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Abstract
X-ray photoelectron spectroscopy was used to study the electronic structure of bulk GdF$_3$, Gd$_2$In and Gd$_5$Si$_4$. The structure of the Gd photoemission core level multiplets was analysed and compared to that one obtained for Gd metal. The line-width and the intensity ratio of the component lines within the multiplets were found to be dependent on the compound. The observed effects have been related to the variation of the valence band structure and various hybrydization effects between the 4f electrons and conduction or valence ones. The most modified multiplet structure in relation to Gd metal was found in the ionic compound GdF$_3$.

1. Introduction

Exchange splitting of the photoemission lines is a result of the interaction between a photo-hole created in a core level and a local spin momentum from an unfilled shell. Gd is a model material to investigate this effect since its half-filled 4f shell exhibits a well localized, pure spin momentum. In spite of the fact that the phenomenon is known since many years and the physical basis is understood, there are several problems, which need detailed study based on good quality spectra. The core s-levels of magnetic rare earths form doublets and the splittings calculated in the Hartree–Fock approximation agree with the experiment only for the 5s shell. The experimental splitting of the 4s shell, reduced in comparison to the theory, is explained as the influence of the configurational interaction between the 4f and 4s shells [1]. The s-level splitting was found to be approximately the same in some Gd metallic compounds but the spectra were not of good enough quality to perform reasonable fitting and analysis of line-width and intensity ratio [2]. Much more was done for the 4d multiplets where the spin–orbit interaction is of the same order as the exchange and the spectra are more complex. The calculation using the atomic configuration model was successful in explaining the structure of this multiplet, but some discrepancies with the experiment still need to be clarified [3–5]. Our studies with synchrotron radiation have shown that the origin of the high binding energy part of the 4d photoemission should be attributed rather to the electron energy losses [6]. Some variation of the 4d spectra was obtained in different Gd intermetallic compounds [7]. There are

no results in the literature about the detailed analysis of photoemission multiplets in Gd ionic compounds. Ogasawara *et al* [3] suggested that the calculated structure of the 4d multiplet obtained for the heavy rare earth metals is expected also for oxides.

With this work we show the results of the XPS investigation of the Gd multiplets and valence band in single crystalline GdF_3 and compare them to the results obtained for Gd metal, Gd_2In and Gd_5Si_4. Both metallic compounds exhibit a valence band close to the Fermi level modified with respect to Gd metal [8]. In Gd_5Si_4 the covalent bonds are formed and the density of states at the Fermi level is lower than in Gd. The influence of solid state effects on the photoemission from Gd core levels is discussed. A discussion is focused on differences between photoemission from Gd and its metallic and ionic compounds and the relation to the structure of the valence band and its modification due to chemical bonding.

2. Experimental details

The XPS measurements were performed with a Physical Electronics PHI 5700 ESCA spectrometer, using monochromatized Al Kα radiation, at a vacuum during measurements of about 10^{-10} Torr. The sample of GdF_3 was a single crystal cleaved in UHV just before taking the spectra. It was obtained by the Czochralski method. The melt was obtained from the GdF_3 powder of 99.9% purity, placed in the induction heated tantalum crucible. A seed was formed on a molybdenum spike. Photoemission measurements from the powder sample have been also performed. The samples of Gd, Gd_2In and Gd_5Si_4 were mainly single crystals obtained by the Czochralski method from a levitated melt or consisted of large monocrystalline grains. They were cleaved in the UHV chamber just before taking the spectra. To ensure a surface free from contaminants some metallic samples were sputtered with a low energy Ar ion beam (up to 1 kV). The influence of sputtering on the chemical composition and to the shape of peaks was checked. The spectra of s levels are characterized by low intensity of photoemission so the final analysis was done on the spectra obtained by adding results from the acquisition short enough to avoid contamination of the surface.

