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Magnetic ordering in HoNiAl-single crystal study

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Abstract

We present a single-crystal study of the magnetic behaviour in HoNiAl. It orders magnetically below $T_{\mathrm{ord}}=13$ K and undergoes an additional magnetic phase transition at $T_1=5$ K. Below T_1, holmium moments create a canted magnetic structure which consists of a ferromagnetic component along the *c*-axis and an antiferromagnetic component within the basal plane. Between T_1 and $T_{\mathrm{ord},}$ the magnetic structure in HoNiAl is, in the case of our sample, a simple ferromagnet with holmium moments aligned along the *c*-axis, what is considerably different from the previous polycrystalline data. The magnetocrystalline anisotropy in HoNiAl is very weak.

Keywords: Rare-earth intermetallic compounds; Magnetic properties; Neutron diffraction

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1. Introduction

HoNiAl belongs to a large group of the *RTX* intermetallic compounds (*R*=rare earth, *T*=transition metal, *X*=p-metal) crystallizing in the ZrNiAl-type hexagonal structure (space group *P*-62 *m*). It orders magnetically below $T_{\mathrm{ord}}=13$ K and undergoes an additional magnetic phase transition at $T_1=5$ K. Let us denote the magnetic phase below T_1 as the low-temperature (LT) phase and the phase between T_1 and T_{ord} as the high-temperature (HT) phase. As inferred from neutron powder diffraction [1,2], the magnetic structure of HoNiAl consists of two components: a ferromagnetic one (μ_{F}) oriented along the *c*-axis in both magnetic phases, and an antiferromagnetic one (μ_{AF}), described by a propagation vector $\boldsymbol{k}=(^1/_2, 0, ^1/_2)$. In the LT phase, μ_{AF} lies within the basal plane, what leads to a canted magnetic structure, similar as in several other isostructural compounds, e.g. DyNiAl [3] or DyPdIn [4]. The direction of μ_{AF} in the HT phase is controversial: two independent powder diffraction experiments reveal considerably different results. μ_{AF} lying within the basal plane is proposed in Ref. [2]. Its magnitude increases continuously with decreasing temperature and it is considerably reduced on one third of the Ho-sites. It results in a canted magnetic structure as in the LT phase, although the spin arrangement is somewhat different. On the contrary, μ_{AF} oriented along the *c*-axis, i.e. parallel to μ_{F}, is concluded in Ref. [1]. Its magnitude on one third of the Ho-sites is also considerably reduced. This leads to a complex amplitude modulated magnetic structure. The observed temperature dependence of μ_{AF} is also completely different. It increases by decreasing temperature below T_{ord}, reaching a maximum around 9 K and then diminish to nearly vanish at T_1. In order to solve this disagreement, we have performed a neutron diffraction study on HoNiAl single crystal. We present also the results of magnetization, specific heat and electrical resistivity measurements on HoNiAl single crystal.

2. Experimental

The HoNiAl single crystal has been grown by the Czochralsky method in a tetra-arc furnace from the stoichiometric melt of the constituent elements (purity 4 N for Ho, 5 N for Ni and 6 N for Al). The final single-grain crystal had a cylindrical shape with a diameter of 3 mm and a length of≈40 mm.

Neutron diffraction experiment was performed on the D10 diffractometer at the Institute Laue-Langevin (ILL), Grenoble, at a wavelength $\lambda=1.25$ Å. The crystal used for the neutron diffraction had a size≈1×2×3 mm. All the reflections were measured as ω-scans. Program MXD [5] was used for the refinement of the nuclear and magnetic structures. The scattering factors and absorption cross

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sections tabulated in [6] and the magnetic form factor of Ho^{3+} ions given in [7] have been used in the analysis.

