

## HYDROGENATION OF $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$ INTERMETALLIC COMPOUNDS: FREE ELECTRON MODEL FOR MAGNETIC SUSCEPTIBILITY AND THERMOELECTRIC POWER

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**ABSTRACT.** The magnetic susceptibility and thermoelectric power of  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  intermetallic compounds were investigated as functions of hydrogen content. The alloys are paramagnetic, with magnetic susceptibility and Seebeck coefficient increasing with the amount of stored hydrogen. The susceptibility is proportional to the Seebeck coefficient and to the d-electron concentration, consistent with a free-electron model. The susceptibility of alloys with lower iron concentration suggests exchange-enhanced Pauli paramagnetism. However, Curie-Weiss paramagnetism likely coexists in alloys with higher iron content. Magnetic and electronic measurements may be used to assess the ability of an alloy to store hydrogen.

**Keywords:** Electronic Band Structure, Hydrogen Storage Materials, Intermetallic Compounds, Magnetic Susceptibility, Metal Hydrides, Nondestructive Electromagnetic Testing, Pauli Paramagnetism, Phase Diagrams, Seebeck Coefficient, Thermoelectric Effects, Thermopower

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### INTRODUCTION

The  $AB_2$  class of intermetallic compounds, of which  $(Zr-Ti)(Cr-Fe)_2$  is an example, are contemplated as possible materials for metal-hydride batteries and hydrogen storage devices [1]. Zr and Ti are hydride-forming elements, whereas Cr and Fe are non-hydride-forming. Magnetic and electronic measurements may be used to determine the amount and state of hydrogen in candidate metal-hydride alloys [2]. Here, a correlation is found among magnetic susceptibility, thermopower, *d*-electron concentration, and the amount of stored hydrogen in  $(Zr-Ti)(Cr-Fe)_2$ .

A phase diagram of hydrogenation is represented by the pressure-composition isotherm (PCT) diagram [3] as shown in Figure 1(a). It shows the relationship between the hydrogen equilibrium partial pressure and the hydrogen content in a material at different temperatures. The solid line shows the variation of the equilibrium hydrogen partial pressure of absorption with the amount of absorbed hydrogen. Hydrogen initially dissolves

in a metal, forming a solid solution phase ( $\alpha$  phase). The hydrogen concentration increases with increasing hydrogen partial pressure until a higher concentration hydride ( $\beta$  phase) precipitates. As the phase conversion is completed, the  $\alpha$  phase totally disappears. The system regains a degree of freedom and the pressure again rises as a function of hydrogen content. A steep increase in pressure is necessary to alter the composition of the hydride phase. The dashed curve in the figure indicates the two-phase region where the isotherms show a constant pressure.

As described by Termsuksawad et al. [2], the first hydrogen to enter a transition-metal-rich solid solution ( $\alpha$  phase) has a positive heat of mixing (endothermic reaction). These hydrogen atoms contribute their electrons to the metal  $d$ -band according to the “proton” and the “screened proton” models [4,5]. As the hydrogen activity (and content) increases in the solid solution, the heat of mixing becomes negative for these transition-metal-rich alloys. This thermodynamically describes a lowering of energy by the shared (covalent) or transferred (ionic) electron to the hydrogen ion, resulting, to some degree, in a bound hydrogen atom. The more negative the heat of mixing, the more irreversible is the hydrogen binding. This  $\beta$  phase is characterized by hydrogen as an electron acceptor; it promotes negative hydrogen ion localization to the positive metal matrix ion, resulting in hydride formation.

Hydrogen absorption causes a change in the Fermi energy level, which affects the chemical potential of the soluble (protonic) hydrogen in metals. The effect of hydrogen absorption on the electronic structure was reviewed by Gelatt [4]: in the pure metal, electron energy states are confined to a partially filled, narrow  $d$ -band and a broad conduction band. As hydrogen enters the lattice, new metal-hydrogen bonding states are formed below the  $d$ -band, depleting states near the bottom of both the  $d$ -band and the conduction band, and raising the Fermi level. This behavior is the desired characteristic of a hydrogen storage electrode for a reversible battery.

