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Magnetic and Crystallographic Characteristics of $CeNi_{5-x}M_x$ (M = Fe, Mn) Alloys and Their Hydrides*

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Measurements of magnetization and lattice parameters were made on $CeNi_{5-x}M_x$ (M = Fe or Mn) ternaries and their hydrides. Replacement of Ni by 10–35% Fe and 15% Mn in $CeNi_5$ expands the lattice and produces a significant change in magnetic properties. Magnetic ordering temperatures determined for the $CeNi_{5-x}Fe_x$ series range from 115 to 290 K. Absorbed hydrogen leads to a large increase in unit cell volume without a change in the crystal structure. Upon hydrogenation the ferromagnetism is suppressed in the Fe-substituted compounds whereas it is enhanced in Mn-substituted compounds. The magnetic characteristics of the $CeNi_{5-x}Fe_x$ system indicate that Fe induces a moment on the neighboring Ni atoms. These moments are dependent on iron content. The existence of Ni moments is indicative of strong coupling between the 3*d* Fe atoms and the induced Ni moments.

Introduction

The magnetic characteristics of RNi_4Fe ternaries, in which R is magnetic (Pr or Nd) (*1*) and nonmagnetic (Ce, La, or Y) (*2*), were studied earlier. These compounds exhibited ferromagnetic behavior with Curie temperatures ranging between 195 and 270 K. The sizeable saturation magnetization observed for RNi_4Fe alloys was deemed to be too high to be ascribed only to Fe sublattice moments. It had been established previously that the nonmagnetic rare earth compounds, i.e., $CeNi_5$, $LaNi_5$, or YNi_5, all are Pauli paramagnets (*3–5*). Electron transfer from Ce, La, or Y to Ni is sufficient to nearly fill the nickel *d* band, supporting the conclusions reached somewhat earlier by Wallace and Aoyagi (*6*).

The present study is concerned with the investigation of the bulk magnetic and crystallographic properties of the ternary alloys represented by the formula $CeNi_{5-x}M_x$, where M is a 3*d* transition element Fe or Mn and x ranges from 0.5 to 1.75. As indicated below, $CeNi_{5-x}Fe_x$ and $CeNi_{4.25}Mn_{0.75}$ have been found to exhibit ferromagnetism with reasonably high Curie temperatures and magnetizations. The present work was undertaken to ascertain the effect of the partially substituted Fe on the moment of the neighboring Ni atoms in the $CeNi_{5-x}Fe_x$ system. The influence of the hydrogen on the magnetization and magnetic ordering temperatures of the systems studied, which

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was found to be drastic, has also been investigated.

Experimental Detail

A. Sample preparation. The $CeNi_{5-x}Fe_x$ ($x = 0.5, 1.0, 1.5$, and 1.75) and $CeNi_{5-x}Mn_x$ ($x = 0.75$) were prepared by melting the constituents Ce (99.9%), Ni (99.99%), and Fe (99.99%) or Mn (99.96%) in a water-cooled copper boat using rf induction heating. A continuous flow of Ti-gettered argon was maintained during melting. The ingots were turned over and remelted several times to insure homogeneity. The samples were annealed at ~1200°C for ~6 hr to obtain single-phase materials. Crystal structures of the alloys were established by conventional powder X-ray diffraction techniques using Cu*K*α radiation and a graphite X-ray monochromator. All investigated samples were single phase (within the detection limit of X-ray diffraction).

B. Hydrogenation. The hydride samples were obtained by exposing the host materials at room temperature to ~60 atm of pure hydrogen. After an induction period of ~1 hr the samples absorbed hydrogen and were converted to a fine powder (~50 μ). A portion of the sample was utilized for the crystallographic measurements. For this purpose the sample was hydrogenated to saturation and then quenched in liquid nitrogen. The hydrogen remaining in the vapor state was removed and the sample was then poisoned with SO_2 gas. The compounds with compositions $x = 1.5$ and 1.75 in $CeNi_{5-x}Fe_x$ and $x = 0.75$ in $CeNi_{5-x}Mn_x$ were hydrogenated to concentrations of hydrogen of 4, 2.6, and ~6 per formula unit, respectively. They were poisoned and used for the magnetic measurements. X-ray diffraction patterns for these hydrides showed that they were in the β-phase region. The vapor pressure of hydrogen in the compounds with $x = 0.5$ and 1 in $CeNi_{5-x}Fe_x$ were found to be high, i.e., $P_{H_2} \geq 10$ atm. Therefore, with the present experimental setup we were not able to proceed with the magnetization measurements of these hydrides.

