

# Resonant Photoemission Spectroscopy Study of the $d$ and $f$ States in $\text{GdNi}_{5-x}\text{Cu}_x$ Intermetallics

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**Abstract**—The electronic structure of the  $\text{GdNi}_{5-x}\text{Cu}_x$  ( $x = 0, 1, \text{ and } 2$ ) compounds is studied by resonant photoemission spectroscopy, the main regularities of the electronic structure transformation upon substitution of copper for nickel are established, and the energies of the  $d$  and  $f$  states that form its valence bands are measured. X-ray absorption and resonant photoemission spectra at the gadolinium  $M_{4,5}$  and  $N_{4,5}$  edges and nickel and copper  $L_{2,3}$  edges are recorded. It is shown that a core photohole and an excited electron in gadolinium decay along the elastic channel; in the final state, one hole forms in the valence band and Gd  $4f$  photoemission is enhanced tenfold. Since the inelastic Auger-type relaxation channel dominates in the transition elements with the formation of two holes in the valence band, the resonant photoemission spectrum allows us to measure the energy of two-particle interactions. The intra-atomic repulsion energy in nickel and copper is found to be  $\sim 7$  eV.

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## INTRODUCTION

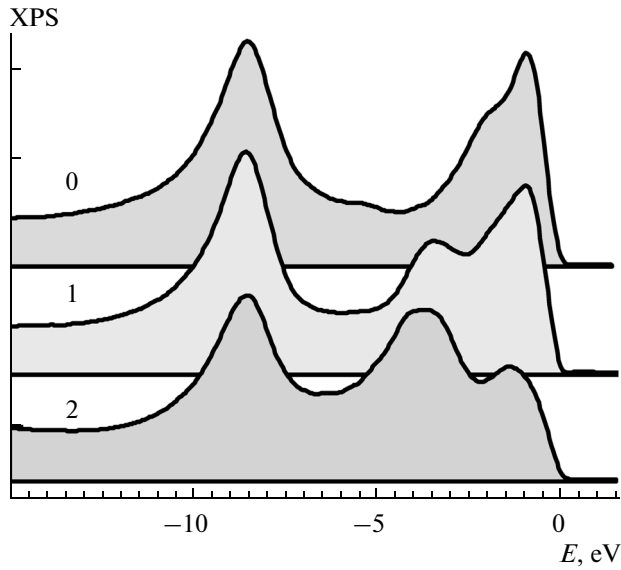
Intermetallic compounds of rare-earth elements ( $R$ ) with  $R\text{Ni}_5$ -type nickel exhibit a variety of magnetic structures and electronic characteristics. The unique physicochemical properties of these alloys make them promising candidates for use as functional materials for permanent magnets and devices based on the magnetothermal, magnetostriction, and magnetoresistive effects [1–3]. Study of these compounds is of special interest due to their ability to absorb and store atomic hydrogen [4]. It has been established that many physical properties of the  $R\text{Ni}_5$  compounds change greatly upon substituting  $d$ - and  $p$ -metal atoms for Ni. The  $R\text{Ni}_{5-x}M_x$  ( $M = \text{Al, Cu, Fe, or Co}$ ) pseudo-binary alloys in particular are characterized by nonmonotonic concentration dependences of their crystal, electronic, magnetic, thermodynamic, and electrochemical properties [5]. Some electronic and magnetic properties of the  $\text{GdNi}_{5-x}\text{Cu}_x$  pseudo-binary compound were studied in [6–8]. The optical properties in the spectral range  $0.22\text{--}15\ \mu\text{m}$  were investigated and spin-polarized partial densities of states were calculated [9].

The aim of this work was to experimentally investigate the interaction between the  $f$  and  $d$  elements and its effect on the formation of electronic structures in  $\text{GdNi}_{5-x}\text{Cu}_x$  ( $x = 0, 1, 2$ ) intermetallics over a wide range of energies. X-ray photoelectron spectroscopy (XPS) allows us to separate the contributions from different components to the valence bands. Using this technique, not only can the ground state can be inves-

tigated but excited two-particle states, responses to external factors, and relaxation of the electronic system as well [10, 11]. Our experiments were conducted on the BESSY-II synchrotron at the Russian–German Laboratory in Berlin. Resonant photoemission spectra were recorded with the use of synchrotron radiation at photon energies of 100 to 1300 eV. The energy resolution of the facility is 0.1 eV. A high-quality working surface was prepared by sample splitting directly in the ultra-high vacuum chamber of the spectrometer.