Another model for the electronic effect on hydrogen absorption in metals was proposed by Bernauer et al. [6]. This model pointed out that hydrogen absorption for the cubic and hexagonal transition-metal alloys depends only on the average number of  $d$ -electrons, which is described by  $H/M = 5 - \text{DEC}$ . Here,  $H$  is the number of stored hydrogen atoms,  $M$  is the number of metal atoms, and DEC is the average number of  $d$ -electrons (before hydrogen is introduced), calculated from  $\text{DEC} = (\text{sum of } d\text{-electrons}) / (\text{number of metal atoms})$ . According to this model, soluble hydrogen will be stored until the  $d$ -band is half full; after that, absorbed hydrogen will cause hydride formation.

*Pauli paramagnetism* of the conduction electrons in transition metals may be described by electron band theory [7]. The energy band structure is simply a parabolic distribution, with half-bands of electrons of opposite spin occupied up to the Fermi level. An applied magnetic field reverses electron spins at and near the Fermi level, so only a small fraction of the total number of electrons contributes to a net spin magnetic moment. Accordingly, the resulting magnetization of a Pauli paramagnetic metal is small. In the  $\alpha$  phase, additional electrons donated from the soluble hydrogen to the  $d$ -band raise the Fermi level.

The magnetic susceptibility is a function of the number of electrons at and in the vicinity of the Fermi level  $E_F$ . The volume susceptibility  $\chi$  is expressed in SI units (dimensionless) as [8]

$$\chi = \frac{3n\mu_0\mu_B^2}{2E_F}, \quad (1)$$

where  $n$  is the electron concentration,  $\mu_0$  is the permeability of vacuum, and  $\mu_B$  is the Bohr magneton. For Pauli paramagnets,  $n$  is on the order of  $10^{28} \text{ m}^{-3}$  and  $\chi$  is on the order of  $10^{-5}$  (SI, dimensionless). To convert  $\chi$  from SI (or rationalized MKS) units to CGS units (or EMU), divide by  $4\pi$ .

In the *thermoelectric (Seebeck) effect*, a temperature gradient causes a potential difference across a material. The Seebeck coefficient  $S$  involves the generation of the Seebeck electromotive force  $\Delta V$  under an applied temperature difference,  $\Delta T$  [9]:  $\Delta V = S \Delta T$ .

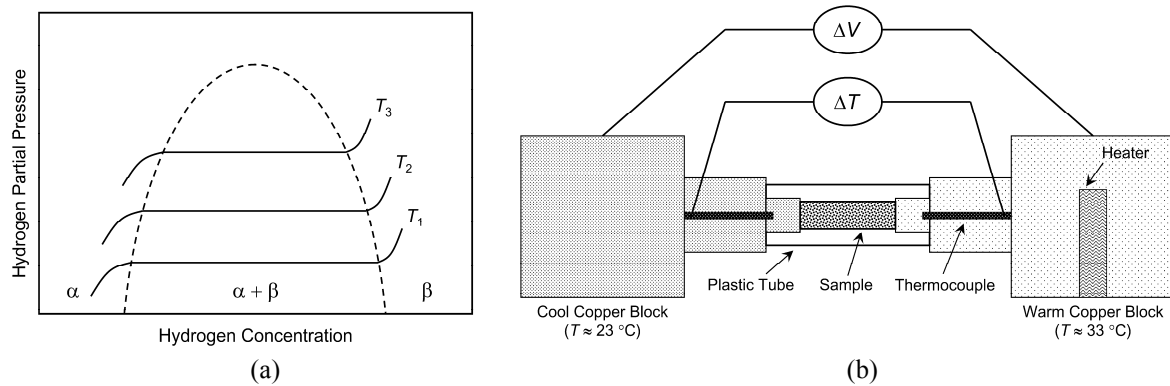
The temperature gradient affects the electron system and the crystal lattice of the material. The electron and phonon contributions to the Seebeck effect are assumed to be independent of each other. The total Seebeck coefficient is then the combination of the diffusion thermopower (electronic contribution) and the phonon-drag thermopower (phonon contribution) [10].

In metals, the lattice effect is significant only at temperatures below the Debye temperature [11]. At normal temperature, the thermal conduction by the lattice is dominated by the electronic contribution. The diffusional Seebeck coefficient  $S_d$  is predicted with its magnitude and sign depending on how the conductivity  $\sigma$  changes with electron energy  $E$  at the Fermi surface  $E_F$  [12]:

$$S_d = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial}{\partial E} \ln \sigma(E) \right|_{E=E_F}, \quad (2)$$

where  $k_B$  is Boltzmann's constant,  $e$  is the electron charge, and  $T$  is temperature.

