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## Ab Initio Investigation of the Spin-Reorientation Phase Transition in $\text{PrCo}_{5-x}\text{Ni}_x$ ( $x = 0-5$ )

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*The series  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x = 0-5$ ) was investigated within the LDA+U+SO method taking into account strong correlations and spin-orbit coupling in Pr-4f, as well as in Ni(Co)-3d states. We give a detailed description of total energies, electronic structure and magnetic moments directions and values for all ions and concentrations considered. It was obtained that the system pass through a continuous spin transition from planar ab to the c axis directions of the Pr ion in agreement with experiments.*

*Keywords: strong correlations, LDA+U+SO, spin transition, electronic structure.*

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Physical properties of intermetallic compounds of the series  $\text{RNi}_5$ , where R is a rare-earth metal, are well-known to be significantly transformed by substitutional d or p metals due to some changes in the electronic structure, exchange interactions and crystalline field [1]. In some cases, impurities and substitutions can induce changes of electronic, magnetic and crystal parameters that improve functional properties of these alloys. This gives the possibility of their practical application using, e.g., magnetocaloric effect [2], hydrogen storage [3] and other applications. Anomalous behavior of some physical characteristics of these compounds is related with the transformation of their electronic structure [4].

The concentration changes of the electronic and magnetic properties in the pseudobinary systems  $\text{PrNi}_{5-x}\text{Cu}_x$  [5] and  $\text{PrNi}_{5-x}\text{Co}_x$  [2] have been found to be substantial at the temperature and increase of the impurity ions concentration. The growth of the substitution ion concentration results in the non-monotonous behavior of spontaneous magnetic moment, magnetic susceptibility, Curie temperature, as well as structural and electronic parameters in this system. In the parent binary compound  $\text{PrNi}_5$  for all temperatures the total magnetic moment of the Pr ion is frozen. At the same time even small concentrations of Co or Cu in this compound give rise to the ferromagnetic state with the increase of the 3d band susceptibility and exchange interactions in the 3d subsystem.

In the  $\text{PrNi}_{5-x}\text{Co}_x$  system the Curie temperature has very high values and grows from 60 up to 540 K for the cobalt concentration range  $x=1.95\div 3$ . In  $\text{PrCo}_5$  magnetic moment is along the easy axis c, this trend remains for a slight substitution of cobalt by nickel ( $\text{PrCo}_4\text{Ni}$ ), continue at high concentrations of nickel  $\text{PrCo}_2\text{Ni}_3$  (in  $\text{PrCoNi}_4$  and  $\text{PrNi}_5$ ) were it is found in the plane ab, the intermediate case  $\text{PrCo}_3\text{Ni}_2$  can implement one of the both directions according to

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the temperature measurements. When the temperature rises, in  $\text{PrCo}_3\text{Ni}_2$  magnetic moment becomes directed along the  $c$  axis [6]. This combination of very high ordering temperatures and large magnetostriction in this system makes it promising for magnetic refrigerator applications [7].

The electronic structure calculations of  $\text{PrCo}_{5-x}\text{Ni}_x$  in this work were performed for the hexagonal crystal structure of the  $\text{CaCu}_5$ -type with spatial symmetry group  $\text{P6}/\text{mmm}$ . The parameters of the crystal lattice were taken as experimentally determined in [6]. The unit cell contains one  $\text{PrCo}_5$  formula unit with one atom of praseodymium in the crystallographic position (1a) (0, 0, 0). Transition metal atoms are located at the positions of two types: (2c) (1/3, 2/3, 0) and (3g) (1/2, 0, 1/2).

To account for the strong electron-electron interactions between the 4f-electron atoms Pr of approaching local electron spin density in the method used by  $\text{LDA}+\text{U}+\text{SO}$  [8]. The basis of the linearized muffin-tin orbitals used in this package together with the atomic sphere approximation, included 6s, 6p, 5d and 4f-state Pr and 4s, 4p and 3d-state Ni or Co. The radius of the sphere of nuclear power Pr was 3.7 a.u., and for the transition metal atoms in both positions (2c) and (3g) were 2.6 a.u. For Pr 4f-electron Coulomb interaction was taken into account the parameters of direct  $U = 6$  eV and exchange  $J = 0.6$  eV interactions for the 3d-shell of a transition metal  $U = 2$  eV and  $J = 0.9$  eV. In the calculations a ferromagnetic ordering was modeled in accordance with the experimental data for  $\text{PrCo}_{5-x}\text{Ni}_x$ .

