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Author: A. Szajek, Z. Śniadecki, P. Skokowski, Grażyna Chełkowska, B. Szymański, T. Luciński i in.

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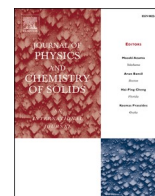
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Intermediate valence of CeNi₂Al₃ compound and its evidences: Theoretical and experimental approach

A. Szajek^a, Z. Śniadecki^{a,*}, P. Skokowski^a, G. Chełkowska^b, B. Szymański^a, T. Luciński^a,
A. Kowalczyk^a

^a Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179, Poznań, Poland

^b A. Chełkowski Institute of Physics, University of Silesia in Katowice, ul. Uniwersytecka 4, 40-007, Katowice, Poland

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ABSTRACT

We present measurements of magnetic, transport and electronic properties obtained for polycrystalline CeNi₂Al₃ intermetallic compound. Magnetic susceptibility $\chi(T)$ was investigated in the range from 2 to 700 K, and its behavior is characteristic of a compound with unstable valence, varying between Ce³⁺ and Ce⁴⁺. In the temperature range down to 2 K there was no trace of magnetic order, no anomalies in the temperature dependence of the specific heat were found. The Sommerfeld coefficient extracted from the linear term of the heat capacity takes a value of $\gamma = 21$ mJ/(mol K²). The dependence of $S(T)$ is linear up to about 25 K, which is symptomatic of a thermopower in the Fermi's liquid regime.

The structure of satellites in the Ce(3d) electron spectrum obtained by the X-ray photoelectron spectroscopy (XPS) method indicates that the states of Ce(4f) are of mixed valence character. Analysis of Ce(3d) states based on Gunnarsson-Schönhammer theory shows that the energy of hybridization of Ce(4f) states with a conduction band is about 78 meV. For more detailed information about electronic states the fully relativistic band structure was calculated within the density functional theory (DFT) for the first time. Below Fermi's energy, the density of states is mainly formed by Ni(3d) states hybridized with Ce(4f) ones.

1. Introduction

Ce-, Eu-, and Yb-containing systems are studied mainly to evaluate their potential for thermoelectric applications and/or with respect to fundamental problems like an intermediate valence (IV) phenomenon [1]. Issues with unstable valence of compounds with strongly correlated electrons are one of the most difficult in solid state physics. Rare-earth elements are characterized by an incompletely filled 4f shell, which may carry a magnetic moment. Various factors contribute to the complexity of these fascinating systems: the strong Kondo interactions, the crystal electric fields of *f*-orbitals, which may individually hybridize with the conduction band, as well as the ultimate coherence effects and magnetic interactions introduced by the periodicity of the Kondo lattice. In strongly correlated electron systems based on unstable ions of rare earth elements, the density of electron states at the Fermi level is very high, thus being important for attaining high values of the thermopower. The thermopower of compounds based on Ce and Yb often show dependencies on temperature that deviate from the typical dependencies

for metals. Linear temperature dependence provided by the diffusion mechanism may be modified by the Kondo effect, CEF effect and scattering of carriers on the narrow *f*-band. It is generally assumed that $S(T)$ often exhibits a single broad peak in the case of mixed valence compounds.

Study of isostructural compounds of cerium and ytterbium is particularly interesting, due to the internal structure of the 4f level of these elements. Ytterbium is the hole counterpart of cerium, since the trivalent Ce has a 4f level occupied by one electron, while Yb⁺³ lacks one electron to completely fill this level. Unusual ground states in cerium intermetallic compounds originate from competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and Kondo effect. The magnetic exchange interaction between the conduction and 4f electrons leads to either magnetic or nonmagnetic ground states at low temperatures depending on the strength of interactions [2].

The magnetic structure that is actually realized depends on the anisotropy of the RKKY interaction and the crystalline electric field (CEF). Thermoelectricity is a consequence of the fundamental

* Corresponding author.

E-mail address: sniadecki@ifmpan.poznan.pl (Z. Śniadecki).

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relationship between the electronic and thermal properties of the system. Materials with strong electron correlations, especially heavy electron ones, are intensively studied due to their potential as a new highly efficient generation of thermoelectric materials.

CeNi₂Al₃ is the compound of interest. Its magnetic and electronic properties suggest that Ce is in an intermediate valence state, *i.e.* the ground state of each cerium ion is a quantum combination of the Ce³⁺ ($4f^1$) and Ce⁴⁺ ($4f^0$) configurations [3,4]. Upon Cu doping at Ni site the compound shows simultaneous improvement of thermoelectric parameters [5–7] and transition from paramagnetic state to antiferromagnetically ordered one [7].

In this manuscript the magnetic and electronic transport properties of the hexagonal CeNi₂Al₃ compound are demonstrated and discussed in details. In order to improve our understanding of the electronic states, the results of X-ray photoelectron spectroscopy (XPS) measurements are presented in a combination with the density functional theory (DFT) calculations.

2. Experimental

The CeNi₂Al₃ intermetallic compound was synthesized with arc-melting in Ar atmosphere using high purity Ce (99.9%), Ni (99.9%) and Al (99.999%) elements. The preparation details were given in the previous paper [8]. The crystal structure was determined by a powder X-ray diffraction technique, using Cu-K α radiation. The CeNi₂Al₃ crystal structure was found to be hexagonal of the PrNi₂Al₃-type, symmetry $P6/mmm$ (space group no. 191) [8]. The lattice parameters are $a = 5.329$ Å and $c = 4.052$ Å [8].

The magnetic and transport properties were measured using the Quantum Design Physical Property Measurements System (PPMS). Heat capacity was investigated in the 1.9–300 K temperature range by relaxation method using the two- τ model, while the magnetic susceptibility was studied up to 700 K. A bar-shaped sample, of the $1 \times 1 \times 8$ mm³ size, was prepared and a standard four-probe technique was used for the electrical resistivity and thermopower studies.

The X-ray photoemission spectra were obtained with Al-K α source using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with energy resolution of about 0.3 eV. The Fermi level $E_F = 0$ was referred to the gold $4f$ -level binding energy at 84 eV. All emission spectra were measured in a vacuum of 10^{-10} Torr immediately after breaking the sample. The XPS data were analyzed by use of MultiPak software (Version 9.6.1.7) from Physical Electronics.

3. Computational details

The calculations of the electronic band structure for CeNi₂Al₃ compound were performed based on the full potential local-orbital code (FPLO) [9]. In this paper we considered one case only, where Ni and Al atoms occupy the 2c and 3g sites, respectively. Our earlier calculations, where chemical disorder was taken into account, showed that the ordered case was more stable [8]. The utilized FPLO14 version of the code allows fully relativistic calculations solving Dirac's equation. In our calculations the generalized gradient approximation (GGA) and the correlation-exchange potential in the form proposed by Perdew, Burke and Ernzerhof (PBE) [10] were used. Furthermore, to improve the description of correlation effects for Ce($4f$) and Ni($3d$) electrons, the on-site Coulomb energy U correction was introduced within the GGA + U approach [11]. Starting from the GGA results we tested the Coulomb repulsion energies U varied from 0 to 6 eV and from 0 to 3 eV within the Ce($4f$) and Ni($3d$) electron shells, respectively. These are typical values used in *ab-initio* calculations and their justification can be found in the article [12]. More details of the procedure used are described in Ref. [13].