The dependence on the electrical conductivity indicates that the Seebeck coefficient depends on the electron concentration, the scattering mechanism, and the features of the band structure at the Fermi energy level, which is characterized by the effective mass  $m^*$ . Both the Seebeck coefficient and the magnetic susceptibility are properties of materials related to  $d$ -electron concentration and band structure, and can be used to assess the change in electronic level of the alloy during hydrogenation. The thermoelectric power of a material is relatively easy to measure, but is rather difficult to interpret because it is strongly influenced by subtle details of the electronic structure. Complemented by magnetic measurements, a rough understanding of the electronic states in hydrogenated compounds is possible.



**FIGURE 1.** (a) Pressure-composition isotherm (PCT) diagram of a metal under hydrogenation [3]. (b) Schematic of Seebeck coefficient measurement system.

## EXPERIMENT

An experimental investigation was undertaken to compare the magnetic susceptibility and Seebeck coefficient of  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  intermetallic compounds as functions of hydrogenation in the context of a free-electron model. The effect of hydrogen on the electronic state of an alloy is based on the assumption that hydrogen will serve either as an electron donor or an acceptor, depending on the alloy composition and the hydrogen content.

$Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  samples with  $x = 0.6, 0.8$  and  $1.0$  were prepared [13] by melting the elements in an arc furnace under a helium atmosphere. They were annealed in helium gas at  $900\text{ }^\circ\text{C}$  for three days. For these compounds, the DEC numbers are:  $DEC = [0.9(2) + 0.1(2) + x(4) + (2-x)(6)] / 3$ .  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  has the hexagonal C14 Laves phase structure (MgZn<sub>2</sub> type) [14]. The  $Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4}$  alloy is the same as “Alloy 4” in Termsuksawad et al. [2].

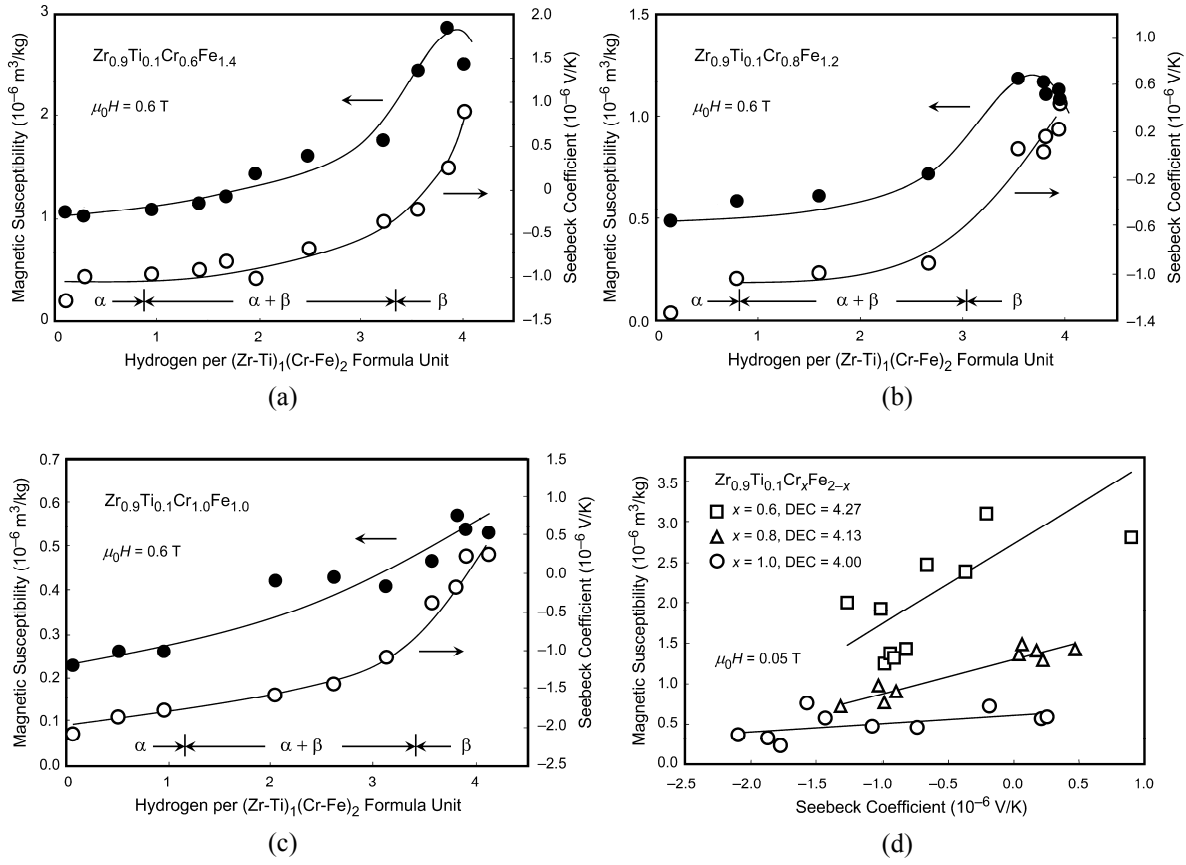
Hydrogen charging was carried out in a Sieverts-type facility on crushed, powdered samples at a pressure of  $1\text{ MPa}$  ( $7800\text{ torr}$ ,  $150\text{ psi}$ ) of high purity hydrogen gas. The system was evacuated to  $7\text{ mPa}$  ( $5 \times 10^{-5}\text{ torr}$ ,  $10^{-6}\text{ psi}$ ) before hydrogen gas was introduced. The amount of hydrogen in the metal was measured with a “hydrogen determinator,” which combusts the samples at  $2500\text{ }^\circ\text{C}$ . The released hydrogen is carried by argon gas through a molecular sieve for separation, and then quantified in a calibrated thermal conductivity detector. The amount of hydrogen was recorded in parts per million and later converted to hydrogen per formula unit.

