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Hydrogenation of CeNi: hydride formation, structure and magnetic properties

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Abstract

The hydrogenation at different temperatures and hydrogen pressures of the binary intermetallic compound CeNi was studied. A hydride with the composition CeNiH_{2.9(1)} was obtained by hydriding the host alloy at 293 K and P_{H₂} = 1 MPa. With increasing temperature of hydriding a reaction of hydrogenolysis of CeNi occurred with formation of a stable two-phase product composed of CeH_{2.51} and CeNi₅. The newly prepared hydride CeNiH_{2.9(1)} was found to be isostructural with CeNi (orthorhombic, CrB-type, S.G. *Cmcm*). On the basis of refinement of the XRD patterns of both the intermetallic compound and its hydride, the atomic positions of Ce and Ni and the interatomic distances were determined. The probable sites of hydrogen intersertion in the host structure were proposed. Moreover, a valence transition of cerium from intermediate valence (CeNi) to the trivalent state (CeNiH_{2.9}) was evidenced by magnetization measurements.

Keywords: A. Rare-earth intermetallics; B. Crystal chemistry of intermetallics; B. Magnetic properties; F. Diffraction (electron, neutron and X-ray)

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1. Introduction

Hydrogen is an ideal non-polluting vector of energy for the future. Its use is closely associated with the methods of its storage. Among them the reversible bonding of hydrogen with some metals and alloys, forming hydrides, is of special interest. The 7.6 wt.% absorption capacity of magnesium determines it as a very attractive material for hydrogen storage in the form of MgH_2 . However, the use of pure magnesium is prevented by its very poor hydrogen absorption and desorption kinetics. For that reason, a large number of investigations have been aimed at improving the kinetic characteristics of hydriding and dehydriding of magnesium by preparing composites on its basis with an absorption capacity close to that of pure Mg. A survey of the literature on this subject is given in some recent papers of the authors [1-3].

Nakhl et al. [4] were the first to study the hydrogen sorption properties of materials composed of Mg and an equiatomic intermetallic compound, YNi , containing a rare earth and a VIII group transition metal. No reaction between the components of the composite was observed during its preparation by mechanical grinding but it was shown that the presence of YNi led to an improvement of magnesium hydriding kinetics even at relatively low temperatures. The X-ray diffraction patterns of the products obtained at 300°C after several hydriding-dehydriding cycles showed formation of MgH_2 , Mg_2NiH_4 , YH_2 and YNiH_3 .

In connection with the above results it was of interest to investigate the hydriding processes of magnesium-based composites containing RNi intermetallics of nickel with other rare earths. However, the authors are of the opinion that such investigations should be preceded by studies on the behaviour of the pure intermetallics during hydriding.

A survey of the crystal structures of RE_xT intermetallics where RE is a rare earth, $\text{T} = \text{Co, Ni, Rh, Pd}$ and $x \geq 1$ is given in a review paper of Parthé and Moreau [5]. It is shown that nickel forms equiatomic RENi compounds with Y, La, Ce, Pr, Nd, Sm, Gd and Tb. Of them only YNi crystallizes with monoclinic symmetry in the space group $P2_1/c$ [6]. All the remaining compounds, excepting TbNi have a CrB-type (S.G. $Cmcm$) orthorhombic structure. Depending on the way of preparation, TbNi crystallizes in space group $Pnma$ or $P2_1/m$ [7]. Irrespective of the available differences, all the above structures of equiatomic RENi compounds contain a common structural unit with nickel in the centre of trigonal prisms which are stacked differently to form each structure. Recently, Palumbo et al present a systematic study of the thermodynamics of Ce-Ni system [8].

The data available in the literature concerning the interaction of some RENi intermetallics with hydrogen are rather scarce and contradictory. Thus, there are communications on the preparation of LaNi hydrides with the composition $\text{LaNiH}_{2.60}$ [9], $\text{LaNiH}_{3.6}$ [10] and $\text{LaNiH}_{3.85}$ [11]. More recently Verbetskii et al. [12] established hydriding at room temperature and a hydrogen pressure of 0.05-0.1 MPa to lead to synthesis of $\text{LaNiH}_{3.5}$ hydride with the same structure as that of the initial alloy. With increasing pressure up to 3MPa, the hydride obtained in the range from room temperature to 673 K has the composition $\text{LaNiH}_{2.8}$ and a structure analogous to that of LaH_3 . The same authors have found the intermetallic compound ErNi to begin

interacting with hydrogen at room temperature only at $P(\text{H}_2) \geq 0.3\text{-}0.5$ MPa. A hydride with the composition $\text{ErNiH}_{3.4}$ and a structure differing from that of the initial compound is formed.

