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Study of magnetic susceptibility of CeNiAl and its hydrides

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Magnetic-susceptibility measurements have been performed in some Fe_2P-type intermetallic compounds, viz., YNiAl and CeNiAl and their hydrides in the temperature range 77–300 K. YNiAl and its hydride exhibit Pauli paramagnetism; moreover hydrogenation does not appreciably alter the magnetization of YNiAl. CeNiAl also exhibits a temperature-independent susceptibility indicating that the cerium ion in this compound is in tetravalent state. Hydrogenation of this compound, however, alters the magnetization such that it becomes temperature dependent and follows Curie's law. With increase in hydrogen concentration (x), μ_{eff} per formula unit of the hydride increases continuously from $0.5\mu_B$ for $x=0.4$ to $2.14\mu_B$ for $x=2.04$, the latter being close to the free-ion value of Ce^{3+}. On the other hand, the temperature-independent contribution (χ_1) to the total susceptibility (χ) decreases with x. Results further indicate that the hydrogenation in CeNiAl alters the band structure in such a way that the decrement in χ_1 and increment in the temperature-dependent part, $\chi(T)$, follow a regular fashion.

I. INTRODUCTION

Hydrogen-absorption properties of the intermetallic compounds of the type AXAl ($A \equiv$Zr, Y, Th, U, etc., and $X \equiv$Ni, Cu, and Mn) have recently been studied.[1,2] They belong to Fe_2P-type crystal structure with the space group $P\bar{6}2m$.[3] In an earlier report,[4] it has been shown that the hydrogen dissolved in UNiAl is responsible for shifting and broadening the magnetic susceptibility maximum of UNiAl from 23 to 34 K in $UNiAlH_x$. Furthermore, an antiferromagnetic transition for the hydride of UNiAl has also been revealed[4] through the observation of susceptibility maximum at 122 K and a simultaneous disappearance of ^1H nuclear-magnetic-resonance (NMR) signal.

Rare earth M^{RE} (except lanthanum), $X=$Ni or Cu, and aluminum can be combined to form $M^{\text{RE}}X$Al-type compounds which also belong to the Fe_2P-type structure.[3] Interestingly, it has been observed from the lattice parameter measurements that among all the rare-earth ions in $M^{\text{RE}}X$Al series, cerium is in a trivalent state when alloyed with copper, but exhibits a higher valence state when alloyed with nickel.[3] We intend to study the magnetic properties of the compounds $M^{\text{RE}}X$Al and their hydrides. In the present paper, the results of magnetic susceptibility measurements on CeNiAl and its hydrides in the temperature range 77–300 K have been reported. For comparison, measurements have also been made on YNiAl and its hydride, CeCuAl and YCuAl. The results indicate that CeNiAl, itself being Pauli paramagnetic, shows a temperature-dependent magnetic moment on hydrogenation. In contrast, both YNiAl and its hydride remain Pauli paramagnetic.

II. EXPERIMENTAL

The intermetallic compounds CeNiAl, CeCuAl, YNiAl, and YCuAl were prepared by arc melting the constituent elements (purity $>99.7\%$) on a water-cooled copper hearth under an argon atmosphere. The process of melting in each case was repeated several times to ensure good homogeneity. The materials were then annealed at 700 °C for 48 h. Crystal structures were verified from x-ray powder diffraction studies. The hydrides were prepared in a Sievert-type gas-doping apparatus, described elsewhere.[5] Each sample was thoroughly degassed at 500 °C for three hours and then cooled down to 250 °C, wherein purified hydrogen gas was allowed to react with the sample. Of the two compounds CeNiAl and YNiAl, the former was found to absorb hydrogen more readily to form stable hydrides. Even at 20 atm hydrogen pressure, YNiAl could be hydrided only up to a concentration of 0.4 per formula unit. Hydrides with different hydrogen concentrations, viz., $CeNiAlH_x$ with $x=0.45$, 0.63, 0.88, 1.45, and 2.04 and $YNiAlH_x$ with $x=0.4$, were obtained by hydriding the samples at various hydrogen pressures ranging from near atmospheric to about 20 atm. The concentrations were calculated directly from the increment of weight of the samples on hydrogenation. Values of x were uncertain by a maximum of ±0.05. The prepared hydrides were stored in normal air. ^1H NMR studies on these hydrides during several weeks did not reveal any hydrogen loss.

