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Synthesis, crystal and electronic structure of the ternary indide $PrNi_2In$

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The ternary indide $PrNi_2In$ was synthesized from the elements by arc-melting and subsequent annealing at 870 K. Single crystals were grown through special annealing procedures in a sealed tantalum container in a resistance furnace. The structure was solved from X-ray single-crystal data: $PrCo_2Ga$-type structure, *Pmma*, $Z = 2$, *oP*8, $a = 5.2143(12)$ Å, $b = 4.1068(10)$ Å, $c = 7.127(2)$ Å, $R1 = 0.0205$, $wR2 = 0.0580$, 250 F^2 values, 17 variables. The crystal chemistry of $PrNi_2In$ is discussed from a geometrical point of view and supported by electronic structure calculations.

Single crystals / Crystal structure / Ternary indide / Density of states

Introduction

Intermetallic rare-earth (R) – transition metal (T) – indium compounds, *i.e.* indides have attracted considerable interest in recent years due to their peculiar crystal chemistry and intriguing physical properties. More detailed investigations of the ternary systems R–T–In, including construction of complete isothermal sections, determination of crystal structures, physical properties, and chemical bonding have been performed over the last 30 years by the groups of *Ya. Kalychak* in Lviv and *R. Pöttgen* in Münster, *e.g.* the phase relations in the systems with cobalt, nickel, and copper as 3*d*-transition metal components [1-4]. Especially the nickel-based systems are extremely rich in compounds. With the early rare-earth metals, more than ten different intermetallics form in these systems.

Ternary indides of composition RT_2In ($T = 3d$-transition metal) form in ternary systems with Co [5,6], Ni, and Cu [7,8] and are representatives of the structure types $MnCu_2Al$ [9] and $PrCo_2Ga$ [10] (Table 1).

Kalychak and Zaremba [6] reported the existence of the compound $PrNi_2In$, which crystallizes with a $PrCo_2Ga$-type structure [10], but they only gave the lattice parameters without specifying the coordinates of the atoms. We have synthesized single crystals of this compound and completely refined its crystal structure.

Experimental details

Starting materials for the synthesis of the title compound were ingots of praseodymium (Aldrich, 99.9 %), nickel pellets (Onyxmet, 99.99 %), and indium tear drops (Onyxmet, 99.99 %). Before preparing the alloy, the praseodymium ingots were cut into smaller pieces and arc-melted to small buttons (about 0.5-0.7 g) under argon. Titanium sponge was used as a getter material. Subsequently, the melted praseodymium buttons were mixed with pieces of nickel and indium tear drops at the composition $Pr_{0.25}Ni_{0.50}In_{0.25}$ and arc-melted under the same conditions. The product pellet was re-melted twice to ensure homogeneity. The total weight loss after the melting procedure was smaller than 0.5 %. Then the button was sealed in an evacuated quartz tube and annealed at 870 K for 750 h. After the arc-melting and the annealing procedures the sample was obtained as a polycrystalline material.

A special thermal treatment was used to obtain single crystals for structural investigations. The alloy of composition $Pr_{0.25}Ni_{0.50}In_{0.25}$ was crushed into small pieces and placed into a small tantalum container that was then sealed in an evacuated silica tube for protection against oxidation. The sample was first heated in a muffle furnace to 1323 K within 15 h and held at that temperature for 3 h. Subsequently,

Table 1 Distribution of RT_2In ternary indides by structure type.

RE *T*	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Co	–	○	–	–	○	○	○	–	○	○	○	○	–	–	–	–
Ni	▨	–	○	–	○	○	–	–	–	–	–	–	–	–	–	–
Cu	▨	▨	▨	▨	▨	▨	▨	–	▨	▨	▨	▨	▨	▨	–	▨

○ $PrCo_2Ga$-type structure; ▨ $MnCu_2Al$-type structure; – compound does not exist

the temperature was lowered at a rate of 5 K/h to 1073 K, then at a rate of 5 K/h to 873 K and held at that temperature for another 12 h, and finally cooled to room temperature by switching off the furnace. The temperature was controlled by a CrNi/Ni thermocouple with a "Eurotherm 118" thermoregulator. As a result, single crystals of irregular shape were obtained (Fig. 1). The sample could easily be separated from the container material. No reaction with tantalum was observed. The sample after the thermal treatment was stable in air over weeks. The single crystals exhibited metallic luster while the ground powder was dark gray.

