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MEASUREMENT AND INTERPRETATION OF ELECTRICAL PROPERTIES OF ZIRCONIUM HYDRIDE FOR HYDROGEN-TO-METAL RATIOS BETWEEN 1.5 AND 2

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MEASUREMENT AND INTERPRETATION OF ELECTRICAL PROPERTIES OF ZIRCONIUM HYDRIDE FOR HYDROGEN-TO-METAL RATIOS BETWEEN 1.5 AND 2

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ABSTRACT

Electrical resistivity and Hall effect measurements have been carried out between 1.1 and 300°K on zirconium hydride for hydrogen-to-metal ratios ranging from 1.54 to 1.96. In addition, the thermoelectric power was determined between 0 and 100°C. The data support the belief that for these compositions zirconium hydride is a metallic compound. $ZrH_{1.96}$ *exhibited a room temperature resistivity of 24.7 micro-ohm-cm, which is considerably less than the value (42.6 micro-ohm-cm) characteristic of high-purity zirconium. On the basis of an observed rapid decrease of electrical resistivity as* ZrH_2 *is approached, it is predicted that the thermal conductivity will increase rapidly as the hydrogen-to-metal ratio approaches 2. Hall coefficient measurements revealed majority hole conduction for a face-centered cubic sample* ($ZrH_{1.54}$) *and majority electron conduction for a face-centered tetragonal sample* ($ZrH_{1.81}$)*. Plots of resistivity and thermoelectric power* vs *composition exhibited maxima in the vicinity of* $ZrH_{1.6}$*, and X-ray studies showed this composition to lie within a two-phase region. The data allow some speculation on the nature of the bonding in zirconium hydride.*

I. INTRODUCTION

The high hydrogen density achievable in zirconium hydride has given rise to a lively interest in this system as a nuclear reactor moderator material. In view of this interest, exploratory electrical property measurements have been carried out in an attempt to characterize the electronic structure and bonding of zirconium hydride. Although the work is incomplete, it is believed that the results are of sufficient interest to warrant publication at this time.

This investigation began with the measurement of the electrical resistivity and Hall coefficient as functions of temperature (from 1.1 to 300°K) and composition for hydrogen-to-metal ratios (H/M) greater than 1.5. Based upon information obtained from neutron diffraction and scattering experiments,[1,2] it is generally believed that for these compositions the hydrogen and zirconium atoms form separate sublattices. Later, partly because of some uncertainty regarding the influence of microcracks on these properties, the scope of the study was enlarged to include measurement of thermoelectric power, a property less sensitive to the presence of such defects, from 0 to 100°C. The data obtained demonstrate the metallic nature of zirconium hydride, shed interesting light on the phase diagram, hint that electronic states associated with the hydrogen might form a band below the Fermi level, and suggest that for H/M approaching 2, zirconium hydride should be a markedly better thermal conductor than pure zirconium.

II. EXPERIMENTAL METHODS

A. SAMPLE PREPARATION AND ANALYSIS

The amount of hydrogen that will combine with a specimen of zirconium is a function of the purity of the zirconium and hydrogen, the temperature, the hydrogen pressure, and the surface conditions.[3] The samples used in this study were prepared by a massive hydriding technique.[4] Clean specimens of reactor grade zirconium were placed within a vacuum furnace and brought to hydriding temperature, typically 1450 to 1650°F. Purified hydrogen was then admitted in sufficient amount to achieve the desired H/M. Hydriding time for a typical specimen was of the order of 40 hours, including cooling time.

An accurate knowledge of hydride composition is necessary if reliable interpretations are to be made from the electrical properties of the samples. In this study, the composition of each sample was determined from weight gain and also from vacuum fusion measurements. If any serious discrepancy existed, the sample was re-analyzed by the vacuum fusion method, which should have a reliability of ±1%. In all cases, the vacuum fusion analysis is the one reported.

The as-hydrided specimens, either in the shape of small rectangular plates or cylindrical rods, were first cut to approximate size with a diamond cutoff wheel. Next, the sample was shaped to the desired dimensions by means of a polishing block and metallurgical paper. When finished, the samples were ⅞ in. long by ⅛ in. wide by 20 to 40 mils thick. These dimensions were established by the electrical and cryogenic equipment available for performance of the measurements. Since zirconium hydride is very brittle, especially for large H/M, it was necessary to handle the samples with great care throughout the preparation and data gathering phases. In addition, it was found that unless the samples were etched, proper electrical contact could not be established. A suitable etchant consists of 5 parts HF, 45 parts HNO_3, and 50 parts H_2O by volume.

