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Concentration and temperature dependence of electrical resistivity in $Zr_{1-x}Ho_xCo_2$ ($0 \leq x \leq 1$) intermetallic compounds and their hydrides

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The electrical resistivity studies have been carried out on the C 15-type Laves phase intermetallic compounds $Zr_{1-x}Ho_xCo_2$ ($0 \leq x \leq 1$) and their hydrides in the temperature range 16–300 K. The first-order magnetic transition occurring for $x=1$ disappears for lower Ho concentrations. Anomalies in the form of resistivity minima observed for the intermediate x values are attributed to the spin fluctuations in the vicinity of the magnetic ordering temperature. On hydrogen absorption, the first-order transition observed for $x=1.0$ as well as the anomalies observed for the other x values disappear at higher hydrogen concentrations. A concentration-dependent metal-semiconductor-like transition has been observed in all cases. This may be a consequence of charge transfer taking place between hydrogen and the $3d$ band, which leads to a strong decrease in the conduction electron density. The activation energy is evaluated from the $\ln \rho$ vs $1/T$ plots.

I. INTRODUCTION

The cubic Laves phase compounds $RECo_2$ (RE =rare earth) have attracted a great deal of attention because of their striking magnetic properties arising out of the itinerant electron magnetism of the $3d$ atoms induced by the localized moments of the RE atoms.¹ Electrical resistivity and thermopower measurements carried out on $RECo_2$ compounds^{2,3} indicated pronounced discontinuity at T_c , characterizing the first-order magnetic transitions that arise due to the collective metamagnetic behavior of the $3d$ electrons.

$RECo_2$ (RE =Dy, Ho, and Er) compounds show a variety of magnetic properties when the RE atoms are replaced by nonmagnetic atoms.^{4–6} For instance, the gradual substitution of Y in the $(Ho,Y)Co_2$ system leads to first order transition followed by second-order transition and spin freezing as obtained by magnetic,^{4,7} electrical resistivity,^{4,7} thermal expansion,⁴ specific heat,^{8,9} and thermopower⁷ measurements. The onset of induced itinerant Co moment and long range order occurs at a critical concentration x_c . Appreciable anomalies in the form of resistivity minima have been observed in the intermediate concentration range and explained in terms of spin fluctuations and a possible Kondo scattering mechanism.^{8,10,11} In these compounds, the end compound YCo_2 is strongly exchange-enhanced paramagnetic.¹²

These properties will be drastically affected if Zr, instead of Y , is substituted for Ho in $HoCo_2$ since the end compound $ZrCo_2$ is weakly Pauli paramagnetic. In other words, when a magnetic atom is substituted in a Pauli paramagnetic compound, the magnetic contribution to electrical resistivity is significantly altered and therefore the measurement of electrical resistivity is useful in investigating its magnetic properties.¹³

It is well known that many intermetallic compounds absorb large quantities of hydrogen. Apart from their technological applications, the metal hydrides are of special interest because of the profound influence of the absorbed hydrogen

on various physical properties.¹⁴ Particularly, in the Laves phase compounds $RETM_2$ (RE =rare earth and TM =Fe, Co), hydrogen absorption leads to charge transfer between hydrogen and the $3d$ band, thereby modifying the various exchange interactions,^{15–17} which will affect the magnetic scattering contribution to electrical resistivity significantly. Furthermore, the electrical resistivity studies on RE hydrides^{18–20} have revealed order-disorder and metal-semiconductor transitions as the hydrogen concentration is increased. A metal-semiconductor-like transition has been reported in $REFe_2-H$ based systems.²¹

Recently, we have reported the structural and thermodynamic properties of the system $Zr_{1-x}Ho_xCo_2H_y$.^{22,23} The diffusion parameters were evaluated through hydrogen absorption kinetics.²⁴ In connection with this, we have studied the temperature variation of electrical resistivity in the Laves phase pseudobinary compounds $Zr_{1-x}Ho_xCo_2$ ($0 \leq x \leq 1$) and their hydrides and the results are presented in this paper.