The hydrogenation of CeNi was also studied by Verbetskii et al. [12]. They noticed that under identical conditions hydrogenation of CeNi differed from that of LaNi in spite of the structural similarity of both intermetallics. Thus, CeNi hydride formation was found to start at room temperature and a hydrogen pressure of 0.005 MPa. Up to a pressure of 0.1 MPa, $\text{CeNiH}_{3.7}$ was formed.

Increase of hydrogen pressure up to 3MPa leads to the formation of a hydride with the composition $\text{CeNiH}_{2.9}$. If the temperature is enhanced up to 673 K at the same pressure, hydrogenolysis of CeNi proceeds according to the reaction



The present work represents a detailed study of the hydriding of CeNi and the resulting changes in structure and oxidation state of cerium.

2. Experimental

The starting intermetallic compound CeNi was synthesized by arc-melting under high-purity argon of a stoichiometric mixture of the elements with a 99.9% purity. To ensure homogeneity, the samples obtained were turned and remelted several times. After that they were annealed at 873 K for two weeks in evacuated silica tubes. Microprobe backscattering analyses showed the presence in the samples of CeNi_2 as a parasitic phase. X-ray powder diffraction patterns needed for phase identification and structural analysis of the samples were obtained using a Philips PW 1050 diffractometer with a Bragg-Brentano geometry (CuK_α radiation). In determining the ternary hydride structure, the Rietveld method for refinement was applied [13], the diffraction patterns being analyzed by a whole pattern fitting procedure using the programme FULLPROF [14].

Hydrogen sorption properties were investigated with the use of an automatic Sievert type volumetric apparatus (HERA, Hydrogen Storage System, Québec, Canada) in the temperature range between room temperature and 723 K. Hydriding experiments were carried out at $p = 1\text{MPa}$ while desorption proceeded at $p = 0.03$ MPa. A detailed description of the volumetric method for hydrogen sorption measurements is given in [15].

Magnetic susceptibility measurements were carried out with both the CeNi alloy and its hydride using a Superconducting Quantum Interference Device (SQUID) magnetometer in the temperature range 1.8–300 K under an applied field of 4T.

3. Results and discussion

To study the hydrogenation process, the CeNi sample in small blocks was put in the hydriding reactor which was closed in a glove box under argon to avoid air

contamination. After that the reactor was evacuated for about 15 min and hydrogen was introduced. The results of the first and second cycle of CeNi hydriding at room temperature and $p = 1$ MPa are shown in Fig. 1. The presence of an activation period during the first cycle is clearly visible. Obviously, this period is associated with the necessity to obtain cracks in the blocks, which would facilitate hydrogen diffusion. Subsequently CeNi begins to absorb hydrogen very quickly and an absorption capacity of 1.41(5) wt.% H_2 is achieved. This value corresponds to a composition $CeNiH_{2.9(1)}$. This result is very far from that found by Verbetskii et al [12] who proposed the formula $CeNiH_{3.7}$ for the product obtained under similar experimental conditions.

Practically no desorption of hydrogen from the sample hydrided at room temperature was observed and, as a result, a negligible absorption capacity during the second cycle was registered. The above pressures of absorption and desorption were used for performing hydriding/dehydriding cycles at 373, 473, 573, 623, 673 and 723 K, respectively. In all cases there was no significant desorption. Even at the highest temperature about 0.1 wt.% hydrogen were desorbed (Fig. 2). The X-ray pattern revealed the presence of a hydride of cerium, $CeH_{2.51}$, and the intermetallic compound $CeNi_5$, i.e. hydrogenolysis of CeNi had taken place according to the probable reaction



which differs from reaction (1) proposed by Verletskii et al [12].

The investigations showed proceeding of reaction (2) already at hydriding and dehydriding temperatures far below the maximum temperature applied in the present paper (723 K). This can be seen in the X-ray patterns shown in Fig. 3. The first pattern (Fig. 3a) corresponds to the $CeNiH_{2.9(1)}$ hydride which is obtained after hydrogenation of the alloy at room temperature (298 K). The rise of the hydriding/dehydriding temperature up to 373 K, however, leads to a product representing a not well crystallized (almost amorphous) mixture of $CeH_{2.51}$ and $CeNi_5$ (Fig. 3b). A similar hydrogen-induced amorphization (HIA) at relatively low temperatures accompanied by appearance of two new phases has been observed many times during hydriding of intermetallics of Laves phase type, AB_2 , where at least one of the metals forms a hydride [16-20]. Here one should note that the registered low temperature of hydrogenolysis of CeNi may not be quite correct. It may in reality be higher due to the strong exothermal effect of hydriding which can provoke appearance of local overheatings.