All samples studied were polycrystalline and contained appreciable numbers of microcracks as revealed by microscopic examination at magnifications of the order of 250x. Figure 1 is a photomicrograph of

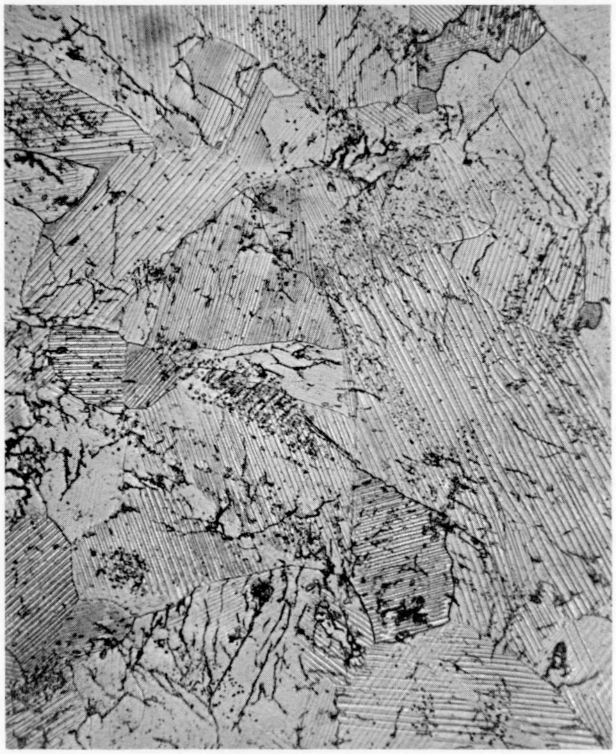

Figure 1. Photomicrograph of Zirconium Hydride. H/M = 1.81, 250x, Bright Field.

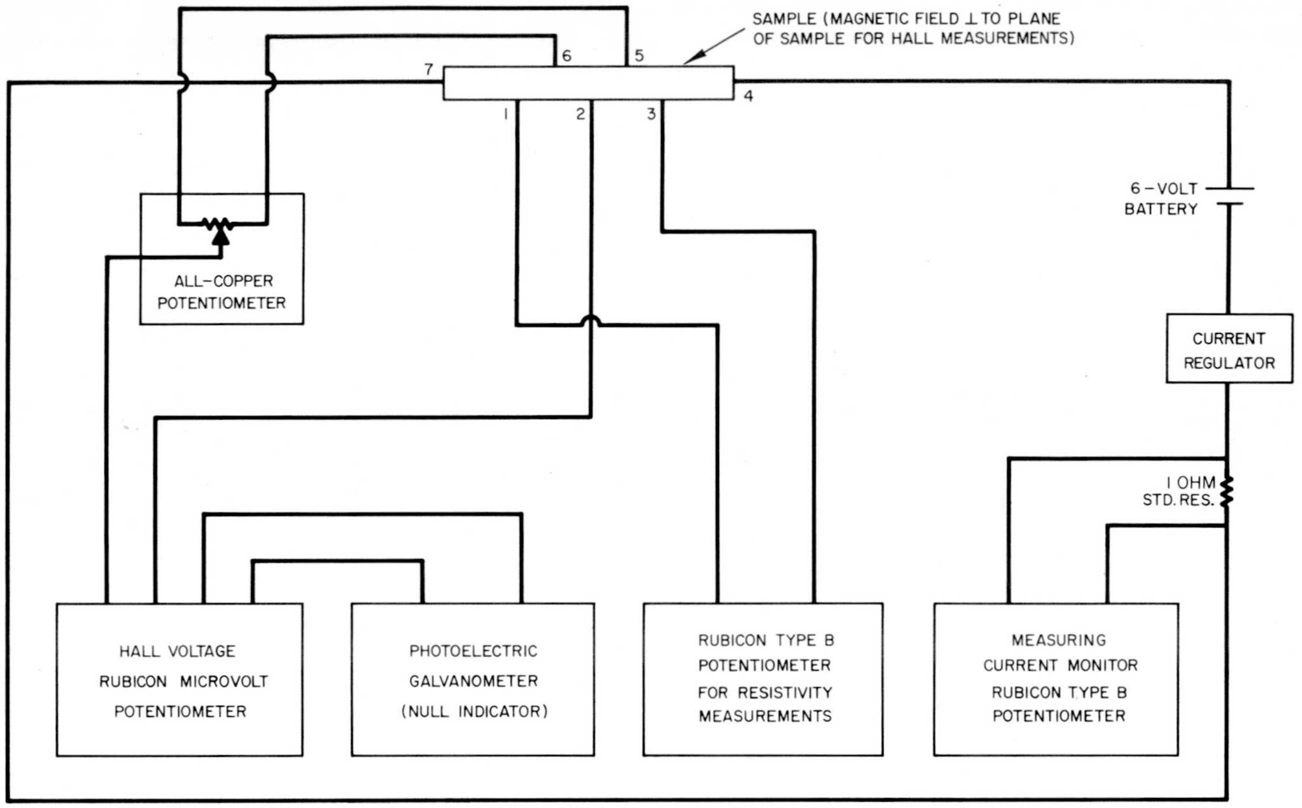

Figure 2. Schematic Circuit Diagram for Resistivity and Hall Effect Measurements.