## VALENCE STATES IN $\text{GdNi}_{5-x}\text{Cu}_x$

Figure 1 shows XPS data (photoelectron yield intensity vs binding energy  $E$ ) of the valence bands in the  $\text{GdNi}_{5-x}\text{Cu}_x$  system with copper concentration  $x = 0, 1, \text{ and } 2$ . The spectra recorded at a nonresonant photon energy of 400 eV are normalized to the Gd  $4f$  peak value (8.5 eV). It is clearly seen that upon substituting copper for nickel, the Cu  $3d$  peak with a binding energy of 3.5 eV arises and grows; the Ni  $3d$  state's contribution falls in response (1 eV). Comparing the spectra of compounds with different copper and nickel concentrations thus allows us to determine with precision the energies of the Cu and Ni states that form valence bands. The Ni  $3d$  states reach the Fermi level and the Cu  $3d$  states are mainly located 3.5 eV lower than  $E_F$ . The question then arises of how to separate the gadolinium's contribution.



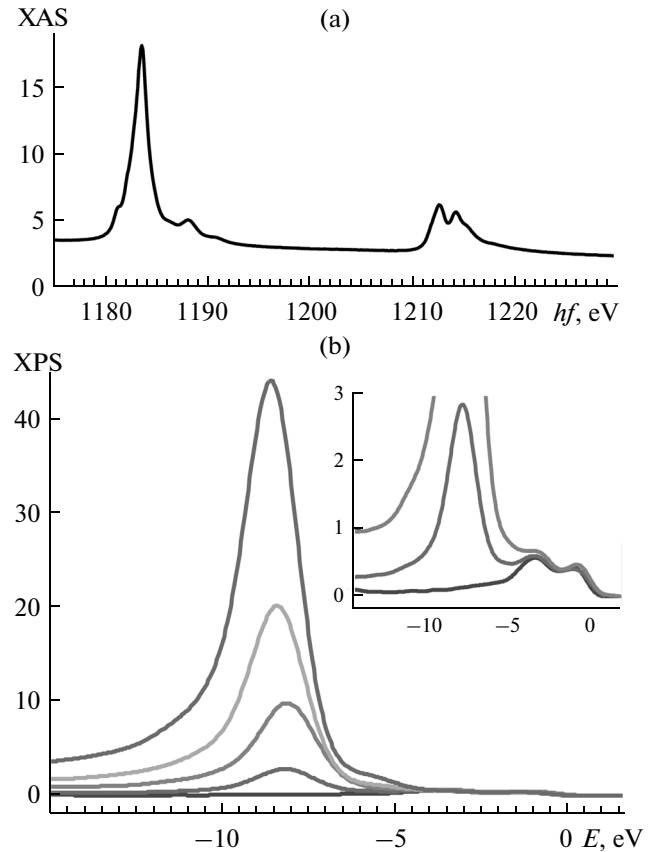
**Fig. 1.** Intensity of photoemission from the valence band vs binding energy  $E$  in the  $\text{GdNi}_{5-x}\text{Cu}_x$  ( $x = 0, 1,$  and  $2$ ) intermetallics upon nonresonant excitation with photon energy  $hf = 400$  eV. The spectra are normalized to the Gd  $4f$  peak (8.5 eV).

