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Research articles

Magnetic properties of $HoCoC_2$, $HoNiC_2$ and their solid solutions

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ABSTRACT

Magnetic properties of single crystalline $HoCoC_2$ and the evolution of magnetic and structural features in a series of polycrystalline solid solutions $HoCo_{1-x}Ni_xC_2$ $(0 \leqslant x \leqslant 1)$ are investigated by means of X-ray diffraction, magnetization, magnetic susceptibility and specific heat measurements. The crystal structures of all investigated samples refers to the $CeNiC_2$-type structure (space group *Amm*2 and Pearson symbol oS8). Non-isoelectronic substitution of Co by Ni causes a non-linear increase of the unit cell volume and especially a non-monotonous variation of the *a* and *c* lattice parameters as well as a pronounced reduction of the C–C bond length of carbon dimers. Temperature dependent magnetization and specific heat measurements reveal a crossover from a ferromagnetic for $HoCoC_2$ with $T_C = 10.6(1)$ K to an antiferromagnetic ground state for $HoNiC_2$ with $T_N = 2.78(6)$ K and a non-monotonous variation of the magnetic ordering temperature with a minimum at intermediate compositions. Crystalline electric field effects of $HoCoC_2$ and $HoNiC_2$ are analysed using combined thermodynamic and magnetic susceptibility data. The electrical resistivity of $HoNiC_2$ displays a distinct anomaly near room temperature which indicates the formation of a charge density wave (CDW) state as earlier reported for several other rare earth nickel dicarbides.

1. Introduction

Carbide intermetallics containing rare earths and 3*d* transition metals attract enduring interest with respect to their large variety of 4*f*-3*d* magnetic states as well as with respect to charge density wave phenomena, especially in $RNiC_2$ [1,2], and unconventional superconductivity in $LaNiC_2$ [3,4]. Respective ternary dicarbides, RTC_2 with $R =$ rare earth and $T =$ Fe, Co, and Ni occur in two structure types. The iron and nickel containing rare earth carbide intermetallics, $RFeC_2$ ($R =$ Sm, Gd–Er, Lu) and $RNiC_2$ ($R =$ La–Lu), crystallize in the non-centrosymmetric orthorhombic $CeNiC_2$-type structure, space group *Amm*2 [5,6]. $RCoC_2$ compounds display two structure types. Those with light rare earths ($R =$ La–Sm) adopt the monoclinic $CeCoC_2$-type structure, space group *Bb* [6,7], while those with heavy rare-earths ($R =$ Gd–Lu) crystallize in the orthorhombic $CeNiC_2$-type structure. Both structure types are closely related to each other, i.e., the monoclinic type can be regarded as a distorted version of the orthorhombic one. Contrary to the $RFeC_2$ carbides, those with Co and Ni are remarkably stable in air.

The magnetic structures of $RCoC_2$ and $RNiC_2$ with $R =$ Pr, Nd, Tb–Tm have been extensively studied by powder neutron diffraction (PND). A survey of these results was compiled by Schäfer et al. [8]. The majority of $RCoC_2$ compounds adopt a ferromagnetic (FM) ground state at low temperatures, e.g. $HoCoC_2$ with a reported Curie temperature $T_C \simeq 9$ K [9], whereas $RNiC_2$ compounds show different types of antiferromagnetic (AFM) ground state configurations, e.g. $HoNiC_2$ adopts a two-component non-collinear AFM structure at a Néel temperature reported as $T_N \sim 4$ K [10]. In all $RCoC_2$ and $RNiC_2$ compounds magnetic order is essentially confined to the rare earth 4*f* moments while 3*d* moments remain negligible.

Our present interest lies in the crossover from FM to AFM ordering of the rare earth sublattice in quasi-binary systems $RCo_{1-x}Ni_xC_2$ as well as in the crystallographic peculiarities caused by non-isoelectronic substitution of Co by Ni. Recently, the crystal structure and evolution of magnetic properties in the solid solution series $DyCo_{1-x}Ni_xC_2$ isotypic with orthorhombic $CeNiC_2$ have been reported [11]. In this series, the substitution of Co by Ni causes a remarkable deviation of the unit cell volume from Vegard's rule and a non-monotonous variation of the *a* and *c* lattice parameters with extrema at $x \sim 0.35$. A crossover from FM to AFM ordering is accompanied with a significant reduction of the magnetic ordering temperature at intermediate compositions near $DyCo_{1/3}Ni_{2/3}C_2$.

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Here, we report on crystallographic characteristics and on magnetic properties of the series $HoCo_{1-x}Ni_xC_2$ ($0 \leqslant x \leqslant 1$) as well as a single crystal study of $HoCoC_2$.

2. Material and methods

2.1. Synthesis

The polycrystalline samples $HoCo_{1-x}Ni_xC_2$ with compositions $x = 0$, 0.25, 0.50, 0.75, 1.0 have been prepared by arc melting with subsequent homogenization at 1070 K for one month using a procedure described earlier [11]. Commercially available elements, Ho sublimed bulk pieces (Alfa Aesar, 99.9 at.%), powders of electrolytic nickel and cobalt (Strem Chemicals, purity of 99.99 at.%) and graphite powder (Aldrich, 99.98 at.%), were used. Single crystalline $HoCoC_2$ has been grown from stoichiometric polycrystalline starting material via the Czochralski technique in a tetra-arc furnace from Techno Search Corp.