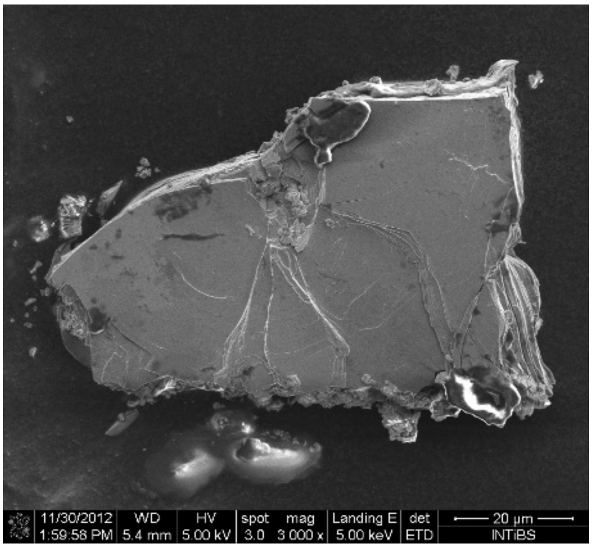


Fig. 1 Growth of single crystals in the $Pr_{0.25}Ni_{0.50}In_{0.25}$ sample.

Irregularly shaped single crystals were selected from the sample by mechanical fragmentation. They were investigated by the Laue method on an RKV-86 camera (white molybdenum radiation, photo technique) in order to check the quality for intensity data collection and to establish the symmetry. A complete data set was recorded at room temperature using an Oxford Xcalibur3 diffractometer (CCD area detector) with graphite monochromatized Mo $K\alpha$ radiation (Laboratory of Crystallography, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland). An empirical absorption correction was applied to the data set [11]. Crystallographic parameters and relevant data for the data collection and refinement are listed in Table 2.

The single crystals investigated on the diffractometer were analyzed using a FEI scanning electron microscope equipped with an EDAX Genesis XM4 spectrometer with PrF_3, Ni, and InAs as standards. No impurity elements heavier than sodium were observed. The composition of the $PrNi_2In$ crystal as determined by EDX (26±2 at.% Pr : 49±2 at.% Ni : 25±2 at.% In) is in good agreement with the refined composition (25 : 50 : 25).

Results and discussion

Structure refinements

The isotypism of the investigated compound with $PrCo_2Ga$ [10] was already evident from the powder patterns (powder diffractometer PANalytical XPert, Cu $K\alpha$ radiation). The diffractometer data set confirmed a primitive orthorhombic lattice and the systematic extinctions were in agreement with space group *Pmma* (No 51). The analysis of Laue photos from various single crystals confirmed orthorhombic symmetry. The atomic parameters of $TbCo_2In$ [5] were taken as starting values and the structure was refined using SHELX (full-matrix least-squares on F^2) [12] with anisotropic atomic displacement parameters for all the atoms. As a check for the correct composition and site assignment, the occupancy parameters were refined in separate series of least-squares cycles. All the sites were fully occupied within two standard deviations. The ideal values were used in the final cycles. The final difference Fourier synthesis was flat and revealed no significant residual peaks (Table 2). The positional parameters and interatomic distances from the refinement are listed in Tables 3 and 4.

Table 2 Crystal data and structure refinement for $PrNi_2In$.