The X-ray patterns of the samples subjected to hydriding and dehydriding at higher temperatures show a much better crystallization of the product obtained after treatment at 573 K (Fig. 3c). At 723 K the characteristic peaks of $CeH_{2.51}$ and $CeNi_5$ are quite distinct in the X-ray pattern (Fig. 3d).

It is worth noting that no absorption was observed after hydriding CeNi even for a very long time at a low hydrogen pressure (e.g. 0.1 MPa). This contradicts the results of Verbetskii et al. [12] according to which the above pressure along with room temperature should lead to formation of a hydride with the composition $CeNiH_{3.7}$, which was, however, not observed in the present study.

It was of interest to investigate the structure of the hydride $CeNiH_{2.9(1)}$ obtained for the first time in the present work. For that purpose, the X-ray diffraction pattern of

both the intermetallic compound and its hydride were scanned in the range from 5 to 120° (2 θ) in steps of 0.02°. It was established that CeNiH_{2.9(1)} crystallized in the same structure as CeNi (CrB-type, S.G. *Cmcm*). The good agreement between the calculated and the experimentally obtained pattern of the hydride is illustrated in Fig. 4 and the refined parameters are given in Table 1. In the case of CeNi, the refinement results are not as good as for the hydride due to a lower crystallinity of the sample but they show a sufficiently good agreement with published data.

The data in Table 1 show a considerable increase in parameters *b* and *c* of CeNiH_{2.9(1)} as compared to CeNi (12.77 and 10.66%, respectively) whereas parameter *a* displays a more moderate increase (3.78%) as a result of hydrogen insertion. The unit cell volume increase is 29.5%. This value is very high as compared to the 22% increase in the case of LaNi₅ which absorbs more than twice as large quantity of hydrogen. The logical explanation of this result is the more compact crystal structure (type CrB) of CeNiH_{2.9(1)}. It is also worth noting that comparison between the values of $\Delta y/y(\text{Ce})$ and $\Delta y/y(\text{Ni})$ evidences that the cerium atom positions are less affected by hydrogenation than is the case of the nickel positions. Finally, in CeNi all Ce-Ni distances are equal to 2.97 Å while in CeNiH_{2.9(1)} the hydrogen occupancy induces an anisotropic change, as a result of which each Ni atom is surrounded by 4 cerium atoms at a distance of 3.15 Å (in the *a-c* plane) and 2 cerium atoms at 3.37 Å (in the *b* direction). This change in the Ni environment proves that the hydrogen atoms are located in the [Ce₃Ni] tetrahedra as was to be expected on the basis of the parameter changes. Moreover, for the isostructural ZrNi compound, the hydrogenation also induce a huge increase of the volume cell (i.e. the parameter *a*, *b* and *c* increase respectively of 7.9, 5.5 and 4.7% which lead to a increase of the volume cell of about 19.2%).

The structure under consideration can be described as an alternative stacking of Ni-Ce and Ce-Ni planes. The Ce and Ni displacement values given in Table 1 (*y* = 0.12866 and 0.4237 in CeNi and *y* = 0.13470 and 0.40521 in CeNiH_{2.9(1)} for Ce and Ni, respectively) led to an enhancement of the distance between two planes. This permits location of the hydrogen atoms in [Ce₃Ni] tetrahedra between these planes. By analogy with the isostructural compound ZrNi it may be assumed that the 8*f* sites in the structure are occupied by hydrogen, the hydrogen-metal distances being comparable to those reported for ZrNiH₃ [21]. A similar occupation has also been reported for the equiatomic CeNiIn [22].

However, to achieve agreement with the formula CeNiH_{2.9(1)}, the hydrogen should also occupy other sites. By analogy again with the hydride of ZrNi, these are assumed to be sites 4*c* in the trigonal bipyramide [Ce₃Ni₂]. Such occupation, which would lead to an increase of the three lattice parameters, was reported recently concerning some hydrides of the ternary cerium-based intermetallics [23, 24].

In most intermetallic compounds containing cerium, hydrogen absorption leads to a valence change of cerium atoms. This was the reason for carrying out magnetic susceptibility measurements on CeNi and CeNiH_{2.9(1)}. The results are presented in Fig. 6. The binary compound CeNi exhibits a fluctuation valence behaviour (large minimum around 140 K in the curve $\chi_m^{-1} = f(T)$), already reported by Clementiev et al. [25]. However, after hydrogenation with CeNiH_{2.9(1)} formation, this behaviour becomes the behaviour of a paramagnetic substance with a paramagnetic Curie

