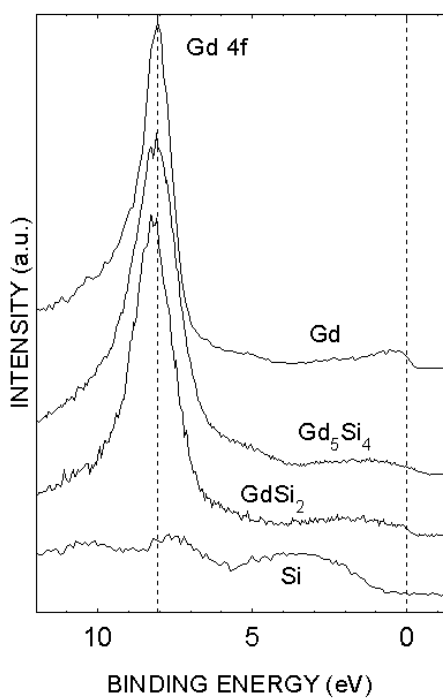

Figure 4. XPS spectra of Gd–Si compounds. Gd metal and Si spectra are added.

at the Gd site. We have discussed this problem for the Gd–Cu group of compounds [9]. Gadolinium has a low electronegativity and there is a tendency to transfer electrons to other metal sites. However, one could expect the transferred charge to depend on the number of
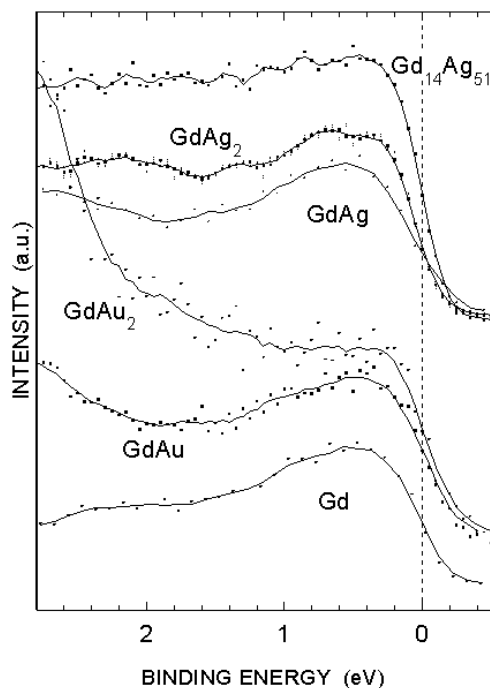
Figure 5. Valence band XPS spectra close to the Fermi level for Gd–noble-metal compounds. The spectra are normalized relative to the intensity of the Gd 4f peak.

unlike neighbours. This is not the case for the compounds examined, and this means that for a metallic bonding which involves gadolinium there is a more or less constant value of the charge which is transferred away from a Gd atom.

The shift observed for the Ag 3d line has a low value and the same sign as was found for Gd lines. This situation is different to that for Gd–Cu compounds, and this means that any model involving charge transfer cannot be applied, as the basic requirement in these models is charge neutrality or charge correlation [12]. This result suggests that Gd–Ag and Gd–Au bondings have partly different character to Gd–Cu bonding. The charge distribution in the compounds with silver and gold prevents one from using the simple models which are based on the point charge assumption.

The spectral weight of the Ag 4d level shifts to lower binding energies when the quantity of silver in the compound increases. Passing from GdAg to GdAg$_2$ one can observe splitting of the 4d level which may be attributed to the formation of the band due to the decreasing distance between nearest-neighbouring silver atoms and increasing coordination number. The broadening of the 4d band is clearly visible for Gd$_{14}$Ag$_{51}$.

For the Gd–Au compounds the shift of the binding energy of the core levels is very large and is of the same sign for the two component elements of the compound (table 2). The Au core levels are shifted in the same direction as those of Gd by more than 0.6 eV. For the Au levels the composition of the compounds and their different crystallographic structures do not influence the chemical shifts. The large positive shift of the Au levels is unexpected, and we think that the effect may be correlated with the strong bonding between Gd and Au atoms. The melting temperatures of Gd–Au compounds are much higher than those of the elements. We observed also a strong exothermic reaction during the induction melting of the raw metals before the Czochralski crystal growth process started. This increase of the potential for both atoms in the compound means that the simple model of charge transfer is not applicable. We assume that the charge is transferred to the interstitial positions in the crystal structure. The

charge distribution at the Au site seems to be very different in the compounds to that in Au metal. This is also confirmed by a different Au 5d band spectrum. Unlike the Ag 4d spectrum, the Au 5d spectrum hardly changes with increasing Au content in a compound (figure 2) but is quite different to that for Au metal.