2.2. Diffraction and sample characterization

Powder X-ray diffraction (XRD) patterns for full profile refinements of the series $HoCo_{1-x}Ni_xC_2$ were collected on a STOE STADI P powder diffractometer with monochromated Cu-$K_{\alpha1}$ radiation ($10^\circ \leqslant 2\Theta \leqslant 100^\circ$, step size 0.05°) to check the samples homogeneity. For precise lattice parameters refinements the data were collected at room temperature on a Siemens D5000 powder diffractometer with graphite monochromated Cu-K_α radiation ($20^\circ \leqslant 2\Theta \leqslant 120^\circ$, step size 0.02°) a powder of germanium (99.9999%, $a_{Ge} = 5.657905$ Å) served as internal standard. All polycrystalline samples $HoCo_{1-x}Ni_xC_2$ were examined using energy dispersive X-ray spectroscopy analysis with a scanning electron microscope REMMA-102–02, whereby only Ho, Ni and Co concentrations were examined.

Czochralski grown, single crystalline $HoCoC_2$ was oriented by means of a standard Laue technique and cut accordingly into a set of three bar shape single crystals with their longest edges oriented parallel to the principal *a*, *b* and *c* axis directions, with masses of 10 to 20 mg. Another crystal was cut in approximately cubic shape with a mass near 70 mg.

2.3. Low temperature physical properties

Specific heat measurements on polycrystalline samples of about 1 g were performed by means of a home-made adiabatic step heating technique at temperatures ranging from 2 K to 140 K and in magnetic fields up to 2 T (see Ref. [12] for details of the set-up). Additional specific heat measurements based on relaxation-type technique were carried out with a Quantum Design PPMS for a $HoCoC_2$ single crystal oriented with *a*-axis parallel to the externally applied field (2 – 200 K and 0 to 5 T). Single crystal and polycrystal specific heat data of $HoCoC_2$ are essentially matching, just the adiabatic measurement of the polycrystalline sample provides a much higher resolution in the temperature steps. For $HoNiC_2$ additional zero-field heat capacity data down to 0.4 K were collected using a PPMS ^{3}He heat capacity inset. Temperature and field dependent magnetic measurements were carried out on a CRYOGENIC SQUID magnetometer with a temperature range from 3 K to room temperature applying static magnetic fields up to 6 T. Additional field dependent isothermal magnetization measurement at 2 K and fields up to 9 T were performed for $HoCoC_2$ single crystals with principal crystallographic orientations parallel to the applied field using a PPMS vibrating sample magnetometer. Temperature dependent resistivity measurements for polycrystalline $HoNiC_2$ were performed using a Quantum Design PPMS set-up in a temperature range from 2 – 360 K. All other samples of the series $HoCo_{1-x}Ni_xC_2$ including a $HoCoC_2$ single crystal (current parallel to the orthorhombic *a* axis) were measured in a home-made set-up in the temperature range from 4.2 K to room temperature. All resistivity measurements were conducted with a four-point ac measuring technique on bar shape samples with spot welded gold contacts.

3. Results and discussion

3.1. Structural characterization

XRD data of the $HoCo_{1-x}Ni_xC_2$ series were indexed in the $CeNiC_2$ structure type, space group *Amm*2, thus, confirming a continuous solid solubility between $HoCoC_2$ and $HoNiC_2$. Refined cell parameters of the series are summarized in Table 1. The present results of $HoCoC_2$ and $HoNiC_2$ are in good agreement with earlier reported data in Ref. [6].

The unit cell parameters of pseudo-ternary series $HoCo_{1-x}Ni_xC_2$ are displayed in Fig. 1. The unit cell volume increases with increasing Ni content with a negative deviation from Vegard's rule, as it was observed for the related series $DyCo_{1-x}Ni_xC_2$ [11]. Again, a non-linear variation of the *a* and *c* lattice parameters is observed which may result from the non-isoelectronic substitution of Co by Ni where one extra electron is progressively added in the series $HoCo_{1-x}Ni_xC_2$. The latter may also be responsible for a systematic reduction of the C–C bond length which is indicated by the present XRD results. The C–C interatomic distances of $HoCoC_2$ and $HoNiC_2$ have, of course, been determined more accurately via earlier PND studies [9,10] yielding 1.422 Å and 1.373 Å, respectively, thus, indicating a change of the bonding character of C–C dimers by Co/Ni substitution. Reference values of single and double C–C bond lengths are e.g. 1.54 Å in diamond and 1.34 Å in alkene, respectively. This indicates some change of the electronic structure due to Co/Ni substitution in the series $HoCo_{1-x}Ni_xC_2$.

3.2. Specific heat and magnetic susceptibility of the solid solution series $HoCo_{1-x}Ni_xC_2$

The evolution of magnetic ordering temperatures in the solid solution $HoCo_{1-x}Ni_xC_2$ is revealed by the specific heat results depicted in Fig. 2. The magnetic phase transition temperatures determined from the magnetic specific heat anomalies display a

Table 1
Room temperature lattice parameters of solid solutions $HoCo_{1-x}Ni_xC_2$ as labeled. Structure type $CeNiC_2$, space group *Amm*2.

x(Ni)	Lattice parameters (Å)			V (Å^3)
	a	*b*	*c*	
0.00	3.5156(1)	4.5087(1)	6.0262(1)	95.5197(3)
0.25	3.5098(2)	4.5076(2)	6.0424(2)	95.5954(6)
0.50	3.5149(1)	4.5063(2)	6.0447(2)	95.7432(5)
0.75	3.5287(2)	4.5054(2)	6.0340(2)	95.9298(6)
1.00	3.5465(1)	4.5003(2)	6.0285(1)	96.2157(4)