Magnetism and electronic structure of RTIn (R = Ce, Pr, Nd; T = Ni, Cu, Pd, Au) ternary compounds

Ł. GONDEK[1], A. SZYTUŁA[2]*, D. KACZOROWSKI[3], Ya. KALYCHAK[4], B. PENC[2], J. HERNANDEZ-VELASCO[5], Yu. TYVANCHUK[4]

[1] *Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Mickiewicza 30, 30-059 Kraków, Poland*
[2] *M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland*
[3] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O.Box 1410, 50-50 Wrocław, Poland*
[4] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya 6, 79005 Lviv, Ukraine*
[5] *BENSC, Hahn-Meitner Institute, Glienicker Str. 100, 14-109 Berlin-Wannsee, Germany*
* *Corresponding author. Tel.: +48 12 663 55 46; fax: +48 12 633 70 86; e-mail: szytula@if.uj.edu.pl*

Magnetic and X-ray photoemission spectroscopy (XPS) measurements were performed on polycrystalline samples RTIn where R is Ce, Pr, Nd and T is Ni, Cu, Pd, Au. All these compounds crystallize in the hexagonal ZrNiAl-type crystal structure. The magnetic data indicate various magnetic properties. Among the CeTIn compounds those with T = Ni and Cu are paramagnets down to 1.9 K, while those with T = Pd and Au order antiferromagnetically at low temperatures. Both PrTIn (T = Ni, Au) phases are paramagnets, while the NdTIn compounds are ferromagnetic for T = Ni and Pd, antiferromagnets for T = Cu and paramagnets for T = Au. The analysis of the XPS data concentrates on the valence bands and R $3d_{5/2}$ and R $3d_{3/2}$ spectra. The valence band spectra indicate a strong hybridization of the R 4f and T states, which causes the absence of any magnetic order in some of these compounds. From the R 3d spectra the values of the hybridization energy have been determined.

Rare earth alloys and compounds / Intermetallics / Magnetically ordered materials / Magnetic measurements / Neutron diffraction / Electronic properties

Introduction

During recent years intermetallic compounds containing rare earth elements have been intensively studied because of their interesting physical properties [1-3]. The family of compounds described by the formula RTX (R – rare earth; T –d-electron transition element; X – p-electron element) is one of the numerous families of ternary intermetallic compounds that have been reported in the literature. In this work the results of investigations of magnetic properties and electronic structure of the RTIn (R = Ce, Pr, Nd; T = Ni, Cu, Pd, Au) compounds are reported. These compounds crystallize in the hexagonal crystal structure of the ZrNiAl type [4-6]. The atoms occupy the following positions in the crystal unit cell (space group *P*-62*m*): rare earth atoms the 3(*f*) site: x_R, 0, 0; T atoms the 1(*a*) site: 0, 0, 0 and the 2(*d*) site: ⅓, ⅔, ½;

and In atoms the 3(*g*) site: x_{In}, 0, ½. The ZrNiAl-type crystal structure leads to a triangular coordination symmetry of magnetic rare earth ions stacked in "magnetic layers" (see Fig. 1), that causes geometrical frustration of the exchange integrals and leads to complex magnetic structures [6].