In all compounds the magnetic moment of Pr was about  $2 \mu_B$ , at the Ni ions was  $0.3 \mu_B$  in alloys with cobalt. The magnetic moment of Co ions is oriented parallel to the one of Pr and is  $1.0\text{--}1.2 \mu_B$ . Then, substituting cobalt ions give rise to the total magnetic moment to  $4.2 \mu_B$  in  $\text{PrNi}_4\text{Co}$  and  $5.3 \mu_B$  in  $\text{PrNi}_3\text{Co}_2$ . The appearance of the magnetic moments of cobalt ions in the 3d-sublattice  $\text{PrNi}_5$  leads to the increase of exchange interactions that contributes to the increase in the Curie temperature. Figs. 1 and 2 show the total and partial electronic density of states of alloys  $\text{PrCo}_{5-x}\text{Ni}_x$ . Electronic state to about 6 eV below the Fermi level and 2 eV

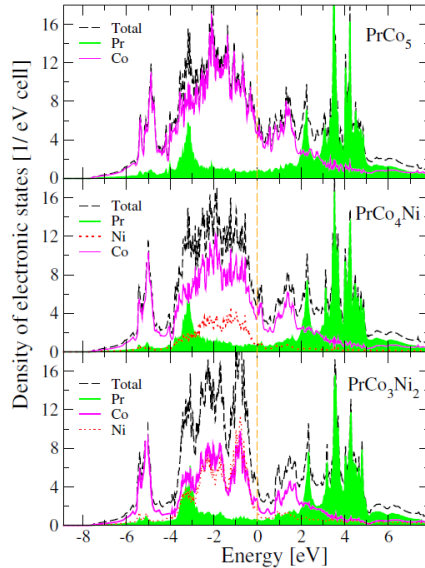


Fig. 1. The  $\text{LDA}+\text{U}+\text{SO}$  calculated densities of the electronic states of  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x = 0\text{--}2$ )

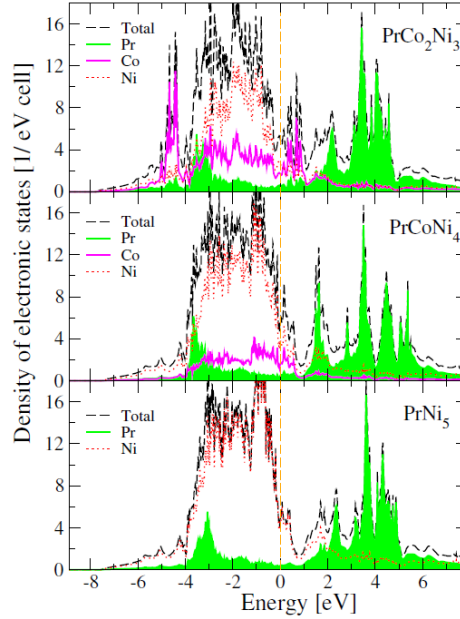


Fig. 2. The LDA+U+SO calculated densities of the electronic states of  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x = 3-5$ )

above it are mainly related to 3d-bands of Ni and Co, forming quite broad bands, that agree with optical measurements [9]. The shaded areas characterized by sharp peaks indicate the partial density of empty and filled 4f-states of the praseodymium, respectively located above (1–5 eV) and lower (3 eV) the Fermi level. Also the state of nickel and cobalt are given. The calculations resulted in the following direction of spin moments of the praseodymium ion characterized by the minimum of total energy: in  $\text{PrCo}_5$ ,  $\text{PrCo}_4\text{Ni}$  directed along the  $c$  axis or close to it for the low temperature structure (4.2 K), in  $\text{PrCo}_2\text{Ni}_3$ ,  $\text{PrCoNi}_4$ ,  $\text{PrNi}_5$  located in the  $ab$  plane with no  $c$  axis component. For pure  $\text{PrNi}_5$  the total energy difference between the  $ab$  and  $c$  directions of the Pr-4f spin moments gives the energy difference 30–80 meV depending on the structural parameters taken for 4.2–800 K experimental data. This concentration transition of spin moments gives the spin reorientation of the Pr-4f moment in the  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x = 0\div 5$ ) series.

In the present work the concentrational transition in the  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x\div 0-5$ ) system was investigated within the ab initio band method LDA+U+SO, which takes into account strong Coulomb correlations in the 4f-subshell and their spin-orbit coupling, as well as in Ni (Co). The usage of this method allowed us to give a detailed description of total energies and moments directions for all ions and concentration considered. It was obtained that the system pass through a continuous spin-reorientation transition from planar  $ab$  to the  $c$  axis directions of the Pr ion as seen in available experiments. Our detailed analysis of the magnetic and spin moment dynamics in the Co concentration range from 0 to 5 revealed good agreement of the calculated and experimental data.

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## Неэмпирическое исследование спин-переориентационного фазового перехода в $\text{PrCo}_{5-x}\text{Ni}_x$ ( $x = 0-5$ )

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*Серия  $\text{PrCo}_{5-x}\text{Ni}_x$  ( $x = 0-5$ ) исследовалась в рамках метода  $\text{LDA}+U+SO$  с учетом сильных корреляций и спин-орбитальной связи в  $\text{Pr}4f$ , а также  $\text{Ni}(\text{Co})3d$  электронных состояниях. Приводится детальное описание полных энергий, электронной структуры и направлений и величин магнитных моментов всех ионов для рассмотренных концентраций. Обнаружено, что в системе происходит непрерывный спиновый переход на ионе Pr из плоскостного направления  $ab$  в направлении вдоль оси  $c$  в согласии с экспериментами.*

*Ключевые слова:* сильные корреляции,  $\text{LDA}+U+SO$ , спиновый переход, электронная структура.