temperature of 19 K. The value obtained for the effective magnetic moment, $\mu_{\text{eff}} = 2.46 \mu_{\text{B}}$, is very close to that of Ce^{3+} ($\mu_{\text{eff}} = 2.54 \mu_{\text{B}}$), which indicates that cerium in the hydride is in the trivalent state. Such a valence change has already been observed [26] with other Ce-based intermetallics. The increase of the unit cell volume induced by the hydrogenation leads to a decrease of the hybridization between 4f (Ce) states and conduction electron responsible of the intermediate valence behaviour of CeNi. It is important to notice that in case of processing, even to a small extent, of $\text{CeNiH}_{2.9(1)}$ dissociation to $\text{CeH}_{2.51}$ and CeNi_5 , the magnetic measurement will at once reveal the presence of CeNi_5 because this compound is a strongly magnetic one as compared to the ternary hydride. The foregoing permits the conclusion that the hydride obtained by CeNi hydriding at room temperature and $p = 1 \text{ MPa}$ contains no admixtures of dissociation products.

4. Conclusion

The results of the present investigation showed that hydrogenation of the intermetallic compound CeNi at room temperature and a hydrogen pressure above 0.1 MPa, resulted in a hydride with the composition $\text{CeNiH}_{2.9(1)}$. Hydriding at higher temperature led to hydrogenolysis of CeNi and formation of a two-phase mixture of $\text{CeH}_{2.51}$ and CeNi_5 . All hydriding products were stable and practically no hydrogen desorption from them occurred up to 723 K.

The $\text{CeNiH}_{2.9(1)}$ hydride was isostructural with the binary intermetallic host compound (orthorhombic, S.G. *Cmcm*). Structural refinement showed that, as a result of hydride formation, all parameters increased, an increase of 29.5 % of the unit cell volume being observed. It was established that the nickel atom positions were more strongly affected by hydrogenation than were cerium atoms. This resulted in a change of the nickel environment, the hydrogen atoms being located in the tetrahedral [Ce_3Ni] 8f sites and the trigonal bipyramidal [Ce_3Ni_2] 4c sites. Hydrogenation of CeNi with ternary hydride formation resulted in stabilization of the trivalent cerium state in the product.

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Figure captions

- Fig. 1** The first (I) and second (II) cycle of hydriding of CeNi at room temperature and $P = 1$ MPa
- Fig. 2** Hydrogen absorption of CeNi and desorption of the hydride $CeNiH_{2.9(1)}$ at 723 K and pressures of 1MPa and 0.03 MPa, respectively
- Fig. 3** X-ray diffraction patterns of: (a) $CeNiH_{2.9(1)}$; (b) a product hydrided at $T = 373$ K and $p = 1$ MPa after dehydriding at the same temperature and $p = 0.03$ MPa; (c) a product hydrided at $T = 673$ K and $P = 1$ MPa after dehydriding at the same temperature and $n = 0.03$ MPa;(d) a product hydrided at $T = 723$ K and $p = 1$ MPa after dehydriding at the same temperature and $p = 0.03$ MPa

Fig. 4 Experimental (+) and calculated (solid line) X-ray diffraction patterns of $\text{CeNiH}_{2.9(1)}$ and difference between them (bottom line)

Fig. 5 Representation of both CeNi and $\text{CeNi}_{2.9(1)}$ structures with highlight of the possible sites occupied by hydrogen. Stars represent the H in 8f site as triangles represent the H in 4c site.

Fig. 6 Magnetic susceptibility vs. temperature relationships for CeNi and $\text{CeNiH}_{2.9(1)}$