II. EXPERIMENTAL DETAILS

$Zr_{1-x}Ho_xCo_2$ ($x=0.0, 0.2, 0.4, 0.6, 0.8, 0.9$, and 1.0) samples were prepared by arc melting the constituent elements under argon atmosphere and subsequent annealing at 900 °C for ten days. X-ray power diffractograms showed the formation of materials in single phase with a C 15-type Laves phase structure. The lattice constant has been found to vary linearly with x , obeying Vegard's law.²²

The dc electrical resistivity measurements were performed using a four-probe technique in the temperature range 16–300 K using a closed cycle helium refrigerator.²⁵ The samples required for the measurements were suitably cut from the ingots, polished, and then annealed at 600 °C for one day to relieve any strain produced in the process.

Hydrides of different concentrations were prepared using the pressure-composition isotherm data of the compounds $Zr_{1-x}Ho_xCo_2$.²³ Electrical resistivity measurements were

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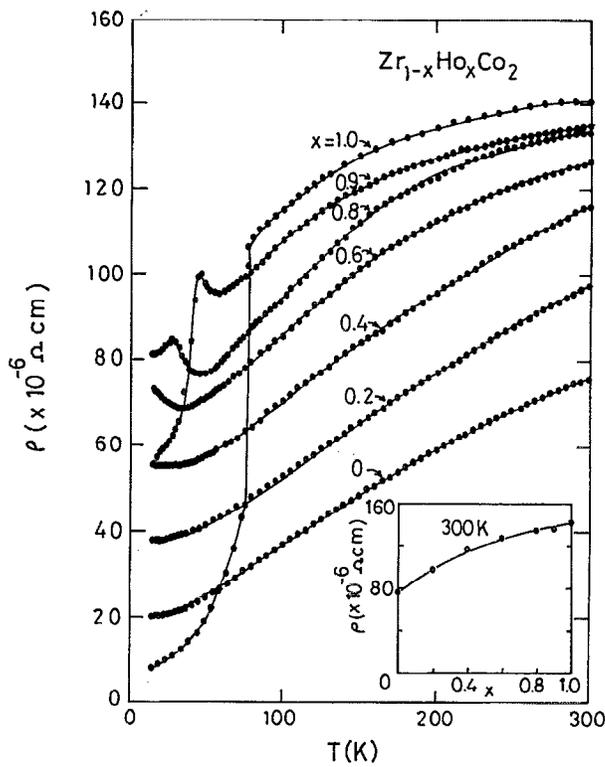


FIG. 1. Temperature variation of resistivity in $Zr_{1-x}Ho_xCo_2$ ($0 \leq x \leq 1$) system. The closed circles are the experimental points and the solid line in each case represents the best fit. The inset shows the resistivity values at 300 K.

performed on the compressed pellets of the hydrided samples. Thermo-emf was measured using a Pt-Pt 13% Rh thermocouple.

III. RESULTS AND DISCUSSION

A. $Zr_{1-x}Ho_xCo_2$ -host materials

Figure 1 shows the electrical resistivity as a function of temperature for different values of x in $Zr_{1-x}Ho_xCo_2$ compounds. The resistivity at 300 K increases with x , as shown in the inset. The $\rho(T)$ curves of $ZrCo_2$ and $Zr_{0.8}Ho_{0.2}Co_2$ show a T^3 dependence in the low temperature region below 50 and 30 K, respectively. This may be due to the s - d scattering by phonons¹³ and indicates that these compounds are weakly Pauli paramagnetic.

A sharp transition is observed at 77 K for $HoCo_2$,³ characteristic of a first order magnetic transition at T_c . On the other hand, the transition observed for other x values are of the second order and for $x \leq 0.2$ there is no magnetic ordering observed, as seen in Fig. 1. The isostructural $Y_{1-x}Ho_xCo_2$ compounds have also been found to exhibit similar properties for different values of x .^{4,7,8}

As seen in Fig. 1, the anomalous behavior of the ρ vs T curves in the form of resistivity minima has been observed in the intermediate concentration range $0.4 \leq x \leq 0.9$. These minima could be due to the enhancement of spin fluctuations in the vicinity of T_c and could be explained by considering the magnetic contributions to electrical resistivity.

