

MAGNETIC PROPERTIES AND CRYSTAL STRUCTURE OF *RENiAl* AND *UNiAl*
HYDRIDES.

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Introduction

RENiAl (RE = rare-earth metal) and *UNiAl* compounds crystallising in the hexagonal *ZrNiAl*-type structure (space group $P\bar{6}2m$) can absorb up to 2 and 3 hydrogen (deuterium) atoms per formula unit, respectively. Hydrogenation leads to a notable lattice expansion and modification of magnetic properties. However, the impact of hydrogenation on magnetism is the opposite for *4f*- and *5f*-materials: $T_N(T_C)$ is lowered in the case of rare-earth hydrides, while for *UNiAlH(D)_x* it increases by an order of magnitude [1-4]. Here we present results of magnetic and structure studies performed of these compounds, focusing on the correlation between magnetic and structural variations and discussing possible reasons of the striking difference in effect of hydrogenation on rare-earth and actinide intermetallics.

Experiment.

Hydrides (deuterides) have been synthesised using a two-stage process. First the parent intermetallics were arc-melted from the constituent elements under Ar atmosphere, and the phase purity was verified by means of X-rays diffraction. Secondly the material was crushed

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and hydrogenated, by means of activating the specimen in a vacuum of 10^{-6} Torr at 350°C for 1 hour, followed by exposure to $\text{H}_2(\text{D}_2)$ at 20 atm pressure for HoNiAl and 55atm pressure for UNiAl . The synthesis of $\text{HoNiAlH}_{2.0}$ was initiated by raising the temperature in the reaction chamber to 50°C . The amount of absorbed D(H) was determined by monitoring the decrease of pressure in a calibrated volume. In order to avoid sample decomposition material was stored in sealed quartz or glass ampulas. Magnetic measurements were performed using an Oxford Instruments Faraday balance and SQUID magnetometer from Quantum Design.

Results and discussion.

HoNiAl has the highest absorption capability among the whole $RENiAl$ series. It forms $\text{HoNiAlH}_{2.0}$, which contains by 30 % more hydrogen than the remaining RE -compounds, achieving typically $[\text{RE}]/[\text{H}] = 1.4$ [3,4]. Hence, $\text{HoNiAlH}_{2.0}$ is the only compound among the $RENiAl$ -hydrides, which approaches U-based counterpart by hydrogen content. For this reason it may be convenient to choose it as the model representative of the series for comparison with UNiAlH_x .

The cusp on the magnetic susceptibility curve shown on Fig.1 and its displacement towards lower temperatures at higher fields demonstrates that $\text{HoNiAlH}_{2.0}$ orders antiferromagnetically at $T_N = 6$ K, while the critical temperature of the parent compound is 13 K [5]. These two materials also display different magnetic phase diagrams: the hydride undergoes only one magnetic phase transition within the experimentally achievable temperature range (*i.e.* down to 1.8 K), while HoNiAl experiences spin re-orientation from amplitude-modulated ferromagnetic phase to a canted ferromagnetic structure at $T_N = 4.9$ K [5,6]. The absence of the latter transition in the hydride may be either due to its shift below 1.8 K or due to the modification of the magnetic structure by the incorporation of hydrogen. For $T > 11$ K, the temperature dependence of magnetic susceptibility, $\chi(T)$, of $\text{HoNiAlH}_{2.0}$ follows the Curie-Weiss law with $\mu_{\text{eff}} = 10.9 \mu_B/\text{f.u.}$ and $\Theta_P = -11$ K, compared to 10.7

$\mu_B/\text{f.u.}$ and 7.2 K for HoNiAl. We can conclude that the effective moment remains approximately unaffected by the hydrogenation, and the paramagnetic Curie temperature changes its sign, retaining the same order of magnitude.