Magnetic measurements were made on loose powder using the Faraday technique. The temperature dependence of the magnetization in the range 4–300 K was measured in an applied field of 4 and 20 kOe, and the field dependence of the magnetization M was measured at 4.2 K. The Curie temperature, T_C, was determined by plotting M^2 vs T and extrapolating to $M^2 = 0$. Saturation magnetization, μ_s, was obtained from Honda plots (M vs $1/H$).

Results and Discussion

A. Crystallography

The prepared $CeNi_{5-x}M_x$ (M = Fe or Mn and $x = 0.5$, 1.0 and 1.75 or 0.75) alloys crystallize in the hexagonal structure of the $CaCu_5$ type with space group *P6/mmm*. The lattice constants and the unit cell sizes increase with the partial replacement of Ni by the larger atoms Fe or Mn in $CeNi_5$. In the RNi_5 systems, R atoms lie in the 1*a* position with point symmetry 6/*mm* and Ni atoms occupy the 2*c* and 3*g* positions with point symmetries $\bar{6}2m$ and *mmm*, respectively. It is expected that in the case of our present well-homogenized samples of $CeNi_{5-x}M_x$ (M = Fe or Mn) compounds, Ce atoms lie in the 1*a* position and Fe (or Mn) partially occupies both 2*c* and 3*g* sites. Mössbauer spectra for the isostructural system $LaNi_{5-x}Fe_x$ observed by Lamloumi *et al.* (*7*) have shown that in these compounds Fe is distributed over both sites. Campbell *et al.* (*8*) has also concluded that there is a similar Fe site occupation in the latter series.

The homogeneity range in $CeNi_{5-x}Fe_x$ is $0 \leq x \leq 1.75$ and in $CeNi_{5-x}Mn_x$ is $0 \leq x \leq 0.75$ (*9*). The crystallographic data for these alloys are given in Table I. For the

TABLE I

CRYSTAL STRUCTURE DATA FOR $CeNi_{5-x}$ (M = Fe or Mn; x = 0.5,1.0,1.5,1.75 or 0.75) AND THE HYDRIDES

Material	a (Å)	c (Å)	V (Å)^3	$V_H{}^a$ (Å)^3	Hydrogen capacity H atoms/f.u.
$CeNi_5$	4.887	4.003	82.80	—	~6.5
$CeNi_{4.5}Fe_{0.5}$	4.912	4.022	84.14	—	—
$CeNi_4Fe$	4.927	4.038	84.90	—	—
$CeNi_{3.5}Fe_{1.5}$	4.941	4.050	85.63	102.70	4
$CeNi_{3.25}Fe_{1.75}$	4.948	4.055	85.98	100.60	2.6
$CeNi_{4.25}Mn_{0.75}$	4.921	4.054	85.02	106.65	6

[a] V_H is the unit cell volume of the hydride of composition cited in column 6.

$CeNi_{5-x}Fe_x$ system, the unit cell volume measured in (Å)^3 increases linearly with increasing iron concentration for x between 0.5 and 1.75, according to the equation

$$V(x) = 1.47x + 83.4.$$

The linear dependence of $V(x)$ vs x for $CeNi_{5-x}Fe_x$ is exhibited in Fig. 1. This behavior suggests that Fe substitution probably does not alter the Ce valence state in $CeNi_5$. Earlier observations on the low-temperature susceptibility measurements of the $CeNi_{5-x}Cu_x$ system showed that Ce in $CeNi_5$ is quadripositive (*4*). The linearity of $V(x)$ has also been observed for the isostructural system of $CeNi_{5-x}Mn_x$ by Pourarian and Wallace (*9*) and for La $Ni_{5-x}Fe_x$ by Lamloumi *et al.* (*7*).