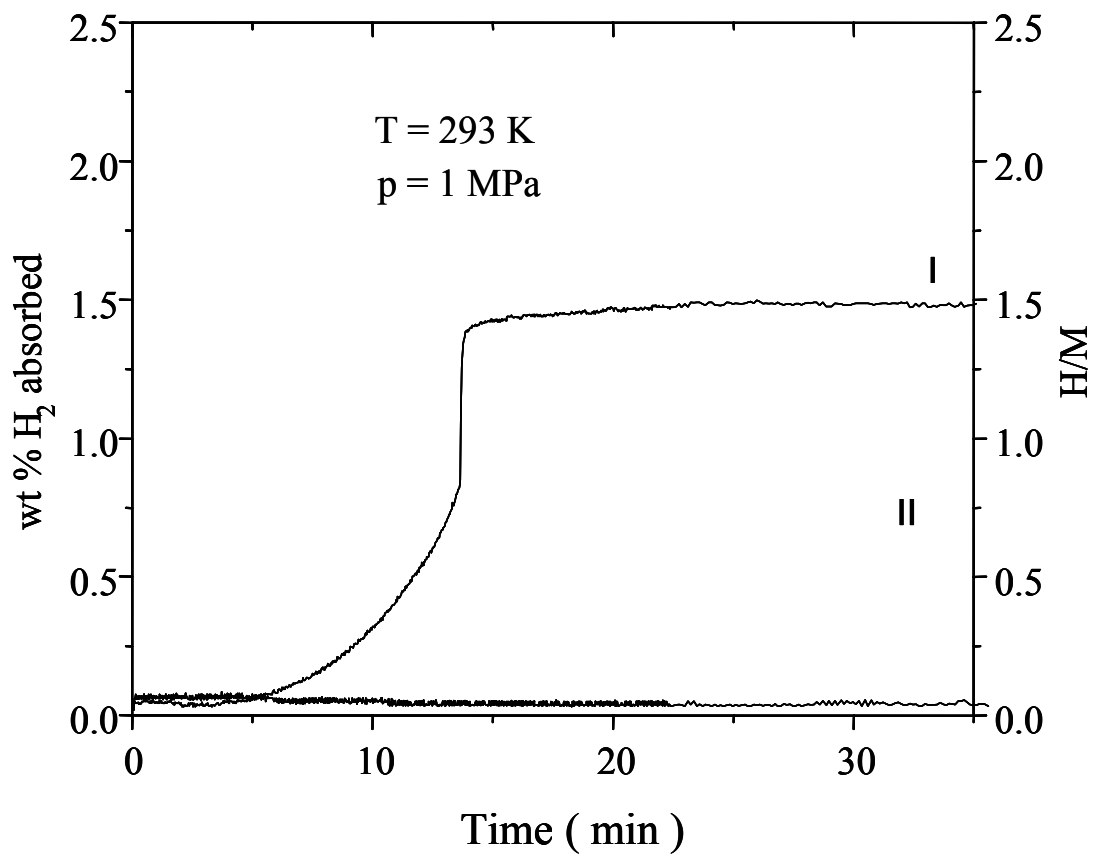
Table 1
 Refined structural parameters of CeNi and CeNiH_{2.9(1)}

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i> (Å ³)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (nm ²)
CeNi	3.794(5)	10.546(6)	4.367(4)	174.79	Ce	0	0.13866	1/4	0.03213
					Ni	0	0.42370	1/4	0.98007
CeNiH _{2.9(1)}	3.938(4)	11.893(7)	4.832(4)	226.39	Ce	0	0.13470	1/4	-0.83631
					Ni	0	0.40521	1/4	1.01424

$\Delta a/a = 3.78\%$; $\Delta b/b = 12.77\%$; $\Delta c/c = 10.66\%$; $\Delta y/y(\text{Ce}) = 2.8\%$; $\Delta y/y(\text{Ni}) = 4.36\%$

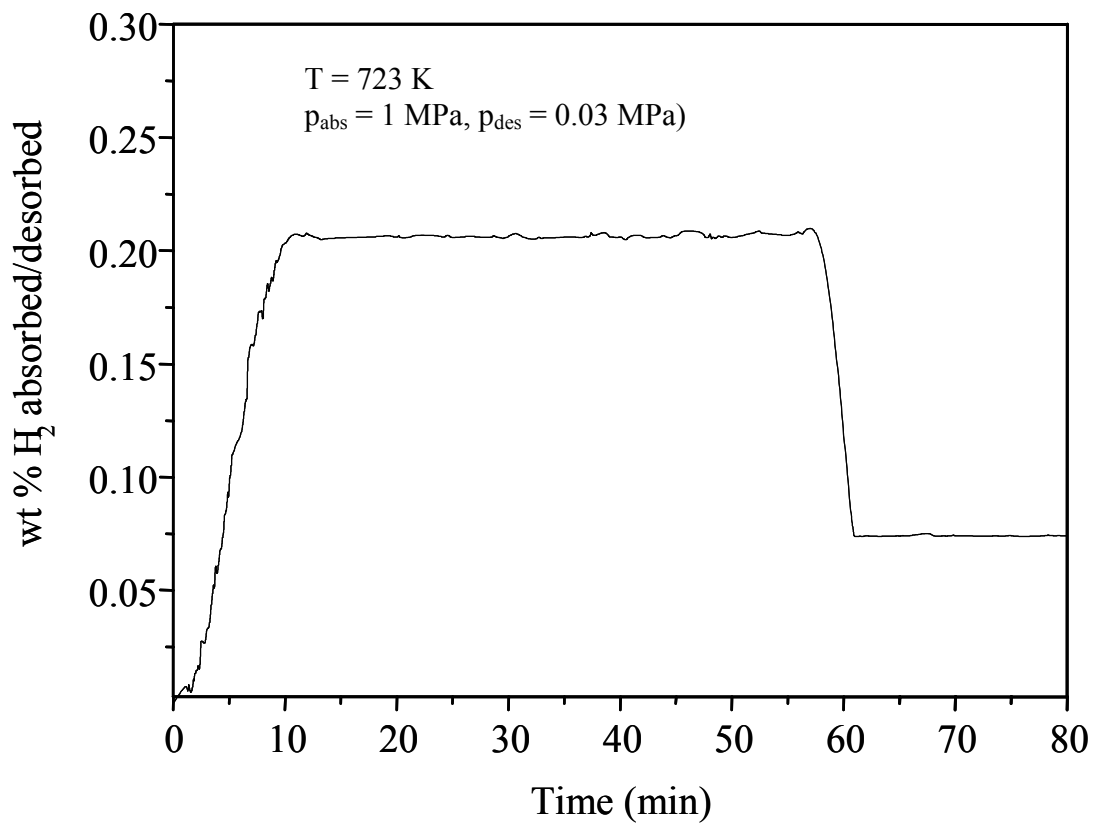
For CeNi: $R_{\text{Bragg}} = 10.95\%$; $R_{\text{wp}} = 32.9\%$; $R_{\text{f}} = 6.63\%$