The simulated XPS spectra were computed based on the calculated partial densities of states for each atomic orbitals, multiplied by the

proper photoelectron cross sections [14] and then convoluted by Gaussian profile of 0.3 eV width, which corresponds to the experimental resolution of the hemispherical mirror analyzer.

The calculations were performed for the experimental lattice constants. For integrations within the irreducible wedge of the Brillouin zone we used the tetrahedron method [15] and the mesh containing 484 irreducible k-points. The calculations were carried out until two convergence criteria were fulfilled: 10^{-8} Ha/cell for energy and 10^{-6} for charge density.

4. Results and discussion

Unstable valence of Ce ions determines different phenomena observed in cerium based ternary compounds. The valence fluctuations depend on the strength of hybridization between the valence and $4f$ electrons. Strong hybridization decreases the localization of the Ce($4f$) electrons and causes non-magnetic intermediate behavior.

In Fig. 1 we present the temperature dependence of magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ in the range of 2–700 K measured in a magnetic field of 0.1 T. Both curves strongly depend on temperature in the entire tested range. The very low value of susceptibility and its temperature characteristic up to 30 K indicate that Ce ions are in fluctuating valence state. Similar temperature characteristics have been observed for other valence fluctuating Ce-based compounds [16–18]. Deviation from the Curie-Weiss behavior is observed above 12 K, while linear dependence was confirmed below this value (see inset in Fig. 1). An effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p were found from linear fit of experimental data to be $0.77 \mu_B/f.u.$ and -8.62 K, respectively. The μ_{eff} is lower than the magnetic moment of the free Ce³⁺ ion ($2.54 \mu_B$) although it is higher than in the case of nonmagnetic Ce⁴⁺.

The Sommerfeld coefficient γ in the specific heat provides an information about the density of states (DOS) at the Fermi level. Fig. 2 presents the temperature dependence of the specific heat in the range of 4–300 K without magnetic field. No sign of magnetic order is observed down to 2 K.

Analyzing combined electronic and phonon contributions $C = \gamma T + \beta T^3$ to the specific heat within the temperature range $10 \text{ K} < T < 20 \text{ K}$ one can obtain $\gamma = 21 \text{ mJ}/(\text{mol K}^2)$ and $\beta = 0.344 \text{ mJ}/(\text{mol K}^4)$. The value of the Sommerfeld coefficient is consistent with the literature data [6,7] and does not classify CeNi₂Al₃ as the heavy fermion (HF) system, in contrast to the isostructural compound UNi₂Al₃, where $\gamma = 120$

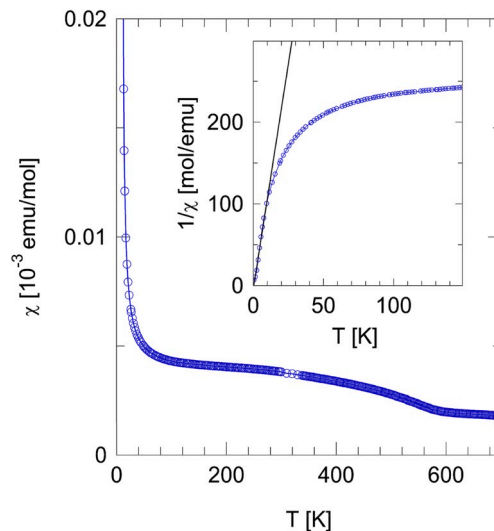


Fig. 1. Temperature dependence of the magnetic susceptibility $\chi(T)$ and inverse magnetic susceptibility $\chi^{-1}(T)$ of CeNi₂Al₃. The straight solid line is a fit to the Curie-Weiss law.

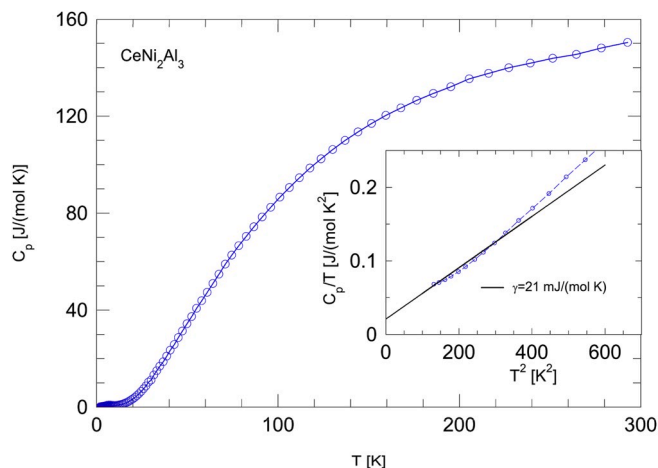


Fig. 2. Temperature dependence of the specific heat of CeNi₂Al₃. The solid line visible in the inset is a linear fit to the experimental $C_p(T)/T$ vs. T^2 dependence.

mJ/(mol K²) [19]. Debye temperature θ_D for CeNi₂Al₃ was estimated based on β , using the relationship:

$$\theta_D = \left(\frac{12\pi^4 nR}{5\beta} \right)^{1/3} \quad (1)$$

where R is molar gas constant and $n = 6$ is the number of atoms per formula unit (f.u.). Thus, the Debye's temperature for CeNi₂Al₃ was determined to be $\theta_D = 324$ K. From our *ab initio* calculations it follows that the density of states at the Fermi level $N(E = E_F)$ is equal to 6.00 or 7.58 states/(eV f.u.) for GGA and GGA + U approach, respectively. More details on the results of the band structure calculations are given below along with discussion of the transport properties of CeNi₂Al₃.

The calculated electronic specific heat coefficient γ , derived from $N(E_F)$ using the relation $\gamma = \frac{\pi^2 k_B^2}{3} N(E_F)$, where k_B is the Boltzmann constant, is equal to $\gamma_{\text{theor}} = 18$ mJ/(mol K²) within GGA + U approach ($\gamma_{\text{theor}} = 14$ mJ/(mol K²) for GGA). The γ value calculated from the band theory is smaller than the experimental one $\gamma_{\text{exp}} = 21$ mJ/(mol K²).

The analysis of the temperature dependence of the electrical resistivity ρ was shown in our earlier paper [8]. $\rho(T)$ is characterized by metallic behavior with a low value at room temperature (about 50 $\mu\Omega$ cm). Resistivity at low temperatures shows the AT^2 relationship characteristic of Fermi's liquid. Above 100 K, the resistivity is almost linear with respect to temperature, which indicates the predominance of phonon scattering processes [8]. The temperature characteristic of electrical resistivity is analogous to that described for another compound with intermediate valence, YbNiAl₄ [20].