Magnetization hysteresis loops were measured with a transverse-field vibrating-sample magnetometer at room temperature in maximum applied fields of  $0.6\text{ T}$ . Magnetization was computed as magnetic moment per unit mass of metal, not including hydrogen. The exclusion of hydrogen causes an uncertainty of  $0.1$  to  $2$  percent in the mass determination. Magnetic susceptibility was calculated as specific magnetization divided by applied field. Uncertainty arising from random effects is estimated to be on the order of the size of the data points in the graphs below. Uncertainty arising from systematic effects is estimated to be less than  $5$  percent of the reported values.

The thermopower measurement setup is shown in Figure 1(b). Powdered samples were used. One of the blocks was maintained at room temperature and the other at around  $10\text{ }^\circ\text{C}$  higher. The absolute thermopower of the alloy material (Seebeck coefficient,  $S_a$ ) can be determined as:  $S_a = \Delta V / \Delta T + S_{Cu}$ , where  $\Delta V$  is the voltage difference measured between probes,  $\Delta T$  is the temperature difference of  $10\text{ }^\circ\text{C}$ , and  $S_{Cu}$  is the known Seebeck coefficient for copper,  $1.83\text{ }\mu\text{V/K}$  at  $300\text{ K}$  [15].

## RESULTS

The magnetic susceptibility at  $0.6\text{ T}$  and the Seebeck coefficient as a function of hydrogen content of the  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  compounds are plotted for  $x = 0.6, 0.8$  and  $1.0$  in Figures 2(a), (b) and (c), respectively. The curves are simply a guide for the eye, but perhaps they suggest a fall-off in susceptibility at the highest hydrogen concentrations. In each compound the variation of the magnetic susceptibility and the Seebeck coefficient as functions of hydrogen content exhibit the same graphical features. Both quantities gradually change with dissolved hydrogen content. Plots of magnetic susceptibilities at  $0.05\text{ T}$  vs. Seebeck coefficients for  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  are illustrated in Figure 2(d). A generally linear relationship between the magnetic susceptibility and the Seebeck coefficient is apparent. To convert mass susceptibility from SI (or rationalized MKS) units of  $\text{m}^3/\text{kg}$  to CGS units (or EMU) of  $\text{cm}^3/\text{g}$  (or  $\text{emu/g}$ ), multiply by  $1000/4\pi$ .



**FIGURE 2.** (a) Magnetic susceptibility and Seebeck coefficient of  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  for  $x = 0.6$  as a function of hydrogen content. (b) For  $x = 0.8$ . (c) For  $x = 1.0$ . (d) Magnetic susceptibility at 0.05 T and Seebeck coefficient of  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  with  $x = 0.6, 0.8,$  and  $1.0$  for different hydrogen content.

The slopes of the linear fits are tabulated in Table 1 (with mass susceptibility converted to volume susceptibility), along with the slopes for susceptibilities at 0.6 T. These slopes also depend on the  $d$ -electron concentration (DEC number) of the host alloys. The compounds with larger DEC numbers have larger slopes. The slopes at the two applied magnetic fields are similar for all three compounds.