Empirical formula	$PrNi_2In$
Formula weight ($g\cdot mol^{-1}$)	373.15
Crystal system	orthorhombic
Space group	*Pmma* (No 51)
Pearson symbol, *Z*	*oP*8, 2
Unit-cell dimensions (Å)	a = 5.2143(12) b = 4.1068(10) c = 7.127(2)
Unit-cell volume (Å^3)	V = 152.62(7)
Wyckoff sequence	f^2ea
Calculated density ($g\cdot cm^{-3}$)	8.120
Absorption coefficient (mm^{-1})	34.949
F(000) (e)	328
θ range for data collection (deg)	2.86-29.26
Range in *hkl*	±6, ±5, ±9
Total number of reflections	1857
Independent reflections /$R_{int.}$	250
Reflections with $I > 2\sigma(I)$	195
Data / parameters	250 / 17
Goodness-of-fit on F^2	1.179
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0205 / 0.0412
$R1$ / $wR2$ [all data)]	0.0320 / 0.0580
Largest diff. peak / hole (e·Å^{-3})	1.445 / -1.229

Table 3 Atomic coordinates, equivalent and anisotropic displacement parameters (Å^2) for $PrNi_2In$.

Atom	Wyckoff position	x	y	z	$U_{eq.}$ (Å^2)
Pr	$2f$	¼	½	0.7218(2)	0.0128(3)
Ni1	$2a$	0	0	0	0.0101(4)
Ni2	$2f$	¼	½	0.1094(4)	0.0137(5)
In	$2e$	¼	0	0.3458(2)	0.0127(3)

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Pr	0.0089(4)	0.0118(4)	0.0176(5)	0
Ni1	0.0072(8)	0.0065(8)	0.0166(11)	-0.0020(9)
Ni2	0.0140(10)	0.0078(9)	0.0193(12)	0
In	0.0114(6)	0.0100(5)	0.0167(7)	0

Table 4 Interatomic distances (δ, Å) in the structure of $PrNi_2In$. All distances within the first coordination spheres are listed.

Atom		CN	δ (Å)	Atom		CN	δ (Å)
Pr	1 Ni2	17	2.763(3)	Ni2	4 Ni1	11	2.554(1)
	2 Ni2		2.871(1)		2 In		2.656(2)
	4 Ni1		3.138(1)		1 Pr		2.763(3)
	4 In		3.353(1)		2 Pr		2.871(1)
	2 In		3.376(1)		2 Ni2		3.038(2)
	2 Pr		4.098(1)	In	2 Ni2	12	2.656(2)
	2 Pr		4.107(1)		2 Ni1		2.788(1)
Ni1	4 Ni2	12	2.554(1)		4 Pr		3.353(1)
	2 Ni1		2.607(1)		2 Pr		3.376(1)
	2 In		2.788(1)		2 In		3.410(1)
	4 Pr		3.138(1)				