The Kadowaki-Woods (KW) relation $A/\gamma^2 = \text{const}$ [21] is satisfied in many Ce- and Yb-based compounds, where A is a quadratic term in the resistivity and γ is the linear term in the specific heat. Therefore, the KW relation can be considered as one of the exceptionally solid Fermi liquid signatures regardless of the value of the effective mass m^* . In fact, Kadowaki and Woods [21] have shown that the KW ratio has value close to the universal one of $1.0 \times 10^{-5} \mu\Omega \text{ cm mol}^2 \text{ K}^2 \text{ mJ}^{-2}$ for many heavy fermion and valence fluctuation systems.

Later Tsujii et al. [22] proposed to scale this ratio with $2/N(N-1)$, where N is the degeneracy of the orbital state of the f element. For an intermediate valent cerium system $N = 6$ and gives $A/\gamma^2 = 0.67 \times 10^{-6} \mu\Omega \text{ cm (mol K/mJ)}^2$. The experimentally estimated Kadowaki-Woods ratio A/γ^2 for CeNi₂Al₃ ($A = 8.16 \times 10^{-4} \mu\Omega \text{ cm/K}^2$ [8]) amounts to $0.19 \times 10^{-5} \mu\Omega \text{ cm (mol K/mJ)}^2$, being one order of magnitude smaller than theoretically predicted value. We obtained similar values of the Kadowaki-Woods relation for other intermediate valence compounds [23,24]. The values of A and γ locate the studied Ce-based compounds far from the heavy fermion systems, which occupy the upper part of

Fig. 1 in Ref. [22]. Instead, they are close to the values for the compounds which exhibit a mixed valence behavior (lower part of Fig. 1 in Ref. [22]). Similar remarks have been made in the work by Sankararao et al. [25].

The $S(T)$ dependence of CeNi₂Al₃ is shown in Fig. 3. It is typical of intermediate valence compounds and reaches the highest value of ~ 46 $\mu\text{V/K}$ in the range of 200–300 K [8], similarly to Refs. [6,7]. Thermopower $S(T)$ has positive values, indicating holes as the dominant carriers in the whole temperature range. The thermopower of CeNi₂Al₃ shows a linear dependence of $S = aT$, up to approximately 25 K with $a = 0.49$ $\mu\text{V/K}^2$. The linear dependence can be attributed to a diffusion thermoelectric power predicted for a normal metal. The low temperature part of the thermopower was discussed in our earlier paper [8].

For many cerium systems, to describe their low-temperature thermoelectric behavior, a phenomenological resonance model can be used [26], where a $4f$ quasiparticle band of a Lorentzian form scatters the conduction electrons. It leads to the thermopower formula of the form:

$$S_B(T) = \frac{AT}{B^2 + T^2} \quad (2)$$

with

$$A = \frac{2\Delta}{|e|} \quad \text{and} \quad B^2 = 3 \frac{\Delta^2 - \Gamma^2}{\pi^2 k_B^2} \quad (3)$$

The parameter $\Delta = E_0 - E_F$ is a measure of the location of the $4f$ peak in DOS in respect to the Fermi level and Γ is the width of the $4f$ band. Equation (2) has been successfully used for the description of valence fluctuating systems characterized by large values of Kondo temperature T_K . In Ref. [26], the plot of thermoelectric data for intermediate valence compound in the form T/S vs. T^2 is considered. We present in the inset of Fig. 3 similar characteristic showing linear behavior in the range of 100–300 K, and thus satisfying eq. (2). As a result one can estimate the parameters, $\Delta = 12.9$ meV and $\Gamma = 41$ meV. This means that the peak in DOS should be just above the Fermi level. This is consistent with the results of *ab-initio* calculations shown in Fig. 4, which indicate that the Fermi level lies on the left side of the $4f$ peak. The estimated Δ and Γ values are similar to those obtained for many heavy fermion compounds and Kondo systems based on Ce, Yb and U atoms [27,28]. The thermopower of a free electron gas is linear as a function of temperature ($S(T) = aT$). The value of the coefficient a is directly proportional to the density of states at the Fermi energy and thereby to the Sommerfeld coefficient γ . The initial slope of the $S(T)$ curve is closely related to γ also at zero limit temperatures [29]. It is known that for HF and IV compounds with an enhanced γ value, one can usually observe a very large initial slope of $S(T)/T$. Additionally Behnia et al. [29] showed that one

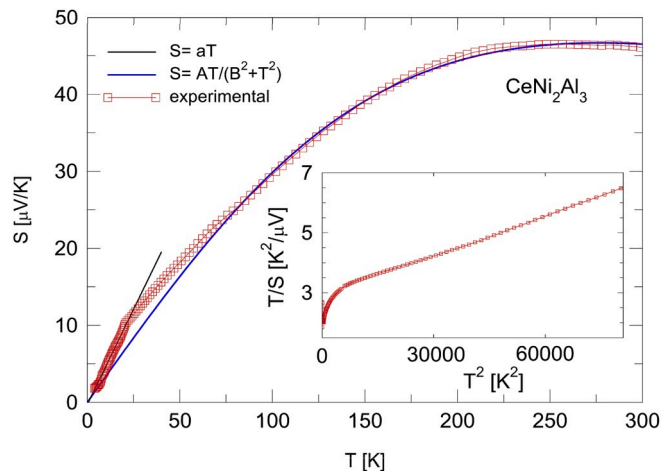


Fig. 3. Temperature dependence of the thermoelectric power S for CeNi₂Al₃. Inset: thermoelectric data in the form T/S versus T^2 plot.