In recent years magnetic properties have been studied for some RTIn compounds. Among cerium CeTIn compounds different properties are observed. The compounds with T = Ni and Cu do not order down to low temperatures [7-9], while those with Pd and Au are antiferromagnets with the Néel temperature equal to 1.8 K for T = Pd and 5.7 K for T = Au [10]. No samples with R = Pr have been investigated. Ferromagnetic properties have been reported for NdTIn (T = Ni, Pd) [11], SmPdIn [12] and GdTIn (T = Ni, Pd) [13]. In turn, GdCuIn is an antiferromagnet [14].
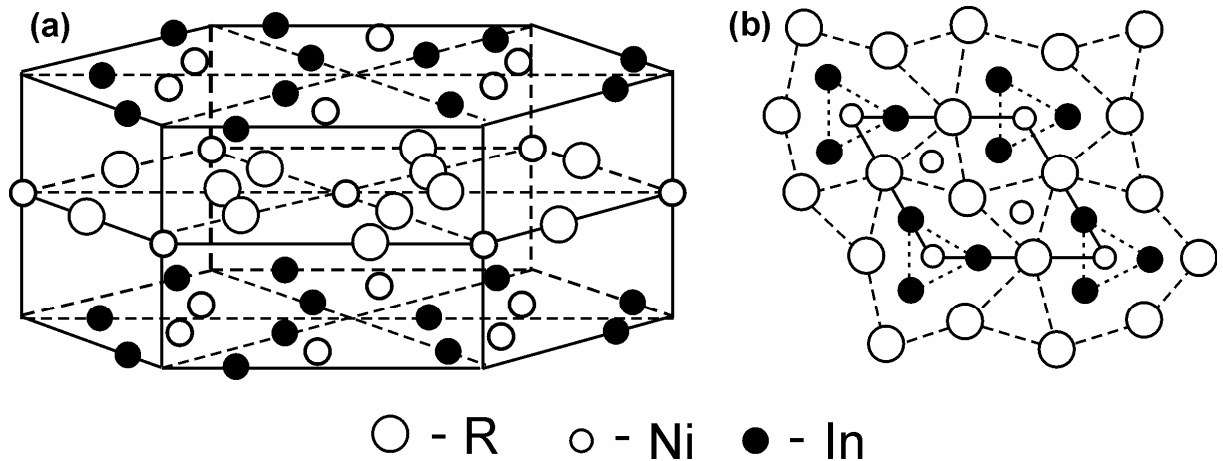
Fig. 1 (a) Hexagonal ZrNiAl-type crystal structure and (b) its projection on the basal plane.

Experimental

Polycrystalline samples were prepared from high-purity rare earth (3N), nickel, copper, palladium, gold (4N) and indium (5N) elements by arc-melting in a purified argon atmosphere. The samples were annealed in high vacuum at 800 °C for 1 week. In order to check the quality of the samples, X-ray diffraction measurements (CuK$_\alpha$ radiation) were performed using a Philips PW-3710 apparatus.

Magnetic susceptibility and magnetization data were collected using a SQUID magnetometer (Quantum Design MPMS) in magnetic fields up to 5 T and in the temperature range 1.72-300 K.

Neutron diffraction experiments were performed at the BER II reactor at the BENSC Hahn-Meitner Institute using the E6 diffractometer. The incident neutron wavelength was 2.44 Å. The measurements were performed in the temperature range 1.5-50 K. For processing the collected data, the Rietveld-type program Fullprof was used [15].

X-ray photoemission (XPS) measurements were carried out at room temperature using a Leybold LHS10 spectrometer with MgK$_\alpha$ (hv = 1253.6 eV) and AlK$_\alpha$ (hv = 1486.6 eV) radiation in a vacuum of about 10^{-9} mbar. The total energy resolution of the spectrometer with a hemispherical energy analyzer was about 0.75 eV for Ag 3d. The binding energies were referred to the Fermi level (E$_F$ = 0). The spectrometer was calibrated using the Cu 2p$_{3/2}$ (932.5 eV), Ag 3d$_{5/2}$ (368.1 eV) and Au 4f$_{7/2}$ (84.0 eV) core-level photoemission spectra. The surface of the samples was mechanically cleaned by scraping with a diamond file in a preparation chamber under high vacuum (10^{-9} mbar). Then the samples were immediately moved into the analysis chamber. This procedure was repeated until the C 1s and O 1s core-level peaks were negligibly small or remained unchanged after further scrapings. Such a cleaning procedure was performed before each XPS measurement. The Shirley method [16] was used to subtract the background and the experimental spectra

prepared in this manner were numerically fitted using an 80% Gaussian and 20% Lorentzian model.

Results

The X-ray diffraction measurements confirmed that all the investigated samples have hexagonal crystal structures of the ZrNiAl type. The determined lattice parameters are in good agreement with the data reported in [4,5].

The magnetic properties of the RTIn compounds are summarized in Table 1. CeTIn (T = Ni, Cu), PrTIn (T = Ni, Au) and NdAuIn do not order down to 1.7 K, while CeTIn (T = Pd, Au) and NdCuIn order antiferromagnetically, and both NdTIn (T = Ni, Pd) phases order ferromagnetically.