Field dependencies of magnetisation $M(H)$ are quite different for HoNiAlH_{2.0} and HoNiAl: magnetisation of hydride reaches lower value (5.9 $\mu_B/\text{f.u.}$) at the maximum field of 5 T, than that of pure compound ($\sim 7.6 \mu_B/\text{f.u.}$ [5]), the latter also has a remnant magnetisation, whereas $M(H)$ of HoNiAlH_{2.0} shows zero remanence. Qualitatively new feature, the inflection point at 0.5 T, appears on the M vs. H dependence of hydride, while for HoNiAl it has not been observed up to $\mu_0 H = 40$ T [5].

UNiAl hydride was first obtained by Drulis *et al.* [2], and the first magnetic characterisation was done by Zogal *et al.* [1]. Larger number of anomalies on $\chi(T)$ reported in [1] may be attributed to the presence of impurity phase, but the ordering temperature above 100 K looks realistic. We have studied both hydride and deuteride, UNiAlH_{2.3} and UNiAlD_{2.1}, indicating antiferromagnetic order at 99 K and 94, respectively (Fig. 2). The origin of the discrepancy in the values of T_N between the Ref. [1] and present results for UNiAlH_{2.3} is not quite clear at this moment. It may be connected either with the difference in H-composition or with the difference in crystal structures between two samples. At the temperatures above 100 K, both compounds show modified Curie-Weiss behaviour with a temperature independent term χ_0 , which originates from the strong uniaxial anisotropy of the compound [7]. Fitting gives the following values of the effective moments, paramagnetic Curie temperatures and χ_0 : $\mu_{\text{eff}} = 2.42 \mu_B/\text{f.u.}$ and $2.43 \mu_B/\text{f.u.}$, $\Theta_P = -42$ K and -50 K, $\chi_0 = 7 \cdot 10^{-9} \text{ m}^3/\text{mol}$ and $8 \cdot 10^{-9} \text{ m}^3/\text{mol}$, for deuteride and hydride, respectively. Due to polycrystalline structure and strong magnetic anisotropy of the hydride the calculated effective moment represents some value averaged over all crystallographic directions and can serve only as an estimate of the true μ_{eff} . Still it may be interesting to mention a weak

increase of μ_{eff} , compared with the previously obtained value of $2.2 \mu_B/\text{f.u.}$ for polycrystalline UNiAl [8,9].

Field dependence of magnetisation of both hydride and deuteride is linearly proportional to field, and no metamagnetic transition have been observed up to 5 T. The absence of the metamagnetic transition on $M(H)$, which was observed for the parent UNiAl at 11.25 T [7] is most likely connected with the relatively low fields available in the experiment.

In spite the similarity of the crystal structure of the parent compounds and the amount of absorbed hydrogen the crystal structures of $\text{HoNiAlH}_{2.0}$ and $\text{UNiAlH}_{2.3}$ are quite different. Non-uniform expansion in the basal plane, accompanying hydrogenation, leads to the orthorhombic distortion of the HoNiAl lattice (Table 1.). Besides that the unit cell is contracted along the c -axis but due to higher multiplicity of the a -axis the total volume is increased: $\Delta V/V = 5.8 \%$. The latter value is lower than the maximum volume increase in the RENiAlH_x series observed for $\text{SmNiAlH}_{1.2}$: 8.7% [4]. In spite of notably lower deuterium content in $\text{HoNiAlD}_{0.97}$ the unit cell volume remains approximately the same $\Delta V/V = 6.0 \%$, but the orthorhombic distortion is weaker and b/a ratio approaches $\sqrt{3}$, typical for hexagonal symmetry. Hydrogenation of UNiAl leads to similar non-uniform deformation of the unit cell but its symmetry remains unchanged, and the volume increase is twice higher than in for $\text{HoNiAlH}_{2.0}$.