$ZrH_{1.81}$, a typical sample. The influence of these defects on the properties studied will be discussed later. The "banding" shown in this photograph is typical of high-hydrogen-content zirconium hydride. The effect of oxygen impurity variations on the electrical properties of the samples was not investigated.[5]

B. ELECTRICAL RESISTIVITY AND HALL EFFECT MEASUREMENT TECHNIQUES

Standard potentiometric techniques were used for the resistivity measurements, and the three-probe geometry[6] was employed for the Hall effect measurements. The instrumentation and circuitry are illustrated in Figure 2. The Hall voltage V_H was taken as one-half the difference in voltage measured by the microvolt potentiometer for forward and reverse magnetic field directions. Field reversal was actually accomplished by a 180° rotation of the sample about its long axis. In terms of the measured quantities, the Hall coefficient is given by $R_H = V_H t/IH$ where t is the sample thickness, I the measuring current, and H the magnetic field strength.

The voltage drops between resistivity probes varied from a few hundred to a thousand microvolts for measuring currents between 0.2 and 0.4 ampere. Hall voltages amounted to a few tenths of a microvolt and were reproducible to about 0.005 microvolt or better.

Electrical contacts (1, 2, 3, 5, and 6, Figure 2) to the edges of the sample were accomplished by means of spring clips. Even though the sample holder was constructed in such a way as to minimize constraint during thermal expansion and contraction of the samples, fracture of the brittle samples sometimes occurred. This difficulty is not easily overcome through the use of thicker samples, because the Hall voltage (which is small at best) is inversely proportional to the sample thickness.

The cryogenic and magnetic apparatus and procedures used in this investigation have been described elsewhere.[7,8]

C. THERMOELECTRIC POWER MEASUREMENT TECHNIQUES

The thermoelectric power measurements do not suffer from complications arising from the brittle nature of zirconium hydride, inasmuch as thin samples are not required, and microcracks are certain to be of less influence. The experimental apparatus is illustrated schematically in Figure 3. With this arrangement, which was intended only for rapid exploratory measurements, it was possible to make measurements between 0 and 150°C. It was not convenient to vary each junction temperature separately, but this proved to be of little consequence because the thermoelectric

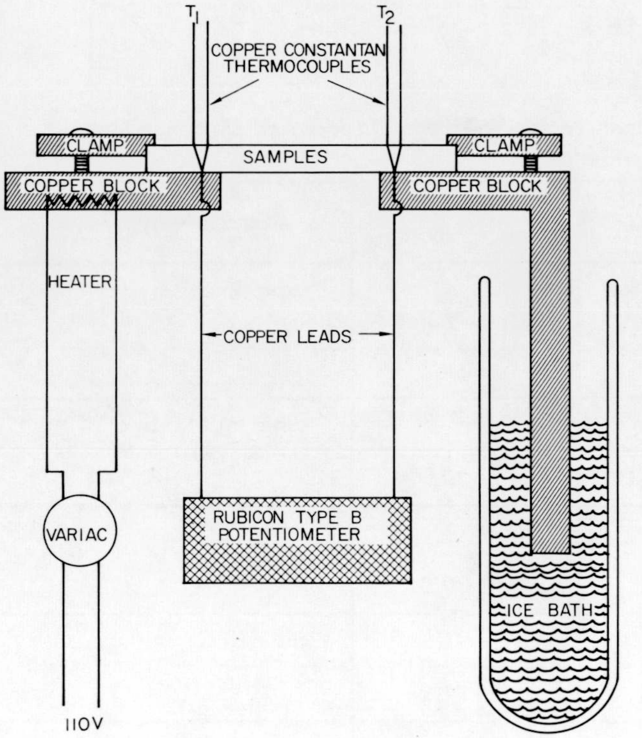

Figure 3. Schematic Circuit Diagram for Thermoelectric Power Measurements.