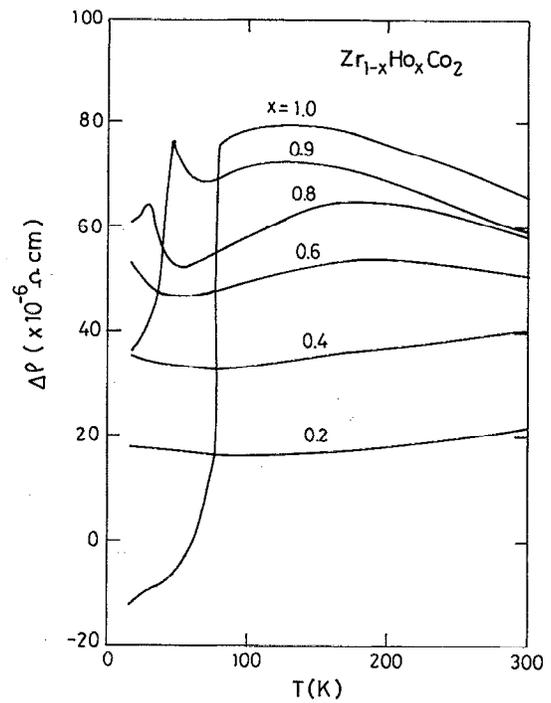


FIG. 2. The variation of excess resistivity $\Delta\rho = \rho_{Zr_{1-x}Ho_xCo_2} - \rho_{ZrCo_2}$ with temperature.

Assuming the validity of Mathiessen's rule, the total resistivity of these compounds can be written as

$$\rho_{total} = \rho_0 + \rho_{ph} + \rho_{mag}, \quad (1)$$

where ρ_0 is the residual resistivity, ρ_{ph} is the phonon contribution, zero and ρ_{mag} is the magnetic contribution to the electrical resistivity.

ρ_{ph} can be eliminated by subtracting the resistivity of the isostructural Pauli paramagnetic $ZrCo_2$ from the total resistivity of the $Zr_{1-x}Ho_xCo_2$ compounds. This will enable us to separate the magnetic contribution to resistivity (ρ_{mag}) arising out of the substituted $4f$ moments in a non-magnetic $ZrCo$ matrix. The excess resistivity $\Delta\rho$ ($= \rho_{Zr_{1-x}Ho_xCo_2} - \rho_{ZrCo_2}$) reflects the magnetic contribution since ρ_0 is temperature independent. $\Delta\rho$ was determined for all the compounds in the series $Zr_{1-x}Ho_xCo_2$ and the temperature variation of $\Delta\rho$ is plotted in Fig. 2.

$\Delta\rho$ vs T curves given in Fig. 2 show a broad minimum for $x=0.2$ and 0.4 and a minimum followed by a broad maximum for $x=0.6, 0.8,$ and 0.9 . For $x=0.2$ and 0.4 , where the magnetic Ho atoms are randomly distributed in a non-magnetic $ZrCo_2$ matrix, the minima seem to be caused by spin fluctuations due to short range correlations between the RE moments. As the Ho concentration is increased further, the increasing molecular field of Ho starts inducing moments on Co atoms, causing spin fluctuations in the vicinity of the transition temperatures. These spin fluctuations might increase the magnetic contribution to resistivity with decrease in temperature until the ordering temperature is attained, below which the spin fluctuations are frozen, and resulting in a pronounced decrease in resistivity. The increase in $\Delta\rho$ with a