For CeNiH_{2.9(1)}: $R_{\text{Bragg}} = 6.55\%$; $R_{\text{wp}} = 17.6\%$; $R_{\text{f}} = 3.1\%$



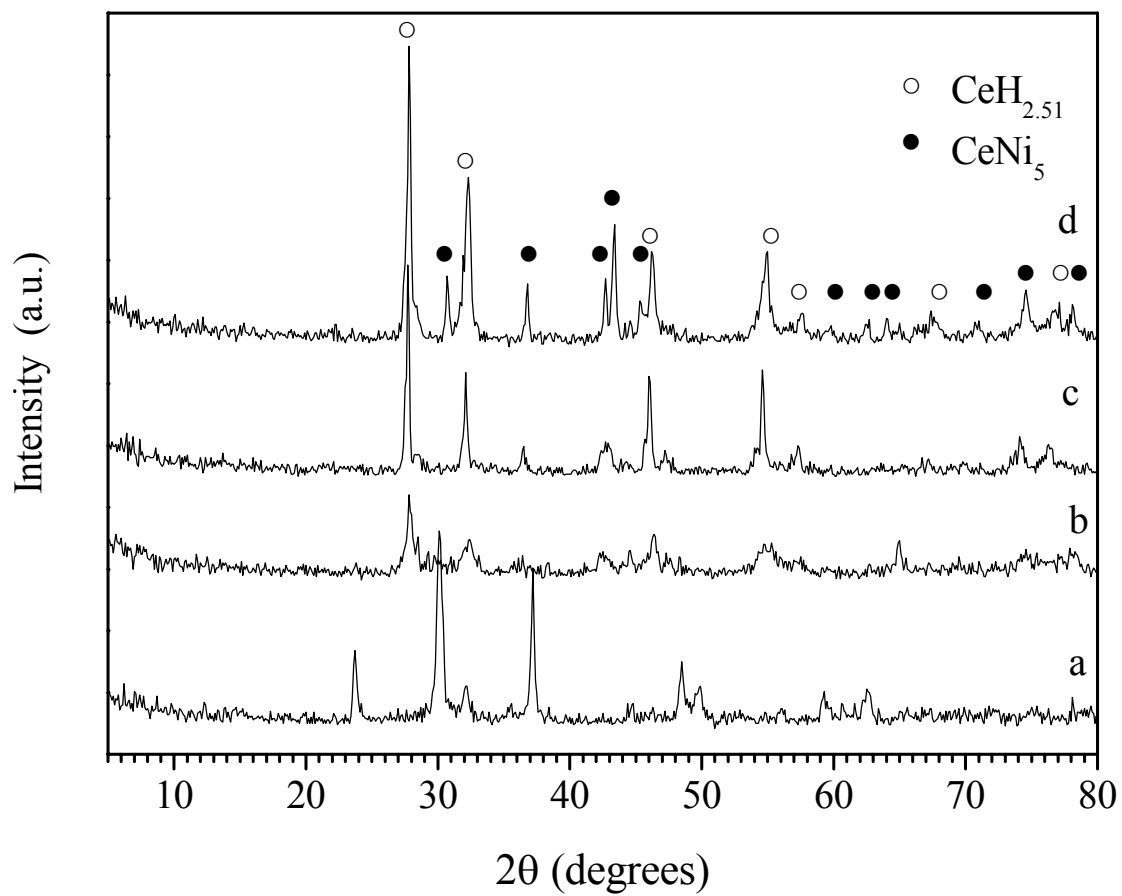
Bobet et al.