The region of binding energy close to the Fermi level is characterized for all compounds by a clearly visible contribution from the 5d band with increasing intensity of photoemission when approaching E_F (figure 5). In the set of spectra presented, over the range of binding energy -1 to 4 eV, the intensity is normalized relative to the intensity of the Gd 4f peak. This allows a comparison to be made between the Gd contributions to the EDC near the Fermi energy. However, it is worth noting that spectra normalized in this way contain a contribution from components other than Gd increasing with the increase of the M/Gd ratio. The spectral shape looks like a superposition of those for Gd and noble-metal states. We may however expect that, due to the transfer of the s-like charge away from Gd atom, a relative increase of the d character of the electrons, localized at Gd atom, will take place. The shapes of the valence band close to the Fermi level, similar for all Gd–noble-metal compounds, accord with the similar magnetic properties. All of the compounds are antiferromagnetic and they all exhibit an excess of the effective moment per Gd atom which may be attributed to the earlier-mentioned increase of the d character of the electrons.

3.2. Gd–In compounds

For both Gd–In compounds investigated, the observed binding-energy shifts of the Gd and In XPS lines have opposite signs. This means that, contrary to the case for the Gd–Ag and Gd–Au systems, local charge neutrality may be applicable for these materials. There is a charge transfer from Gd to In sites and this leads to a positive potential at the Gd site, which is independent of the composition. For the In levels there is a difference between the behaviour of the 4d and 3d levels which is probably related to lower sensitivity of the deeper level to the
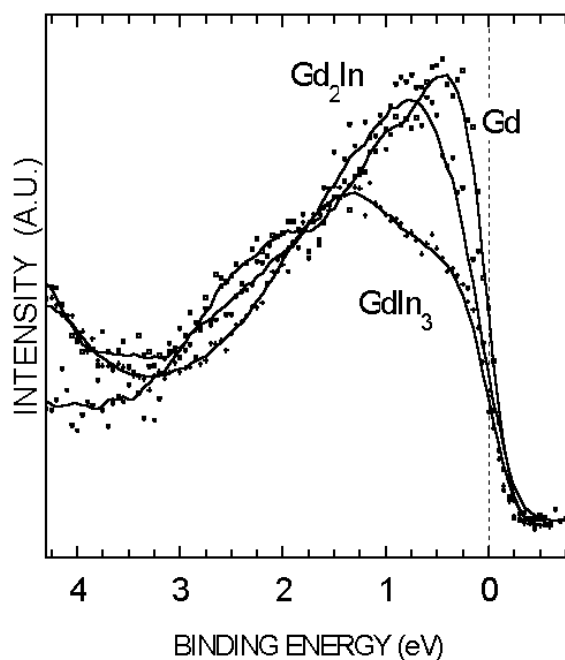

Figure 6. Valence band XPS spectra close to the Fermi level for Gd–In compounds

changes in the charge distribution which take place in the outer parts of the atomic volume. The shift of the $4d_{5/2}$ level was determined with a very good accuracy, and its dependence on the composition indicates the applicability of charge-correlation requirements at the In site. This means that the local potential depends on the number of Gd neighbours.

The observation of the valence band close to the Fermi level (figure 6) reveals quite different features to those for Gd–noble-metal series. For the two compounds the shapes of the spectra are similar, with characteristic maxima situated at about 1–1.5 eV below the Fermi level. As the contribution to the spectra from the conduction electrons at the In site is very small, the observed features may be related to the Gd 5d band. The contribution of the In states at the Fermi level may be estimated by relating the photoemission intensity in this energy range to the intensity of the In 4d peak. The possible relation between the observed electron structure and the unusual magnetic properties for Gd_2In was discussed in our earlier paper [3]. The presence of a peak at a binding energy of about 1 eV is in agreement with the recent calculation carried out using the LMTO method [13]. Also, for $GdIn_3$ the *ab initio* calculation by Grechnev *et al* [14] gives a pronounced peak in the density of states situated about 1.4 eV below the Fermi level, in good agreement with our experimental photoemission result.