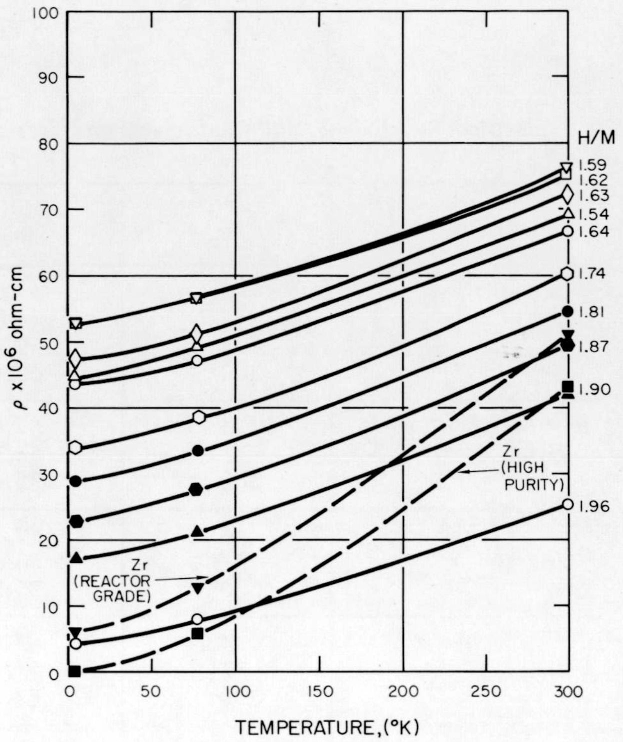

Figure 4. Resistivities of Zirconium Hydride Samples at 4.2, 77, and 300°K.

force ΔE was measured for a temperature difference $\Delta T = T_1 - T_2$, and plots of $\Delta E/\Delta T$ *vs* average temperature $(T_1 + T_2)/2$ were linear in all cases. Under these circumstances, a plot of $\Delta E/\Delta T$ *vs* $(T_1 + T_2)/2$ is equivalent to a plot of thermoelectric power dE/dT *vs* T.

It should be noted that all thermoelectric power measurements were made against copper. Between 0 and 100°C, the absolute thermoelectric power of copper in microvolts/°C is given[9,10] approximately by $dE/dT = 1.5 + .0069T$. Hence, to reduce the values reported herein for zirconium hydride against copper to absolute thermoelectric power, it is necessary to add the copper value.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. ELECTRICAL RESISTIVITY

The results of experimental determinations of the electrical resistivity ρ for zirconium hydride as a function of composition and temperature are summarized in Table I along with data on the crystal structure and the Hall coefficient R_H. Data on high-purity and reactor-grade zirconium are included for comparison.

As previously noted, the zirconium hydride samples contained fair numbers of microcracks. Nevertheless, considerable confidence in the values listed in Table I is justified, because specimens cut from different portions of the same bar of zirconium hydride yielded resistivities in agreement within one percent or better, resistivity *vs* concentration curves followed a regular course, and the observed resistivity at 4.2°K approached zero as H/M approached 2.

The metallic nature of zirconium hydride is strikingly evident in Figure 4, where electrical resistivity is plotted as a function of temperature for the samples listed in Table I. Indeed, as ZrH_2 is approached, zirconium hydride is a considerably better electrical conductor than is pure zirconium. The fact that all the zirconium hydride curves are nearly parallel throughout so large a range of composition is quite surprising. On naïve reasoning, such behavior might be interpreted as evidence that the major effect of changing hydrogen concentration *in this range* is to change the number of scattering centers (i.e., hydrogen vacancies), thus altering the residual resistivity (i.e., the resistivity at 4.2°K) while leaving the number of charge carriers nearly unchanged. This further implies that in the range of composition $H/M > 1.5$ the electronic energy levels in the vicinity of the

TABLE I

Electrical Resistivities, Hall Coefficients and Crystal Structures of Zirconium Hydrides and Zirconium Samples

Sample	T °K	$\rho \times 10^6$ ohm-cm	$R_H \times 10^5$ cm^3/coulomb	Structure by X-rays
$ZrH_{1.54}$	1.1	44.5		cubic (fcc)
	4.2	44.5	+29.9	
	77	49.2	+37.3	
	300	69.1	+34.8	
$ZrH_{1.59}$	4.2	52.4		cubic and tetragonal
	77	56.7		
	300	75.6	+39.0	
$ZrH_{1.62}$	4.2	52.8		cubic (fcc)
	77	56.6		
	300	75.3	+39.0	
$ZrH_{1.63}$	4.2	47.4		cubic (fcc)
	77	51.1	+11.2	
	300	73.2	+21.2	
$ZrH_{1.64}$	1.1	43.8		cubic and tetragonal
	4.2	43.8	+39.8	
	77	47.3	+39.8	
	300	66.6	+42.0	
$ZrH_{1.74}$	4.2	33.8		tetragonal (fct)
	77	38.7	−32.2	
	300	60.2	−17.7	
$ZrH_{1.81}$	1.1	28.9		tetragonal (fct)
	4.2	28.9	−48.7	
	77	33.2	−50.4	
	300	54.7	−39.0	
$ZrH_{1.87}$	4.2	22.8		no information—assumed to be tetragonal
	77	27.6	−52.0	
	300	49.5	−45.8	
$ZrH_{1.90}$	4.2	16.5		tetragonal (fct)
	77	19.3	−66.0	
	300	38.4	−61.2	
$ZrH_{1.96}$	1.1	4.31		no information—assumed to be tetragonal
	4.2	4.31		
	77	7.82	−65.9	
	300	24.7	−67.9	
Zr (high purity)	4.2	0.213		hexagonal
	77	6.08		
	300	42.6		
Zr (reactor grade)	4.2	5.97		hexagonal
	77	12.8		
	300	50.8		