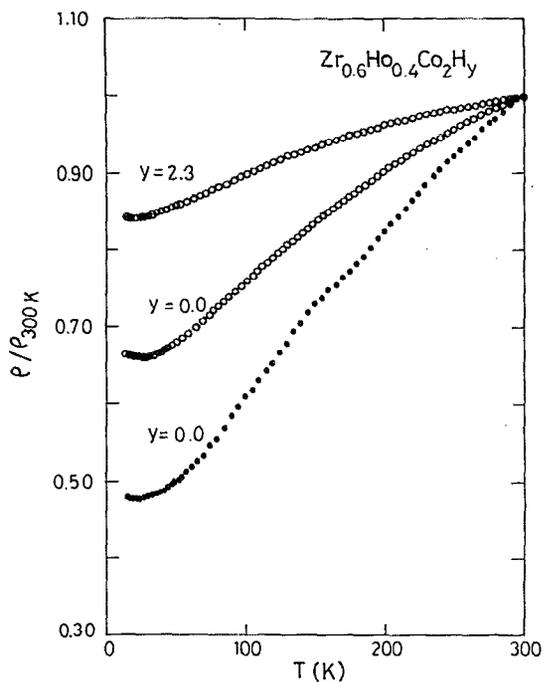


FIG. 3. The temperature variation of resistivity normalized to resistivity at 300 K in $Zr_{0.6}Ho_{0.4}Co_2H_y$ (open circles correspond to the pellets and closed circles to the ingot).

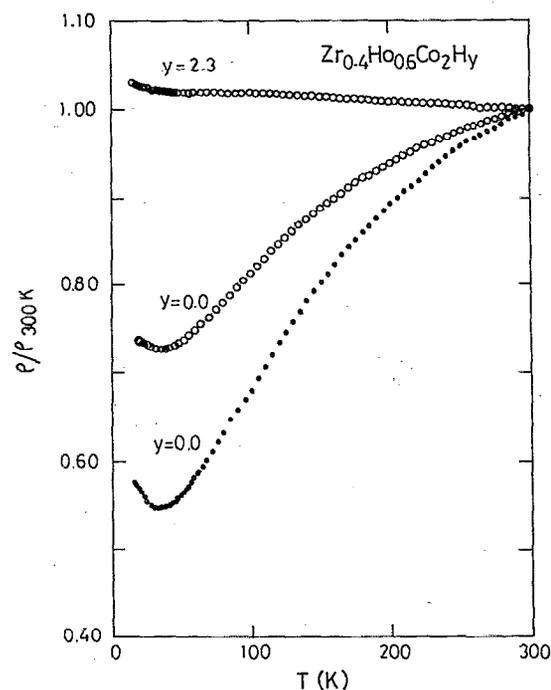


FIG. 4. The temperature variation of resistivity normalized to resistivity at 300 K in $Zr_{0.4}Ho_{0.6}Co_2H_y$ (open circles correspond to the pellets and closed circles to the ingot).

decrease in temperature for $x \geq 0.6$ in the high temperature regions, as shown in Fig. 2, indicates that the spin fluctuations are present not only in the vicinity of T_c but also in the paramagnetic temperature region in addition to the spin disorder scattering. The isomorphous compounds $Y_{1-x}RE_xCo_2$ (RE=Er, Dy, Tb, and Gd) with higher x values also exhibit an increase in the excess resistivity with a decrease in temperature in the paramagnetic region,¹¹ which has been attributed to spin fluctuation scattering.

The other possible reason for a decrease in ρ_{mag} with an increase in temperature in the high temperature regions may also be due to the deviations from the Matheissen's rule, which become pronounced and influence the temperature dependence and concentration dependence of resistivity in the high temperature regions.²⁶ In the case of systems that do not exhibit strong magnetic interactions, the break-up of the local magnetic clusters at high temperatures will give rise to a decrease in ρ_{mag} with increasing temperature.²⁷

B. $Zr_{1-x}Ho_xCo_2H_y$ hydrides

The temperature variation of resistivity curves, normalized to ρ at 300 K, obtained for the hydrides of $Zr_{1-x}Ho_xCo_2$ ($x=0.4, 0.6, 0.8$, and 1.0) compounds are presented in Figs. 3–6, respectively. The normalized ρ vs T curves of the corresponding host materials obtained for the ingots are also given in the same figures, for comparison.

As seen in Fig. 6, the sharp first-order transition observed at the magnetic ordering temperature (T_c) for $HoCo_2H_y$ with $y=0$ becomes broad and disappears at higher hydrogen concentrations ($y > 1.8$). The T_c (obtained by the