### RESONANCE ON A GADOLINIUM ATOM

Let us consider the processes that accompany the transition of electrons from the Gd  $3d$  to Gd  $4f$  state above the Fermi level. An absorbed photon transfers the core  $3d$  electron to the unoccupied state with energy  $E^*$ . The resulting photohole creates two scattering channels. In the first channel, the excited electron returns to its initial  $3d$  state. The released energy is used to emit a valence photoelectron whose state is analogous to that of a valence photoelectron that absorbs a photon directly, without participation of the internal level. The total intensity is in this case determined as the squared sum of amplitudes of both transitions, enhancing the XP spectrum of the valence band at the resonant frequency. In the second channel, the  $3d$  hole is filled with the valence electron, and the energy is transmitted to the other valence electron, which is detected. The final photoemission state thus contains the excited electron with energy  $E^*$  and two holes in the valence band, mainly on one atom, since the Auger transition requires the wave function overlap.

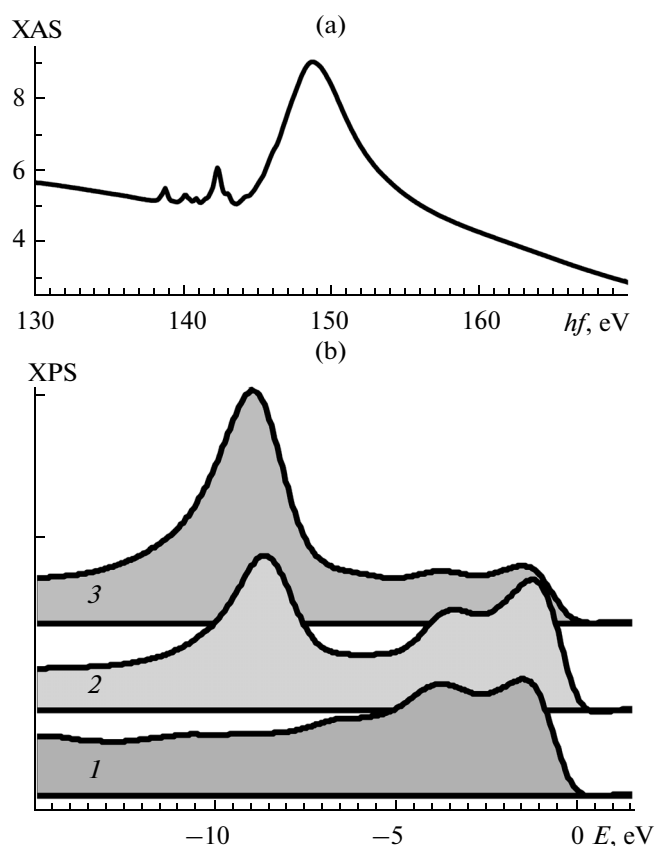
The experiment showed clearly that the first scenario occurs on the gadolinium atom. Figure 2a shows the dependence of the absorption coefficient (rel. units) on photon energy  $hf$  near the Gd  $M_{4,5}$  edges in the  $\text{GdNi}_3\text{Cu}_2$  compound. The strong spin-orbit interaction splits the Gd  $3d_{5/2}$  and Gd  $3d_{3/2}$  internal levels by 29 eV. Each level in turn splits into several eV due to interaction between the core  $3d$  photohole and the valence  $4f$  electrons.

Let us now consider the XPS behavior upon variation in the energy of exciting photons near the binding



**Fig. 2.** (a) Intensity of X-ray absorption of photons with energy  $hf$  in  $\text{GdNi}_3\text{Cu}_2$  near the Gd  $M_{4,5}$  edges. (b) Intensity of photoemission vs binding energy  $E$  upon excitation near the Gd  $M_5$  edge at photon energies  $hf$  of 1175, 1181, 1182, 1183, and 1184 eV upward. The insert shows the first three spectra enlarged. Invariable Ni and Cu contributions (peaks 1 and 3.5 eV, respectively) are observed.

energy of the Gd  $3d_{5/2}$  level. Figure 2b presents spectra of the  $\text{GdNi}_3\text{Cu}_2$  valence band at photon energies of 1175, 1181, 1182, 1183, and 1184 eV. We can see a huge (by a factor of 350) rise in the intensity of the spectrum with a binding energy of 8.5 eV. The insert shows the first three spectra enlarged. In the spectrum with 1175 eV, there are only two peaks (1 and 3.5 eV) formed by the nickel and copper states and no Gd peak. Approaching the Gd  $3d_{5/2}$  level excitation threshold, the contribution from the Gd  $4f$  states with a binding energy of 8.5 eV grows and starts to dominate. With a further increase in the photon energy (not shown in the figure), this peak weakens by a factor of 30. The dependence of the photoemission peak intensity on the photon energy qualitatively reproduces the X-ray absorption spectrum (XAS) shown in Fig. 2a; however, the quantitative photoemission growth at the resonance exceeds many tens of times the corresponding rise in absorption intensity. Due to the strong spatial localization of the  $3d$  wave function, the cross section of photoemission from the valence band is much smaller than the cross section of the  $3d-4f$