Measurements of magnetic moments were performed with a vibrating sample magnetometer VSM model 155 of EG&G, Princeton Applied Research. Magnetic field was supplied by a Varian Associates V7400 15-in. electromagnetic. Temperature variation was achieved by controlling the temperature of precooled nitrogen gas using a Varian V4540 temperature controller. Measurements at 77 K were performed using a fixed liquid-nitrogen bath.

III. RESULTS AND DISCUSSIONS

The intermetallics YNiAl, YCuAl, CeNiAl, and CeCuAl exhibit paramagnetic behavior at 300 K as observed

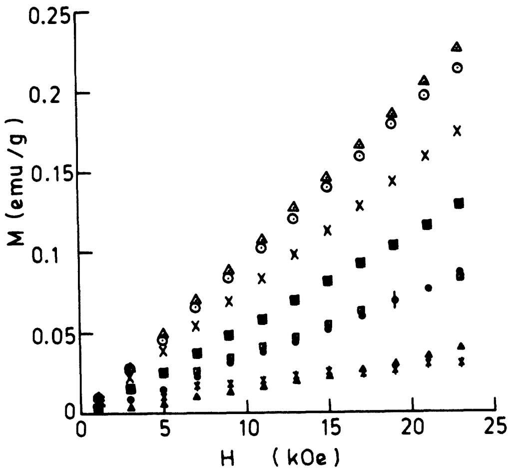

FIG. 1. Magnetic-field dependence of the magnetization M at room temperature for different samples: ▲, YNiAl; ●, CeNiAl; *, $YNiAlH_{0.4}$; ■, $CeNiAlH_{0.63}$; ×, $CeNiAlH_{0.88}$; △, $CeNiAlH_{2.04}$; □, degassed $CeNiAlH_{2.04}$; and ○, CeCuAl.

from the respective magnetic-field dependence of their magnetization (Fig. 1). In general, the magnetic susceptibility of these compounds at any temperature consists of several independent contributions

$$\chi=\chi_1+\chi(T)+\chi_{MI}(T)\ , \tag{1}$$

where $\chi_1=\chi_P+\chi_0+\chi_{dia}$. χ_P contains contributions from the Pauli spin susceptibilities of the d-p and s-p bands. χ_0 is the orbital contribution to the susceptibility, i.e., Van Vleck term. χ_{dia} contains the diamagnetic contribution of the ion cores and the filled portion of the d-p and/or s-p bands. Thus χ_1 represents the total temperature-independent contribution to the susceptibility. The term $\chi(T)$ is the paramagnetic susceptibility of a magnetic material, arising out of its $3d$ or $4f$ localized electrons together with the s-d or s-f exchange-enhanced temperature-dependent susceptibility of the conduction electron bands. $\chi_{MI}(T)$ is the contribution from ferromagnetic or superparamagnetic impurities.

