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Hydrogen-induced structural and valence change in CeIrAl

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The compound CeIrAl crystallizes in the orthorhombic ε-TiNiSi-type structure in which the cerium ions are in a mixed-valent state as inferred from its weakly temperature dependent magnetic susceptibility. This compound absorbs hydrogen at ambient temperature to form $CeIrAlH_2$. A structural transformation from orthorhombic to hexagonal structure takes place on hydrogen absorption. Further, the magnetic susceptibility of the hydride exhibits Curie-Weiss behavior, typical of local moment on Ce^{3+} ions. Thus hydrogen absorption brings about dramatic changes in the structure and the valence state of cerium in CeIrAl.

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I. INTRODUCTION

Studies on metal hydrogen systems have been of considerable interest ever since the discovery that Pd, a nonsuperconducting metal, becomes superconducting on hydrogen absorption.[1] It was soon observed that many rare earth intermetallic compounds absorb large amounts of hydrogen at moderate pressures and ambient temperatures and result in many interesting changes in the physical and electronic properties of the compounds.[2–6] In contrast to the case of Pd metal mentioned above, hydrogen absorption by superconducting Th_7Fe_3 (Ref. 7) and Zr_2Rh (see Ref. 8, and references therein) leads to suppression of superconductivity. The compound Th_6Mn_{23} which is a Pauli paramagnet, exhibits magnetic ordering on hydrogen absorption while Y_6Mn_{23} which is ferromagnetic exhibits antiferromagnetic ordering on hydrogen absorption.[9] The absorbed hydrogen leads to an expansion in the lattice or cell volume. These in turn can modify the magnetic and superconducting interactions in the system under investigation.

Recently, the equiatomic ternary rare earth compound CeIrAl has been found to show interesting properties.[10] In this compound, the Ce ions are found to be in a mixed-valent state. It is interesting to see the effect of hydrogen absorption on the magnetic behavior of cerium ions in this compound. We report the results of our hydriding studies in this paper. It is observed that CeIrAl absorbs hydrogen to form $CeIrAlH_2$. On hydrogen absorption, the crystal structure of CeIrAl changes from orthorhombic to hexagonal. Also, the Ce ions are no longer in a mixed-valent state in the hydride. Instead, the susceptibility of the hydride is seen to follow a Curie-Weiss behavior typical of a local moment on Ce ions.

II. EXPERIMENTAL DETAILS

The polycrystalline sample of CeIrAl was prepared by melting together stoichiometric amounts of the constituent elements in an arc furnace in a continuous flow of argon gas. The sample was turned over and melted several times to ensure homogeneity. The phase purity of the sample was checked using x-ray diffraction technique, employing monochromatic Cu K_α radiation. A portion of the above sample was hydrided in the conventional volumetric equipment. A known amount of sample was contained in a stainless steel reactor and hydriding was carried out using the standard procedure involving the activation of the compound followed by gradual increase in hydrogen pressure to a maximum of 45 atmosphere. The sample temperature was cycled between room temperature and $\cong$473 K several times. The amount of hydrogen in the sample was estimated by (i) monitoring the change in H_2 pressure in the absorption process and (ii) by complete decomposition of a part of the hydride sample in an evacuated and calibrated chamber. Our estimate along the two routes agreed within $\pm3\%$.

X-ray diffraction analysis on the hydride was also carried out to check for its single-phased nature and determine the volume expansion. The sample surface was poisoned using CS_2, so that the sample could retain hydrogen when taken out for x-ray and magnetic studies. Magnetization measurements on the parent and the hydride samples were carried out using the SQUID magnetometer (Quantum Design) in the temperature range 2–300 K and in applied fields up to 5.5 T.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the observed x-ray patterns of the CeIrAl and $CeIrAlH_2$, respectively The compound CeIrAl is a single phase material which crystallizes in the orthorhombic ε-TiNiSi-type structure (space group Pnma with 4 formula units per unit cell). Rietveld analysis of the observed diffraction pattern yields lattice parameters $a = 6.8954$ Å, $b = 4.3211$ Å, and $c = 7.9411$ Å. Various atoms are at the following positions in the structure: Ce at [0.9648, 0.25, 0.8194], Ir at [0.7339, 0.25, 0.1160], and Al at [0.8640, 0.25, 0.4304]. Hydrogen absorption brings about a dramatic change in the x-ray diffraction pattern with the