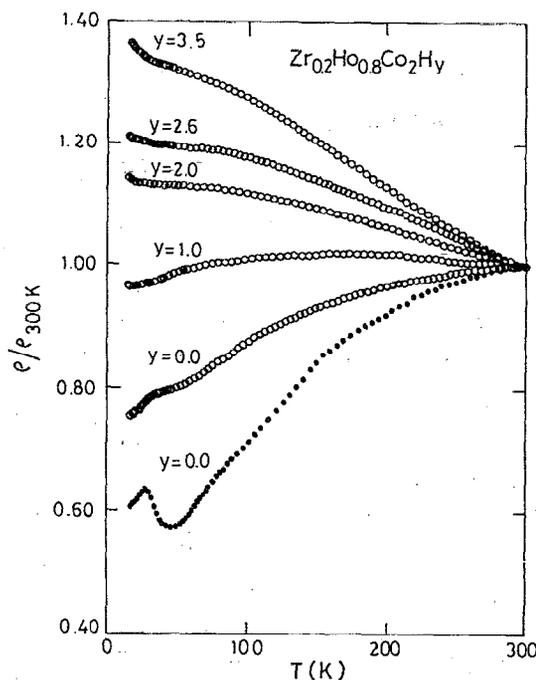


FIG. 5. The temperature variation of resistivity normalized to resistivity at 300 K in $Zr_{0.2}Ho_{0.8}Co_2H_y$ (open circles correspond to the pellets and closed circles to the ingot).

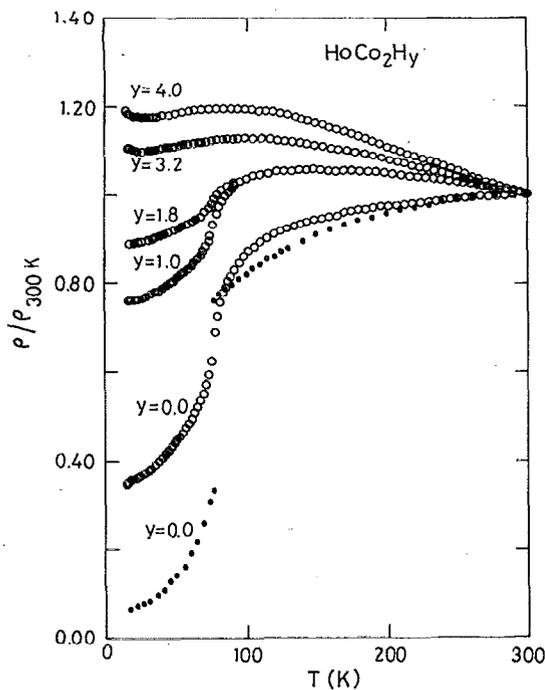


FIG. 6. The temperature variation of resistivity normalized to resistivity at 300 K in HoCo_2H_y , (open circles correspond to the pellets and closed circles to the ingot).

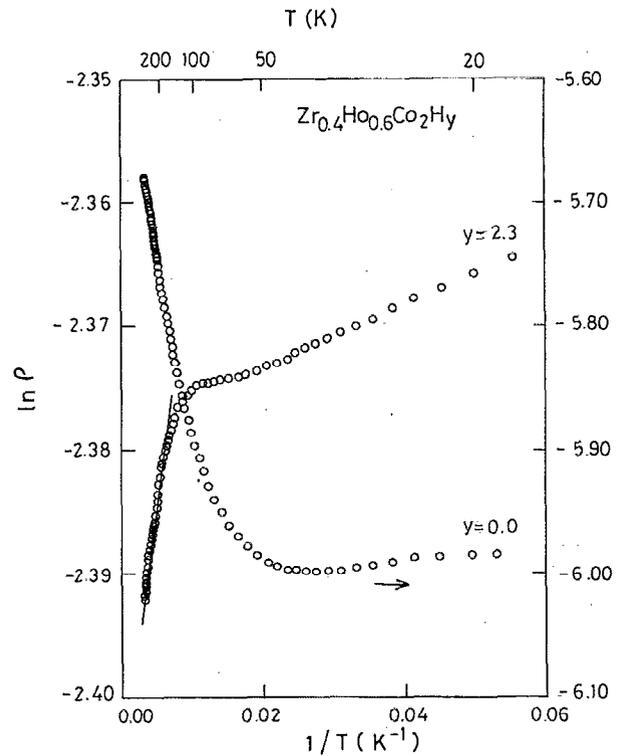


FIG. 7. $\ln \rho$ vs $1/T$ plot for $\text{Zr}_{0.4}\text{Ho}_{0.6}\text{Co}_2\text{H}_y$.