3. Results and discussion

All Gd core levels which are exchange split exhibit some different features in GdF_3 than in Gd metal and its metallic compounds. Figures 1, 2 and 4 show the 4s, 5s and 4d levels with the results of fitting. Spectra of GdF_3 were obtained with the same spectrometer, at similar conditions to other metallic compounds. We used the same method for fitting the experimental spectra. The only difference was the kind of line used for fitting. It was an asymmetrical Doniach–Šunjić shape [9] for metallic samples and a mixture of Gaussian and Lorentzian for GdF_3. To estimate the quality of fitting we performed it for various parameters set free, e.g. Gauss broadening, asymmetry of the line, type of background etc. For the 4d photoemission the discussion is given later in the text. The estimation of the error bar for the s levels is given in table 1.

The exchange interaction, which is responsible for the splitting of Gd s levels, may be described using the Heisenberg model in a simple form:

$$H_{ex} = -2J\,\vec{S}\vec{s}$$

where J is the exchange constant, which may be given by the Slater integral G.

$$J = \frac{1}{2l+1}G^2(4s(5s), 4f)$$

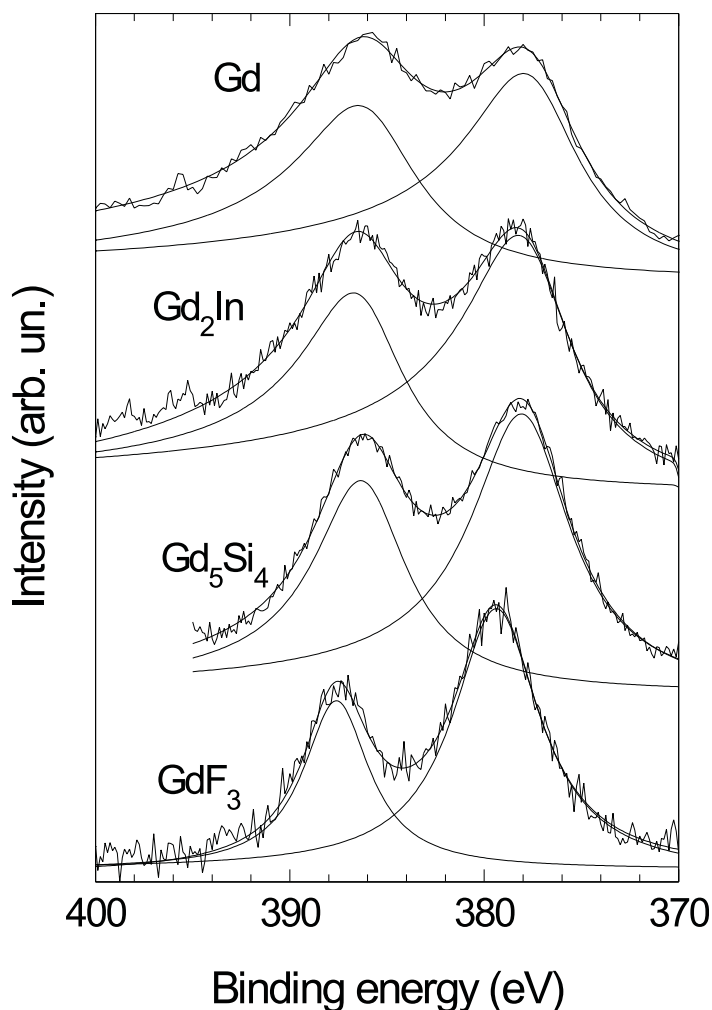where l is the orbital momentum of the unfilled shell.

Figure 1. Photoemission from Gd 4s level for GdF$_3$, Gd$_5$Si$_4$, Gd$_2$In and Gd metal with the result of fitting. Details of the fitting procedure are in the text.

This then leads to the exchange splitting observed in photoemission

$$\Delta E_{ex} = J(2S + 1)$$

which should be equal to $8J$ for the Gd s levels.

