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Chromium sublattice magnetic ordering in a compound of the $ThCr_2Si_2$ type structure: $HoCr_2Si_2$

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Abstract

A neutron diffraction investigation of the intermetallic compound $HoCr_2Si_2$ has been carried out over the temperature range 1.7–470 K. The data clearly demonstrate that the Cr sublattice in this compound is ordered for the whole range of temperatures investigated. Chromium atoms at *4d* sites are aligned anti-parallel along the *c* axis. The refined value of the ordered Cr moment is 1.48(4) μ_B at 293 K and 1.60(4) μ_B at 25 K. The magnetic space group is $I4'/m'm'm$, with G_Z^- Mn magnetic modes at *4d* sites. The Ho and Cr sublattices order independently, with Ho moments at *2a* sites ordering below 1.7 K.

Keywords: Magnetic neutron powder diffraction; Magnetic structure; RCr_2Si_2 intermetallic compounds

I. introduction

Rare earth intermetallics which crystallize in the tetragonal $ThCr_2Si_2$ structure (space group $I4/mmm$) display an enormous variety of magnetic structures [1]. Compounds of the type RMn_2Si_2 have been of particular interest, since numerous neutron diffraction investigations clearly prove that the Mn sublattice orders anti-ferromagnetically below 500 K [2]. In contrast, RT_2Si_2 compounds (with T = Fe, Ni, Co) are classified as weak Pauli paramagnets, since the T sublattice does not order. Magnetization data reported for the series RCr_2Si_2 (R = Gd, Tb, Dy, Ho, Er and Tm) [3] indicate that the R ions in this series order at very low temperatures and that the ordering temperatures scale approximately with the de Gennes factor. Self-consistent band structure calculations of the valence electron contribution to the EFG (electric field gradient) and experimental determinations of the EFG for the series show that the 2nd order crystal field coefficient A_2° changes sign when passing from RCr_2Si_2, RFe_2Si_2, RNi_2Si_2 ($A_2^\circ > 0$) to RCu_2Si_2 compounds ($A_2^\circ < 0$) [4,5]. The CF interaction, which is generated by a square prism of eight X atoms and eight almost equidistant T atoms, is an important source of these magnetic phenomena. Since these two types of atoms can present a large variation in their electronic properties, an equally large variation in their magnetic properties can be expected. An inelastic neutron scattering investigation of the crystal field interaction in $HoCr_2Si_2$ has confirmed the sign change in RCr_2Si_2 compounds [6].

Magnetization measurements on the mixed series $RFe_{2-x}Cr_xSi_2$ [7] have indicated the presence of anti-ferromagnetic interactions for Cr rich compounds with ordering temperatures up to 700 K, whilst low ordering temperatures were observed for Fe rich compounds. Up until now, no definitive neutron diffraction studies have been reported for the pure series RCr_2Si_2. Evidence of a magnetic moment on the transition metal sublattice in the Cr rich series $RFe_{2-x}Cr_xSi_2$ has been recently reported [8]. During the course of a neutron diffraction investigation of the low temperature magnetic structure of the Ho sublattice in $HoCr_2Si_2$, clear evidence of a magnetic ordering of the Cr sublattice in this compound has emerged. In this paper, the details of this investigation, performed in the temperature range 1.7–470 K, are reported. The Cr sublattice is shown to order anti-ferromagnetically, whilst the Ho sublattice is observed to order independently of the Cr sublattice, with Ho atoms ordering anti-ferromagnetically below 1.7 K.

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2. Experimental

A sample of $HoCr_2Si_2$ was prepared by arc melting starting materials of at least 3N purity. The resulting ingot was then wrapped in Ta foil, sealed into an evacuated quartz tube and annealed for several weeks at 700°C. X-ray diffraction measurements showed that the sample was single phase, characteristic of a material that crystallizes in the tetragonal $ThCr_2Si_2$ structure (space group I_4/mmm). Neutron powder diffraction measurements were performed on the multi detector powder diffractometer E9 located at the BER II reactor, Berlin Neutron Scattering Centre, Hahn Meitner Institute, Germany. Data were collected in a temperature range from 1.7 to 470 K. The angular range of 2θ was from 5 to 158° using an incident neutron wavelength of 1.79636 Å. Approximately 25 g of material was used in the experiment.