sudden change of slope in the ρ vs T curves) does not seem to be altered with an increase in hydrogen concentration, at least up to $y=1.8$ in HoCo_2H_y . However, the magnetization measurements carried out on $\text{HoCo}_2\text{H}_{3.5}$ have shown that the T_c and the Co moment decrease in the hydrides.¹⁵ In the RECo_2 system, the hydrogen absorption leads to weakening of the RE-Co magnetic interactions. The hydrogen atoms occupying the interstitial sites lead to large expansion in the unit cell volume, thereby affecting the exchange mechanisms between the RE and the Co atoms. Hydrogen absorption in RECo_2 compounds has been found to bring about destruction of long range atomic order and formation of Co clusters that are embedded in a magnetically disordered matrix.^{16,17,28}

As seen from Figs. 3–6, the magnitude of resistivity values at 16 K (the lowest experimental temperature) increases considerably as the hydrogen concentration (y) is increased. For instance, the typical value of resistivity at 16 K for $\text{HoCo}_2\text{H}_{4.0}$ is found to be about $10^{-2} \Omega \text{ cm}$. This could be due to the increase in the number of scattering centers and the decrease in the conduction electron density with an increase in y . Furthermore, in Ho-rich compounds, hydrogen absorption leads to a high degree of distortion in the host lattice and these materials become almost amorphous at hydrogen concentrations $y > 3.0$.²³

The ρ vs T curves for $x \geq 0.6$ shown in Figs. 4–6 are characterized by a change in sign of the temperature coefficient of resistance (α) from positive to negative as the hydrogen concentration is increased. For lower Ho concentrations, the change in sign of α occurs at higher y values. For instance, in $x=0.4$ (Fig. 3), the sign of α remains positive

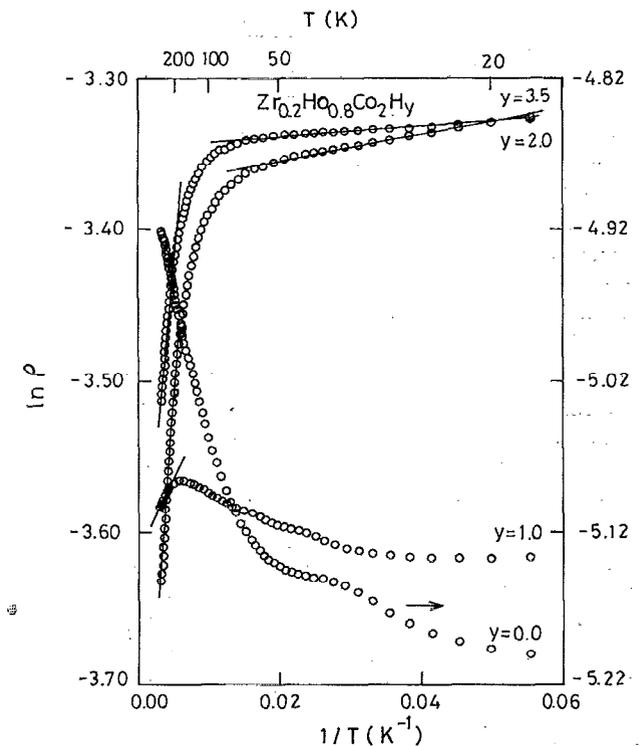


FIG. 8. $\ln \rho$ vs $1/T$ plot for $\text{Zr}_{0.2}\text{Ho}_{0.8}\text{Co}_2\text{H}_y$.