## FREE ELECTRON MODEL

A relationship between the magnetic susceptibility and the Seebeck coefficient may be demonstrated by use of a free electron model (FEM). In the model, the valence electrons of many atoms in a unit volume become conduction electrons and freely move through the metal with no ion-electron interactions. A conduction electron is scattered only infrequently by other conduction electrons. The relaxation time  $\tau$  is independent of an electron's position and velocity. Therefore, the concentration of free electrons  $n$  is a

**TABLE 1.** For different Zr-Ti-Cr-Fe alloys, slope  $d\chi/dS_d$  from Figure 2(d), with mass susceptibility converted to volume susceptibility using an approximate density of  $7000 \text{ kg/m}^3$ .

$Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$	DEC	$d\chi/dS_d \text{ (K/V)}$	
		at 0.05 T	at 0.6 T
$x = 0.6$	4.27	6900	6400
$x = 0.8$	4.13	2900	2800
$x = 1.0$	4.00	700	1000

function only of energy  $E$  [16]:

$$n = \frac{1}{3\pi^2} \left( \frac{2m_e E}{\hbar^2} \right)^{3/2}, \quad (3)$$

where  $m_e$  is the electron mass (not effective mass  $m^*$ , because the electrons experience only a constant potential). The electrical conductivity  $\sigma$  of a metal is as expressed as

$$\sigma = \frac{ne^2\tau}{m_e}. \quad (4)$$

Combine (3) and (4):

$$\sigma = \frac{e^2\tau}{3\pi^2 m_e} \left( \frac{2m_e E}{\hbar^2} \right)^{3/2}. \quad (5)$$

Take the natural logarithm of each side and partially differentiate with respect to  $E$ :

$$\left. \frac{\partial}{\partial E} \ln \sigma(E) \right|_{E=E_F} = \frac{3}{2E_F}. \quad (6)$$

Combine (2) and (6):

$$S_d = \frac{\pi^2 k_B^2 T}{2eE_F}. \quad (7)$$

Equation (7) includes only the diffusion term, not the phonon drag term. The equations for the Seebeck coefficient (7) and the susceptibility (1) have the reciprocal of  $E_F$  in common. Thus,

$$\chi = \frac{3ne\mu_0\mu_B^2}{\pi^2 k_B^2 T} S_d. \quad (8)$$

In the FEM, the paramagnetic volume susceptibility is proportional to the free electron concentration and the Seebeck coefficient. For Pauli paramagnets with  $n$  on the order of  $10^{28} \text{ m}^{-3}$ ,  $\chi$  on the order of  $10^{-5}$ , and measurements at ambient temperature, values of  $S_d$  on the order of  $10^{-5} \text{ V/K}$  are expected.

## DISCUSSION

The fact of the matter is, (8) fails to adequately describe Figure 2(d): (a) the sign of  $S_d$  would be expected to be positive, the same as that of  $\chi$ ; (b) the linear fits to the data should go through the origin; and (c) the measured values of  $\chi$  are up to four orders of magnitude larger than predicted. We address each of these points.

In the single hydride ( $\beta$ ) phase, the filling of electrons at the Fermi energy level competes with the consumption of electrons from the conduction band to form the hydride-

bonding band [4]. The magnetic susceptibility increases to a maximum and then decreases, possibly due to the  $d$ -band becoming half-filled; further addition of hydrogen would reduce the number of unpaired electrons, reducing the magnetic moment. This behavior is present in all the  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  compounds. In contrast, the Seebeck coefficient keeps rising with the amount of stored hydrogen, indicating further filling of electron bands when the compounds enter the hydride ( $\beta$ ) phase region. At high hydrogen concentrations, electrons donated by the hydrogen can shift the Fermi level to the upper portion of the energy band. This can make the sign of the Seebeck coefficient positive, in analogy to the effect in semiconductors.