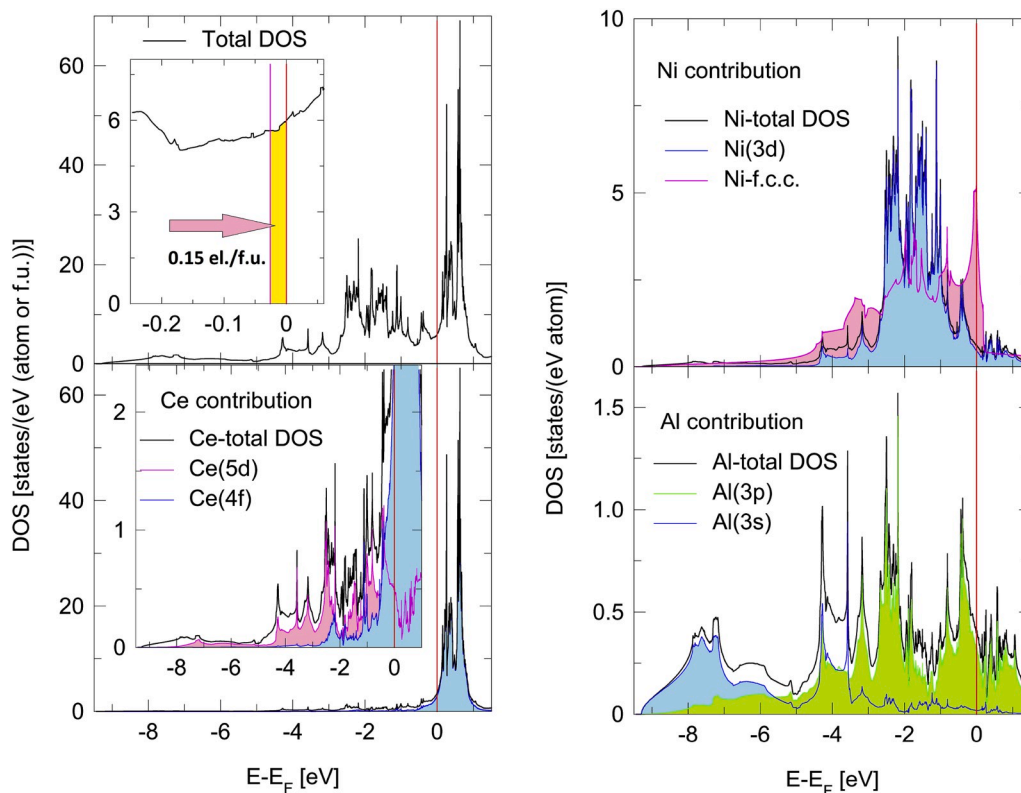


Fig. 4. DOS plots per f.u. for CeNi_2Al_3 compound and local contributions calculated per atom.

can relate $S(T)/T$ and dimensionless number q defined as:

$$q = \frac{S}{T} \frac{N_{Av} |e|}{\gamma} \quad (4)$$

where N_A is the Avogadro number and e is the electron charge, while the product in the nominator is called the Faraday number. The value and sign of q depends on the density and type of carriers, respectively. In the case of metals q is close to ± 1 and the sign of q depends on the type of carriers. The above defined ratio is not the only one which describes heavy fermion or intermediate valence systems. We could mention the following quasi-universal ratios: χ_0/γ [30] and A/γ^2 [21]. The Fermi liquid state is characterized by $q \sim 1$ [28]. We should keep in mind that this model works best below 2 K (not achievable in utilized experimental setup). In our case $q = 2.3$, which is close to the line represented by $q = 1$ [29] and confirms reasonability of the Fermi-liquid description. Determined value is consistent with the general trend pointing out that the absolute magnitude of q is expected to be proportionally larger than unity when the density of carriers is lower than $1 \text{ e}^-/\text{f.u.}$. In this paper results of *ab-initio* calculations based on FPLO code, with full potential and with regard to fully relativistic mode, are presented for CeNi_2Al_3 for the first time. The results based on the GGA approach will be discussed at first and followed by GGA + U results.

The total density of states (DOS) per formula unit and the contributions of particular atoms are presented in Fig. 4. The carrier density at the low temperatures can be estimated on the basis of the DOS in the vicinity of the Fermi level and amounts $0.15 \text{ e}^-/\text{f.u.}$. For GGA + U calculations, this value is slightly modified to $0.17 \text{ e}^-/\text{f.u.}$. However, this change does not qualitatively contribute to the discussion on q parameter (see eq. (4)). This value was estimated from the DOS marked as yellow area in the inset of Fig. 6 (left upper panel). The yellow area is limited by the Fermi level and the energy equal to $0.026 \text{ eV} = 300 \text{ K}$. The width of the valence band, measured from the bottom of band to the Fermi level, is equal to 9.3 eV . The value of DOS at the Fermi level, equal to $5.997 \text{ states}/(\text{eV f.u.})$, is an important parameter characterizing

transfer of charge and heat. Using the relation between the theoretical and experimental Sommerfeld coefficients, $\gamma_{\text{exp}}/\gamma_{\text{theor}} = 1 + \lambda$, the electron phonon coupling parameter was calculated to be equal to 0.49. The largest contribution to this value of 59.4% ($3.564 \text{ states}/(\text{eV atom})$) is provided by cerium atom. Two Ni and three Al atoms contribute equally with about 20.3% (0.610 and $0.405 \text{ states}/(\text{eV atom})$, respectively). The subband of cerium is formed mainly by $4f$ electrons (occupation $4f^1$ and $\text{DOS}(E_F) = 2.975 \text{ states}/(\text{eV atom})$) and $5d$ ones (occupation $5d^{1.6}$ and $\text{DOS}(E_F) = 0.506 \text{ states}/(\text{eV atom})$). The band of 4.5 eV width is mainly formed by Ni $3d$ electrons (occupation $3d^{8.8}$ and $\text{DOS}(E_F) = 0.457 \text{ states}/(\text{eV atom})$). We must emphasize that the energy position of the Ni $3d$ contribution in the valence spectra is significantly shifted from the Fermi level and is narrower when compared with the spectrum of pure Ni metal. Such a behavior may be qualitatively understood by taking into account the $3d$ band-filling effect caused by charge transfer from Ce and Al atoms during the compound formation. The characteristics of the aluminum band are following: occupation $3s^{1.2}$, $3p^{1.8}$ and $\text{DOS}(E_F) = 0.018, 0.322 \text{ states}/(\text{eV atom})$ for Al($3s$) and Al($3p$) electrons, respectively. The calculations that account for spin polarization and were started with large initial magnetic moments for Ce, Ni and Al atoms indicate a nonmagnetic solution.

Ab-initio calculations in GGA + U approach are usually performed with U parameters selected in a way to improve the compatibility of the calculation results with the experimental data, while keeping the U values in reasonable range. Reference should be made to previous calculations for similar compounds [31] or to theoretical databases for simple monoatomic systems [12]. The results presented in Fig. 5 (lower panel) were obtained for $U_{4f} = 6 \text{ eV}$ and $U_{3d} = 3 \text{ eV}$. U_{3d} slightly alters the position of the Ni($3d$) band, while Ce($4f$) peak near the Fermi level was formed after consideration of U_{4f} parameter. The image presented for GGA + U calculations is typical for the partially filled Ce($4f$) band, lying below and above the Fermi level. Electrons from the part of the filled band shift in the direction of higher binding energies. In turn, the unfilled states are shifted in the opposite direction. Unfortunately, the

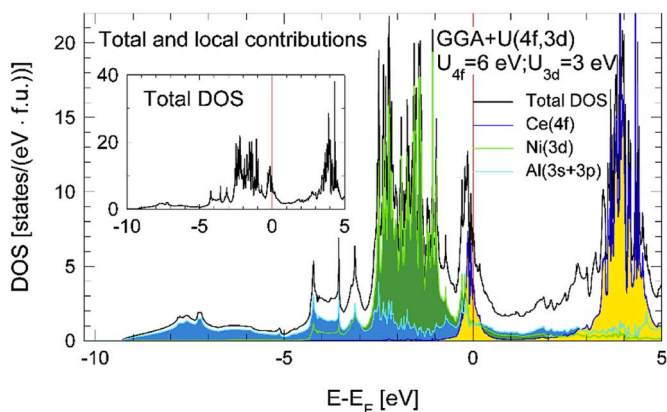
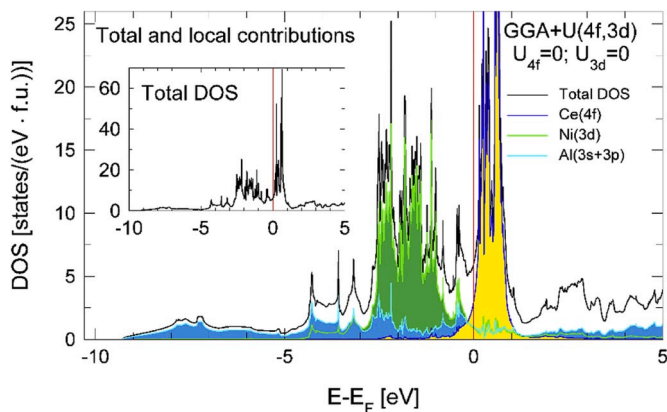