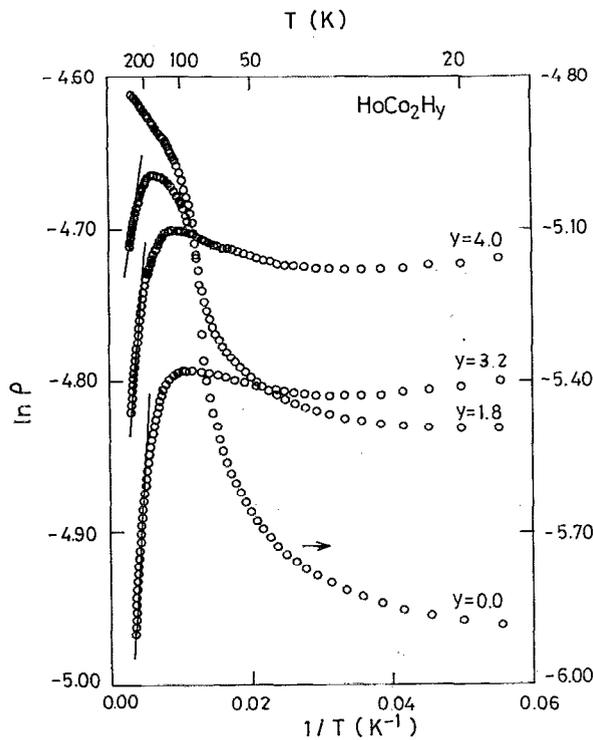


FIG. 9. $\ln \rho$ vs $1/T$ plot for HoCo_2H_y .

even at the maximum hydrogen concentration of $y=2.3$. The decrease in resistivity with an increase in temperature is characteristic of a semiconducting material. This effect is seen clearly in the $\ln \rho$ vs $1/T$ plots shown in Figs. 7–9. In $\text{Zr}_{0.4}\text{Ho}_{0.6}\text{Co}_2\text{H}_y$ (Fig. 7), $y=0$ exhibits a metallic behavior and $y=2.3$, a semiconducting behavior. In $\text{Zr}_{0.2}\text{Ho}_{0.8}\text{Co}_2\text{H}_y$ (Fig. 8), $y=0$ shows a metallic behavior. As the hydrogen concentration is increased above 1.0, the metallic nature is lost and for $y \geq 2.0$, the material behaves like a semiconductor. Similarly, in HoCo_2H_y (Fig. 9), the curve for $y=0$ shows metallic and that for $y > 1.8$, semiconducting behaviors.

The $\ln \rho$ vs $1/T$ curves for the higher hydrogen concentrations fit into two straight lines with different slopes in the high and low temperature regions. For instance, the $\ln \rho$ vs $1/T$ plots for $\text{Zr}_{0.2}\text{Ho}_{0.8}\text{Co}_2\text{H}_y$ with these straight line portions are shown in Fig. 8. This is analogous to the extrinsic and intrinsic conductivities of a typical semiconductor in the low and high temperature regions, respectively. However, for HoCo_2H_y ($y \geq 2.0$) as shown in Fig. 9, the nonlinearity in the low temperature region may be due to the magnetic interactions.

It can be seen from Figs. 8 and 9 that the $\ln \rho$ vs $1/T$ curves exhibit a maximum for $\text{Zr}_{0.2}\text{Ho}_{0.8}\text{Co}_2\text{H}_{1.0}$ and $\text{HoCo}_2\text{H}_{1.8}$ at 155 K and they are considered to be weakly metallic. The nature of resistivity differs on both sides of the peak at 155 K. However, for higher values of y , both the compounds exhibit a semiconducting behavior throughout the temperature range studied. A similar effect has been reported for $\text{LaH}_{2.9}$, where α is positive in the low temperature region and negative in the high temperature region and for

TABLE I. Activation energy for the $\text{Zr}_{1-x}\text{Ho}_x\text{Co}_2\text{H}_y$ system.

x	y	$E_a (\times 10^{-3} \text{ eV})$
0.6	2.3	0.5
0.8	1.0	1.0
	2.0	5.9
	2.6	3.5
	3.5	7.3
1.0	1.0	3.2
	1.8	3.2
	3.2	6.1
	4.0	4.5

the maximum y value of 2.9 it is negative throughout the temperature range studied.²⁹

A change in the electronic structure involving a strong decrease in the conduction electron density may lead to a metal-semiconductor transition as the hydrogen concentration is increased. Hydrogen absorption in RETM_2 ($\text{TM}=\text{Fe}, \text{Co}$) systems leads to a decrease in the conduction electron density due to charge transfer taking place between hydrogen and the $3d$ band.^{30,31} Further increase in y above a critical concentration may decrease $N(E_F)$ to zero which could lead to opening up of a small band gap at the Fermi level and therefore the material would behave like a semiconductor.