For all the compounds, except NdPdIn, the paramagnetic Curie temperatures are negative, thus indicating predominance of antiferromagnetic interactions. The values of the effective magnetic moments are close to the free R^{3+} ion values, however, for the NdCuIn compound some lowering of the magnetic moment was observed. These results indicate that only the rare earth atoms carry magnetic moments. The values of the magnetic moments at T = 1.7 K and H = 5 T are smaller than the free R^{3+} ion values.

The neutron diffraction experiments provide the following information on the magnetic structures of the compounds:

− in CePdIn the magnetic ordering is described by the propagation vector **k** = (¼, 0, 0); a small cerium moment of a few tenths of μ$_B$ [11] has been reported,

− in CeAuIn the antiferromagnetic order is described by the propagation vector **k** = (0, 0, ½); the Ce magnetic moments of 1.2(1) μ$_B$ lie in the a-b plane [18],

− in NdNiIn the Nd magnetic moments of 2.2(1) μ$_B$ order ferromagnetically in the a-b plane,

Table 1 Magnetic properties of RTIn (R = Ce, Pr, Nd; T = Ni, Cu, Pd, Au) compounds.

Compound	Type of the magn. ordering	$T_{C,N}$ (K)	Θ_p (K)	μ_{eff} (μ_B)		μ_s (μ_B)		Ref.
				exp.	theor.	exp.[a]	theor.	
CeNiIn			-56	2.40	2.54		2.14	[8]
CeCuIn			-15	2.40		0.7		[14]
CePdIn	AF	1.7	-43	2.61				[11]
CeAuIn	AF	6.0	-8.1	2.39(5)		0.24		[8]
PrNiIn			-42	3.7(2)	3.58	1.0	3.2	this work
PrAuIn			-5.4	3.54		1.2		this work
NdNiIn	F	14.5	-43	3.8(1)	3.62	1.6	3.27	this work
NdCuIn	AF	4.9	-7.2	2.96		0.8		[14]
NdPdIn	F	32.5	+2	3.59		1.96		[17]
NdAuIn			-18.9	3.68		0.6		this work

[a] *Value determined from the magnetization at* T = 1.7 K *and* H = 5 T.

Table 2 Positions of the R 4f states (E_{4f}) with respect to the energy of the T nd state (E_{nd}) and the corresponding energy difference δ (all in eV).

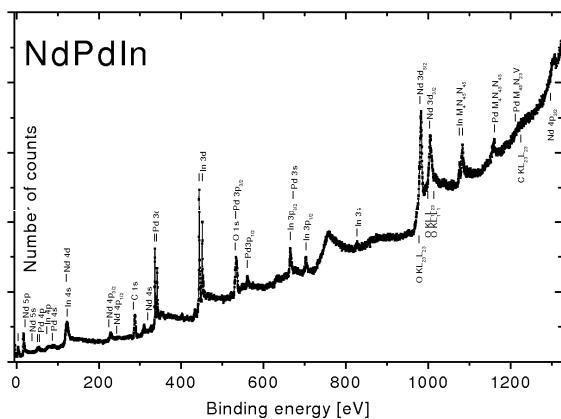|	RNiIn			RCuIn			RPdIn			RAuIn		
	E_{4f}	E_{3d}	δ	E_{4f}	E_{3d}	δ	E_{4f}	E_{4d}	δ	E_{4f}	E_{5d}	δ
Ce	1.9	1.3	0.6	2.0	4.1	2.1				2.5	5.5	3.0
Pr	2.9	1.1	1.8							3.8	5.8	1.9
Nd	4.9	1.3	3.6	4.8	3.8	1.0	5.7	3.8	1.9	4.6	5.2	0.6

− in NdPdIn the Nd magnetic moments change direction from the basal plane (below 15 K) to the *c*-axis direction (above 15 K). At 1.5 K the Nd magnetic moment is equal to 1.8(1) μ_B.

Fig. 2 presents a photoelectron spectrum of the NdPdIn compound collected in the wide (0-1300 eV) binding energy range. The binding energies are referred to the Fermi level (E_F = 0 eV). In order to obtain information on the electronic state of the rare earth elements, two parts of the measured spectrum: the valence band and R 3d states, have been analyzed.