The compounds $CeNi_{5-x}M_x$ with M = Fe and x = 1.5 and 1.75 and for M = Mn and x = 0.75 are found to absorb hydrogen with a capacity of 4, 2.6, and 6 H/f.u., respectively. The hydrogen absorption does not alter the structure of the compounds but is accompanied by a large expansion in the unit cell volume, ranging from 18 to ~25%. Results for the hydrides studied are also included in Table I. It can be noted that there is a decrease in hydrogen capacity as the Fe content is increased beyond x = 1.5. This reduction in the hydrogen concentration can be accounted for using the reasoning employed in our recent analysis of the paradigm system $LaNi_{5-x}Cu_x$ (or $CeNi_{5-x}Cu_x$) (*10*). The amount of hydrogen which can be incorporated in the lattice is controlled by the number of metal–hydrogen bonding states and these, in turn, are controlled by the number of Ni or Fe 3*d* states.

B. Magnetic Characteristics

1. $CeNi_{5-x}Fe_x$ system. Field dependence and temperature dependence (at H = 4 and 20 kOe) of the magnetization, M, of the $CeNi_{5-x}Fe_x$ system, with x ranging between 0.5 and 1.75, are shown in Figs. 2–4. As

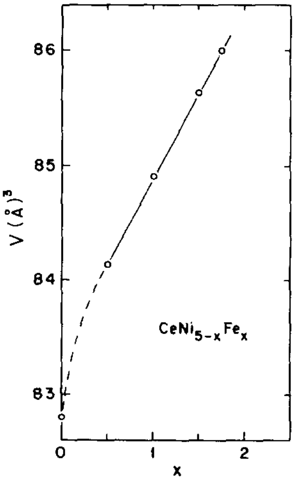

FIG. 1. Dependence of the unit cell volume, V_c, of $CeNi_{5-x}Fe_x$ as a function of iron content, x.

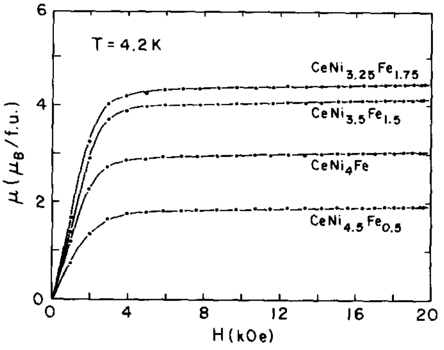

FIG. 2. Field dependence of the magnetization of $CeNi_{5-x}Fe_x$ ($0 < x \leq 1.75$) at 4.2 K.

noted in the Introduction, all the alloys studied order ferromagnetically. This is established from the behavior of M vs H at 4.2 K and also M vs T at 4 and 20 kOe. The determined magnetic ordering temperatures, T_C, of the compounds studied are found to vary between 115 and 293 K. The behavior of T_C vs x is shown in Fig. 5.

As noted above, $CeNi_5$ is a Pauli paramagnet at 4.2 K (*4*). Its susceptibility is only weakly dependent on temperature. Thus the Ce atom in $CeNi_5$ is in the nonmagnetic Ce^{4+} state and the Ni d band is filled. The partial replacement of Ni (between 10 to 35%) by Fe results in the development of ferromagnetism in the $CeNi_{5-x}Fe_x$ system. The magnetic moment of the latter increases upon progressive replacement of Ni by Fe.

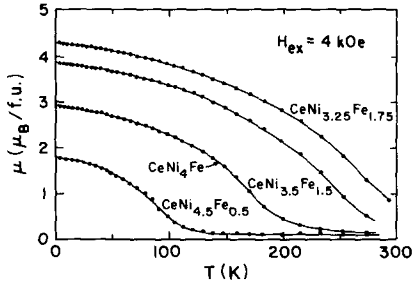

FIG. 3. Temperature dependence of the magnetization of $CeNi_{5-x}Fe_x$ at 4 kOe.