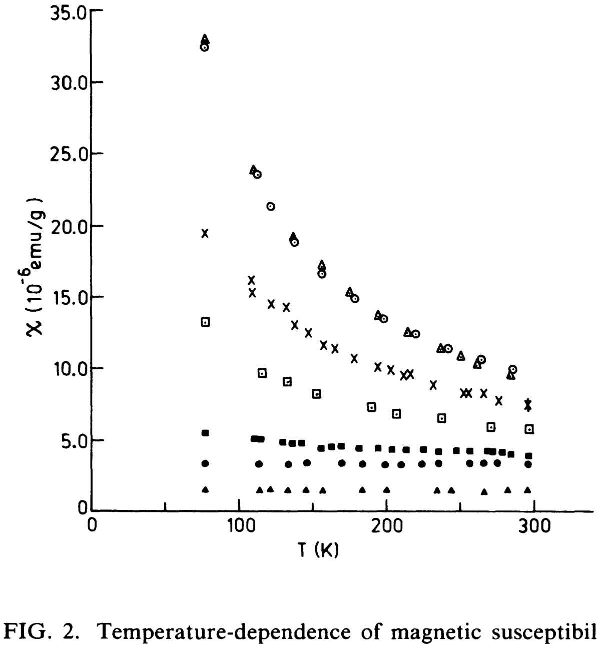

FIG. 2. Temperature-dependence of magnetic susceptibility χ for different samples: ●, CeNiAl; ■, $CeNiAlH_{0.45}$; □, $CeNiAlH_{0.63}$; ×, $CeNiAlH_{0.88}$; △, $CeNiAlH_{2.04}$; ○, CeCuAl; and ▲, $YNiAlH_{0.4}$.

Temperature-dependence studies of magnetic susceptibility reveal that YNiAl and YCuAl are temperature-independent Pauli paramagnets. Thus nickel and copper in these compounds are nonmagnetic, i.e., there is no contribution from localized $3d$ electrons to the susceptibility in these compounds. It is interesting that CeNiAl also exhibits temperature-independent susceptibility in this temperature range (Fig. 2). It appears, then, that magnetism of these compounds is associated only with the conduction electrons; even the $4f$ electron of cerium has become completely delocalized in CeNiAl. In contrast, CeCuAl exhibits normal temperature-dependent susceptibility arising out of localized $4f$ electron of cerium. These observations support the results of lattice-parameter measurements[3] in CeCuAl and CeNiAl, where it has been observed that cerium is in trivalent state in the former compound whereas in the latter it exhibits a higher-valence state. However, these measurements are not sufficient to draw a conclusion that cerium in CeNiAl is in a tetravalent state. Nevertheless, it should be noted that the intermediate value (in between YNiAl and CeCuAl) of the magnetization in CeNiAl as observed in Fig. 1 may arise either from an increased contribution from χ_1 in comparison to YNiAl or if cerium in CeNiAl is not in a completely tetravalent state. However, from all the results mentioned above, it seems that there is an overlap of the cerium $4f$ level with the conduction band in CeNiAl.

A. Measurements on hydrides

It is found that in $YNiAlH_{0.4}$ the magnetization remains almost the same as that of YNiAl (Fig. 1) and exhibits temperature-independent Pauli paramagnetism (Fig. 2) in the temperature range 77–300 K. This indicates that the hydrogen in YNiAl, at least up to this concentration, does not appreciably alter the density of electronic states at the Fermi level. Interestingly, in CeNiAl the magnetization is found to increase continuously with increase in hydrogen concentration (Figs. 1 and 3). At a certain hydrogen concentration, $x\sim2.0$, in $CeNiAlH_x$, the magnetization is found to become close to that of CeCuAl. Furthermore, the susceptibility behavior of CeNiAl is modified on hydrogenation and becomes temperature dependent (Fig. 2). With increase in hydrogen concentration, not only the magnetization is increased as mentioned above, but also the temperature-dependent contribution to the magnetic susceptibility becomes more and more dominant. From these results it seems that both χ_1 and $\chi(T)$ of Eq. (1) are changed with hydrogenation. However, the effect of $\chi_{MI}(T)$, which may arise in metal hydrides, may be ignored in the present case as the magnetization behavior of the dehydrided samples have been found to be the same as that of their respective original intermetallics (Fig. 1).