The valence bands are dominated by the nd states of T elements. In the RNiIn (R = Ce, Pr, Nd) compounds broad peaks due to the Ni 3d states are observed below the Fermi level. This is in good

Fig. 2 XPS spectrum of NdPdIn collected for the 0-1300 eV binding energy range.

agreement with the calculated electronic structures, which reveal a peak corresponding to the Ni 3d states, located at 2 eV below the Fermi level [8]. The Cu 3d and Pd 4d states form single peaks at 4.1 eV and 3.8 eV, respectively. In the Au 5d spectrum a spin-orbit splitting of 1.5 eV is observed. The positions of the R 4f states were analyzed with respect to the T nd states and the results are summarized in Table 2.

In the R $3d_{5/2}$ and R $3d_{3/2}$ spectra the spin-orbit splitting Δ_{SO} dominates the spectral structure (Fig. 3). The value of Δ_{SO} is constant for a given element and increases with increasing number of f-electrons. Within the Gunnarsson-Schönhammer model [19] all the peaks have three final-state contributions f^{n-1}, f^n and f^{n+1}. The appearance of f^{n-1} is a clear evidence for a mixed valence state. The intensity ratio $r_1 = I(f^{n-1})/[I(f^{n-1})+I(f^n)+I(f^{n+1})]$ gives information on the occupation of the final f-states $n_f^{XPS} = 1-r_1$. The f^{n+1} components located on the low-binding energy side of the f^n components give information on the hybridization between the 4f electrons and the electrons of the conduction band. The hybridization energy Δ is defined as $\pi V^2 \rho_{max}$, where ρ_{max} is the maximum of the density of states of the conduction band and V is the hybridization matrix element. Since the intensity ratio $r_2 = I(f^{n+1})/[I(f^n)+I(f^{n+1})]$ has been calculated for Ce in [20] as a function of Δ, it is possible to determine the value of the hybridization. In this procedure the separation of the peaks in the R 3d XPS spectra was made on the basis of the Doniach-Šunjić theory [21]. The so-determined values of n_f^{XPS} and Δ are summarized in Table 3.

Table 3 The 4f-level occupation at room temperature n_f^{XPS} (in %) and hybridization energy Δ (in meV) for RTIn (R = Ce, Pr, Nd; T = Ni, Cu, Pd, Au) compounds.

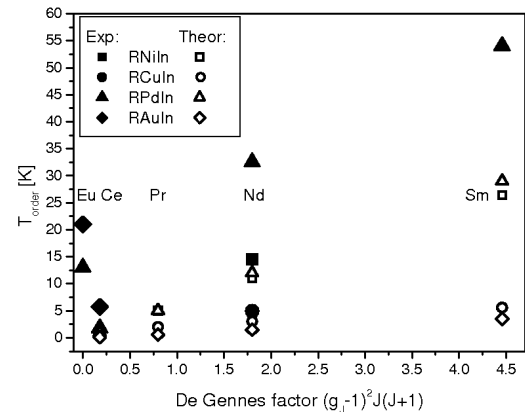| R/T	Ni		Cu		Pd		Au	
	n_f	Δ	n_f	Δ	n_f	Δ	n_f	Δ
Ce	83.9	148	92	170			90.9	123
Pr		130						70
Nd		80		96		119		45
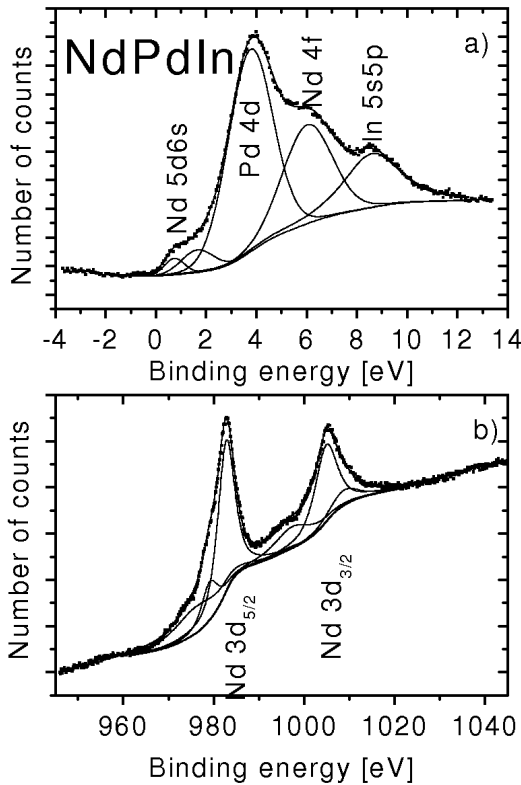
Fig. 3 Deconvoluted Nd 3d X-ray photoelectron spectra of NdPdIn.