3.3. Gd–Si compounds

Gadolinium forms many compounds with silicon—silicides—in various stoichiometries. Some of them were studied with photoemission spectroscopy due to the fundamental and technological interest related to reactive silicon–rare-earth interfaces. The investigations of Braicovich *et al* [15] and Chemelli *et al* [16] aimed to study chemical bonds and stressed the importance of the Gd d–Si sp interaction. The photoemission core-level shifts were analysed for some Gd silicides [17]. With the present investigation, we studied the core and valence photoemission of Gd_5Si_4 and $GdSi_2$ which had not been investigated previously with photoelectron spectroscopy. The available photoemission data and high melting points of silicides indicate strong Gd–Si bonding. However, the observed binding-energy shifts are very
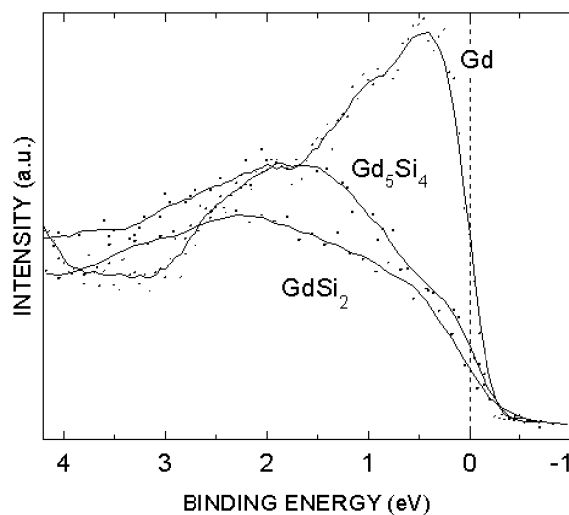
Figure 7. Valence band XPS spectra close to the Fermi level for Gd–Si compounds.

small for Gd and larger for Si lines. This means that the simple charge-transfer model is again not applicable. The covalent-like Gd–Si bonding influences mostly the positions of the Si 2p lines (table 2). The Si 2s line shifts are half the size but show the same tendency with increasing Si content. Our results are in general agreement with those obtained by Braicovich *et al* [15] and Puppin *et al* [17] for other silicides. Also, the valence band spectra in the region close to the Fermi edge show similar shapes and features to those of Gd_3Si_5, GdSi, and Gd_5Si_3. The valence band structure is modified to the largest degree compared to that of the pure elements in comparison with those of the other compounds investigated within this work. This is due to the bonding between Gd and Si. The feature at about 0.5 eV may be assigned mainly to the Gd 5d states and Gd–Gd bonds. The spectral feature at about 2 eV may be related to the covalent mixed Si 3p and Gd 5d states. The relative increase of this feature in $GdSi_2$ indicates that the Si 3p states, which take part in the Si–Si bonds, should be situated in this region of binding energy. According to the recent experimental and theoretical results obtained for 4d and 5d silicides [18], apart from metal d–Si 3p hybridization, one has to take into account Si 3d states which also participate in the bonding and hybridization with metal d states. This effect may also enhance the bonding in the case of gadolinium silicides. Following Braicovich *et al* [15], one can conclude that accumulation of the bonding charge must take place far from the Gd atoms. This would explain the observed negative core-level shift of the Si lines. The lack of a shift at the Gd site indicates that in this case there is instead a 5d-electron transfer to the bonds, and this has a small influence on the potential at Gd core levels. The magnetic properties of the two compounds investigated are quite different. The strong ferromagnetism in Gd_5Si_4 may be related to the magnetization transfer by the 5d electrons involved in the Gd–Si bonds and/or the remaining 5d and 6s states at the Fermi level. Spin-polarized photoemission investigation in a ferromagnetic state could resolve this question.

4. Conclusions

The XPS investigation of Gd intermetallic compounds shows that chemical interactions in the compounds lead to various binding-energy shifts and changes of the valence band structure in relation to those of the pure elements. The Gd core-level shift is always positive and independent of the stoichiometry within a Gd–M series. The sign of the shift may be related to a low electronegativity of Gd and a charge transfer to neighbouring 'unlike' atoms. The Pauling electronegativity for Gd is 1.1 and can be compared with those of Ag—1.9, Au—2.4, In—1.7, and Si—1.8. One can see that the correlation with the values of the Gd shift is only partial. The charge transfer involves mainly s electrons and this results in the increase of the degree of electron d character at the Gd site. This increase may explain the relative enhancement of the conduction electron polarization and the presence of the excess effective magnetic moment per Gd atom, observed for many compounds (table 1). The situation is different for Gd–Si compounds, where d electrons take part in covalent-like bonding which is reflected in the relatively low photoemission intensity near the Fermi level and the low value of the effective magnetic moment. The magnetic orderings are of the same type for all Gd–noble-metal compounds (including Gd–Cu compounds for which the results are published elsewhere [9]) and the electronic structures are also similar. They vary for Gd–Si and Gd–In compounds, for which the maximum of the photoelectron density and Gd 5d electron density is shifted away from the Fermi level.

For most compounds the charge-neutrality and charge-correlation assumptions, invoked successfully for random alloys [12], are not applicable. Both the metallic and the covalent bonding present in the compounds investigated are related to a charge redistribution which seems to be characteristic for a particular Gd–M system. The influence of the composition and

crystal structure is relatively weak. However, the Ag 4d band shows an interesting evolution with the composition of the compounds.

Acknowledgments

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