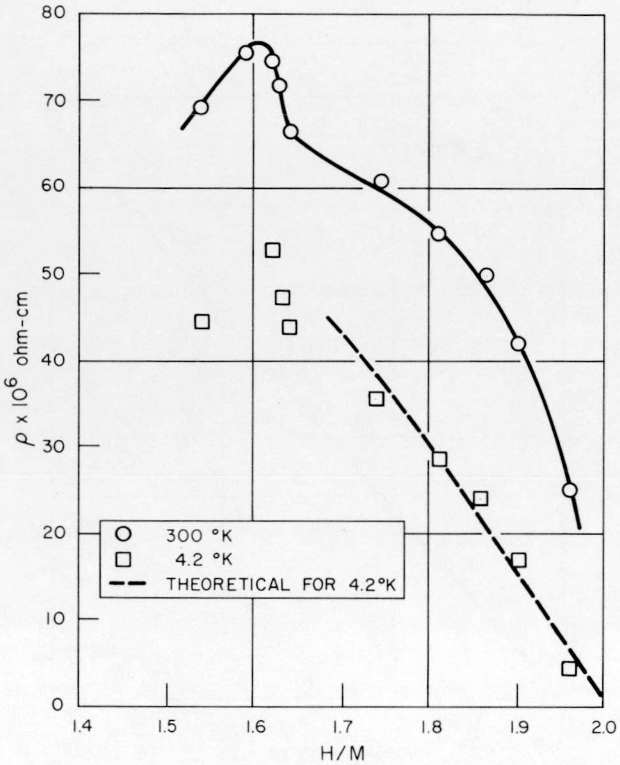

Figure 5. Resistivity of Zirconium Hydride Samples as a Function of H/M Ratio for T = 300°K and T = 4.2°K.

hydrogen lie far enough below the Fermi level that they do not contribute appreciably to conduction; i.e., the hydrogen exists in the lattice as neutral or nearly neutral hydrogen, the electrons associated with the hydrogen forming a band below the Fermi level. In conflict with this simple picture are the facts that the crystal structure changes markedly in this range of composition, going from fcc to a two-phase region (fcc plus fct) to fct, and the Hall coefficient and thermoelectric power are strongly dependent upon composition.

The latter objection might be rationalized by the observation that changes in scattering alone can bring about marked changes in the Hall coefficient and thermoelectric power,[7,11,12] but the former objection remains. Thus, the parallel resistivity *vs* temperature curves could be merely fortuitous consequences of a more complicated change in electronic structure.

Nevertheless, it is of interest to pursue the "nearly neutral" hydrogen hypothesis a bit further. The 4.2°K data in Figure 5 correspond to the residual resistivity. By analogy with the case of simple solid solution alloy theory,[13] in the absence of impurities, changes in lattice parameter, and changes in number of charge carriers, this residual resistivity should be proportional to $x(1-x)$, where x is the fractional concentration of hydrogen vacancies (or in terms of H/M, $x = 1 - H/2M$). Such a dependence (fitted to the experimental point for H/M = 1.81) has been plotted in Figure 5 as the dashed line. The agreement with experiment over an appreciable range of concentrations is surprisingly good in view of the obvious failure of the experimental system to fulfill all of the conditions imposed by the theory. Clearly, it would be premature to accept the possibility of "nearly neutral" hydrogen without additional data.