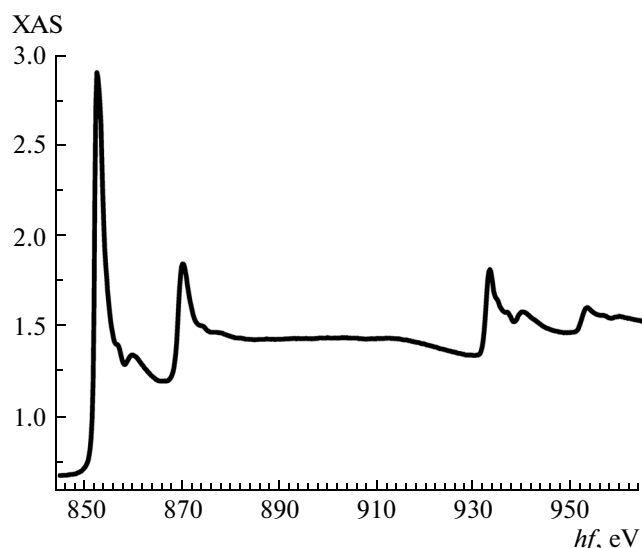


**Fig. 3** (a) Gd  $N_{4,5}$  X-ray absorption spectrum for  $GdNi_4Cu$ . (b) Normalized photoemission spectra obtained at photon energies  $hf = 143.5$  eV below resonance (curve 1),  $hf = 180$  eV above resonance (curve 2), and  $hf = 148.5$  eV at resonance (curve 3).

excitation process accompanied by emission of an electron as a result of the Auger decay of the excited state. The elastic channel is additionally enhanced by the spin selection rules, which determine the cross section of the second-order processes [12–14]. Due to the complete spin polarization of gadolinium, all of the Gd  $4f\uparrow$  states are occupied while all of the Gd  $4f\downarrow$  states remain unoccupied. According to the spin projection conservation upon the absorption of a photon, the core  $3d\downarrow$  hole forms and the excited  $4f\downarrow$  electron and only it (the other seven valence  $4f\uparrow$  electrons do not fit in spin) can fill the hole with the formation of the elastic scattering channel.

#### 4d Giant Resonance

Enhancement of photoemission from the Gd  $4f$  states is also observed at photon energies near the so-called  $4d-4f$  giant resonance, which corresponds to the wide absorption peak in Fig. 3a with an increase in intensity by a factor of 1.5. Figure 3b shows photoemission spectra normalized to their square at three excitation energies: before resonance (143.5 eV), after resonance (180 eV), and at resonance (148.5 eV).



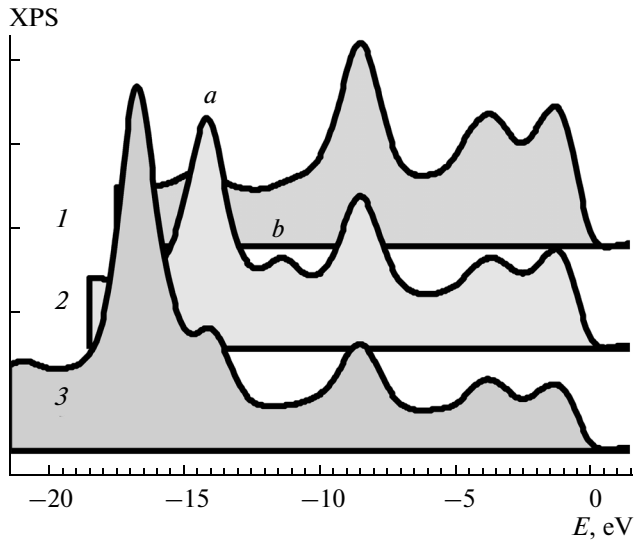
**Fig. 4.** X-ray absorption spectrum of  $GdNi_3Cu_2$  compound near the Ni and Cu  $L_{2,3}$  edges.