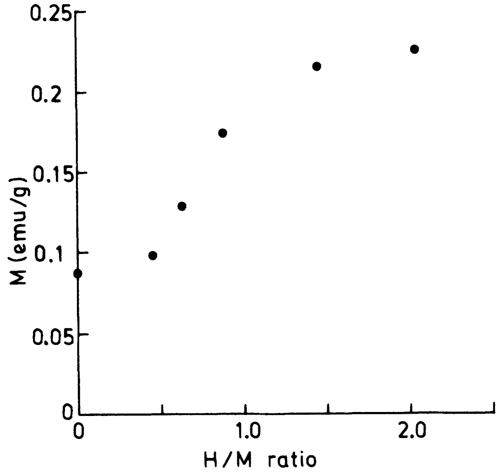

FIG. 3. Magnetization M of CeNiAlH$_x$ ($0 \leq x \leq 2.04$) vs the hydrogen concentration x observed at 23 kOe.

TABLE I. Values of temperature-independent contribution to the susceptibility, χ_1, and the effective moment μ_{eff} for different samples.

Sample	χ_1 (10^{-6} emu/g)	μ_{eff} (μ_B/formula-unit)
YNiAl	1.5±0.3	
CeNiAl	3.4±0.3	
CeNiAlH$_{0.45}$	3.8±0.1	0.50±0.02
CeNiAlH$_{0.63}$	3.2±0.1	1.17±0.02
CeNiAlH$_{0.88}$	2.9±0.1	1.59±0.02
CeNiAlH$_{1.46}$	1.6±0.1	2.11±0.02
CeNiAlH$_{2.04}$	0.9±0.1	2.14±0.02
CeCuAl	1.2±0.1	2.10±0.02

We have estimated the different contributions, viz., χ_1 and $\chi(T)$, to the total susceptibility in the following way. The most general form of the temperature-dependent susceptibility is $\chi(T) = C/(T \pm \Theta)$, where C is the Curie constant and Θ is the paramagnetic Curie temperature. The sign of Θ depends upon whether the system orders ferromagnetically or antiferromagnetically. Neglecting $\chi_{\text{MI}}(T)$, Eq. (1) may be rearranged as

$$\chi = \chi_1 + \frac{C}{T \pm \Theta} . \tag{2}$$

In the plot of χT against T, Θ would be manifested in the nonlinearity of the curve, as otherwise this would be straight line with a slope given by χ_1 and intercept at $T = 0$ K as "C." From C, one can estimate effective moment of the magnetic ion, μ_{eff}, in terms of Bohr magneton per formula unit.

Figure 4 shows the variation of χT with T of CeNiAlH$_x$ at different hydrogen concentrations. The nature of the variation in each case fits well to a straight line without any nonlinearity in the temperature range studied. Thus, Θ may be assumed to be negligibly small in all cases and thus the susceptibilities follow a Curie-type behavior in this temperature range. It is interesting to note that the slopes of these lines, i.e., the temperature-independent contribution to the susceptibility χ_1, decreases continuously with increase of hydrogen concentrations x, whereas the Curie constant C as seen from the intercepts increases with x. Table I shows the values of χ_1 and μ_{eff} for different compounds. The χ values for CeNiAl and YNiAl, for which $\chi = \chi_1$, are also included in Table I. Since in most cases χ_{dia} is not expected to make a significant contribution to χ_1, decrease of χ_1 in CeNiAlH$_x$ with x could reflect reductions in χ_P and/or χ_0. Measurements of NMR Knight shift and electronic specific heat could provide information regarding their individual contribution to χ_1. Apparently it seems that the decrease in χ_1 and increase in $\chi(T)$ observed in CeNiAlH$_x$ are quite independent manifestations of the effect of hydrogenation of CeNiAl. However, from Fig. 5 it is seen that changes in χ_1 and $\chi(T)$ occur in a regular fashion. The reason for this correlation at the microscopic level is not clear at this stage.