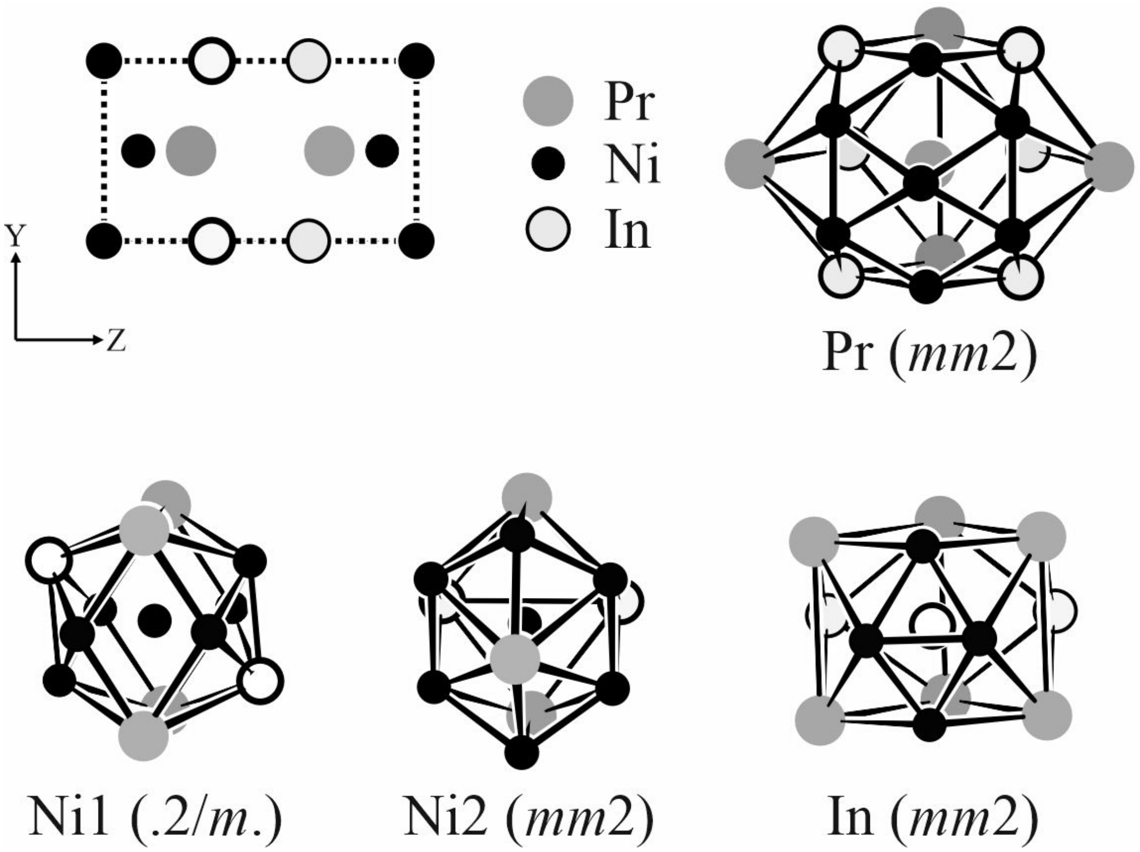


Fig. 2 Projection of the structure of $PrNi_2In$ onto the *YZ* plane and coordination polyhedra of the atoms. The site symmetries are indicated.

A projection of the structure of $PrNi_2In$ onto the YZ plane and the coordination polyhedra of the atoms are shown in Fig. 2. The coordination environment of the praseodymium atoms is a square prism with centered lateral faces and edges (CN = 17). For the nickel atoms it can be considered as a trigonal prism with centered lateral faces and edges (Ni2, CN = 11) or a distorted icosahedron of the $CaCu_5$-type, in which four faces are combined in pairs into two rhombuses (Ni1, CN = 12). The indium atoms are located at the centers of tetragonal prisms with four additional atoms centering the lateral faces (CN = 12). Topologically, this structure can also be considered as a stacking of slabs of distorted icosahedra of the $CaCu_5$-type around Ni1 atoms along the *Y* direction (Fig. 3). On the other hand, the structure can be considered as a stacking of fragments of simpler types, *i.e.* $CaCu_5$-type slabs and fragments of the CsCl-type. The composition of $PrNi_2In$ can be expressed by the following formula: 1PrIn (CsCl-type) + $1PrNi_4In$ ($CaCu_5$-type) = $Pr_2Ni_4In_2$ = $2PrNi_2In$.

It is interesting to compare the structure of $PrNi_2In$ with the structures of $CePd_2In$ [13] and $Sm_2Co_9In_3$ [14]. Fig. 4 shows the projections of these structures, in which it is possible to distinguish columns or layers of icosahedrons formed around the *d*-metal atoms.