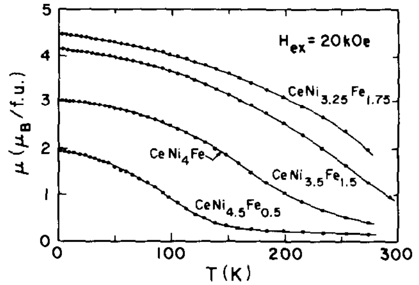

FIG. 4. Temperature dependence of the magnetization of $CeNi_{5-x}Fe_x$ at 20 kOe.

The M vs H behavior at 4.2 K for all the compositions shows that saturation is readily achieved. Results of the saturation moments, μ_s, determined at 4.2 K (using Arrott plots M^2 vs H/M) are shown in Fig. 6. It is interesting to note that the behavior of μ_s with x is found to be linear. The linearity follows the relation

$$\mu_s = 2.1x + 0.91 \qquad \text{for } 0.5 \leq x \leq 1.75.$$

The increase of Curie temperature, T_C, with x in $CeNi_{5-x}Fe_x$ is also found to be linear and follows the expression:

$$T_C = 144.5x + 43.2 \qquad \text{for } 0.5 \leq x \leq 1.75.$$

It is to be noted that the results of T_C vs x and μ_s vs x shift away from linearity when

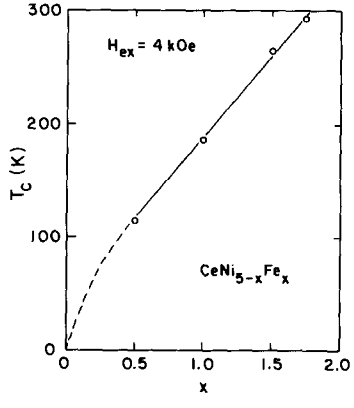

FIG. 5. Curie temperature (T_C) of $CeNi_{5-x}Fe_x$ vs iron content, x.

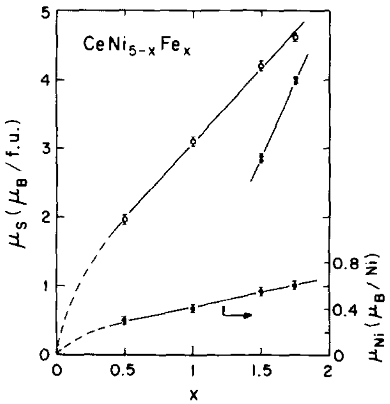

FIG. 6. Saturation magnetization, μ_s, of $CeNi_{5-x}Fe_x$ (O), $CeNi_{5-x}Fe_xH_y$ (×) and induced Ni moment (●) vs iron content, x, at 4.2 K.

Fe concentration is <0.5 (Figs. 5 and 6). In this respect, V_c vs x is observed to behave in a similar fashion (Fig. 1). The sharp increase in the lattice parameter between $x = 0$ and $x = 0.5$ and the drastic increase in the magnetic moment and T_C in the same range may be attributed partially to the alteration of Ce^{4+} to the Ce^{3+} state in the alloy. This mixed valency of Ce atoms has also been observed in the isostructural $CeNi_{5-x}Cu_x$ system (*4*).