The X-ray powder diffraction has been done on a powdered piece of single crystal with a conventional diffractometer working with the Bragg–Brentano geometry. The radiation of a Cu tube was filtered by a nickel filter, thus the whole doublet $K\alpha_1$, $K\alpha_2$ (with the wavelengths 1.54051 Å and 1.54433 Å) was used for the experiment. Due to the small amount of the sample, the powder was put on glass. Although no reduction of diffracted intensity at low diffraction angles was observed (due to the surface roughness), the use of a glass sample holder (thin specimen) can be a reason for overestimating the calculated temperature factors.

Magnetization was measured using a SQUID-magnetometer and the PPMS-14 system (Quantum Design, installed in the Joint Laboratory for Magnetic Studies in Prague) on ≈7 mg samples oriented along the specific directions in the temperature range 2 to 300 K, in magnetic fields up to 6 T.

Electrical resistivity measurement was performed using a standard four-probe ac-method, specific heat measurements were carried out on≈80 mg sample using a quasi-adiabatic step heating technique in the temperature range 2 to 70 K.

3. Results and discussion

The ZrNiAl-type structure consists of two types of layer at $z=0$ and ${}^1/_2$ with the following atomic positions:

3 Ho in 3(g): $(x, 0, {}^1/_2), (0, x, {}^1/_2), (\bar{x}, \bar{x}, {}^1/_2)$

3 Al in 3(f): $(y, 0, 0), (0, y, 0), (\bar{y}, \bar{y}, 0)$

2 Ni in 2(c): $({}^1/_3, {}^2/_3, 0), ({}^2/_3, {}^1/_3, 0)$; (*Ni II*)

1 Ni in 1(b): $(0, 0, {}^1/_2)$; (*Ni I*)

The results of the crystal structure refinement are summarised in Table 1. The determined lattice parameters are in a good agreement with the previously reported data [8]. The site parameter of Ho is very close to the value of $x_{Ho}=0.583(1)$ reported in Ref. [2], and somewhat differs from $x_{Ho}=0.575(1)$ obtained in Ref. [1]. The site parameter of Al determined in this work and both values obtained from the two neutron powder diffraction experiments ($x_{Al}=0.242(4)$ [1], $x_{Al}=0.238(2)$ [2]) are all almost the same.

Table 1
Results of the crystal structure refinement

	X-ray diffraction $T=300$ K	Neutron diffraction $T=25$ K
a (Å)	6.9896(14)	–
c (Å)	3.8261(5)	–
x_{Ho}	0.580(1)	0.5824(3)
x_{Al}	0.232(5)	0.238(1)
B_{Ho} (Å^2)	2.0(2)	0.00(3)
$B_{Ni\ I}$ (Å^2)	3.5(8)	0.18(6)
$B_{Ni\ II}$ (Å^2)	2.3(7)	0.18(6)
B_{Al} (Å^2)	1.9(8)	0.02(3)
	$R_{Bragg}=16.5\%$	$R_{LSQ}=5.8\%$

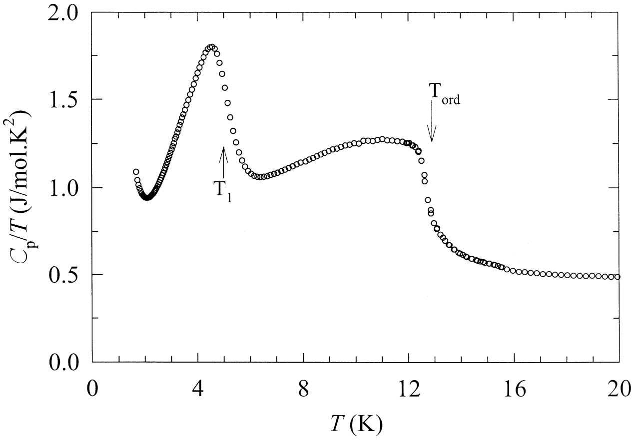

Fig. 1. Specific heat of HoNiAl single crystal.