Due to higher coherent scattering cross-section of deuterium neutron diffraction studies have been performed on $\text{HoNiAlD}_{0.97}$ (Table II) and $\text{UNiAlD}_{2.1}$ (see Table III). The Rietveld analysis of the diffraction patterns has shown that D atoms occupy three different crystallographic positions in each material. Only one of them is similar in both materials: D(3) in $\text{UNiAlD}_{2.1}$ and as D(1) in $\text{HoNiAlD}_{0.97}$. The D(1) deuterium position in $\text{HoNiAlD}_{0.97}$ lays in the centre of the Ho_3Ni_2 -bipyramid, and in $\text{UNiAlD}_{2.1}$ it is found in one of two adjacent U_3Ni -pyramids. In $\text{UNiAlD}_{2.1}$ the site D(3) accommodates the smallest amount of

deuterium, and in $\text{HoNiAlD}_{0.97}$, on the contrary, D(1) has the highest D-occupation. Two other D-atoms in $\text{UNiAlD}_{2.1}$ are located in bipyramid $\text{U}_3\text{Al}_2 - \text{D}(1)$, and pyramid $\text{NiAl}_3 - \text{D}(2)$. In $\text{HoNiAlD}_{0.97}$ the interstitials filled with deuterium are tetrahedron $\text{Ho}_2\text{NiAl} - \text{D}(2)$, and octahedron $\text{Ho}_4\text{NiAl} - \text{D}(3)$.

In general the atomic positions for $\text{UNiAlD}_{2.1}$ presented here, are quite close to those reported by Yamamoto *et. al.* [10]. We have also notable shift of U atoms from $(0.572, 0, 1/2)$ to $(2/3, 0, 1/2)$ and Al atoms – from $(0.231, 0, 0)$ to $(1/3, 0, 0)$ so that the unit cell can accommodate more deuterium. The displacement of the U-atom can be clearly seen by X-rays as well: the peak (010) around $2\theta = 15^\circ$ present on the pattern of UNiAl disappears after hydrogenation (deuteration). Numerical simulations show that this peak comes through the minimal intensity when U atom is located at $(2/3, 0, 1/2)$.

However the conclusion about the shift of Ni(1) atom from $(0, 0, 1/2)$ to $(0, 0, 0)$ made in [10], seems disputable. We assume that one of the reasons for the presumption of such shift of Ni could be the disappearance of the peak (201) on the X-ray pattern of hydride (deuteride). Indeed this peak goes down after hydrogenation, but similar effect can take place due to the disorder in Ni-Al plane mentioned by H. Noel [11]. Moreover, it is still possible to observe some weak intensity on the position of the peak (201) after incorporation of H(D) into crystal lattice. Although it should be mentioned that we have taken into account the Ni-Al disorder only for X-ray patterns simulations but not during neutron data refinement.

Conclusions.

Hydrogenation has noticeable effect on magnetic properties and crystal structure of RENiAl compounds and UNiAl . It leads to the change of the ordering temperatures and expansion of the unit cell in both cases. While the crystal lattice modification has some common features in 4f- and 5f-compounds, *i.e.* expansion in the basal plane, contraction along the *c*-axis, positive value of $\Delta V/V$, magnetic properties are changed in the opposite

manner. The ordering temperature of UNiAlH_{2.3} is higher by almost 100 K compared to its parent compound, Θ_P shifts to more negative values, indicating stronger antiferromagnetic interaction. However, we do not have any reliable estimate for the magnitude of ordered moments μ_U . All these changes can be attributed to the lattice expansion, which leads to decrease of the *5f*-ligand and *5f-5f* hybridisation.

On the contrast to UNiAl, HoNiAlH_{2.0} has lower ordering temperature than HoNiAl, it also has different type of magnetic ordering: AFM vs. FM in parent compound. Θ_P changes its sign after hydrogenation, but retains the same order of magnitude, indicating rather modification of the type of magnetic exchange than its strength. The mechanism leading to these effects in HoNiAlH_{2.0} should be different from that in UNiAlH_{2.3}. As in the rest of *RENiAl* series [3,4] it can be ascribed to the weakening of the RKKY exchange interaction, responsible for the magnetic ordering in *RENiAl*'s due to the decrease of the conduction electron density. Geometrical effect plays a secondary role since *4f*-states responsible for magnetism are located quite far from E_F . The minor importance of the lattice expansion is reflected, for example, in the absence of the direct correlation between $\Delta V/V$ and the decrease of the ordering temperature. For instance $\Delta T_C = -46$ K and $\Delta V/V = 5.9$ % for GdNiAlH_{1.35} [3,4], and almost the same increase of volume in HoNiAlH_{2.0} leads to the reduction of the ordering temperature by 7 K only. The weakening of the exchange interaction cannot be attributed either to the symmetry change under hydrogenation because GdNiAlH_{1.35} and GdNiAlH_{1.06} having orthorhombic and hexagonal unit cell, respectively, show almost identical T_N . The role of the symmetry changes may be quite crucial for the magnetic structures for the incorporation on hydrogen affects local symmetry, thus, altering possibilities for certain arrangement of magnetic moments.