Fig. 5. DOS plots: GGA and GGA + U calculations (upper and lower panel, respectively). The main contributions to the valence band provided by the Ce (4f), Ni(3d) and Al(3s+3p) electrons were marked in the figures with different shades of yellow, green and blue, respectively.

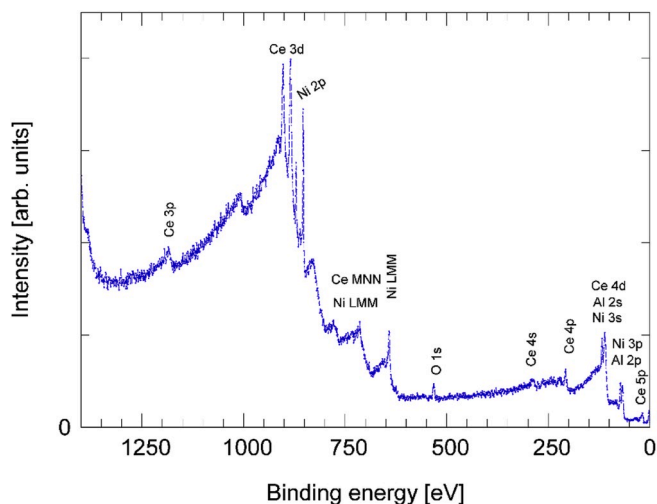


Fig. 6. The XPS spectrum of CeNi₂Al₃ in the energy range of 0–1400 eV.

states above the Fermi level are not visible in Fig. 7, because the XPS method is not dedicated to their detection. The reconstruction of the electron structure of the Ce(4f) subband near low binding energies causes changes of the DOS values at the Fermi level. In our case these values are increased to 7.58 states/(eV f.u.), which implies a change of the calculated Sommerfeld coefficient γ_{theor} to 18 mJ/(mol K²). The calculated value has approached the experimental value, thus decreasing the value of parameter λ responsible for electron-phonon

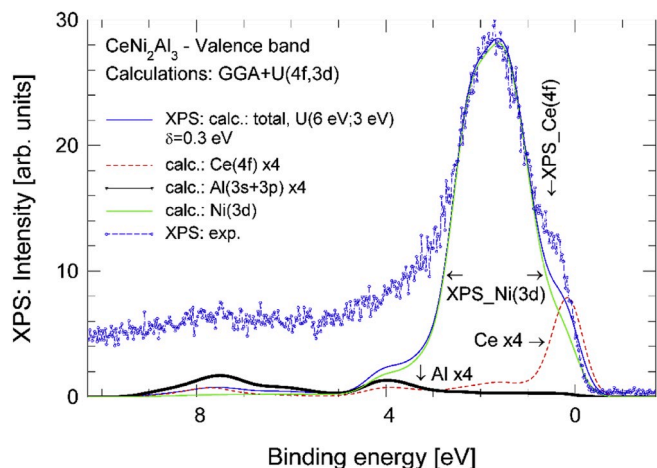


Fig. 7. Valence band region of the CeNi₂Al₃ compound obtained by XPS measurements and *ab-initio* calculations. For better visibility, the Ce and Al spectra were multiplied by factor 4.

coupling, to about 0.18.

The efficiency of a thermoelectric material is generally characterized by a dimensionless figure of merit $ZT = S^2T/\rho\kappa$, where S , T , κ and ρ are thermopower, temperature, thermal conductivity and electrical resistivity, respectively. Power factor ($PF = S^2/\rho$) and the Lorenz number ($L = \rho\kappa/T$) are another useful parameters. A high PF value and low κ are required to maximize ZT values of thermoelectric materials. From the application point of view, it is also important to optimize PF , a parameter that depends only on the electronic properties. There is a class of metallic systems in which PF reaches very high values. These are strongly correlated electron systems.

Power factor for CeNi₂Al₃ reaches value of $\sim 70 \mu\text{W}/(\text{cm K}^2)$ at 150 K [8] and is larger than in the case of the vast majority of modern thermoelectric materials based on Bi₂Te₃ [32]. The power factor value is also greater than the PF values reported for many intermetallic compounds based on rare earth elements [33–35]. This large power factor encourages further studies and makes CeNi₂Al₃ a serious candidate for a potential thermoelectric material. Materials with a high PF coefficient are able to cope with a large amount of heat and can convert heat into electricity and vice versa. In addition, the dimensionless figure of merit ZT reaches a value of 0.1 at 220 K [8], which is one of the highest among cerium-based compounds. Sun et al. [7] reported that the substitution of Cu at the Ni site in Ce(Ni_{1-x}Cu_x)₂Al₃ results for $x = 0.4$ in the simultaneous optimization of all three quantities (S , ρ , κ) determining thermoelectric properties.

The study of the electronic structure of compounds with mixed valence based on cerium is one of the most important tasks in the field of strongly correlated electron systems. In our case, the study of the electron structure of CeNi₂Al₃ is based on the analysis of XPS spectra of the valence band and a series of spectra reflecting the core electrons. Fig. 6 presents the XPS spectrum for CeNi₂Al₃ in the whole measured range of binding energies for Al-K _{α} source of X-ray radiation. Except of the peaks corresponding to the appropriate levels of the elements forming our compound, a very small contamination by oxygen is visible. The oxides that were created in the technological process are the most probable source of this contribution. It is well known that rare earth metals are very reactive. After breaking the sample, even under ultra-high vacuum conditions, the surface can oxidize quickly [36]. The presence of oxygen modifies the measured lines. To avoid this problem all spectra were measured immediately after breaking the sample in vacuum of 10^{-10} Torr and the sample was repeatedly cleaved in situ in about every 10 min. We did not observe any increase of the oxidation effect during the data acquisition time. It was checked by observations of the (O 1s) spectra before and after each measurement.

The valence band spectrum (shown in Fig. 7) is predominated by contribution provided by the Ni(3d) electrons. We have to point out that energy position of the Ni(3d) contribution (~ 2 eV) in the XPS valence spectrum is considerably shifted from the Fermi level, if one compares to that of the pure fcc Ni (~ 0.6 eV).