The specific heat data (see Fig. 1) show well pronounced anomalies at the two magnetic phase transitions at $T_{ord}=13$ K and $T_1=5$ K. Only the ordering temperature, T_{ord}, is reflected in the resistivity data shown in Fig. 2.

Both phase transitions are clearly seen also in the magnetization data represented in Fig. 3. When the magnetic field is applied along the c-axis, magnetization rapidly increases at T_{ord}, and shows a small effect at T_1. In the case of $\boldsymbol{H}$ perpendicular to the c-axis, slight increase at T_{ord} and well pronounced maximum at T_1 are observed. The maximum at T_1 shifts to lower temperatures when increasing the field up to 1 T, and disappears for higher fields. The transition at 14.5 K, observed in Ref. [2] and

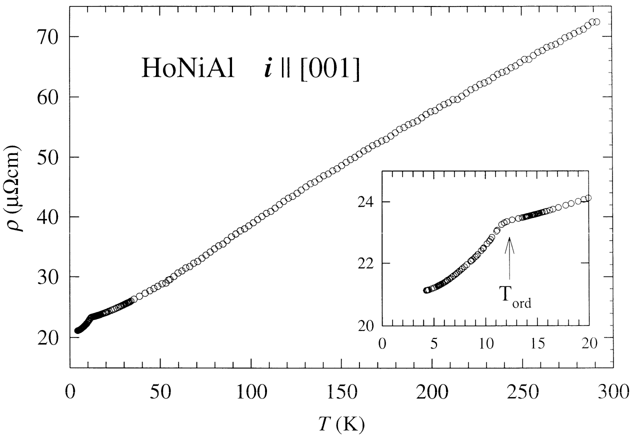

Fig. 2. Temperature dependence of the electrical resistivity of HoNiAl single crystal.

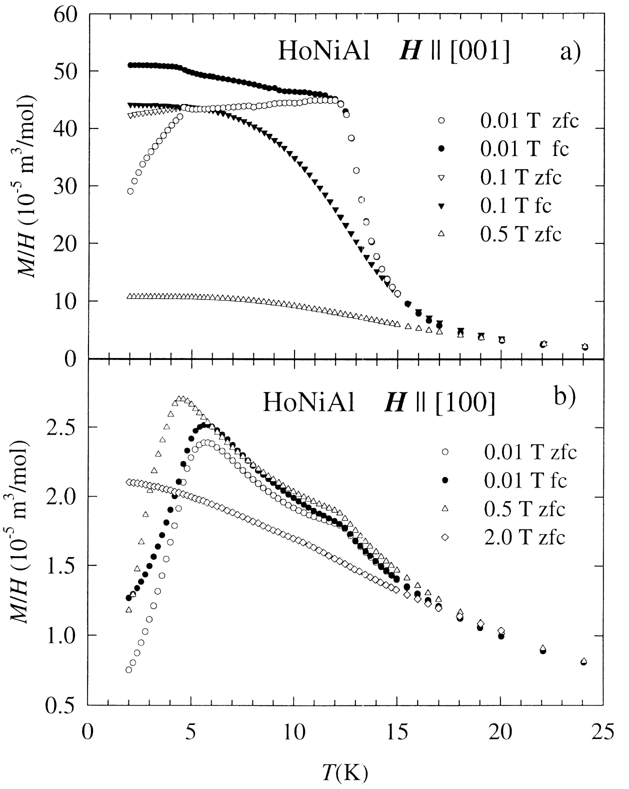

Fig. 3. Temperature dependence of the magnetization in magnetic fields applied along the *c*-(a) and *a*-axis (b); fc and zfc denotes field cooled and zero-field cooled data, respectively.

interpreted as the temperature at which the ferromagnetic component starts to order, is not confirmed by our data. The observed $M(T)$ dependencies, very similar to the single-crystal data reported for the isostructural DyPdIn [9], indicate that the *c*-component of the Ho moment orders ferromagnetically at T_{ord}, while the basal plane component orders antiferromagnetically at T_1.