FIG. 1



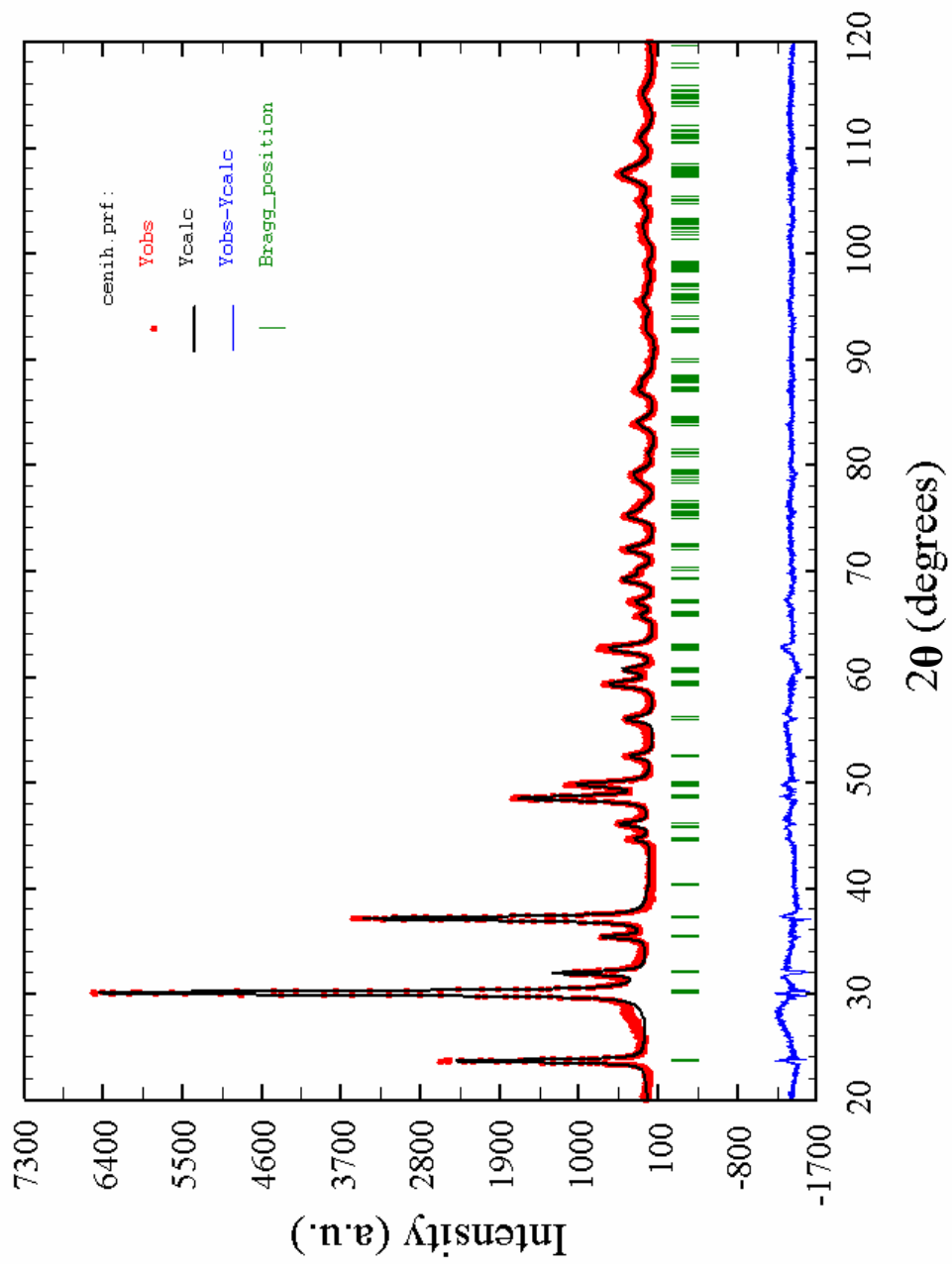
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FIG. 2