For Gd metal the value of the exchange splitting obtained with this work agrees with the former results and is 8.3 eV for the 4s and 3.7 eV for the 5s level. The intensity ratio of two component lines may be compared to the multiplicity of the terms resulting from the final $4s^1 4f^7$ and $5s^1 4f^7$ configurations. For the 4f spin $S = 7/2$ and the spin of a photo-hole $s = 1/2$, the total momentum of the final state may be $J' = 4$ or 3, depending on the final spin of the configuration $S' = S + s$ or $S' = S - s$. The state at the lower binding energy should have higher spin value and higher multiplicity. Thus one expects intensity ratio 9/7 for the exchange split s levels in Gd. Our study for Gd metal has shown that the experimental intensity ratio is lower than that value for both s levels (table 1). The low binding energy peak has the lowest line-width and this effect can be found also in all Gd core levels multiplets.

Table 1. Exchange splitting and parameters of the fitted lines for Gd and some its compounds. Line-width means full width at half maximum—FWHM.

	Exchange splitting (eV)	Intensity ratio—area of the first to the second line	Line-width of the first line at lower binding energy (eV)	Line-width of the second line at higher binding energy (eV)
5s				
Error bar	±0.3	±0.2	±0.2	±0.3
Gd	3.7	0.9	2.3	3.8
Gd_2In	4.1	1.9	4.4	4.1
Gd_5Si_4	3.9	2.8	4.1	2.9
GdF_3	3.5	1.8	2.0	1.6
4s				
Error bar	±0.2	±0.2	±0.2	±0.2
Gd	8.2	1.0	5.2	6.0
Gd_2In	8.5	1.3	5.8	5.6
Gd_5Si_4	8.3	1.4	5.9	5.5
GdF_3	8.2	2.0	5.4	4.1

The situation is opposite in GdF_3. Figures 1, 2 and 4 show that there is a general rule concerning the first, low binding energy lines in the 5s, 4s and 4d levels. In GdF_3 they are of high intensity and broader than the next lines. In the case of the 5s level we had to fit the spectrum with three lines. The broad band with a maximum at 43.4 eV may be related to the satellite from the F 2s level. The analysis of the F 1s line has shown a broad satellite feature at the binding energy higher by 15 eV than the main peak. Figure 3 shows both the F 1s line with a satellite and the region of the F 2s and Gd 5s levels. The binding energy is shown relative to the position of the F 1s and 2s lines. One may expect occurrence of similar satellites for both s levels from fluorine. The binding energy of the F 2s line is 29.5 eV (figure 5) whereas for F 1s it is 684.5 eV. The exchange splitting of the 5s level is 3.5 eV, which is slightly less than the 3.7 eV found in Gd metal. The difference is however within the experimental and fitting error. The line-width of the first line is 2.0 eV whereas the second one is 1.6 eV. The intensity ratio is 1.8, which can be compared to 0.9 obtained for Gd metal. A similar situation is seen with the 4s level (figure 1). The splitting is 8.2 eV, which is roughly the same as in Gd metal, whereas the intensity ratio is about 2. For Gd metal, a value close to 1 was obtained. In GdF_3 the first line has the line-width of 5.4 eV and the second one 4.1 eV. Again the relation is reversed with reference to Gd metal. We included the spectra from Gd_2In and Gd_5Si_4 in figures 1, 2 and 4 to show the evolution of multiplets. It is well visible for the 4s level, for which the fitting is more unique than for the 5s one. The large line-width of the 5s component lines for Gd_2In and Gd_5Si_4 make the analysis in these cases problematic. There is however a clear tendency of the changes in line-width and intensity ratio for the 4s level (table 1). Gd_2In and Gd_5Si_4 show the intermediate values of those parameters.