3. Results and discussion

Inspection of the measured diffraction patterns indicated that the intensities of peaks such as (101), (103) and (211) are different than those expected for the $ThCr_2Si_2$ structure, with Ho and Cr atoms at special positions *2a*, and *4d*, respectively, whilst Si atoms reside at *4e–(00z)* sites, with $z \sim 0.38$. The (101) reflection in particular has a very small calculated nuclear structure factor. The observed intensity of the (101) peak is much greater than that calculated for only a nuclear contribution. In the temperature range 1.7–470 K the (101) peak intensity is observed to decrease by a factor of 30%, a decrease which cannot be simply accounted for by the isotropic Debye Waller factor alone (Fig. 1). The origins of this peak and others such as (103) and (211) are clearly magnetic. The occurrence of magnetic intensity in such peaks, with the reflection condition $h + k = 2n + 1$ satisfies the conditions for an anti-C translation mode, with Cr atoms at positions (0, 1/2, 1/4) and (1/2, 0, 1/4) having magnetic moments pointing in the opposite direction to each other. An analysis of the intensity ratio for (101) and (103) peaks indicates that Cr moments are aligned along the c axis, rather than lying in the (001) plane. With this model of the magnetic structure, the neutron diffraction data reported here were analysed by the Rietveld technique [9], using the FULLPROF package for refinement of crystal and magnetic structure by constant wavelength neutron powder diffraction [10]. The magnetic form factor for metallic Cr was employed in the profile refinement. Neutron nuclear scattering lengths of $b_{Ho} = 0.249 \times 10^{-12}$ cm, $b_{Cr} = 0.775 \times 10^{-12}$ cm and $b_{Si} = 0.458 \times 10^{-12}$ cm were utilized. Parameters that were varied during the initial stage of the refinement included a scale factor, tetragonal lattice parameters and the positional parameter z for the Si atom. In the final stages of the refinement, an overall isotropic Debye Waller parameter for Ho, Cr and Si as well as the Cr magnetic moment were varied. The observed and calculated diffraction pattern at 25 K is displayed in Fig. 2. Refined magnetic and structural parameters, in the temperature range 25–293 K are collected together in Table 1. A large anisotropic line broadening is observed in peaks such as (112) and (118), but the overall R factors are very satisfactory. The diffraction pattern measured at 1.7 K showed a clear build up of diffuse magnetic intensity centered at scattering angles of approximately 7 and 23°. This indicates the onset of magnetic ordering of the Ho sublattice, which takes place independently of the Cr sublattice. The Ho sublattice is hence only fully ordered at a temperature well below 1.7 K.

The Nèel point for this compound most likely lies in the range 580–600 K. Further neutron diffraction measurements in the temperature range 500–700 K are presently underway and will be reported elsewhere. The model for the magnetic structure of the Cr sublattice possesses a $I4'/m'm'm$ magnetic space group, with Cr moments

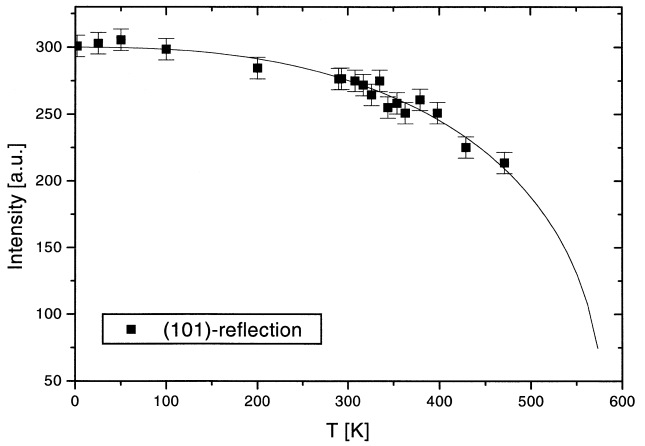

Fig. 1. Temperature dependence of integrated intensities of the (101) reflection in $HoCr_2Si_2$.

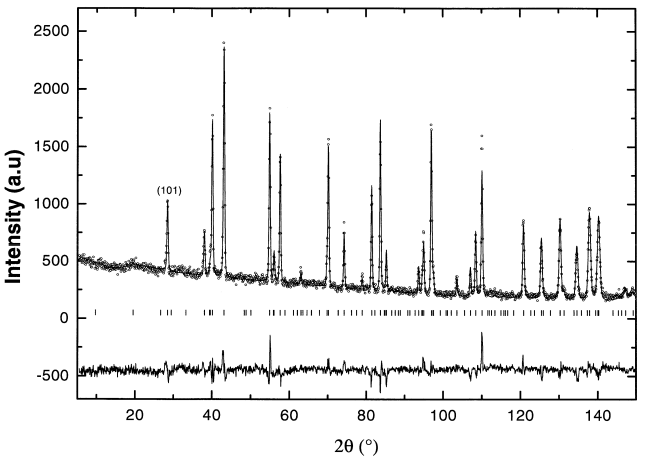

Fig. 2. Observed, calculated and difference neutron diffraction pattern for $HoCr_2Si_2$, measured at 25 K. Tickmarks indicate calculated peak positions.