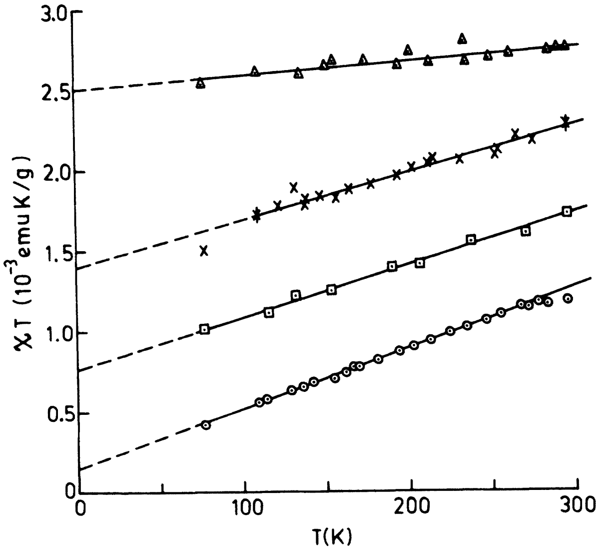

FIG. 4. χT vs temperature for the hydrides of CeNiAl: ○, CeNiAlH$_{0.45}$; □, CeNiAlH$_{0.63}$; ×, CeNiAlH$_{0.838}$; and △, CeNiAlH$_{2.04}$.

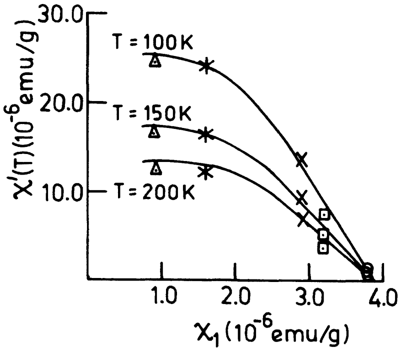

FIG. 5. Values of χ_1 and $\chi(T)$ plotted at different temperatures: ○, CeNiAlH$_{0.45}$; □, CeNiAlH$_{0.63}$; ×, CeNiAlH$_{0.88}$; $*$, CeNiAlH$_{1.46}$; and △, CeNiAlH$_{2.04}$.

From Table I it is seen that μ_{eff} for $CeNiAlH_{0.45}$ is much less than that of the free ion Ce^{3+}. However, it increases gradually with x, and at $x = 2.04$ the value of μ_{eff} becomes close to that of Ce^{3+}. As expected, CeCuAl also exhibits almost the same μ_{eff} with cerium in a trivalent state (Table I). These results indicate that the 4f electron, which was almost delocalized in CeNiAl, becomes more and more localized, depending on the extent of hydrogenation. In intermediate concentrations ($0 \leq x \leq 2.04$), though an effect of localized moment is introduced, as manifested through the temperature-dependent susceptibility, the moment still remains lower than that of Ce^{3+}. Thus it seems that at $x < 2.04$, cerium in $CeNiAlH_x$ is neither tetravalent nor trivalent. This may happen in one of the following ways.

(1) In $CeNiAlH_x$ there may exist two phases. One is a solid solution of CeNiAl and hydrogen and the other is a hydrogen-rich hydride phase containing the trivalent cerium ion. With the increase in hydrogen concentration, the solid-solution phase changes to the hydride phase and finally at $x \sim 2.0$, a complete hydride phase is obtained. This explains the variation of magnetization with x as observed in Fig. 3.

(2) If $CeNiAlH_x$ is in a single phase then there may exist a fluctuation between the two valence states. With increase in hydrogen concentration, the fluctuation is gradually decreased which is also reflected in the increase of temperature-dependent contribution to the susceptibility.

The results presented here, therefore, indicate that hydrogenation modifies the band structure of CeNiAl in such a way that the overlapping of the 4f level with the conduction band is reduced. In particular, hydrogenation of CeNiAl affects the valence state of cerium in the same way as when cerium is alloyed with copper instead of nickel forming CeCuAl. Further microscopic studies such as ^1H NMR, x-ray photoemission spectroscopy, Mossbauer, etc., are necessary in order to have a clear picture about the band structure of these compounds and their hydrides.

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