Before resonance, the Gd line in the valence band can barely be seen; at resonance, it reaches its maximum, and after resonance, it weakens and becomes approximately the same as in the nickel and copper  $3d$  states. Resonant growth of the peak at 8.5 eV is observed for all of the investigated compositions, demonstrating clearly that it is formed by the gadolinium  $4f$  states.

#### $L_{2,3}$ RESONANCE ON TRANSITION ELEMENTS

Figure 4 shows the dependence of the X-ray absorption on photon energy  $hf$  in  $GdNi_3Cu_2$ . The  $GdNi_4Cu$  absorption spectrum looks similar, but of course with a lower copper line intensity (930–965 eV). X-ray absorption in  $GdNi_5$  in the energy range 850–880 eV is also described by the corresponding portion of the curve (Fig. 4). Each line of the spin-orbit doublet has a satellite line with energy over those of the main nickel and copper lines by 7 and 6.4 eV, respectively. The main line corresponds to the final state with a screened core  $2p$  photohole and a high-energy satellite is formed by the transition to the unscreened state. The relative satellite weight for nickel is lower than for copper, due to the presence of the unoccupied nickel  $3d$  state in which the unscreened electron can be found. The copper atom has no such well-localized empty state, so the screening is complicated. The unoccupied Ni  $3d$  states determine the absorption peak height, which is higher for nickel than for copper by a factor of 4.7.

We now consider the XPS behavior in passing the excitation threshold of the  $2p_{3/2}$  copper level, at which absorption grows by 20% (Fig. 4). Figure 5 presents the X-ray photoelectron spectra normalized to the square at the photon energies passing through the

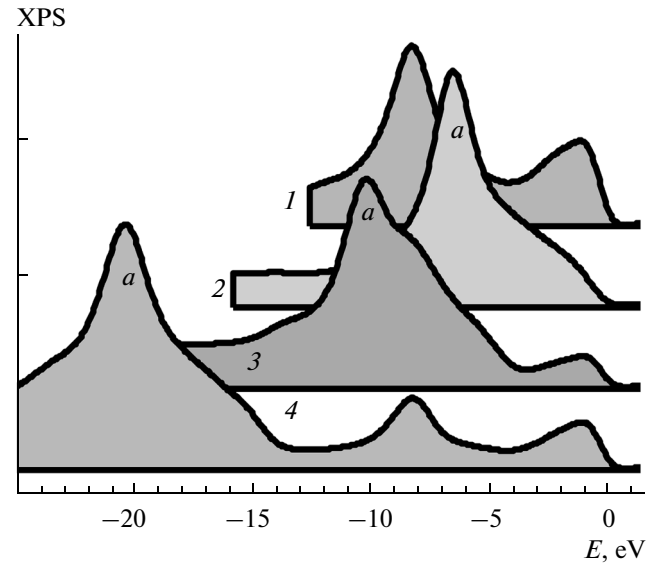


**Fig. 5.** Normalized intensities of photoemission from the  $\text{GdNi}_3\text{Cu}_2$  valence band vs binding energy of electrons  $E$  at exciting photon energies  $hf = 931$  (curve 1), 932 (curve 2), and 935 eV (curve 3) near the Cu  $L_3$  edge.

Cu  $L_3$  excitation edge. In contrast to the Gd resonance, the valence state region from 0 to 9.5 eV remains almost invariable upon copper excitation; i.e., this spectral region is formed by the direct photoemission of valence electrons.