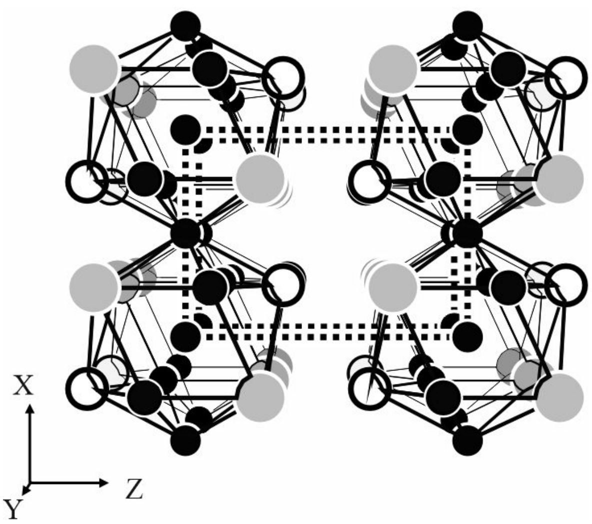


Fig. 3 Stacking columns of polyhedra around Ni1 atoms along the *Y* direction in the structure of $PrNi_2In$.

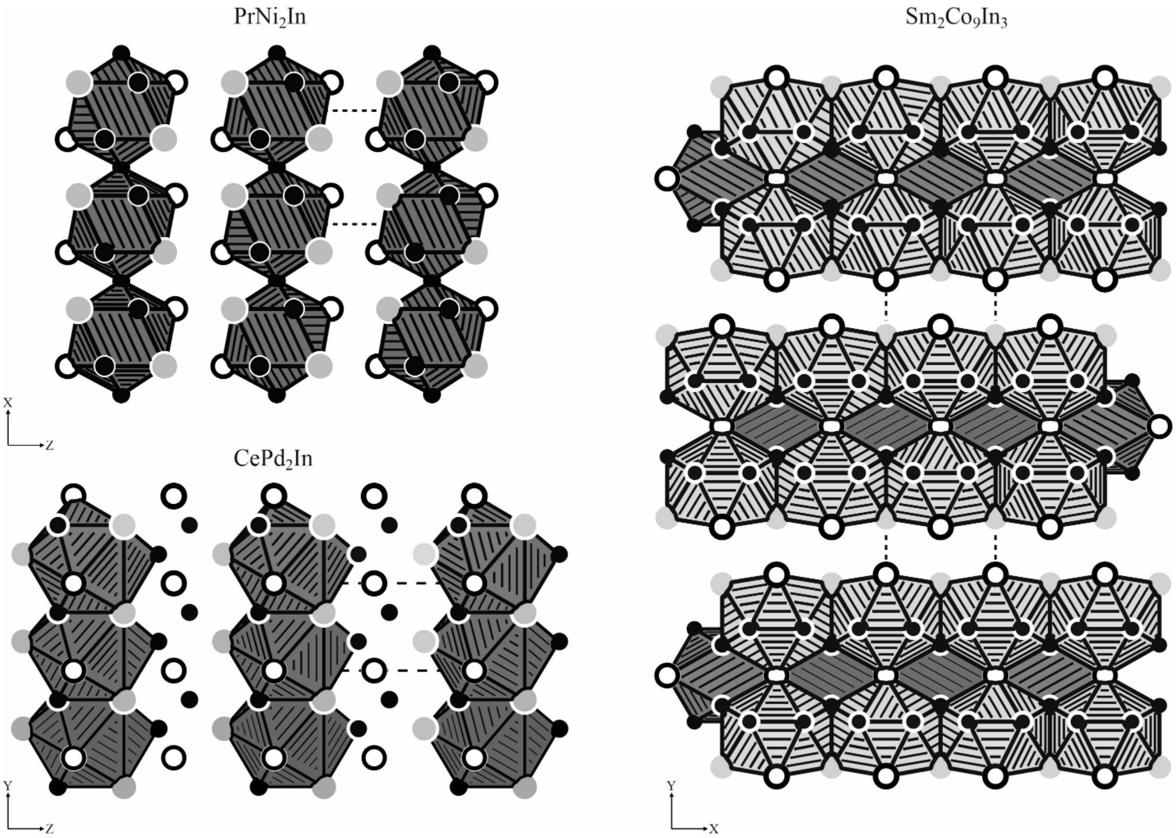


Fig. 4 Projections of the structures of $PrNi_2In$, $CePd_2In$ and $Sm_2Co_9In_3$. Praseodymium, cerium and samarium atoms are drawn as open circles; nickel, palladium and cobalt as black and indium as gray filled circles. The common distorted icosahedral slabs are emphasized.