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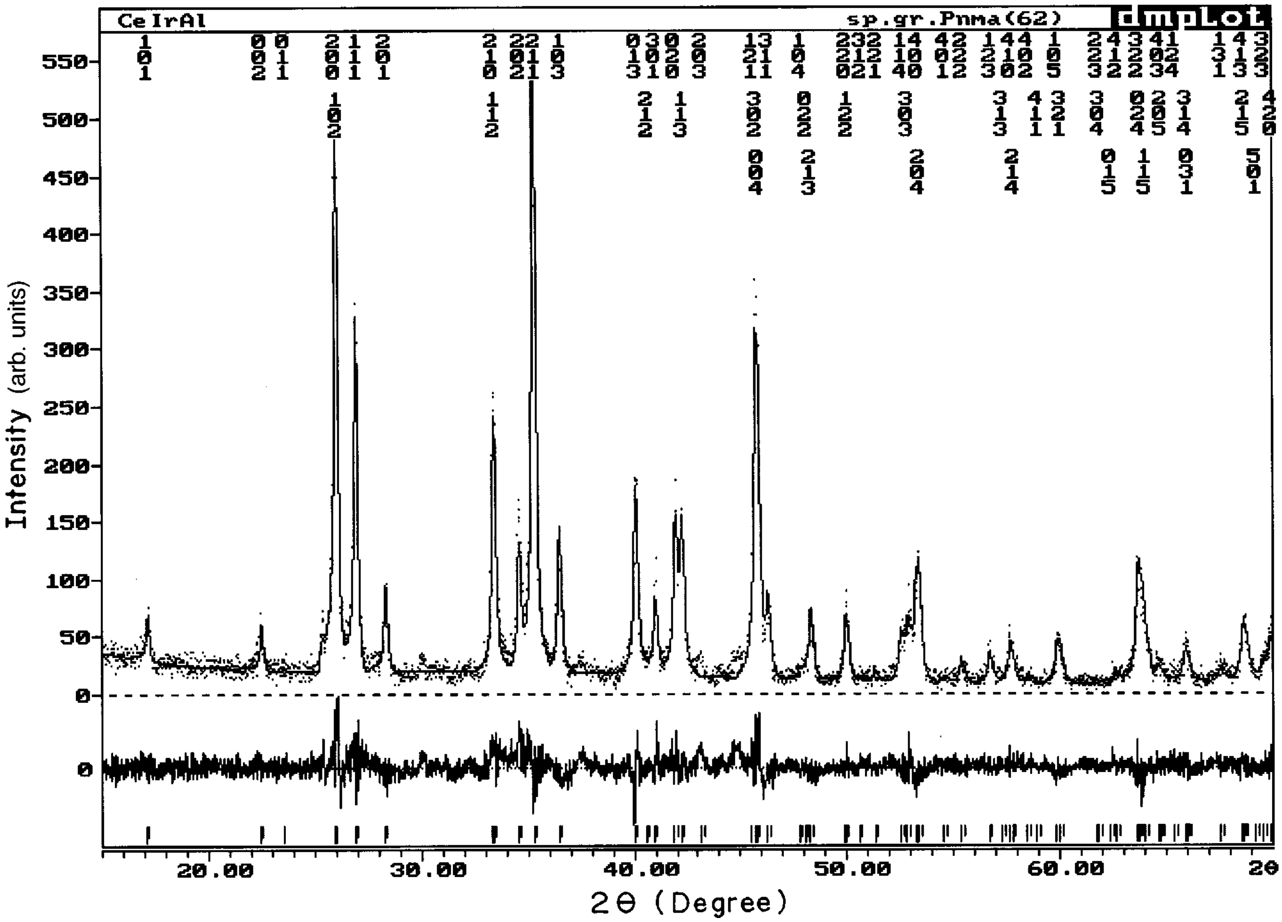

FIG. 1. X-ray diffraction pattern of CeIrAl.

