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Antiferromagnetic-to-ferromagnetic transition in the $GdNiSi_{1-x}Al_x$ compound

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Ternary intermetallics RTX where R – a rare-earth metal and T, X – d or p-elements are being actively investigated because of many interesting properties, such as: giant and large magnetocaloric effect (MCE) and magnetoresistance, metamagnetic transitions, etc. [1, 2]. There are many RTX compounds with magnetic ordering temperatures near room temperature and above, some RNiSi are reported to have giant or large MCE [3]. The gadolinium-based GdTX are of particular interest not only due to MCE, but also due to the variety of structures and magnetic properties [4, 5]. It was found that doping most GdTX compounds can improve their magnetic and other properties [1, 6]. There are transitions that depend on changes in composition, for example, in $GdFe_{1-x}Ni_xSi$ [7]. Recently, the Al-doped $GdNiSi_{1-x}Al_x$ system was first synthesized and experimentally studied in order to improve its magnetocaloric properties, it was found to almost double the values of the relative cooling power for $x = 0.2$ [8].

In this work, the electronic structure and magnetic properties of $GdNiSi_{1-x}Al_x$ have been investigated within the framework of theoretical DFT + U method in Quantum ESPRESSO package [9]. Strong electron correlations in the Gd $4f$ shell were taken into account in the GGA + U approach for the Coulomb parameter as 6.7 eV and Hund parameter as 0.7 eV [1, 7]. The densities of states calculated for GdNiSi are shown in Fig. 1a, b. The total density of two Gd types forming the antiferromagnetic (AFM) ordering are plotted in fig. 1a with the most intense peaks from −8 to −7 eV and from 4.5 to 5.5 eV, symmetrically for both spin projections. Below the Fermi level, from −3 to 0 eV, there are highly intense, symmetrical peaks of the $3d$ states of nickel, indicated in orange.

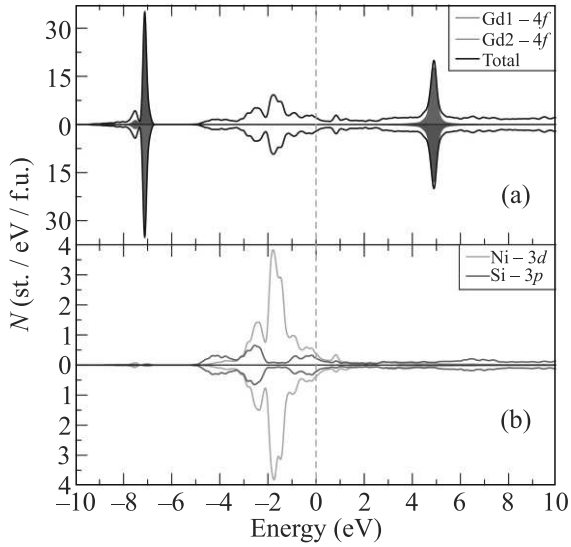

Fig. 1. (Color online) (a) – Total and (b) – partial densities of electronic states of GdNiSi. The Fermi energy is drawn as a vertical dashed orange line at zero energy

Structural data for our calculations were taken from [8]. GdNiSi crystallizes into orthorhombic structure $Pnma$, space group (SG) # 62 [8]. The cell volume decreases with the addition of aluminum, except for the high Al content which is most likely due to the presence of another impurity phase [8]. The distances between the nearest gadolinium atoms gradually decrease when modeling an increase in the concentration of aluminum in the system.

In our self-consistent DFT + U calculations, the theoretical total magnetic moment of $GdNiSi_{1-x}Al_x$ was found to be solely formed by the Gd ion, and Ni, Si, Al are either non-magnetic or have very small magnetic moments. Changing the doping parameters has little effect on the magnetic moments, and the total magnetic moment of all ferromagnetic (FM) compounds does not

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change. The calculations confirmed that GdNiSi has an AFM state in the Gd sublattice as its ground state. This AFM is more stable in GdNiSi than the FM one with the differences in total energy equal to 1.03 meV/f.u.

Doping of GdNiSi even with small amounts of Al dramatically changes the magnetic ordering type. It was found that, starting with the modelled $GdNiSi_{0.9}Al_{0.1}$ compound, the most energy-favorable ordering in the Gd sublattice becomes FM. We checked different types of the AFM orderings of the Gd moments. The energy difference in these cases ranges from 2.32 ($GdNiSi_{0.7}Al_{0.3}$) to 4.02 ($GdNiSi_{0.8}Al_{0.2}$) meV/f.u. From these results, it is possible to estimate the transition point for the Al concentration x equal to 0.024, i.e. 2.4 % Al.

As a result of replacing a small part of silicon atoms with aluminum, there is a decrease in the distances between Gd atoms and the lattice volume as a whole. The decrease of the Gd-Gd distance can be clearly traced for the next-nearest neighbors $d(\text{Gd1-Gd2})_{NNN}$ and $d(\text{Gd1-Gd1})_{NNN}$ for all $x = 0{-}0.3$ structural data. However, for the nearest neighbors $d(\text{Gd1-Gd2})_{NN}$ and the next-nearest neighbors $d(\text{Gd2-Gd2})_{NNN}$ are decreasing for $x = 0{-}0.2$, then grows for $x = 0.3$ which we discuss below. The changes of the Gd-Gd distances are accompanied by with exchange coupling changes. As it is well known, the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction oscillates with the distance [10] and dominates the exchange coupling between the Gd-Gd ions [11]. Then it can govern a transition from AFM to FM ordering for the Al-doped compounds, but the presence of Al is also significant for the AFM formation, as at $x = 0.3$, the FM ordering is preserved despite the increase of some Gd-Gd distances.

From the above theoretical data, an antiferromagnetic-to-ferromagnetic (AFM-FM) transition was found when GdNiSi is doped with Al in our theoretical calculations. The AFM-FM transition takes place in the Gd sublattice, the magnetic moments at the Gd ions remain the same but the type of magnetic ordering changes. It was found that even at concentrations as low as $x = 0.1$, the FM ordering in the Gd sublattice is more favorable in total energy as the ground state which can be ascribed to the shortening of Gd-Gd distances and the oscillating behavior of the RKKY interaction in the Al-doped compositions. The electronic structure demonstrates significant changes in the vicinity of the localized Gd $4f$ states that confirms the presence of the AFM-FM transition using our theoretical results for Al $x > 0.1$ in good agreement with the previous experimental magnetic results. The concentration-driven magnetic transition is promising for the Gd-based compounds and will motivate further research. Therefore, further study of their properties may be useful for various environmentally sustainable applications.

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Conflict of interest. The authors of this work declare that they have no conflicts of interest.

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