Discussion

It is well known that the magnetic properties of rare earth compounds with stable 4f electron states are qualitatively understood by taking into account the isotropic Ruderman-Kittel-Kasuya-Yoshida (RKKY) type exchange interaction between the magnetic moments of R^{3+} ions, the electrostatic interactions of the R^{3+} ions with surrounding, i.e. the crystal electric field (CEF) and the magnetoelastic or biquadratic exchange interaction. In the case of Ce compounds the hybridization effect plays the dominant role. In the RKKY model, the ordering temperatures are proportional to the de Gennes factor $G = (g_J-1)^2 J(J+1)$ [22].

The results presented in this work indicate rather complex magnetic properties of the RTIn compounds. Only in some of them the rare earth moments order at low temperatures. The dependence of the ordering temperatures on the de Gennes factor for the phases investigated in this work is shown in

Fig. 4. The graph shows that the simple RKKY model is not suitable for the description of the magnetic properties of these compounds. The experimental values of $T_{N,C}$ are always higher than the theoretical ones. This finding implies that a local coupling between the 4f shell and the conduction electrons is much stronger than expected, possibly due to a large orbital contribution to the exchange coupling [23]. Another explanation could arise from strengthening the local coupling due to larger spatial extent of the 4f shell for the light rare earths, thus leading to a larger overlap of the 4f and 5d orbitals [24].

Fig. 4 Magnetic ordering temperatures as a function of the de Gennes factor for the RTIn (R = Ni, Cu, Pd, Au) compounds. Solid and open symbols denote the experimental and theoretical values, respectively. The theoretical values are normalized to the Néel temperatures of the isostructural GdTIn compounds.

The analysis of the Ce $3d_{5/2}$ and Ce $3d_{3/2}$ states in the Ce compounds indicates for all of them the existence of a mixed valence state. The hybridization energy Δ is large for CeNiIn and CeCuIn, which are paramagnetic down to very low temperatures. The smallest Δ is found for CeAuIn, which exhibits magnetic ordering. In contrast, for the magnetically ordered NdTIn (T = Ni, Cu and Pd) phases the values of the hybridization energy are similar and larger than that observed for NdAuIn, for which no magnetic ordering is observed. The second factor that influences the magnetic state is hybridization between 4f electrons of the rare earth and nd-electrons of the T transition elements. The values of the hybridization matrix element V_{df}, calculated on

Table 4 The hybridization matrix elements V_{df} (in meV) for RTIn (R = Ce, Pr, Nd; T = Ni, Au) compounds.

T/R	Ce	Pr	Nd
Ni	86	64	52
Au	246	188	168

the basis of the Harrison-Straub [25,26] model for two series: RNiIn and RAuIn, are shown in Table 4. The obtained data indicate a decrease in the V_{df} values from Ce to Nd. The total hybridization V is proportional to the product of V_{df} and ρ_{po}, where ρ_{po} is the density of the states of the f- and d-electrons. To estimate the contribution of the f- and d-states one should analyze the positions of the peaks corresponding to the R 4f and T nd states (see Table 2). For the paramagnetic Ce- and Pr-based compounds, as well as for NdAuIn, the distances between R and T peaks are smaller than those in the magnetically ordered counterparts, thus hinting at stronger hybridization of the respective states. It seems therefore that just this type of hybridization causes the absence of any magnetic ordering in these compounds. The NdCuIn compound seems to be an exception from the above claim as it is magnetic and the separation between Nd 4f and Cu 3d states is close to 1 eV. In fact, it must be stressed that the separation energy δ between R 4f and T nd is not the only parameter that must be taken into account. Since the Cu 3d shell is smaller than the Au 5d one, the hybridization should be suppressed because of better spatial separation between 4f and 3d shells. Such a conclusion can be made based on the intuitive Harrison-Straub model [25,26].