In terms of the Brillouin zone (BZ), the fraction of the BZ occupied by electrons increases with the addition of electrons donated by hydrogen (H). If the concentration of H is high compared to the concentration of host atoms, the filling of the BZ could be considerable. As the occupied volume increases, the Fermi surface moves toward the BZ boundaries, touching the boundaries when the BZ is half or two-thirds filled. Here one can expect a reversal of the sign of the Seebeck coefficient from negative to positive. The metal behavior resembles that of a semiconductor heavily doped with acceptor impurities (high hole concentration). The amount of H required to change the sign of the Seebeck coefficient depends on the electron band occupation before doping. If it is already above half, then the addition of a small amount of H can cause a sign change. For examples, Cu, Ag and Au have positive Seebeck coefficients. To avoid problems with the sign of  $S_d$  and the nonzero intercept in the linear fits in Figure 2(d), we concentrate just on the expected proportionality between  $\chi$  and  $S_d$ . From (8),

$$\frac{d\chi}{dS_d} = \frac{3ne\mu_0\mu_B^2}{\pi^2k_B^2T}. \quad (9)$$

For  $n$  on the order of  $10^{28} \text{ m}^{-3}$  and measurements at room temperature, (9) predicts  $d\chi/dS_d$  on the order of unity, with  $\chi$  equal to the volume susceptibility calculated from the mass susceptibility plotted in the figures. As seen in Table 1, the values of  $\chi$  are much larger than expected from simple Pauli paramagnetism. Pauli paramagnetism refers to the susceptibility of conduction-electron spins in metals. Its signature is a temperature-independent volume susceptibility in the range of  $10^{-5}$  SI or mass susceptibilities on the order of  $10^{-9} \text{ m}^3/\text{kg}$ . Pauli paramagnetism is well established in some cubic C15 Laves phase compounds such as  $ZrCo_2$  [17],  $NbFe_2$ ,  $MoFe_2$  [18],  $YNi_2$ ,  $LuNi_2$ , and  $CeNi_2$  [19].

Several Laves phase compounds are known to have strong *exchange-enhanced* Pauli paramagnetism [20,21,22]:  $YCo_2$  has a mass susceptibility on the order of  $1.9 \times 10^{-7} \text{ m}^3/\text{kg}$  [23];  $ScCo_2$ ,  $1.6 \times 10^{-7} \text{ m}^3/\text{kg}$  [24]; and  $LuCo_2$ ,  $4.5 \times 10^{-7} \text{ m}^3/\text{kg}$  [25].

Our C14 Laves phase  $Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x}$  alloys with low Fe content ( $x = 0.8, 1.0$ ) and low hydrogen concentrations ( $\alpha$  phase and  $\alpha + \beta$  phase) have mass susceptibilities similar to those of the exchange-enhanced Pauli paramagnets. This could explain the much larger measured susceptibilities compared to simple Pauli paramagnets. A further consideration is that, in transition metals, the density of states in the  $3d$ -band at the Fermi level can be orders of magnitude larger than in the FEM, giving rise to magnetic susceptibilities larger than expected for ideal metals.

The  $Zr_{0.9}Ti_{0.1}Cr_{1.0}Fe_{1.0}$  alloy with no hydrogen has a high-field susceptibility of  $1.6 \times 10^{-7} \text{ m}^3/\text{kg}$  at 300 K, consistent with exchange-enhanced Pauli paramagnetism. However, there are also indications of weak Curie-Weiss paramagnetism, probably due to a magnetic moment on the Fe ions: (a) at fields below 0.02 T, slight curvature (but no hysteresis) is present in a plot of magnetization vs. field (not shown), and (b) the low-field susceptibility

at 300 K ( $2.1 \times 10^{-6} \text{ m}^3/\text{kg}$ ) increases by a factor of 2 as temperature decreases to 30 K. Thus, for the alloys with low Fe content and low hydrogen concentration, the magnitudes of the exchange-enhanced Pauli paramagnetism and the Curie-Weiss paramagnetism are comparable. The alloys with higher Fe content ( $x = 0.6$ ) and higher hydrogen concentrations ( $\beta$  phase) may be best characterized as just Curie-Weiss paramagnets.

It is likely that, although it is appealingly simple, the FEM is not adequate for these alloys: The periodic potential in the lattice would cause the energy bands to deviate from simple parabolas, requiring the use of an effective electron mass (the usual modification of the FEM). The Seebeck coefficient derived in (7) is the electronic contribution of the thermopower; the phonon-drag thermopower is not included in the calculation. Finally, the apparent coexistence of Curie-Weiss paramagnetism confounds the interpretation in terms of simple (or even exchange-enhanced) Pauli paramagnetism. Despite these limitations, the linear relation between measured susceptibilities and Seebeck coefficients gives some credence to a FEM approach.

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