The analysis of the 4d splitting confirms the same tendency (figure 4). The background, which is a very important component of this multiplet, spread over a large range of binding energy, was fitted using the exponential function described in our earlier paper [7]. We checked that this kind of function gives the background, which is very similar to the one derived for Gd metal from the electron loss spectroscopy. The spectrum for Gd_2In is less resolved but, apart from the slightly larger line-width of all lines in Gd_2In than in Gd metal, the intensity distribution and line-width increase with binding energy is similar in both metallic samples. Similarly to the previous studies of the 4d photoemission in various compounds, the fitting is not unique within the second main peak at 147 eV. Moreover, the satellite features, visible at
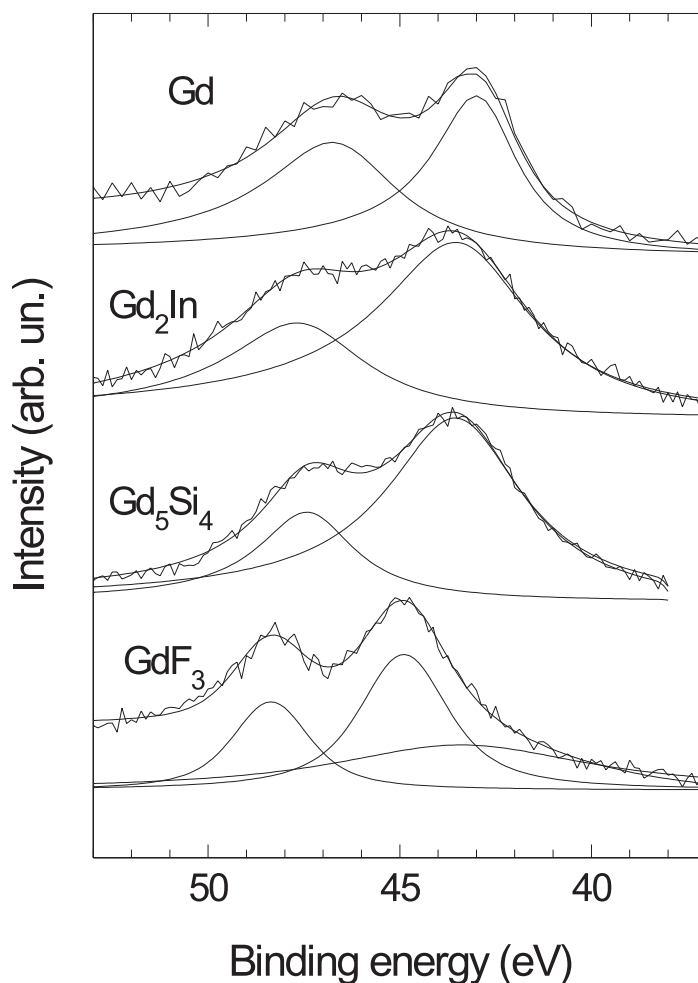
Figure 2. Photoemission from Gd 5s level for GdF$_3$, Gd$_5$Si$_4$, Gd$_2$In and Gd metal with the result of fitting.

about 152–160 eV, depend on the compound [7]. They are most pronounced in Gd$_2$In and are significantly reduced and shifted away from the main peaks for Gd$_5$Si$_4$ and GdF$_3$. The high intensity satellites were found also in GdIn$_3$ and one can relate this fact to the more pronounced energy losses in the valence band which take place in the compounds with indium. This may be induced by the modified electronic structure close to the Fermi level [8].