CeIrAl hydride showing lines very different from those of the parent compound. However, after some trial, all the diffraction lines in the hydride sample could be indexed and the diffraction pattern fitted on the basis of a hexagonal structure (space group $P6_3/\mathrm{mmc}$ with 2 formula units per unit cell). The refined lattice parameters are $a=4.4012$ Å and $c=8.3251$ Å, and various atoms are at the following positions: Ce at [0,0,0]; Ir at [1/3,2/3,0.25]; and Al at [1/3,2/3,0.75]. Thus, hydrogen absorption has transformed the structure of CeIrAl from an orthorhombic to a hexagonal structure, which is accompanied by a volume expansion of about 18%. The hydrogen could be removed from the sample by heating it to ≅600 K, after which the sample reverted back to the original orthorhombic ε-TiNiSi-type structure. Thus the hydrogen absorption and the structural transformation in this compound is reversible.

Magnetic susceptibility measurements on intermetallic compound CeIrAl have already been reported by our group.[10] The magnitude of the susceptibility was found to be small, being of the order of 10^{-3} emu/mol, and it showed only weak temperature dependence. In particular, it did not show the Curie-Weiss behavior typical of local moment systems. Above 100 K, the susceptibility was found to increase with increase in temperature up to 300 K, the upper limit of the range of measurements. This is expected to go through a maximum, at some higher temperature, which is characteristic of the compounds showing mixed-valent behavior of cerium ions with high Kondo temperature. The Kondo temperature for this compound was estimated to be about 1300 K,[10] by comparing its susceptibility with that of Rajan's results[11] (based on the Bethe-ansatz solution of the Coqblin-Schreiffer Hamiltonian[12]). No evidence of magnetic ordering was found in this compound, down to 2 K.

It is interesting to see the effect of hydrogenation on the magnetic behavior of CeIrAl, in particular the effect on the mixed-valent behavior of the Ce ions. Figure 3 shows a plot of susceptibility vs temperature and the inverse of susceptibility vs temperature for $\mathrm{CeIrAlH_2}$. Unlike the case of CeIrAl, the susceptibility (χ) of the hydride is not of the mixed-valent type. In fact, χ^{-1} is found to be linear with temperature above 100 K, typical of local moment systems. Upon hydrogenation, one expects changes in the electronic density of states at the Fermi level, which can in turn affect the hybridization between the conduction electron states and the $4f$ electron states. The unit cell volume increases on hydrogenation, resulting in larger Ce-Ce distances and a tendency towards local moment behavior. Therefore, one may expect the hydrogenation to reduce the Kondo interaction between the $4f$ electrons and the conduction electrons.