The ferromagnetic ordering in $CeNi_{5-x}Fe_x$ cannot be measured to involve only Fe atoms, since the value of the Fe moments (for all cases) seems unreasonably large. This suggests that part of the moment is due to Ni atoms, the induced moment referred to above. This is a point of considerable interest, since the existence of Ni moments is indicative of strong exchange interactions between the localized (3*d*) Fe atoms and the induced Ni moments. The Curie temperature versus x increases strikingly due to such a positive exchange interaction ($T_C = 293$ for $x = 1.75$). This induced Ni moment has also been observed in the isostructural $LaNi_{5-x}Fe_x$ (*7*), $PrNi_4Fe$ and $NdNi_4Fe$ systems (*1*). An attempt was made to estimate the Ni moments in $CeNi_{5-x}Fe_x$, employing the average hyperfine field of Fe in $LaNi_{5-x}Fe_x$ determined by Lamloumi *et al.* using Mössbauer spectroscopy. The latter authors have estimated the moment on the Fe atom for various concentrations of x. Using the moments for $CeNi_{5-x}Fe_x$ and assuming a colinear ferromagnetic coupling between Ni and Fe atoms, we have estimated the moments of Ni in μ_B per Ni atom as a function of the composition x. The results are shown in Fig. 6. It can be seen that upon partial replacement of ~35% of Ni by Fe in $CeNi_5$, an induced moment of ~0.6 μ_B/Ni atom is observed. This is slightly higher than that observed for elemental Ni ($\mu_{Ni} \simeq 0.55\ \mu_B$). It is presumed that both 2*c* and 3*g* Ni sites in the lattice experience the induced moments. It is to be noted that the behavior of μ_{Ni} vs x between $x = 0.5$ to $x = 1.75$ is almost linear.

2. *$CeNi_{5-x}Fe_xH_y$ system.* The magnetization vs applied field curves for the hydrides $CeNi_{3.5}Fe_{1.5}H_4$ and $CeNi_{3.25}Fe_{1.75}H_{2.6}$ compared to their host compounds at 4.2 K are shown in Fig. 7. The Arrott plots (M^2 vs H/M plots) at 4.2 K indicated that these hydrides are ferromagnetic. The temperature dependence of magnetization at a constant applied field of 4 and 20 kOe for the hydrides studied is also compared to the host compounds and is plotted in Figs. 8 and 9. It is clearly shown that both the magnetiza-

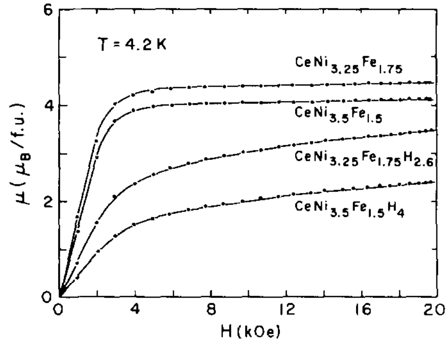

FIG. 7. Comparison of the field dependence of magnetization of $CeNi_{5-x}Fe_x$ with their hydrides at 4.2 K.

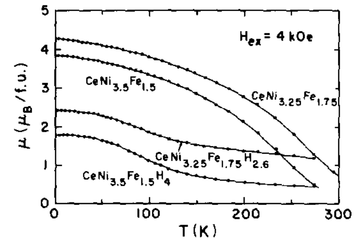

FIG. 8. Comparison of the temperature dependence of magnetization of $CeNi_{5-x}Fe_x$ with their hydrides at 4 kOe.

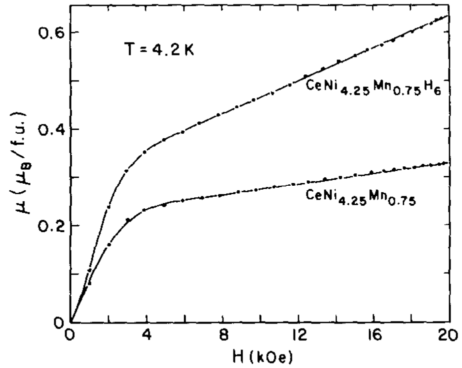

FIG. 10. Field dependence of magnetization of $CeNi_{4.25}Mn_{0.75}$ and their hydrides at 4.2 K.

tion and the magnetic ordering temperature of the compounds are reduced upon hydrogen absorption. The reduction in the saturation magnetization, μ_s (at 4.2 K), is estimated to be ~30 and 14% for $CeNi_{3.5}Fe_{1.5}$ and $CeNi_{3.25}Fe_{1.75}$, respectively. The decrease in μ_s value suggests that hydrogen may have influenced the induced moment on Ni atoms. The reduction in μ_{Ni} in $CeNi_{3.5}Fe_{1.5}H_4$ and $CeNi_{3.25}Fe_{1.75}H_{2.6}$ is estimated to be ~0.38 μ_B and ~0.19 μ_B, respectively. These estimates are valid subject to the proviso that hydrogen has no influence on the Fe moment.