The shape of the main 4d peak changes significantly for Gd$_5$Si$_4$. The fitting is not as unique as for Gd or Gd$_2$In because the splitting is less resolved. We suppose that it is related to the natural intrinsic line-width, which is larger in this compound. We fixed the distance between the first five lines, which was earlier found in Gd and various Gd compounds to be equal to 1 eV [4, 7]. The asymmetry parameter has been fitted and fixed to be the same for all lines within a multiplet; the same assumption was made for the Gaussian broadening. As a result we have obtained a distribution of line-width and intensity within the first main peak, which is very different from that in Gd metal. In contrast to Gd metal, the first line is again of high intensity and relatively high line-width. These effects are not related to the ferromagnetic
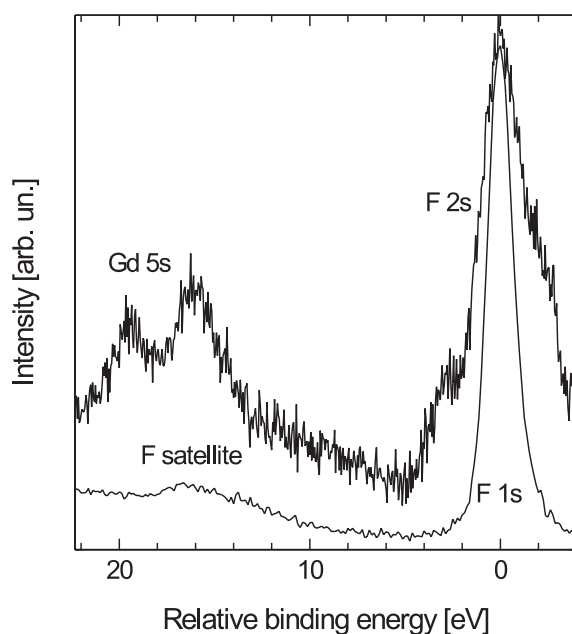
Figure 3. Photoemission from F 1s and 2s levels showing the region of satellites related to fluorine. The binding energy is given in relation to the position of F1s and 2s peaks.

state of this compound at room temperature because we obtained the same shape of the 4d photoemission at a temperature higher by 100 K than the Curie point [11]. The explanation of this effect seems to be related to the modified valence band close to the Fermi level and its influence on the final state of the 4d photoemission. The 4d photoemission for Gd_2In does not differ much to that from Gd metal whereas for Gd_5Si_4 the intensity ratio changes.