Above 50 K, the susceptibility of $\mathrm{CeIrAlH_2}$ can be fitted

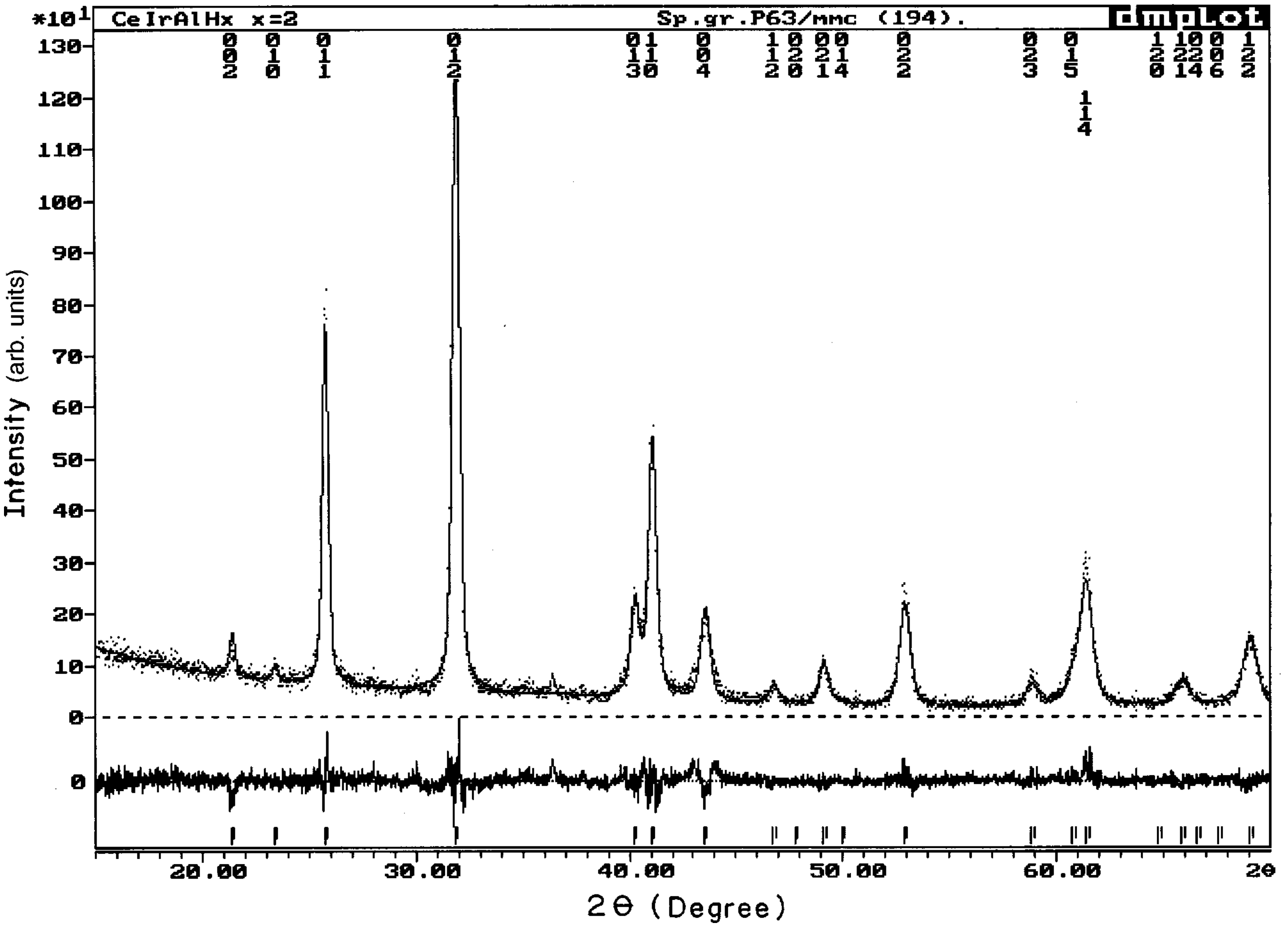

FIG. 2. X-ray diffraction pattern of CeIrAlH$_2$.

to the modified Curie-Weiss type of equation

$$\chi = \chi_0 + C/(T - \theta_P), \tag{1}$$

where χ_0 is the temperature independent susceptibility, C is the Curie constant (related to effective paramagnetic moment), and θ_P is the paramagnetic Curie temperature. The fit yields $\chi_0 = 4.9 \times 10^{-4}$ emu/mol, $\theta_P = -33$ K and $\mu_{\mathrm{eff}} = 1.93\mu_B$/f.u. This indicates the trivalent or near trivalent nature of the Ce ions in this compound. The negative value of θ_P suggests the presence of a sizeable Kondo (antiferromagnetic) interaction in the hydride though considerably reduced compared to that in the parent compound. The effective magnetic moment is somewhat less than that expected for free Ce ion moment of $2.54\mu_B$. This may be due to the partial suppression due to the Kondo interaction and/or crystal field effects in the hydride. The hydride also does not exhibit magnetic ordering down to 2 K. The shortest Ce-Ce distance in CeIrAl is 3.61 Å which is close to the Hill's limit of 3.25–3.4 Å below which the direct Ce-Ce overlap occurs which results in a mixed valent Ce ions in this compound.[13,14] The delocalization of Ce-4f electrons through hybridization with the electrons of the surrounding atoms is also expected to result in similar behavior. However, in the hydride, the Ce-Ce distance expands to 4.16 Å which is very much above the Hill's limit and beyond which Ce-Ce overlap ceases. This drives the Ce ions towards a trivalent local moment state. The changes in band structure due to changes in the crystal structure, increased Ce-Ce distance, and additional electrons and states contributed by hydrogen may also lead to further changes in Ce-4f electron and conduction electron hybridization which influence the Kondo temperature.