The magnetization curves measured in fields applied along the *c*-axis show behaviour typical for a ferromagnetic order (see Fig. 4). We do not observe any metamagnetic transition in the HT phase which could be expected assuming magnetic structure proposed in Ref. [1] (μ_{AF} along *c*). When applying the field perpendicular to the *c*-axis (see Fig. 5), a metamagnetic transition is observed around 0.6 T at 2 K. It means that the antiferromagnetic order of the basal-plane component is broken above 1 T, what is consistent with the M vs. T data. No such clear metamagnetic transition occurs at higher temperatures (a small change of the slope around 1 T can be seen perhaps for 4 and 7 K) which one would expect assuming the antiferromagnetic order of the basal-plane component in the HT phase, as proposed in Ref. [2]. Our magnetization data thus do not support neither of the models of the magnetic structure in the HT phase derived from powder neutron diffraction data [1,2].

Above 20 K, the inverse susceptibility (see Fig. 6) can

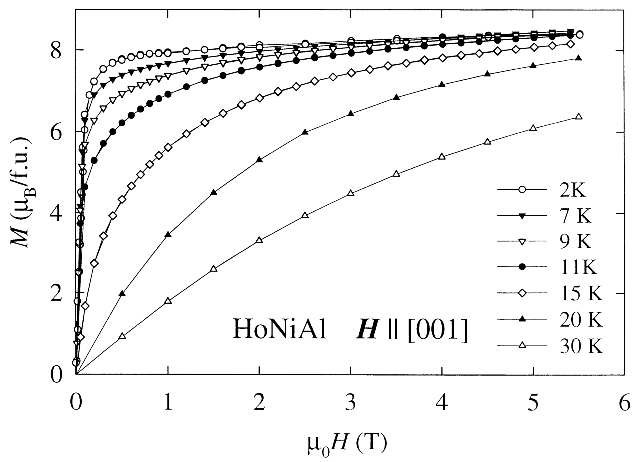

Fig. 4. Magnetization curves at different temperatures for the field applied along the *c*-axis.

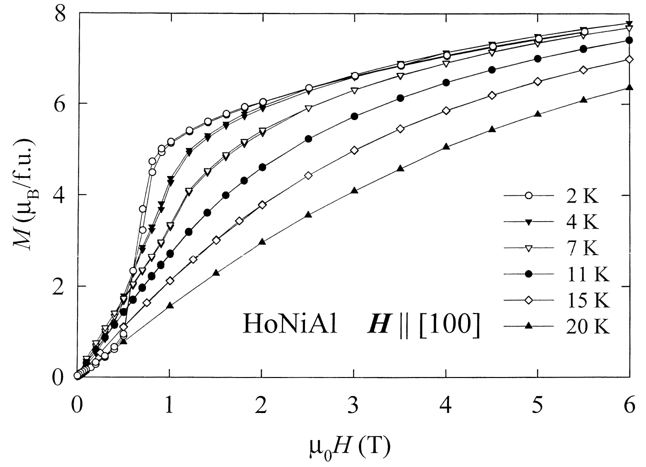

Fig. 5. Magnetization curves at different temperatures for the field applied along the *a*-axis.

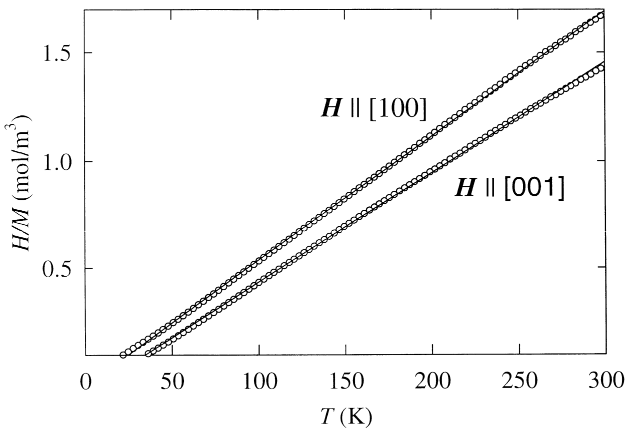

Fig. 6. Inverse magnetic susceptibility measured in field of 1 T applied along the *a*- and *c*-axis; the full line is fit to Curie–Weiss law using parameters given in text.