Electronic structure calculations for $PrNi_2In$

Based on the results of the refinement of the crystal structure of $PrNi_2In$, electronic structure calculations were carried out using the TB–LMTO–ASA method (Tight-Binding Linear Muffin-Tin Orbital) [15-17]. Graphical images from the calculations were obtained using the wxDragon program [18]. Fig. 5 and 6 show the results of these calculations. The density of states (DOS) at the Fermi level indicates metallic type of interaction between the atoms (Fig. 5). The formation of the $PrNi_2In$ compound ensures the overlap of *d*-orbitals of nickel atoms with *p*-orbitals of indium and *f*-orbitals of praseodymium within the valence band, from -4 to -1 eV. The distribution of the electron localization function (ELF) indicates that the Pr atoms are positively polarized as the function of electronic localization tends to zero (Fig. 6a). In contrast, the maximum value of the function of electronic localization ($E = 0.779$ eV) is observed between In atoms (Fig. 6b), which indicates slight covalent In–In interaction. Significant delocalization of electrons around the nickel atoms is also observed.

The Hamilton populations and the interatomic distances confirm the dominance of metallic bonding and some minor partially covalent contributions between In atoms. The integrated crystal orbital Hamilton populations (-iCOHP) exhibit strong chemical bonding for In–Ni ($\delta = 2.656$ Å and -iCOHP = 1.404 eV) and In–In ($\delta = 3.410$ Å and -iCOHP = 0.804 eV). The Pr–Ni and Pr–In interactions are much weaker and their magnitudes are -iCOHP = 0.306 eV ($\delta = 2.763$ Å) and -iCOHP = 0.658 eV ($\delta = 3.353$ Å), respectively.

Conclusions

The structure of $PrNi_2In$, like that of $TbCo_2In$, belongs to the orthorhombic structure type $PrCo_2Ga$. The In atoms occupy the Co1 position (2*f*) in the $PrCo_2Ga$ structure and are characterized by CN12, which corresponds to a coordination polyhedron derived from a cube, which is more characteristic of indium atoms. Therefore, the refined structure $PrNi_2In$ can be considered an anti-type to the parent structure $PrCo_2Ga$. The analysis of the interatomic distances and quantum mechanical calculations indicate the dominance of metallic bonding and some minor partially covalent contributions between In atom.