Table 1
Results of Rietveld profile refinements of neutron diffraction data for $HoCr_2Si_2$[a]

	25 K	50 K	100 K	180 K	293 K
a (Å)	3.89306(3)	3.89284(5)	3.89305(3)	3.89467(3)	3.89662(3)
c (Å)	10.6054(1)	10.6076(2)	10.6105(2)	10.6179(2)	10.6290(2)
z/c, Si (*4e*)	0.3861(3)	0.3859(3)	0.3854(3)	0.3852(3)	0.3850(3)
B_{ov} (Å^2)	0.10(4)	0.13(4)	0.20(4)	0.25(4)	0.31(4)
μ_B, Cr	1.60(4)	1.60(4)	1.60(4)	1.53(4)	1.48(4)
R_{wp} (%)	8.31	8.47	8.61	9.11	8.97
R_{exp} (%)	5.23	5.24	5.24	5.23	5.26
χ^2	2.53	2.61	2.70	3.04	2.91

[a] Errors refer to estimated standard deviations calculated by the Rietveld refinement code (a typical detection limit of μ_B for neutron powder diffraction is $\pm 0.15\ \mu_B$). Observed and calculated neutron intensities and structure factors are available on request from the authors.

aligned along the tetragonal c axis. A G magnetic mode corresponds to a $(+-+-)$ sequence of moment orientations within (001) Cr planes and hence for $HoCr_2Si_2$ the Cr magnetic modes, as determined in the present investigation, are G_z^- with the superscript denoting the anti-C relation and z the ordering direction, which is along [001]. This magnetic structure is displayed in Fig. 3. The magnetic ordering of the Cr sublattice in these compounds has remained, until now, undetected in previously reported magnetization measurements.

In RMn_2Si_2 compounds, an antiferromagnetic coupling within (001) Mn planes is observed when interlayer Mn–Mn distances are greater than a critical distance of about 2.87 Å. The corresponding Cr–Cr interlayer distance in $HoCr_2Si_2$ is smaller, about 2.75 Å. Electronic band structure calculations of RT_2X_2 compounds, for T=Mn, Fe, Ni and Co are in overall agreement with experimentally observed magnetic phenomena for these compounds. Compounds with T=Mn obey the Stoner criterion for magnetic ordering, whilst compounds with, for example T=Co, do not fulfil the Stoner criteria [11]. In the light of the results presented here, it would be of utmost interest to extend such calculations to compounds of the series RCr_2Si_2. Neutron diffraction measurements on $LaCr_2Si_2$ and YCr_2Si_2 compounds would also appear to be of interest, in order to check if competing antiferromagnetic and ferromagnetic interactions, which are extremely sensitive to the interlayer T–T distance, similar to those in $LaMn_2Si_2$ and YMn_2Si_2 compounds, also extend to compounds with T=Cr.

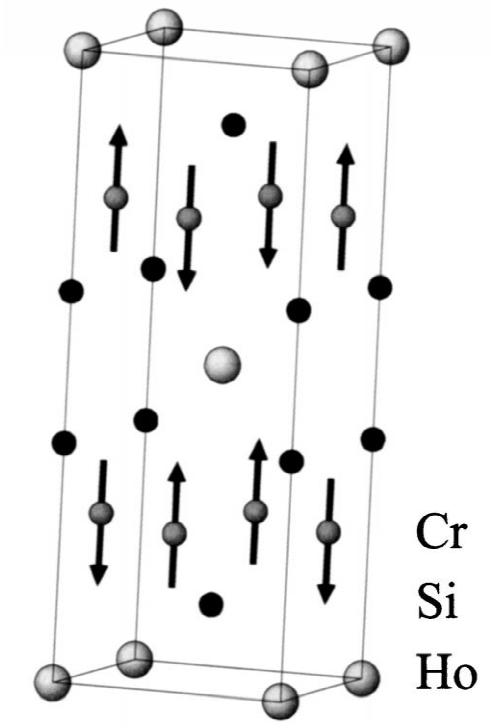

Fig. 3. Schematic of the crystal and magnetic structure of $HoCr_2Si_2$ (magnetic space group $I4'/m'm'm$).

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