3. *$CeNi_{4.25}Mn_{0.75}$ and the hydride.* Results of the field dependent magnetization of $CeNi_{4.25}Mn_{0.75}$ and $CeNi_{4.25}Mn_{0.75}H_{5.8}$ determined at 4.2 K are plotted in Fig. 10. The data do not show saturation up to 20 kOe. The temperature dependencies of the magnetization of the host and the hydride were measured between 4.2 K and room temperature and in applied fields of 4 and 20 kOe. The results are exhibited in Fig. 11. The details of the magnetic ordering cannot be inferred from these data. The Arrott plots were found to have positive y-axis intercepts. The plots at 4.2 K revealed that both the host compound and the hydride are magnetically ordered.

It has been mentioned above that $CeNi_5$ is a Pauli paramagnet; its magnetization is linearly dependent upon field. Partial replacement of Ni (15%) by Mn in the compound has changed the material to a ferro-

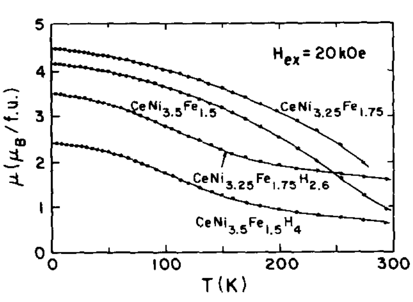

FIG. 9. Comparison of the temperature dependence of magnetization of $CeNi_{5-x}Fe_x$ with their hydrides at 20 kOe.

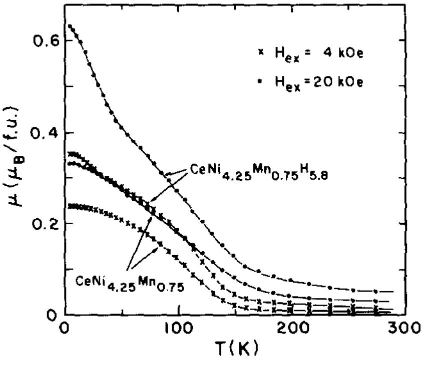

FIG. 11. Temperature dependence of magnetization of $CeNi_{4.25}Mn_{0.75}$ and their hydrides at 4 and 20 kOe.

magnet. The Curie temperature of Ce $Ni_{4.25}Mn_{0.75}$ was determined (plotting M^2 vs T) to be 135 K. The ordering temperature increases slightly to 145 K upon hydrogenation absorption. The magnetic moments of $CeNi_{4.25}Mn_{0.75}$ and its hydride at 20 kOe were obtained to be $0.32 \pm 0.02\ \mu_B$, and $0.62 \pm 0.02\ \mu_B$, respectively. The results show striking behavior, as the moment of the hydride is about a factor of two larger than that of the corresponding host. The saturation magnetization of $CeNi_{4.25}Mn_{0.75}$ has increased from $\sim 0.38 \pm 0.02\ \mu_B$ to $\sim 0.78 \pm 0.05\ \mu_B$ upon hydrogenation.

It is uncertain whether the total magnetic moment of the compound (or the hydride) is attributed to the Mn sublattice or to both Mn and Ni atoms. It remains for neutron diffraction studies to establish the nature of the coupling between Mn and Ni sublattices. Assuming all the contribution to the magnetization to be from the Mn sublattice (no moment is induced on Ni atoms), the estimated μ_{Mn} at 4.2 K and 20 kOe is found to be $\simeq 0.42\ \mu_B$ and $\sim 0.82\ \mu_B$ in the host and the hydride, respectively. Here again hydrogenation produces an increase in the moment of the system, a feature which has also been observed for the $Zr(Fe,V)_2$ system (*11*).

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