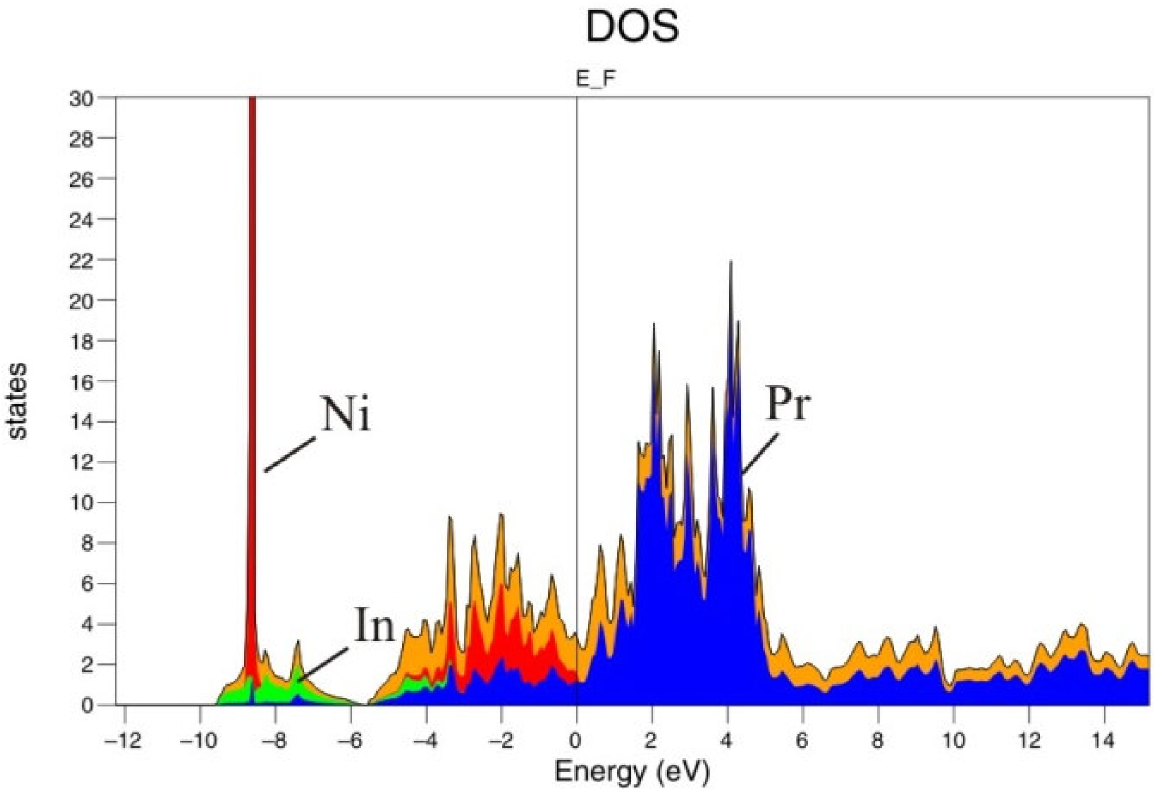
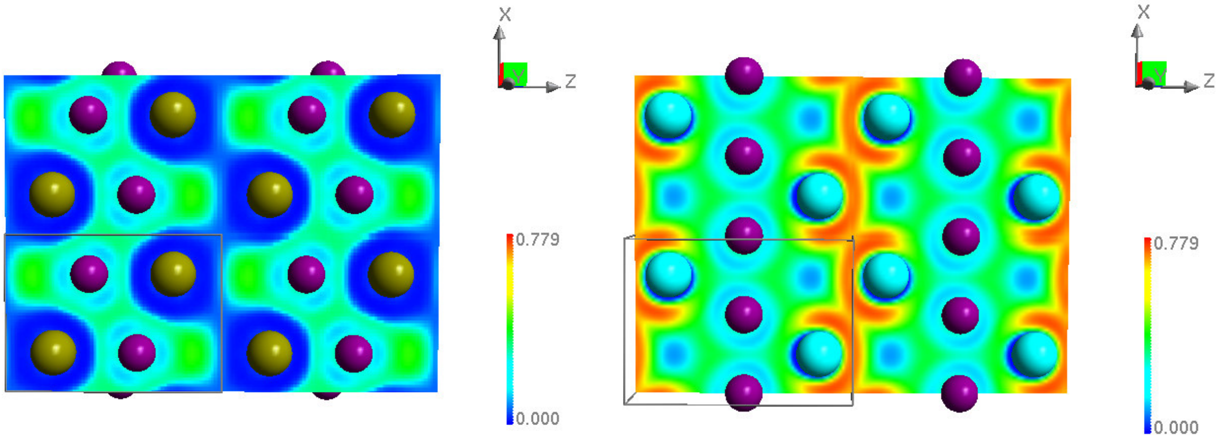


Fig. 5 Density of states (DOS) for $PrNi_2In$ with the contribution of Pr, Ni and In, respectively. The Fermi level (E_F) is represented by a thin line.



a *b*

Fig. 6 Electron localization function (ELF) for $PrNi_2In$ at $y = 0$ (*a*) and $y = 1/2$ (*b*).

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