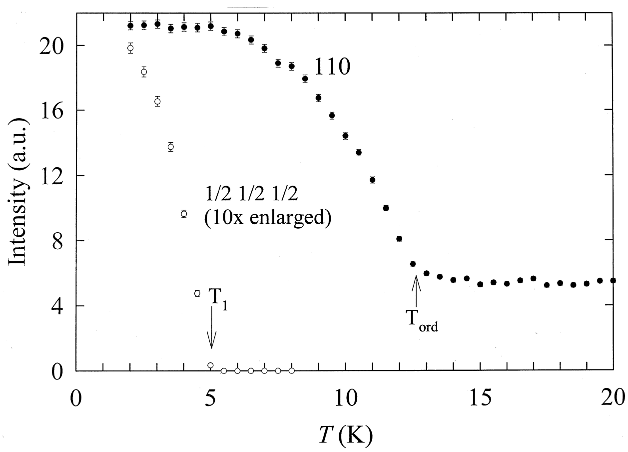

Fig. 7. Temperature dependence of the intensities of (1 1 0) and $({}^1/_2\ {}^1/_2\ {}^1/_2)$ reflections.

be well fitted with the Curie–Weiss law with the following parameters: $\mu_{eff} = 11.16\ \mu_B$, $\theta_p = 14.8$ K for $\boldsymbol{H} \parallel [001]$ and $\mu_{eff} = 10.49\ \mu_B$, $\theta_p = 7.1$ K for $\boldsymbol{H} \parallel [100]$. The value of θ_p corresponds well to the ordering temperature and the effective magnetic moment is relatively close to the Ho^{3+} free-ion value of 10.60 μ_B. The difference between both dependencies originates presumably in the crystal-field effects.

As can be seen from Figs. 4–6, the magnetic anisotropy in HoNiAl is very weak, by far not comparable with the uranium based isostructural compounds [10].

Let us now turn to the single-crystal neutron diffraction experiment. The refinement of the crystal structure ($T = 25$ K) is already summarised in Table 1. Additional magnetic intensities on the positions of nuclear reflections develop below T_{ord}, increase by cooling down to T_1 and stay almost constant below this temperature, as shown in Fig. 7 for the representative (1 1 0) reflection. Surprisingly, in distinction from the powder neutron data [1,2], magnetic intensities described by $\boldsymbol{k} = ({}^1/_2, 0, {}^1/_2)$ do not appear in the HT phase, and develop below T_1 only. We have performed a relatively detailed search for magnetic intensities in the $(h\ k\ {}^1/_2)$ plane at 9 K, but no reflections have been found. It means, the HT phase is a pure ferromagnet. In fact, such observation corresponds well to our magnetization data.

To determine the magnetic structure in the LT phase, set of 320 (94 non-equivalent) reflections described by (0, 0, 0) propagation and 184 reflections described by $\boldsymbol{k} = ({}^1/_2, 0, {}^1/_2)$ measured at 2 K have been analysed. The first set of reflections corresponds clearly to the ferromagnetic ordering of the c-component of the holmium moment. Moments on all the three Ho-positions have the same orientation and magnitude $\mu_F = 6.60(5)\ \mu_B$, in a very good agreement with the previous powder data [1,2]. Our refinement gives the agreement factor of $R = 6.7\%$.