At excitation energy  $hf = 932$  eV, a rather narrow Auger line with two peaks (large peak  $a$  at 14 eV and small peak  $b$  at 11 eV) forms and shifts linearly along the binding energy scale with increasing  $hf$ . Note that the  $\text{GdNi}_4\text{Cu}$  spectra behave in a similar manner. The following scenario obviously occurs: The excited electron leaves the copper atom, since there are no empty localized  $3d$  states there, and does not participate in the further XPS formation, apart from bringing the excess energy received from the photon (if the latter arises). The resulting  $2p$  photohole is occupied by one of the valence  $3d$  electrons with the emission of an Auger electron. Finally, two  $3d$  holes form in the valence band of the copper atom. The probable value of their one-electron energy is the double binding energy of the copper peak (Fig. 1), i.e., approximately 7 eV. To obtain the observed threshold value of main peak  $a$  (14 eV), it is necessary to add hole repulsion energy  $U$  (7 eV). The energy of interaction between holes in the state that forms peak  $b$  is obviously 4 eV. We have thus demonstrated that the resonant photoemission allows us to determine the energy of local two-particle excitations in materials.

Let us move on to the resonance photoemission on the nickel atom. Figure 6 shows the XPS data upon the excitation energy's transition through the Ni  $L_3$  edge in  $\text{GdNi}_5$ . As with copper, the decay of the Ni  $2p_{3/2}$  photohole occurs along the inelastic Auger channel



**Fig. 6.** Variation in the X-ray absorption spectrum of the  $\text{GdNi}_5$  valence band upon the transfer of exciting photon energy through the Ni  $L_3$  absorption edge:  $hf = 849$  (curve 1), 852 (curve 2), 856 (curve 3), and 866 eV (curve 4).

with the formation of two holes in the nickel valence states. Up to excitation threshold  $hf = 849$  eV, the spectrum is formed by the peak of Ni  $3d$  electrons reaching the Fermi level and the Gd  $4f$  peak with a binding energy of 8.5 eV. At the threshold of 852 eV, intense Auger line  $a$  with a binding energy of 6.5 eV arises, covering the entire valence band. As the excitation energy is increased, the Auger line shifts along the binding energy scale and the one-electron spectrum of the valence band recovers. The binding energy at which the Auger line arises (6.5 eV) yields the most probable energy of two interacting holes in the Ni  $3d$  states. The Ni Auger line is much broader than the corresponding Cu line (Fig. 5) and has the only peak. Broadening is due to shaking or the multiple creation of electron-hole pairs near the Fermi level upon the sudden occurrence of the core  $2p$  hole [15, 16]. The probability of this process on a nickel atom is very high, since the Ni  $3d$  state has high partial density at the Fermi level. Shaking on the copper atom is much smaller, since the Cu  $3d$  states are deepened by 3.5 eV. This indicates that with all other conditions being equal, the copper Auger line lies deeper than that of nickel 7 eV, as was confirmed experimentally.

## CONCLUSIONS

We obtained the X-ray absorption and resonant photoemission spectra at the Gd  $M_{4,5}$  and  $N_{4,5}$  edges and the Ni and Cu  $L_{2,3}$  edges in the  $\text{GdNi}_{5-x}\text{Cu}_x$  ( $x = 0, 1, \text{ and } 2$ ) intermetallics. The characteristic features of the valence bands are determined by the  $3d$  states of transition metals and  $4f$  states of gadolinium. The Ni  $3d$  electrons reach the Fermi level and form a distribu-

tion peak with a binding energy of 1 eV, while the Cu 3*d* states are located deeper, near 3.5 eV; finally, the Gd 4*f* states group around 8.5 eV. Photoemission from the latter states grows hundreds of times upon excitation by photons whose energy changes by several eV near the Gd *M*<sub>5</sub> absorption edge (1184 eV) due to the switching on of the resonant emission related to the virtual excitation of a 3*d* electron to the empty 4*f* state and back. Since the valence 3*d* shell is filled on a copper atom and almost filled on a nickel atom, the evolution of the 2*p* → 3*d* excitation occurs along the inelastic channel upon the absorption of a photon. As a result, XPS is determined not by the traditional one-particle state but by the two-particle final state. This allows us to measure the intra-atomic repulsion energy (in our case, 6–7 eV), which is the main parameter in describing correlation effects in a substance.

#### ACKNOWLEDGMENTS

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