It is of interest to compare hydrogen vacancies in zirconium hydride with vacancies in pure metals as regards their effect on residual resistivity. The slope of the dashed line of Figure 5 at ZrH_2 yields a value of 3.3 micro-ohm-cm/atomic percent vacancies relative to the hydrogen sub-lattice, or 2.2 micro-ohm-cm/atomic percent vacancies relative to the entire lattice. Estimates of vacancy resistivities for pure noble metals range from 0.4 to 1.5 micro-ohm-cm/atomic percent vacancies.[14] The values for zirconium hydride are perhaps surprisingly close to those for noble metals, in view of differences in electronic structure as indicated by the much lower ideal resistivities of the noble metals. It should be pointed out that the zirconium hydride measurements enjoy some advantage over the determinations on pure metals, because in the former the vacancy concentration is known quite accurately from the hydrogen concentration. The maximum that occurs in Figure 5 for a H/M ratio of about 1.61 is in a two-phase region and most probably arises from additional contributions to the scattering by phase boundaries and extra microcracks.

Although electrical resistivity measurements were made down to 1.1°K for three zirconium hydride samples (Table I), no evidence of superconductivity was found, nor was a measurable magneto-resistance observable. It is conceivable that both effects might be observed for H/M near 2.

B. RELATION OF ELECTRICAL RESISTIVITY DATA TO THERMAL CONDUCTIVITY

Knowledge of the electrical resistivity permits speculation regarding thermal conductivity, K, for according to the simple free-electron theory these quantities are related by the Lorenz number[15] $L = \rho K/T = \pi^2 k^2/3e^2 = 2.45 \times 10^8$ watt-ohms/(°K)^2, where k is the Boltzmann constant and e is the electronic charge. Experimental values of L for most metals are in fair agreement with this theoretical value in the vicinity of room temperature, and increase slightly with temperature because of lattice contributions to the thermal conductivity.

The rapid decrease of electrical resistivity as ZrH_2 is approached is suggestive of a corresponding increase of thermal conductivity and further implies that for high hydrogen contents, zirconium hydride is a better thermal conductor than pure zirconium. Since this is a matter of considerable importance in the practical utilization of zirconium hydride in nuclear reactor systems, a test of the range of applicability of the Lorenz number to zirconium hydride would be of great interest.

C. HALL COEFFICIENT

Hall effect measurements were carried out on samples with H/M values of 1.54, 1.64, and 1.81. In all instances, the Hall voltage was linear in magnetic field strength, as illustrated in Figure 6 for a typical case. The corresponding Hall coefficient values are listed in Table I. The negative Hall coefficient for the fcc sample $ZrH_{1.81}$ is indicative of majority electron conduction, and the positive value for the fct sample $ZrH_{1.54}$ is evidence for majority hole conduction. Difficulties experienced in fabricating and handling the thin samples required for Hall effect measurements have so far retarded the acquisition of extensive Hall effect data, although additional information of this type should have an important bearing on the question of bonding in zirconium hydride.

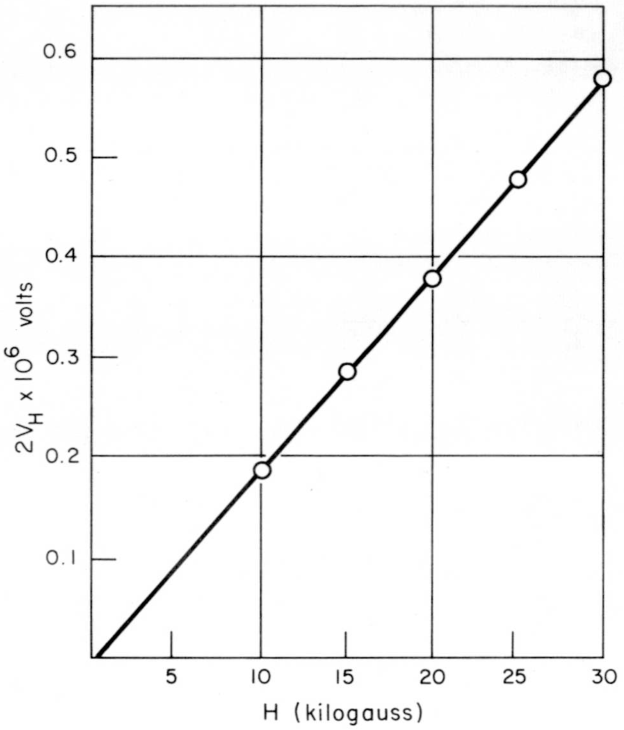

Figure 6. Hall Voltage of $ZrH_{1.81}$ as a Function of Magnetic Field Strength for T = 300°K.