The line-width is related to the photo-hole decay rate and the additional energy broadening effects that come from x-ray energy uncertainty, surface to core shift etc. For Gd metal it was found that the line-width depends on the binding energy within a multiplet indicating the spin dependent decay as an origin of that effect [4, 5, 7]. The state at the lowest binding energy has spin parallel to the 4f one and, according to the $\Delta S = 0$ selection rule, the hole may be filled with an electron, which has the opposite spin. Thus the 4f electrons should not take part in the decay process to the low binding energy states of a multiplet when the electronic state of the 4f shell is ^{8}S. In the case of the 5s hole only 5p electrons with minority spin can contribute to the decay of the high spin states and the valence electrons, which have polarization opposite to the 4f shell. The spin polarization of the 5p states has been found experimentally [5, 10] and one may assume that it is independent of the solid state effects. Thus one may expect that the differences between the compounds result mostly from various polarizations of the valence electrons. This polarization depends mainly on the 4f5d exchange integrals. For Gd metal it was found to be positive. For the 4s level, a decay from the 4p level can additionally contribute but the scheme is similar. For GdF_3 the first low binding energy line is for all discussed levels broader than the next ones. This tendency is visible also for Gd_5Si_4. If we assume that line-width depends mainly on the radiation transitions and Coster–Kronig Auger processes including valence electrons, broadening of the first lines in multiplets, in comparison to Gd metal, may be related to the lower spin polarization or the polarization opposite to the 4f shell. It is reasonable also for ferromagnetic Gd_5Si_4 where a fraction of the valence electrons is involved in covalent bonding with Si atoms [8, 11]. Moreover the effective moment is lower
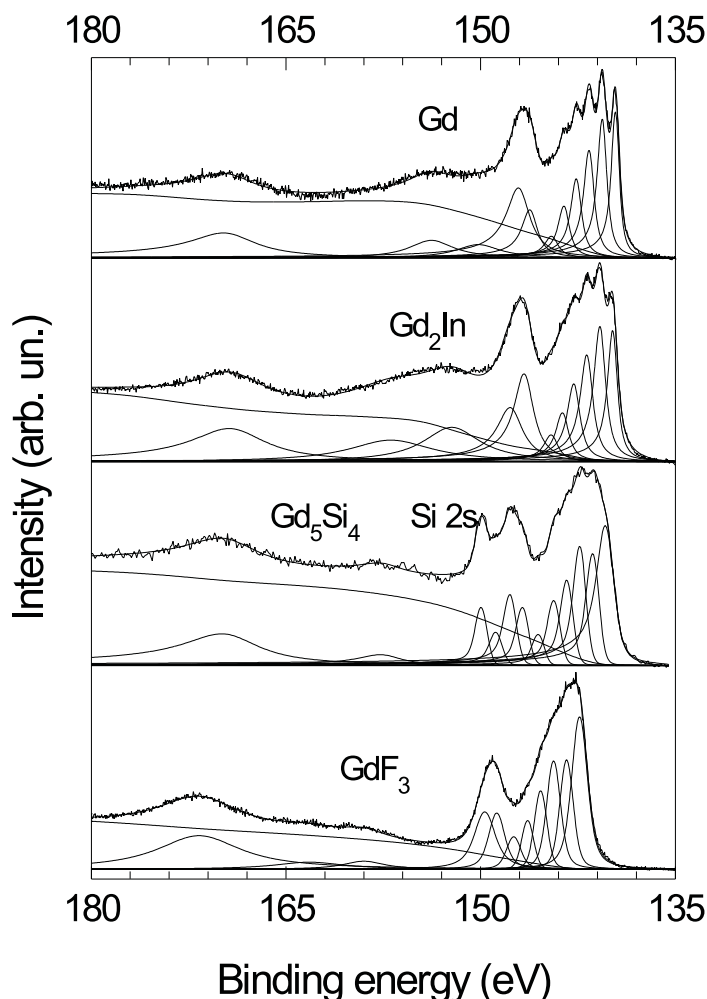
Figure 4. Photoemission from Gd 4d level for GdF$_3$, Gd$_5$Si$_4$, Gd$_2$In and Gd metal with the result of fitting.

than in Gd and it indicates to the polarization of conduction electrons opposite to that of the 4f shell.

In GdF$_3$ all valence electrons are in bonds and their polarization is problematic. The Gd 5d and 6s electrons, hybridized with the F 2p, form a band visible in a broad range of binding energies 5–15 eV (figure 5). Bonding and energetic position mean that exchange interaction with 4f electrons is quite different from that in metal. Certainly there is less screening of photoholes and less decay involving valence (5d, 6sp) electrons, which leads to the relative narrowing of the high BE lines in multiplets.