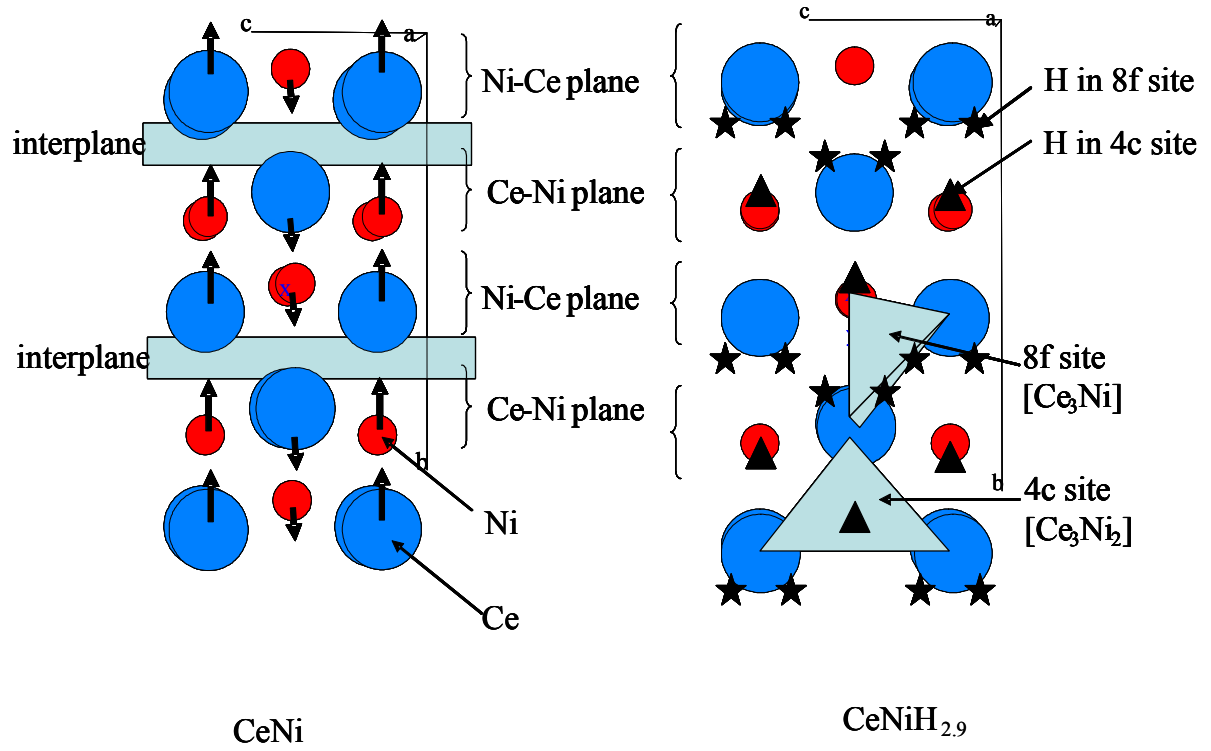


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FIG. 3

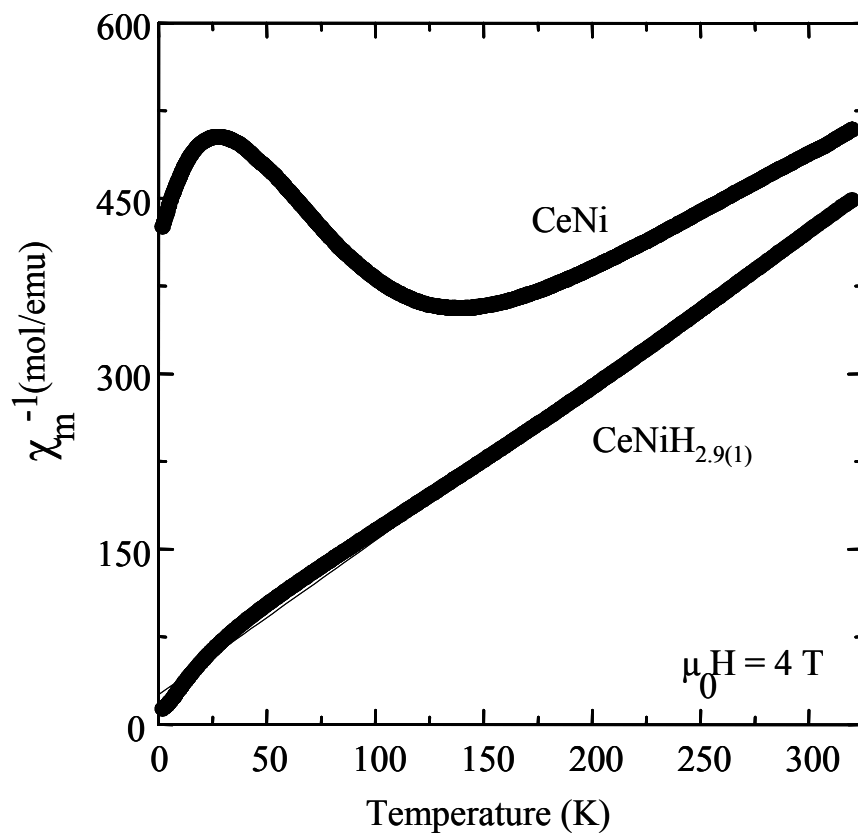


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FIG. 4



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FIG. 5



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Fig.6