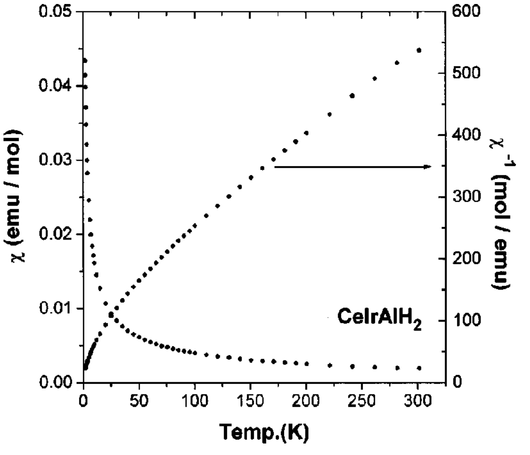

FIG. 3. Temperature dependence of molar magnetic susceptibility and that of its inverse of CeIrAlH$_2$ (applied field = 5 kOe).

IV. CONCLUSIONS

In conclusion, it has been shown that hydrogenation brings about a dramatic change in the crystal structure and magnetic behavior of CeIrAl. While the parent compound crystallizes in the orthorhombic structure in which the cerium ions are in a mixed valent state, the hydride crystallizes in the hexagonal structure in which the cerium ions are largely in the 3+ state.

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[1] Z. Bieganski and B. Stalinski, Phys. Status Solidi **2**, K161 (1970).

[2] K. H. J. Buschow, P. C. P. Bouten, and A. R. Miedema, Rep. Prog. Phys. **45**, 937 (1982).

[3] P. Raj, Indian J. Pure Appl. Phys. **32**, 548 (1994).

[4] P. Raj, K. Shashikala, A. Sathyamoorthy, V. Siruguri, and S. K. Paranjpe, Philos. Mag. B **79**, 1185 (1999).

[5] K. Shashikala, P. Raj, A. Sathyamoorthy, T. V. Chandrasekhar Rao, V. Siruguri, and S. K. Paranjpe, Philos. Mag. B **79**, 1195 (1999).

[6] P. Raj, A. Sathyamoorthy, K. Shashikala, N. Harish Kumar, C. R. Venkateswara Rao, and S. K. Malik, J. Alloys Compd. **296**, 20 (2000).

[7] P. J. Viccaro, G. K. Shenoy, B. D. Dunlap, D. G. Westlake, S. K. Malik, and W. E. Wallace, J. Phys. Colloq. **C5**, C2 (1979).

[8] H. G. Salunke, G. P. Das, P. Raj, K. Shashikala, A. Sathyamoorthy, and S. K. Dhar, Phys. Rev. B **53**, 12 299 (1996).

[9] S. K. Malik, T. Takeshita, and W. E. Wallace, Solid State Commun. **23**, 599 (1977).

[10] N. Harish Kumar, Latika Menon, C. R. Venketswara Rao, S. K. Malik, P. Raj, A. Sathyamoorthy, and K. Shashikala, Solid State Commun. **109**, 345 (1999).

[11] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[12] B. Coqblin and J. R. Schreiffer, Phys. Rev. **185**, 847 (1969).

[13] H. H. Hill, in *Plutonium 1970 and Other Actinides*, edited by W. N. Miner (American Institute of Mechanical Engineers, New York, 1970), p. 2.

[14] D. E. Ellis, in *Handbook on the Physics and Chemistry of Actinides*, edited by A. J. Freeman and G. H. Lander (Elsevier, New York, 1985), Vol. 2, p. 329.