The intensity ratio of the two components of the s levels is also reversed compared with Gd metal. Generally the observed ratio is far from the calculated multiplicity of the final states. One of the possible explanations is connected with some excitations within the 4f shell during a photoexcitation of the core level. A virtual occupation of the ^{6}X states, which are formed when one 4f electron has an opposite spin, may influence the spectra. Intensity may be
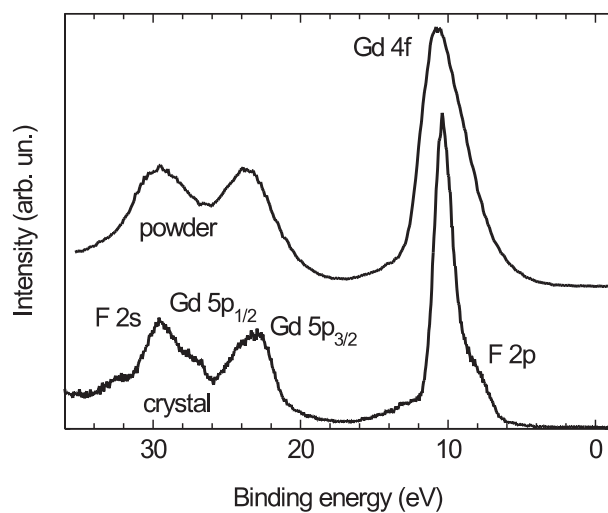
Figure 5. Valence band photoemission from GdF$_3$. A spectrum obtained for the powder sample is shown for comparison.
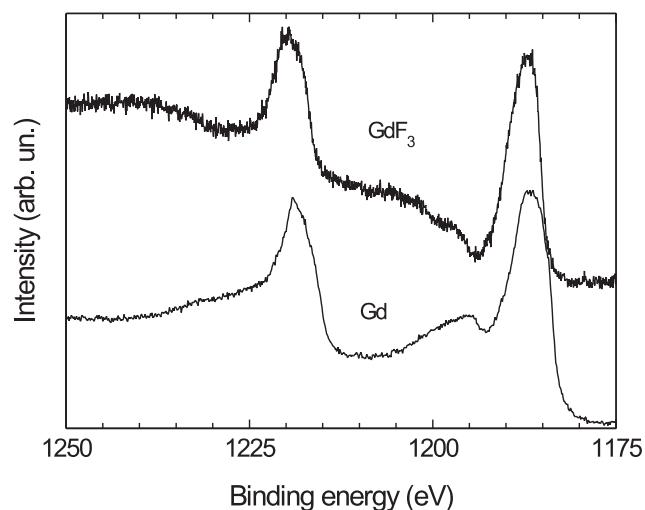

Figure 6. Photoemission from the Gd 3d level for GdF$_3$ and Gd metal.

transferred from the low spin lines of a multiplet to the satellites which are at binding energy higher by several eV. The satellites have usually short life-time and may not be observed within the range of measurements for the s levels. As a result the intensity of the high binding energy lines is lower than expected and the intensity ratio for the s levels may be larger than 9/7. It is however not clear why such process is less effective in Gd metal.

The shape of the photoemission spectrum from the 3d level of GdF$_3$ does not allow reasonable fitting but one can notice a clear difference from the spectrum from Gd metal (figure 6). The structure of the satellite lines, which are visible at about 1200 eV and 1235 eV, is clearly changed and this indicates that a lack of conduction electrons influences also the excitations responsible for these satellites.

Figure 5 shows the difference between the valence band spectra from the powder and the single crystal obtained using the same material. The good quality of the spectrum obtained with a crystal allows to separate the narrow 4f level from the broader band, which originates from the F 2p and hybridized Gd 5d and 6sp electrons. It is also worth mentioning that the structure of the Gd 5p$_{3/2}$ sublevel, visible at energies from 20 to 26 eV, is not resolved as it was found in Gd metal [6]. The reason is probably the same as for the 4d multiplet.

The binding energy of the Gd 4f level (10.4 eV) and its chemical shift (2.3 eV) are larger by 1 eV than the values reported earlier for GdF$_3$ [12]. We obtained the position of the F 1s level equal to 684.5 eV and F 2s 29.5 eV, which are close to the values reported by Raiser and Deville [12]—684.8 and 29.7 eV respectively.

4. Conclusion

Photoemission from Gd core levels shows different structure in GdF$_3$ than in Gd metal whereas the metallic compounds Gd$_2$In and Gd$_5$Si$_4$ show intermediate features. The exchange splitting does not vary from one compound to another but the relative line-width and intensity ratio of the lines within a multiplet show significant changes. Due to the stability of the 4f shell carrying the pure spin momentum the mentioned changes may be related to the changes in the valence band. The spin dependent decay channels including valence electrons are responsible for the line-width behaviour. The relative intensity changes may be related to the excitations in the valence band causing some intensity transfer from the low spin states but this hypothesis has to be verified with further investigations.

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