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Figure captions.

Figure 1. Temperature dependence of magnetic susceptibility of $\text{HoNiAlH}_{2.0}$. The insert shows the inverse susceptibility at 4 T (open squares), and the Curie-Weiss fit (straight line)

Figure 2. a) magnetic susceptibility of $\text{UNiAlH}_{2.3}$ and $\text{UNiAlD}_{2.1}$ vs. temperature; b) inverse susceptibility vs. temperature. Lines represent fitting results, empty circles denote 0.1 T data for hydride, filled circles – 5 T data for $\text{UNiAlH}_{2.3}$, empty triangles – 5 T data for $\text{UNiAlD}_{2.1}$.

Table captions

Table I. Structure parameters of HoNiAl-H and UNiAl-H(D) systems.

Table II. Crystal structure of HoNiAlD_{0.97}. Space group Amm2.

$$a = 3.7996(4) \text{ \AA}, b = 12.433(1) \text{ \AA}, c = 7.2594(7) \text{ \AA}, b/c = 1.713 \text{ (ideal} = \sqrt{3} \\ = 1.732).$$

Table III. Crystal structure of UNiAlD_{2.1}. Space group $P\bar{6}2m$; $a = 7.18069(8) \text{ \AA}$, $c = 3.98849(7) \text{ \AA}$

Table I.

	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$\Delta a/a, \%$	$\Delta c/c, \%$	A/b	$\Delta V/V, \%$
HoNiAl ^[5]	6.985(1)	—	3.8284(9)	—	—	—	—
HoNiAlD _{0.97} *	3.7996(3)	12.433(1)	7.2594(7)	3.9	-0.8	1.713	6.0
HoNiAlH _{2.0}	7.536(5)	12.292(5)	3.694(1)	7.9	-3.5	1.631	5.8
UNiAl ^[7]	6.733	—	4.035	—	—	—	—
UNiAlH _{2.3}	7.182(1)	—	3.9849(8)	6.7	-1.2	$\sqrt{3}=1.732$	12.4
UNiAlD _{2.1}	7.18069(8)	—	3.988849(7)	6.6	-1.1	$\sqrt{3}=1.732$	12.4