Such behavior can be qualitatively understood, taking into account the effect of filling of the 3d band. Fuggle et al. [37–39] studied the valence band of Ni–Al alloys by XPS method. They reported that the centroid of Ni(3d) bands shifts to higher binding energies with increasing Al content. The absence of a 6 eV satellite is further evidence of the full 3d band. Similar behavior was observed for CeNi₂Al₃ by Coldea et al. [4]. There is a peak corresponding to the Ce(4f) and Ce 5d6s² states near the Fermi level ($E_F = 0$ eV). A shift of Ni(3d) peak towards higher binding energies was also observed in case of CeNiAl₄ [31].

The previously mentioned presence of a separate peak near the Fermi level (Fig. 5, upper panel) formed by the Ce(4f) electrons highlighted the hump in the calculated XPS spectrum, which is clearly visible in the experimental part. Calculations in the framework of GGA ($U_{4f} = U_{3d} = 0$) did not give such a clear contribution of Ce(4f) electrons to the XPS spectrum. Overall consistency of calculated and measured results should be noted and indicated as justification for the use of the chosen calculation method within the DFT approach.

The XPS spectrum analysis of the Ce (3d) core level provides more detailed information about the configurations of Ce(4f) shells and the hybridization of these electrons with conduction ones. Fig. 8 shows the Ce(3d) core level photoemission spectrum of CeNi₂Al₃. The fitting process was performed using MultiPak software. The Shirley method [40] was used to subtract background, the spectrum was numerically fitted using the 80% Gaussian and 20% Lorentzian peak-shape. The spectrum is composed of two strong peaks at the binding energies of 884.1 and 902.6 eV. These peaks are assigned to the 3d_{5/2} and 3d_{3/2} spin-orbital coupling components of the 3d⁹4f¹ final states. The main components 3d⁹_{5/2}4f¹ and 3d⁹_{3/2}4f¹ exhibit a spin-orbit splitting $\Delta_{SO} = 18.5$ eV. This value is comparable to those observed in other Ce-based compounds listed by Fuggle et al. in Ref. [41].

Dealing with compounds based on cerium or other ions that show the possibility of different valency, we cannot avoid the question about the valence state of the rare earth ion. Due to the proximity of Ce(4f) states to the Fermi level, a change in the properties can be observed with the shift of the actual position of peak 4f. The main mechanism responsible for changing physical properties is the hybridization of 4f states with conduction electrons. The strength of hybridization influences the

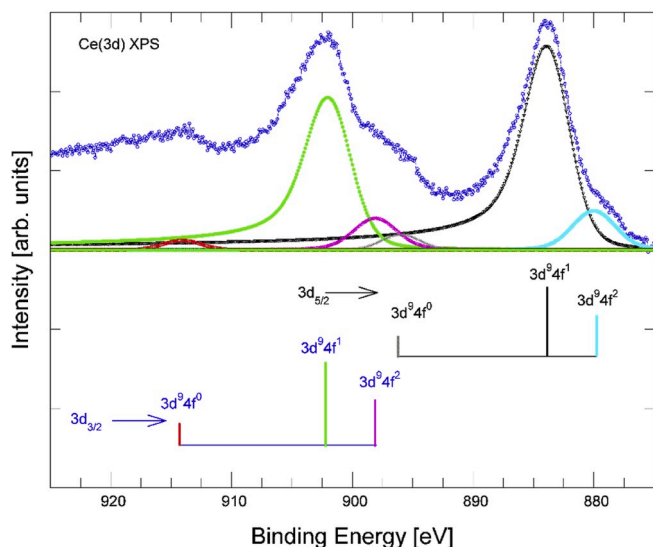


Fig. 8. The Ce(3d) XPS spectrum for CeNi₂Al₃.

degree of localization/delocalization of 4f electrons and is responsible for valence state of Ce. Strong hybridization decreases the localization of the Ce(4f) electrons and results in non-magnetic intermediate valence behavior. Weak hybridization leads to more localized character and deeper position of 4f shell in relation to Fermi's level.

Three final states (f^0, f^1, f^2) are present in a number of Ce-based intermetallics. A mixed valence behavior of Ce can be suggested by the appearance of the f^0 components. In turn, when the core hole is screened by an extra 4f electron, one can observe f^2 peaks located at the low-binding energy side of the f^1 components. It may occur due to hybridization of the 4f shell with the conduction band. In consequence, the ratio of intensities of f^2 and summarized intensities of f^1 and f^2 peaks could reflect the degree of hybridization. Gunnarsson and Schönhammer [42] calculated the XPS spectra based on the Anderson Hamiltonian and discussed how the hybridization energy of the 4f states with the conduction electron system can be estimated from the experimental spectra. Since the intensity ratio $r = I(f^2)/[I(f^1) + I(f^2)]$ is calculated following Ref. [42] as a function of the hybridization Δ , it is possible to estimate this important parameter for the Kondo compounds. This value is similar to that given for CeNi₂Al₃ by Coldea et al. [4] (80 meV) and values for other intermediate valence compounds [23,43].

The Ce(3d) spectrum has a hump around 914 eV. This is trace of the 3d⁹4f⁰ states, characteristic of Ce⁴⁺ ion. The intensity of this hump for CeNi₂Al₃ is weak compared to the other intermediate valence Ce compounds, implying that Ce valence in CeNi₂Al₃ is close to 3+. Based on the Gunnarsson-Schönhammer theory we also estimated the Ce(4f) occupation number n_f from the intensity ratio: $I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$. We obtained $n_f \approx 0.94$ which suggests that the studied system is weakly hybridized, i.e. with tendency to localization.

Further analysis of the XPS core states concerns the Ni(2p) doublet, which is displayed in Fig. 9. The spin-orbit split is equal to 17.25 eV. The presence of a small satellite between the main peaks suggests that the contribution of nickel to the magnetic properties of the compound is negligible due to the filling of the 3d band.

5. Conclusions

Based on the measurements of magnetic, transport and electronic properties, it was confirmed that CeNi₂Al₃ is an intermediate valence system. The Sommerfeld coefficient provided by the heat capacity measurements is equal to 21 mJ/(mol K²). Using a simple band model and the results of thermopower measurements, the position and width of the 4f peak in the vicinity of the Fermi level were estimated. It is located just above E_F . This is consistent with our *ab initio* calculations, which showed that the Fermi level is situated on the left side of the prominent peak formed by Ce(4f) electrons.