The presented analysis does not explain the magnetic properties of NdCuSn, which is antiferromagnetic with a δ value of only 1.0 eV. Such a value suggests a non magnetic state. Further investigations, including calculation of the electronic structure, are planned in order to elucidate this inconsistency.

Acknowledgements

References

[1] P. Rogl, in: K.A. Gschneidner Jr., L. Eyring (Eds.), *Handbook on Physics and Chemistry of Rare Earths*, Vol. 7, North-Holland, Amsterdam, 1984, p. 1.

[2] A. Szytuła, in: K.H.J. Buschow (Ed.), *Handbook of Magnetic Materials*, Vol. 6, Elsevier, Amsterdam, 1991, p. 83.

[3] D. Gignoux, D. Schmitt, in: K.H.J. Buschow (Ed.), *Handbook of Magnetic Materials*, Vol. 10, Elsevier, Amsterdam, 1997, p. 241.

[4] A.E. Dwight, in: C.E. Lundin (Ed.), *Proc. 12th Rare Earth Res. Conf.*, Denver Research Institute, Denver, 1976.

[5] R. Ferro, R. Marazza, G. Rambaldi, *Z. Metallkd.* 65 (1974) 37.

[6] Ł. Gondek, *Thesis*, Jagiellonian Univ., Kraków, 2004.

[7] H. Fujii, T. Juone, Y. Andoh, T. Takabatake, K. Satoh, Y. Maeno, T. Fujita, J. Salmrai, Y. Yamaguchi, *Phys. Rev. B* 39 (1989) 6840.

[8] Ł. Gondek, B. Penc, A. Szytuła, A. Jezierski, *Acta Phys. Pol. B* 34 (2003) 1209.

[9] S.K. Malik, D.T. Androja, B.D. Padalia, R. Vijayaraghavan, *Physica B* 163 (1990) 89.

[10] H. Fujii, H. Nagata, Y. Uwatoko, T. Okamoto, H. Yamamoto, M. Sagawa, *J. Magn. Magn. Mater.* 70 (1987) 331.

[11] H. Fujii, T. Takabatake, Y. Endoh, *J. Alloys Compd.* 181 (1992) 111.

[12] T. Ito, K. Ohkubo, T. Hirasawa, J. Takeuchi, I. Hiromitsu, M. Kurisu, *J. Magn. Magn. Mater.* 140-144 (1995) 873.

[13] K.H.J. Buschow, *J. Less-Common Met.* 39 (1975) 185.

[14] A. Szytuła, Yu. Tyvanchuk, T. Jaworska-Gołąb, A. Zarzycki, Ya. Kalychak, Ł. Gondek, N. Stüsser, *J. Alloys. Compd.,* this volume.

[15] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.

[16] D.A. Shirley, *Phys. Rev. B* 5 (1975) 4708.

[17] Ł. Gondek, S. Baran, A. Szytuła, D. Kaczorowski, J. Hernandez-Velasco, *J. Magn. Magn. Mater.* 285 (2005) 272.

[18] Ł. Gondek, A. Szytuła, B. Penc, J. Hernandez-Velasco, A. Zygmunt, *J. Magn. Magn. Mater.* 262 (2003) L177.

[19] O. Gunnarsson, K. Schönhammer, *Phys. Rev. B* 50 (1994) 12332.

[20] J.C. Fuggle, F.U. Hillbrecht, Z. Żołnierek, R. Lässer, C. Freiburg, O. Gunnarsson, K. Schönhammer, *Phys. Rev. B* 39 (1989) 3380.

[21] S. Doniach, M. Šunjić, *J. Phys. C* 3 (1970) 285.

[22] P.G. de Gennes, *J. Phys. Radium* 23 (1962) 510.

[23] E. Belorizky, J.J. Niez, P.M. Levy, *Phys. Rev. B* 23 (1981) 3360.

[24] E. Belorizky, J.P. Gavigan, D. Givord, H.S. Li, *Europhys. Lett.* 5 (1988) 349.

[25] G.K. Straub, W.A. Harrison, *Phys. Rev. B* 31 (1985) 7668.

[26] W.A. Harrison, G.K. Straub, *Phys. Rev. B* 36 (1987) 2695.