*HoNiAlD_{0.97} has orthorhombic unit cell, space group Amm2

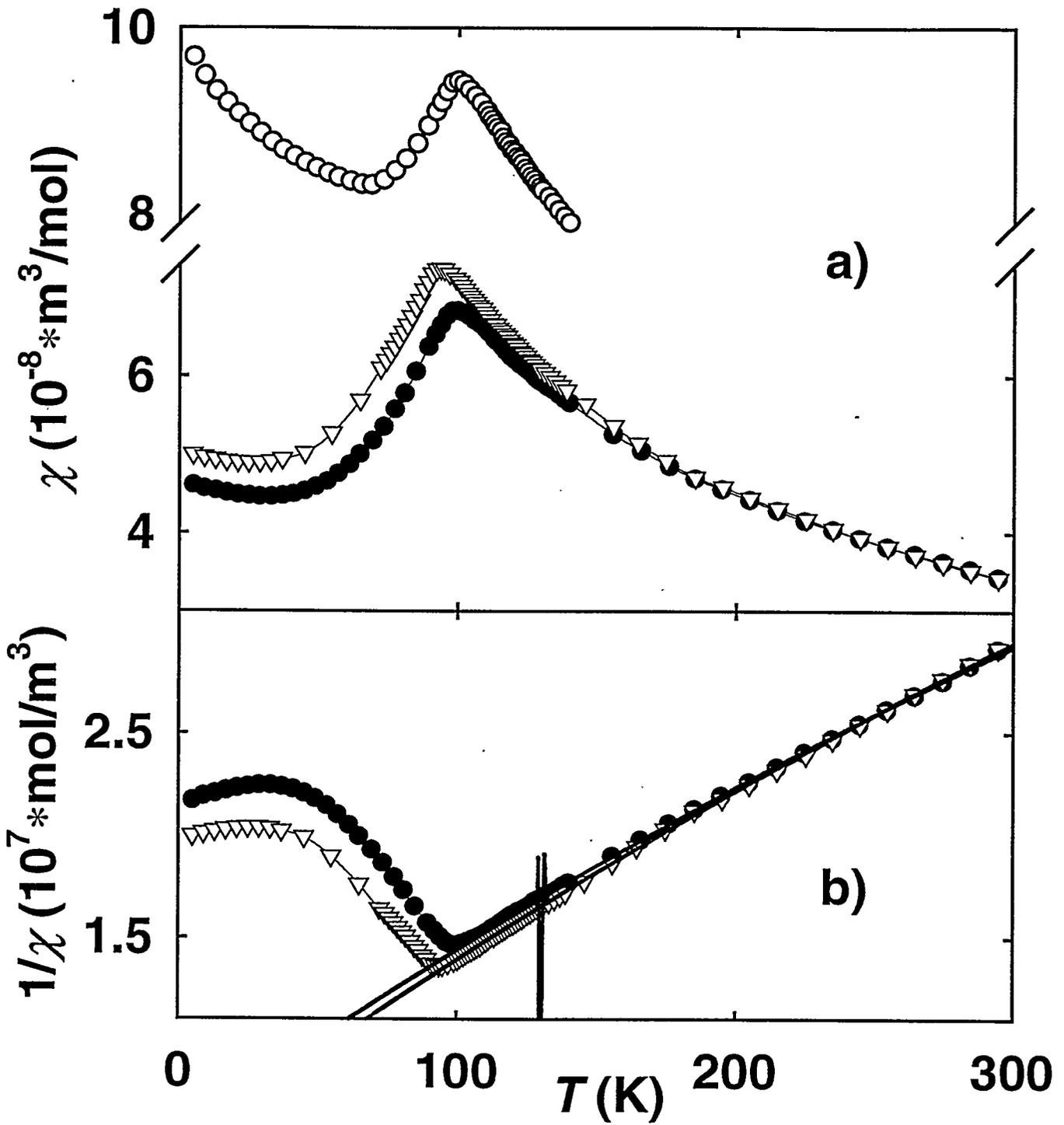
Table II.

	Site	x	y	z	Occupancy
Ho(1)	4e	1/2	0.2098	0.0178	1
Ho(2)	2b	1/2	0	0.6360	1
Ni(1)	4d	0	0.3319	0.2334	1
Ni(2)	2b	1/2	0	0.2304	1
Al(1)	4d	0	0.1197	0.3470	1
Al(2)	2a	0	0	0.0135	1
D(1)	4e	1/2	0.3350	0.2320	0.82
D(2)	4d	0	0.3945	0.0638	0.46
D(3)	4d	0	0.2236	0.1798	0.19

Table III.