The X-ray photoemission spectroscopy measurements revealed the predominance of the Ni(3d) and the Ce(4f) states at the valence band

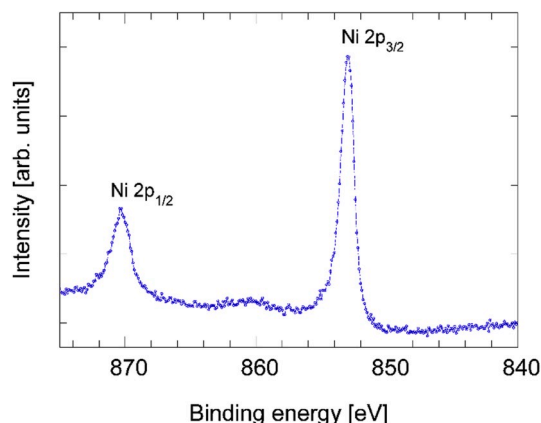


Fig. 9. XPS Ni(2p) doublet with a small satellite peak visible at $E_B = 860$ eV.

region. The Ce(3d) XPS spectrum suggests a mixed valence character of the f states in this compound. It also allowed us to determine the hybridization between conduction band and f -electrons ($\Delta = 78$ meV) as well as f -level occupation parameter ($n_f = 0.94$). Band structure calculations within the density functional theory with and without spin polarization are presented for the first time. The spin polarized calculations, started with initial large magnetic moments for Ce, Ni and Al atoms, gave resultant nonmagnetic solution. The total density of states below the Fermi energy is formed mainly of Ni hybridized with Ce(4f) states. The density of states at the Fermi level is equal to $N(E_F) = 5.997$ states/(eV f.u.), which corresponds to the Sommerfeld coefficient $\gamma_{\text{theor}} = 18$ mJ/(mol K²). The main contributions to this value are provided by Ce(4f) and Ni(3d) electrons, which amounts to 49.6% and 15.2%, respectively. The calculated valence band spectrum coincides well with the measured one.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

A. Szajek: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Z. Śniadecki:** Investigation, Resources, Visualization, Writing - original draft, Writing - review & editing. **P. Skokowski:** Investigation, Formal analysis, Validation. **G. Chelkowska:** Investigation, Formal analysis, Validation, Writing - original draft, Writing - review & editing. **B. Szymański:** Investigation, Formal analysis, Validation. **T. Luciński:** Investigation, Formal analysis, Validation. **A. Kowalczyk:** Supervision, Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing.