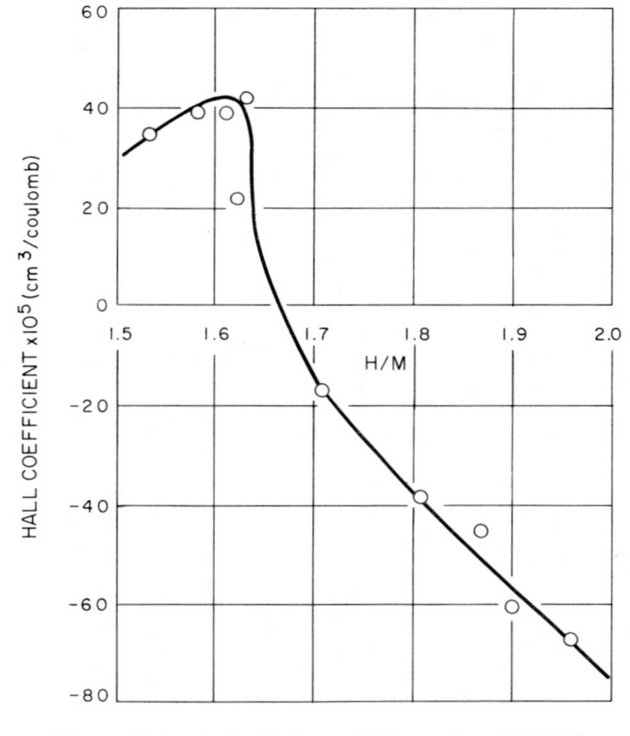

Figure 7. Hall Coefficient of Zirconium Hydride Samples as a Function of Composition for T = 300°K

D. THERMOELECTRIC POWER

As already mentioned, the thermoelectric power was a linear function of temperature between 0 and 100°C for all samples studied and can therefore be represented by an equation of the form $dE/dT = A + BT$, where A and B are constants characteristic of each sample. It should be recalled at this point that all measurements were made relative to copper and are so reported. Because dE/dT for copper is small in comparison to the values reported for zirconium hydride, the distinction between absolute thermoelectric power and thermoelectric power relative to copper is not important in the discussion to follow.

Some typical plots of dE/dT *vs* T are presented in Figure 8 for three samples, and values of A and B are listed in Table II. Thermoelectric power is plotted in Figure 9 as a function of composition for 0 and 100°C (as obtained by small extrapolations). The curves show positive thermoelectric powers for the lower hydrogen-to-metal ratios, maxima in the two-phase region, and negative thermoelectric powers for the higher hydrogen-to-metal ratios. The trends of these curves are qualitatively very similar to trends observed in the Pd-Ag and Pd-Au systems by Geibel.[16] In the latter instances, the behavior was attributed to marked changes in electronic structure with concentration.[16] If this is the case for zirconium hydride, then the thermoelectric power data are in direct conflict with the hypothesis of "nearly neutral" hydrogen. It should be kept in mind, however, that the thermoelectric power is often quite sensitive to very small

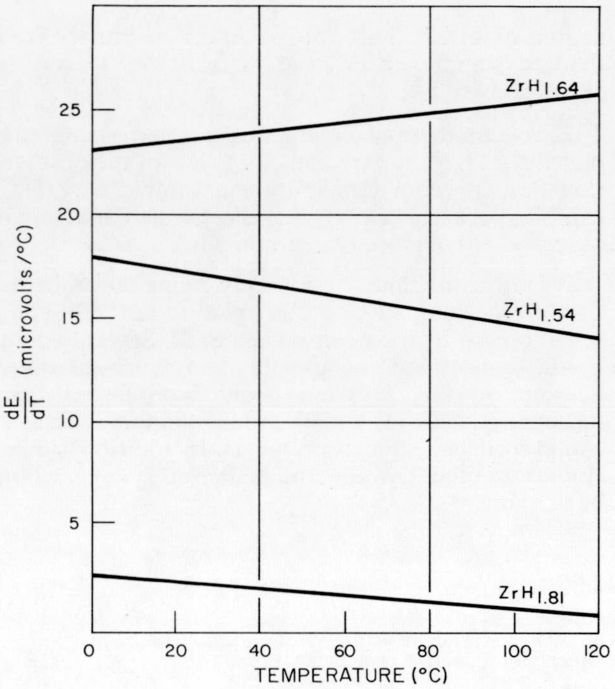

Figure 8. Thermoelectric Power of Zirconium Hydride Samples as a Function of Temperature for H/M Ratios of 1.54, 1.64, and 1.81.