The two arrangements of μ_{AF} in the LT phase, proposed in the previous papers [1,2], are shown in Fig. 8. In both cases, μ_{AF} lies within the basal plane. The main difference concerns μ_{AF} on the $(0, x, {}^1/_2)$ site: it propagates in the same way as μ_{AF} on the remaining Ho-sites and it is perpendicular to them (see Fig. 8b), or μ_{AF} on all the Ho-sites are parallel but that one on $(0, x, {}^1/_2)$ propagates with $\boldsymbol{k}' = (0, {}^1/_2, {}^1/_2)$ (see Fig. 8a). In the hexagonal symmetry, $\boldsymbol{k}'$ is an equivalent vector to $\boldsymbol{k}$. The refinement of our data gives the following results:

Structure on Fig. 8a: $\mu_{AF} = 4.80(4)\ \mu_B$ $R = 6.6\%$

Structure on Fig. 8b: $\mu_{AF} = 4.84(5)\ \mu_B$ $R = 9.3\%$

These results are obtained assuming that μ_{AF} on all the Ho sites have the same magnitude. Allowing different magnitudes does not lead to any substantial improvement of our fits. It is clear that the structure in Fig. 8a gives a considerably better agreement than the other one. Therefore, we suggest this structure as the magnetic structure in HoNiAl in the LT phase.

Let us summarise the results. In the LT phase, the magnetic structure consists of μ_F oriented along the c-axis

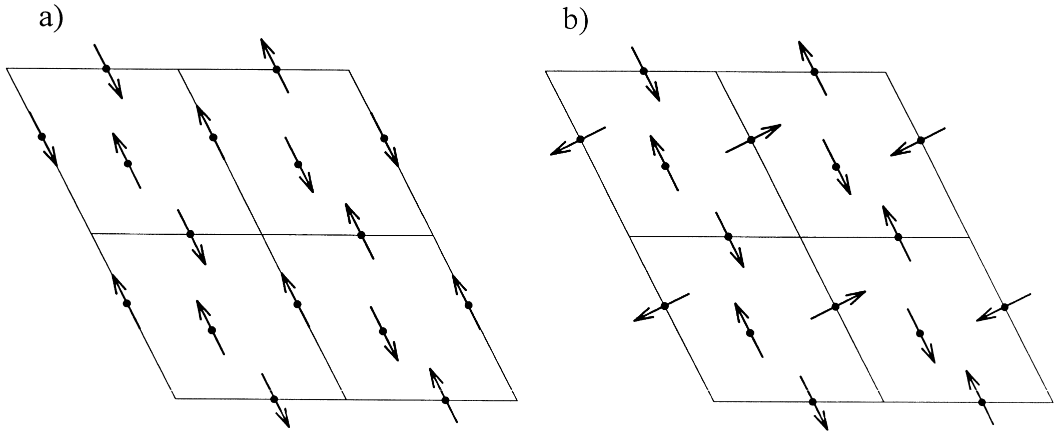

Fig. 8. Antiferromagnetic components in the low-temperature ($T < T_1$) magnetic structure in HoNiAl; our data favour the (a) arrangement.

and μ_{AF} lying within the basal plane and arranged as shown in Fig. 8a). It is thus a canted magnetic structure with the total moment of 8.2(1) μ_B at 2 K. While μ_F is almost constant below T_1, μ_{AF} increases when cooling down below T_1, what leads to an increasing angle between the holmium magnetic moment and the *c*-axis (≈35° at 2 K). This is a common result obtained for all the samples (polycrystalline and single crystal).

As regards the magnetic structure in the HT phase, different results are obtained on different samples. The differences are rather substantial, and cannot be due to different ways of analysis. The dominant ferromagnetic component along the *c*-axis is a common observation. On the other hand, the antiferromagnetic component, μ_{AF}, can probably develop in different ways or it does not develop at all. It could be a result of a delicate balance of magnetic interactions, and can be strongly influenced by actual crystal structure parameters and sample quality. In the case of our single crystal, μ_{AF} does not exist in the HT phase, and the HoNiAl magnetic structure is thus a simple ferromagnet with holmium moments along the *c*-axis.

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