A metal-semiconductor-like transition has been reported for $\text{REFe}_2\text{-H}$ based systems²¹ and this was attributed to the depopulation of conduction electrons by the absorbed hydrogen atoms. A concentration-dependent metal-semiconductor transition has been reported for CeH_x system.^{18,20,32} The temperature variation of resistivity measurements on CeH_x system indicate that it is metallic for $x < 2.8$, semiconducting for $x > 2.8$ and insulating for $x = 3.0$. Libowitz *et al.*^{18,32} have proposed that, as the hydrogen is removed from the insulating CeH_3 composition, hydrogen vacancies are formed that create donor levels just below the conduction band and the hydride acts as an n -type semiconductor. The density of the donor levels increases with further decrease in x until the composition $\text{CeH}_{2.8}$ is reached where the donor levels overlap with each other and form a defect band. This corresponds to a Mott-type semiconductor-metal transition at $x = 2.8$.^{33,34} The formation of the defect band in CeH_x ($2.0 \leq x \leq 3.0$) and the metal-semiconductor transition have been explained using band structure calculations by Fujimori and Tsuda.³⁵

A more appropriate system to compare would be YH_{2+x} , in which the origin of metal-semiconductor transitions has been attributed to the disintegration of the delocalized band into localized defect levels at the Fermi energy due to the collapse of the ordered octahedral H sublattice with increasing temperature.³⁶

Such explanations seem to be applicable to the metal-semiconductor-like transition observed in the $\text{Zr}_{1-x}\text{Ho}_x\text{Co}_2\text{H}_2$ system. However, a quantitative analysis would be of great help in the understanding of metal-semiconductor-like transitions observed in this system.

For the $\text{Zr}_{1-x}\text{Ho}_x\text{Co}_2\text{H}_y$ compounds showing semiconducting behavior, the thermo-emf was measured to determine the sign of the charge carriers. For instance, the value of the

Seebeck coefficient measured for $\text{HoCo}_2\text{H}_{4.0}$ is found to be about $-15 \mu\text{V/K}$ at 300 K. This is consistent with the negative value of the Seebeck coefficient observed for $\text{CeH}_{2.85}$, indicating n -type conductivity.¹⁸

The values of activation energy were calculated from the slopes of the $\ln \rho$ vs $1/T$ plots shown in Figs. 7–9 in the temperature region 250–300 K and are given in Table I. The average values of E_a obtained for $\text{Zr}_{0.4}\text{Ho}_{0.6}\text{Co}_2\text{H}_y$, $\text{Zr}_{0.2}\text{Ho}_{0.8}\text{Co}_2\text{H}_y$, and HoCo_2H_y , are 0.5×10^{-3} eV, 4.7×10^{-3} eV, and 4.6×10^{-3} eV, respectively. Such a low value of E_a has been reported for the $\text{REFe}_2\text{-H}$ system²¹ (4×10^{-3} and 6×10^{-4} eV) and also for the $\text{Yb}_{1-x}\text{Gd}_x\text{Te}$ system³⁷ (5.6×10^{-3}), which exhibits a metal-semiconductor transition at $x \leq 0.2$.

IV. CONCLUSIONS

The electrical resistivity studies carried out on a $\text{Zr}_{1-x}\text{Ho}_x\text{Co}_2$ system indicate that the first-order transition observed for $x=1.0$ disappears for other concentrations. Anomalies in the form of resistivity minima observed for the intermediate Ho concentrations could be attributed to the spin fluctuations due to short range correlations between the RE moments in the vicinity of magnetic ordering temperatures.

In the $\text{Zr}_{1-x}\text{Ho}_x\text{Co}_2\text{H}_y$ system, the first-order transition observed for $x=1.0$ as well as the resistivity minima observed for intermediate x values are found to disappear for higher hydrogen concentrations (y). This may be due to the weakening of magnetic interactions on hydrogen absorption. Concentration dependent metal-semiconductor-like transitions are observed for higher hydrogen concentrations. This could be due to the profound modifications in the electronic band structure of the host compounds arising out of charge transfer effects.

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