References

- V. Zlatić, R. Monner, Theory of the thermoelectricity of intermetallic compounds with Ce or Yb ions, *Phys. Rev. B* 71 (2005), 165109, <https://doi.org/10.1103/PhysRevB.71.165109>.
- G.R. Stewart, Heavy-fermion systems, *Mod. Rev. Phys.* 56 (1984) 755, <https://doi.org/10.1103/RevModPhys.56.755>.
- R.J. Cava, A.P. Ramirez, H. Takagi, J.J. Krajewski, Physical properties of some ternary Ce intermetallics with the transition metals Ni and Pd, *J. Magn. Magn. Mater.* 128 (1993) 124–128, [https://doi.org/10.1016/0304-8853\(93\)90865-Y](https://doi.org/10.1016/0304-8853(93)90865-Y).
- M. Coldea, M. Neumann, V. Pop, M. Demeter, Mixed valence state of Ce ions in CeNi₂Al₃, *J. Alloys Compd.* 323–324 (2001), 431434, [https://doi.org/10.1016/S0925-8388\(01\)01104-5](https://doi.org/10.1016/S0925-8388(01)01104-5).
- Q. Lu, P. Sun, D. Huo, T. Mizushima, Y. Isikawa, J. Sakurai, Magnetic, Thermal and transport Properties of Ce(Ni_{1-x}Cu_x)₂Al₃: the dominant Role of electronic change, *J. Phys. Soc. Jpn.* 73 (2004) 681–686, <https://doi.org/10.1143/JPSJ.73.681>.
- S. Yadam, D. Singh, D. Venkateshwarliu, M.K. Gangrade, S.S. Samatham, V. Ganesan, Enhancement in thermoelectric power of Ce(Ni_{1-x}Cu_x)₂Al₃: an implication of two-band conduction, *Phys. Status Solidi B* 252 (2015) 502–507, <https://doi.org/10.1002/pssb.201451317>.
- P. Sun, T. Ikeno, T. Mizushima, Y. Isikawa, Simultaneously optimizing the interdependent thermoelectric parameters in Ce(Ni_{1-x}Cu_x)₂Al₃, *Phys. Rev. B* 80 (2009), 193105, <https://doi.org/10.1103/PhysRevB.80.193105>.
- A. Szajek, A. Kowalczyk, Thermoelectric properties and band structure calculations of intermediate valence CeNi₂Al₃, *Appl. Phys. A* 125 (2019) 757, <https://doi.org/10.1007/s00339-019-3057-z>.
- K. Köpfernik, H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme, *Phys. Rev. B* 59 (1999) 1743–1757, <https://doi.org/10.1103/PhysRevB.59.1743>.
- J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868, <https://doi.org/10.1103/PhysRevLett.77.3865>.
- V.I. Anisimov, I.V. Solov'ev, M.A. Korotin, M.T. Czyżyk, G.A. Sawatzky, Density-functional theory and NiO photoemission spectra, *Phys. Rev. B* 48 (1993), 16929, <https://doi.org/10.1103/PhysRevB.48.16929>.
- D. van der Marel, G.A. Sawatzky, Electron-electron interaction and localization in d and f transition metals, *Phys. Rev. B* 37 (1988), 10674, <https://doi.org/10.1103/PhysRevB.37.10674>.
- M. Samsel-Czekala, M. Werwiński, A. Szajek, G. Chelkowska, R. Troć, Electronic structure of UGe₂ at ambient pressure: Comparison with X-ray photoemission spectra, *Intermetallics* 19 (2011) 1411, <https://doi.org/10.1016/j.intermet.2011.05.008>.
- J.J. Yeh, I. Lindau, Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leq Z \leq 103$, *Atomic Data Nucl. Data Tables* 32 (1985) 1, [https://doi.org/10.1016/0092-640X\(85\)90016-6](https://doi.org/10.1016/0092-640X(85)90016-6).
- P. Blöchl, O. Jepsen, O.K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, *Phys. Rev. B* 49 (1994) 16223–16233, <https://doi.org/10.1103/PhysRevB.49.16223>.
- A. Kowalczyk, M. Pugaczowa-Michalska, T. Toliński, Electronic band structure of the CeNi₄Ga compound, *Phys. Status Solidi B* 242 (2005) 433–437, <https://doi.org/10.1002/pssb.200460055>.
- S. Layek, V.K. Anand, Z. Hossain, Valence fluctuation in Ce₂Co₃Ge₅ and crystal field effect in Pr₂Co₃Ge₅, *J. Magn. Magn. Mater.* 321 (2009) 3447–3452, <https://doi.org/10.1016/j.jmmm.2009.06.039>.
- C. Mazumdar, R. Nagarajan, S.K. Dhar, L.C. Gupta, R. Vijayaraghavan, B. D. Padalia, Ce₂Ni₃Si₅: a mixed-valence cerium compound, *Phys. Rev. B* 46 (1992) 9009–9012, <https://doi.org/10.1103/PhysRevB.46.9009>.
- C. Geibel, S. Thies, D. Kaczorowski, A. Mehner, A. Grauel, B. Seidel, U. Ahlheim, R. Helfrich, K. Petersen, C.D. Bredl, F. Steglich, A new heavy-fermion superconductor: UNi₂Al₃, *Z. Phys. B Condens. Matter* 83 (1991) 305–306, <https://doi.org/10.1007/BF01313397>.
- A. Kowalczyk, M. Falkowski, T. Toliński, Valence fluctuations in YbNiAl₄ compound, *J. Appl. Phys.* 107 (2010), 123917, <https://doi.org/10.1063/1.3452388>.
- K. Kadowaki, S.B. Woods, Universal relationship of the resistivity and specific heat in heavy-Fermion compounds, *Solid State Commun.* 58 (1986) 507–509, [https://doi.org/10.1016/0038-1098\(86\)90785-4](https://doi.org/10.1016/0038-1098(86)90785-4).
- N. Tsujii H. Kontani, K. Yoshimura, Universality in heavy fermion systems with general degeneracy, *Phys. Rev. Lett.* 94 (2005), 057201, <https://doi.org/10.1103/PhysRevLett.94.057201>.
- T. Toliński, A. Kowalczyk, G. Chelkowska, M. Pugaczowa-Michalska, B. Andrzejewski, V. Ivanov, A. Szweczyk, M. Gutowska, Magnetic, thermodynamic, electronic, and transport properties of CeNi₄Al, *Phys. Rev. B* 70 (2004), 064413, <https://doi.org/10.1103/PhysRevB.70.064413>.
- M. Falkowski, Polish Academy of Sciences, Ph.D. thesis, 2009. Poznan.
- Y. Sankararao, S. Shanmukharao Samatham, D. Venkateshwarlu, M. Gangrade, V. Ganesan, Transport and calorimetric studies on CeNi₂Al₃, *J. Phys.: Conf. Ser.* 534 (2014), 012039, <https://doi.org/10.1088/1742-6596/534/1/012039>.
- U. Gottwick, K. Gloos, S. Horn, F. Steglich, N. Grewe, Transport coefficients of intermediate valent CeNi_x intermetallic compounds, *J. Magn. Magn. Mater.* 47–48 (1985) 536–538, [https://doi.org/10.1016/0304-8853\(85\)90487-1](https://doi.org/10.1016/0304-8853(85)90487-1).
- J.G. Park, M. Ocko, Thermopower studies of doped CeAl₂ and UAl₂, *J. Phys. Condens. Matter* 9 (1997) 4627–4634, <https://doi.org/10.1088/0953-8984/9/22/015>.
- M. Falkowski, A. Kowalczyk, Thermal and electron transport studies on the valence fluctuating compound YbNiAl₄, *J. Appl. Phys.* 123 (2018), 175106, <https://doi.org/10.1063/1.5025236>.
- K. Behnia, D. Jaccard, J. Flouquet, On the thermoelectricity of correlated electrons in the zero-temperature limit, *J. Phys. Condens. Matter* 16 (2004) 5187–5198, <https://doi.org/10.1088/0953-8984/16/28/037>.
- K.E. Wilson, The renormalization group: critical phenomena and the Kondo problem, *Rev. Mod. Phys.* 47 (1975) 773–840, <https://doi.org/10.1103/RevModPhys.47.773>.
- M. Werwiński, G. Chelkowska, A. Szajek, A. Kowalczyk, Electronic Properties of CeNiAl₄ Based on ab initio Calculations and XPS Measurements, *Acta Phys. Pol., A* 133 (2018) 517, <https://doi.org/10.12693/APhysPolA.133.517>.
- I. Terasaki, Y. Sasago, K. Uchinokura, Large thermoelectric power in NaCoO₄ single crystals, *Phys. Rev. B* 56 (1997) R12685–R12687, <https://doi.org/10.1103/PhysRevB.56.R12685>.
- V.H. Tran, W. Miiller, A. Kowalczyk, T. Toliński, G. Chelkowska, YbNi_{0.8}Al_{4.2}: a novel intermetallic compound with an enhanced thermoelectric power factor, *J. Alloys Compd.* 442 (2007) 355–357, <https://doi.org/10.1016/j.jallcom.2006.09.167>.
- Y. Muro, K. Yamane, K.S. Kim, T. Takabatake, C. Godart, P. Rogl, Magnetic and thermoelectric properties of a heterogeneous mixed-valence system, Yb₂Pt₃Sn₅, *J. Phys. Soc. Japan* 72 (2003) 1745–1750, <https://doi.org/10.1143/JPSJ.72.1745>.
- K. Synoradzki, K. Ciesielski, L. Kepinski, D. Kaczorowski, Power factor enhancement in a composite based on the half-Heusler antimonide TmNiSb, *J. Appl. Phys.* 123 (2018), 235101, <https://doi.org/10.1063/1.5038395>.
- G. Chelkowska, M. Neumann, Electronic structure of Gd(Al_{1-x}Co_x)₂ intermetallic compounds, *Solid State Commun.* 91 (1994) 799–801, [https://doi.org/10.1016/0038-1098\(94\)90651-3](https://doi.org/10.1016/0038-1098(94)90651-3).
- J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Żolnierek, P.A. Bennett, Ch Freiburg, Electronic structure of Ni and Pd alloys. I. X-ray photoelectron spectroscopy of the valence bands, *Phys. Rev. B* 27 (1982) 2145, <https://doi.org/10.1103/PhysRevB.27.2145>.
- F.U. Hillebrecht, J.C. Fuggle, P.A. Bennett, Z. Żolnierek, Ch Freiburg, Electronic structure of Ni and Pd alloys. II. X-ray photoelectron core-level spectra, *Phys. Rev. B* 27 (1983) 2179, <https://doi.org/10.1103/PhysRevB.27.2179>.
- P.A. Bennett, J.C. Fuggle, F.U. Hillebrecht, A. Lenselink, G.A. Sawatzky, Electronic structure of Ni and Pd alloys. III. Correlation effects in the Auger spectra of Ni alloys, *Phys. Rev. B* 27 (1983) 2194, <https://doi.org/10.1103/PhysRevB.27.2194>.
- D. Shirley, High-resolution X-ray photoemission spectrum of valence bands of gold, *Phys. Rev. B* 5 (1972) 4709, <https://doi.org/10.1103/PhysRevB.5.4709>.
- J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Żolnierek, P.A. Bennett, C. Freiburg, O. Gunnarsson, K. Schönhammer, Electronic structure of Ce and its intermetallic

- compounds, Phys. Rev. B 27 (1983) 7330, <https://doi.org/10.1103/PhysRevB.27.7330>.
- [42] O. Gunnarson, K. Schönhammer, Electron spectroscopies for Ce compounds in the impurity model, Phys. Rev. B 28 (1983) 4315, <https://doi.org/10.1103/PhysRevB.28.4315>.
- [43] A. Kowalczyk, M. Falkowski, T. Toliński, G. Chełkowska, Valence state and magnetism of CeNi₄Si and YbNi₄Si, Solid State Commun. 139 (2006) 5, <https://doi.org/10.1016/j.ssc.2006.05.013>.