	Site	x	y	z	Occupancy
U	3g	0.666(2)	0	1/2	1
Ni(1)	1b	0	0	1/2	1
Ni(2)	2c	1/3	2/3	0	1
Al	3f	0.333(2)	0	0	1
D(1)	3g	0.332(3)	0	1/2	0.95(2)
D(2)	2e	0	0	0.033(1)	0.80(1)
D(3)	4h	1/3	2/3	0.406(1)	0.337(5)

Figure 2 (Kolomiets *et al.*)



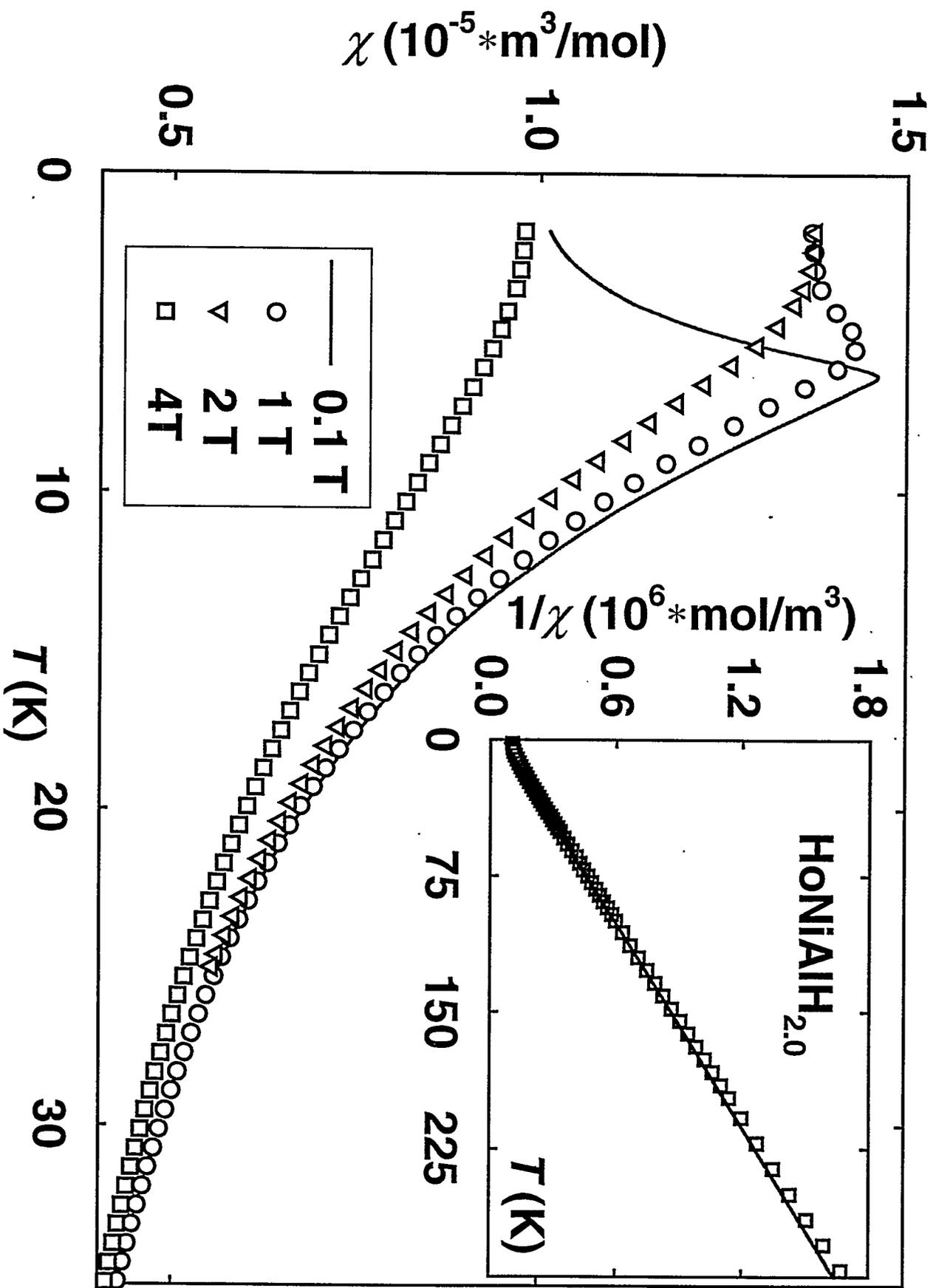


Figure 1 (Kolomiets et al.)