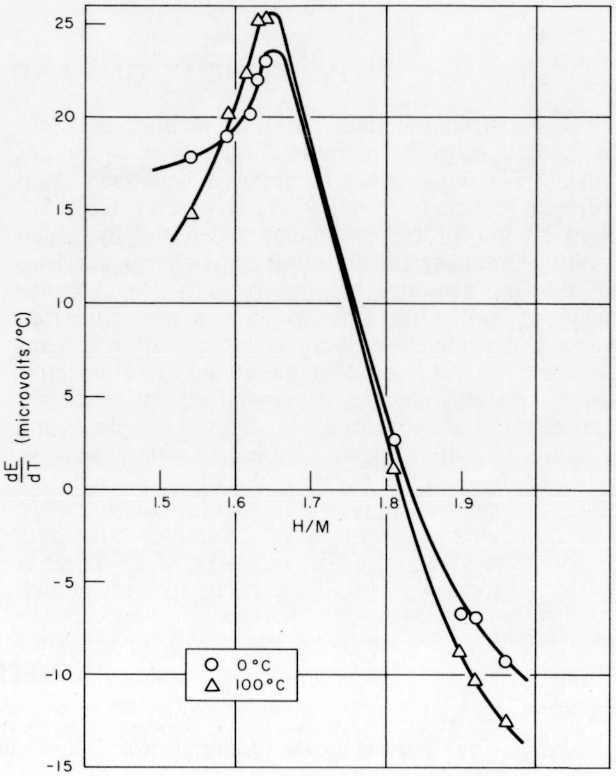

Figure 9. Thermoelectric Power of Zirconium Hydride Samples as a Function of Composition.

and subtle changes in electronic structure, so that large variations in the thermoelectric power are not necessarily indicative of gross changes in electronic structure.

Since the thermoelectric power is so sensitive to structure changes, it is believed that thermoelectric power measurements may be helpful in further elucidating the phase diagram of zirconium hydride in the region of large hydrogen-to-metal ratios. The electrical resistivity, Hall coefficient, and thermoelectric measurements, together with the X-ray data and dissociation pressure work of D. F. Atkins of this laboratory, tend to confirm the existence of a two-phase hydride region at room temperatures for hydrogen-to-metal ratios around 1.62. This is in substantial agreement with the work of Gulbransen and Andrew.[17]

The magnitudes of thermoelectric power for zirconium hydride are comparable with values typical of transition metals. A value of +9 microvolts/°C relative to copper was obtained for reactor grade zirconium at 20°C, whereas Miller[18] reported a value of +11.1 microvolts/°C relative to copper for crystal bar zirconium.

TABLE II

Thermoelectric power of Zirconium Hydride Samples

Sample	$\frac{dE}{dT} = A + BT$		Structure by X-ray Analysis
	$A \times 10^6$ volts/°C	$B \times 10^6$ volts/(°C)^2	
$ZrH_{1.54}$	+17.9	−0.031	fcc
$ZrH_{1.59}$(1)	+19.0	+0.012	fcc + fct
$ZrH_{1.62}$	+20.2	+0.022	fcc
$ZrH_{1.63}$	+22.1	+0.031	fcc
$ZrH_{1.64}$	+23.0	+0.023	fcc + fct
$ZrH_{1.81}$	+ 2.7	−0.016	fct
$ZrH_{1.90}$(2)	− 6.7	−0.021	fct
$ZrH_{1.92}$	− 6.9	−0.034	no information
$ZrH_{1.96}$	− 9.2	−0.034	(3)

(1) *Average of two samples.*

(2) *Average of five samples.*

(3) *Sample whose composition was $ZrH_{1.94}$ was fct by X-ray analysis.*

IV. CONCLUSIONS AND SUGGESTED FUTURE WORK

The experimental data obtained in this investigation demonstrate the metallic character of zirconium hydride. The dependence of electrical resistivity upon hydrogen concentration for H/M greater than 1.5 might be interpreted as evidence that the hydrogen has little influence on the number of charge carriers, and that the presence or absence of hydrogen influences the conduction process only in the sense that hydrogen vacancies are very efficient scattering centers. On the other hand, Hall effect and thermoelectric power data and changes in crystal structure clearly demonstrate the existence of changes in the electronic structure. Perhaps all that can be said with conviction is that changes in the number of hydrogen vacancies influence the electrical resistivity to a far greater extent than do changes in electronic structure. The data support the view that for large H/M, zirconium hydride is indeed a metallic compound with a high degree of order. This can be inferred directly from the rapid approach of residual resistivity to zero as H/M approaches 2.

Excellent thermal conduction properties are predicted for H/M approaching 2 in view of the observation that at room temperature a sample of $ZrH_{1.96}$ exhibited nearly twice the electrical conductivity observed for high-purity zirconium.

It is obvious that considerably more experimental data are needed before a clear picture of the bonding in zirconium hydride can be achieved. Several curves in this report are incomplete, and much of direct bearing on this problem could be inferred from nuclear magnetic resonance and low-temperature electronic specific heat measurements. In addition, similar studies on other hydride and deuteride systems would be of value.

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