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Localized Magnetic Impurity States in Ti, Zr, and Hf†

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An experimental study of localized moments on "magnetic" impurities (≈ 0.2 at.% of Cr, Mn, Fe, Co, or Gd) in the group IV transition elements Ti, Zr, and Hf has been carried out. From magnetic-susceptibility measurements we find a localized moment on Mn of $\approx 3.5\ \mu_B$ in each of the solvents Ti, Zr, and Hf. Chromium forms a moment in Zr ($0.2\ \mu_B$) and in Hf ($1.7\ \mu_B$) but not in Ti. Iron forms a moment in Hf ($0.7\ \mu_B$) but not in Ti or Zr. Thus the tendency towards localized-moment formation on these $3d$ ions increases in the sequence Ti-Zr-Hf, possibly because of the decreasing solvent electronic-state density. Negative magnetoresistance is produced by each d-shell impurity for which magnetic-susceptibility measurements indicate a localized moment. The magnetoresistivity and susceptibility data are shown to be correlated in the weak-field limit by the elementary molecular-field description and the assumption that the magnetoresistance is proportional to the square of the magnetization. Resistivity minima are observed in "pure" (arc-cast, iodide process) Ti and Ti-Cr, -Mn, and -Fe; Zr-Mn; and Hf-Cr, -Mn, and -Fe. It thus appears that there is no strict correlation of resistivity minima and localized moments for the d-shell impurities. The resistivity-versus-temperature curves are not explained by the recent theory of Kondo. It is suggested that this apparent disagreement can be accounted for in part if one assumes a substantial temperature dependence of the nonmagnetic impurity-potential scattering, which was not included in Kondo's theory. For Gd in the group IVB solvents, a nearly free-atom moment is observed in Zr ($7.0\ \mu_B$) and Hf ($6.1\ \mu_B$), (Ti-Gd was not examined). No resistivity minima and only a very small negative magnetoresistance are observed in the alloys with Gd, suggesting a much weaker conduction-electron interaction with the localized magnetic states of the f-shell ions than with the localized moments on the d-shell impurities.

I. INTRODUCTION

An extensive literature exists on the subject of localized magnetic states associated with magnetic impurities in the noble metals, and other nontransition metals.[1] A well-known example is Cu containing a dilute addition of Mn.[2–7] At low temperatures an alloy of this type is expected to exhibit some of the well-known "anomalies" including negative magnetoresistance, resistivity maxima and/or minima, and an anomalous contribution to the specific heat, to name a few. Some of these anomalies have been explained on the basis of the s-d interaction model. For example, the s-d theories of Yosida[8] and Kasuya[9] have been used to explain the observed negative magnetoresistance of several nontransition metal solvents containing Mn or Fe.[5,10]

Recently, Kondo[11] has carried the s-d exchange-scattering calculation to second order in the Born approximation. This leads to a spin-dependent resistivity term proportional to $\ln T$ which when combined with the lattice- and impurity-potential resistivities affords an explanation of the resistivity-minimum phenomenon. The theory seems to explain adequately the temperature dependence of the resistivities[12] of some dilute Au-Fe alloys which showed a resistivity minimum.

Low-temperature anomalies similar to those observed in noble-metal-based alloys have been observed in several transition-metal-based alloys.[13–16] Detailed studies[17–20] have been carried out on dilute Ti alloys with "magnetic" impurities. By now most of the well-known anomalies have been seen in these Ti alloys and they have been observed to be qualitatively similar to those found for nontransition metal solvents. On account of the similarity of these anomalies to those observed in the noble metals, they have been ascribed to conduction-electron-localized-moment interaction presumably similar to the s-d interaction. A detailed study of magnetic impurities in the transition metals seems pertinent, therefore, with the purpose of shedding light on (a) the conditions favorable to moment localization, (b) the applicability of the s-d interaction theories to the transition-metal-based alloys, (c) those fundamental interactions of localized moments which are the origins

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of ferromagnetism, and (d) the interrelationship of superconductivity and magnetism in the transition metals.

In the present paper we report on an experimental survey of localized magnetic states in the transition elements of the IVth column, Ti, Zr, and Hf. Essentially an extension of earlier work,[17–20] the present study consisted of a search for resistive anomalies in the group IV metals containing dilute quantities of Gd, or Cr, Mn, Fe, or Co. (In the following the latter four will be referred to collectively as the "*d*-shell" impurities.) For each alloy we have sought to correlate the transport measurements with a localized moment as determined by measurement of its magnetic susceptibility. It is observed that Mn gives rise to large localized moments in each base metal and that the predilection towards formation of localized moments increases in the sequence from Ti to Zr to Hf, possibly reflecting the decreasing electronic-state density of the solvents. For the *d*-shell impurities, it is observed that in each instance where a localized moment is evidenced by the susceptibility, negative magnetoresistivity is observed. The familiar phenomenological (molecular-field) approach coupled with a development[21] of the assumption that the scattering power of an impurity depends on the relative spin orientation of the ion and the conduction electron is found to correlate satisfactorily the magnitude of the *d*-shell moments with the observed negative magnetoresistance. The resistivity minima, on the other hand, are not found to occur in one-to-one correspondence with the observed localized moments. Rather, the minima are most prevalent in Ti and least in Zr.

In contrast to the *d*-shell impurities, Gd produces barely perceptible resistive anomalies in these transition metals even though susceptibility measurements are indicative of localized-moment formation. These results are suggestive of a very weak conduction-electron interaction with the Gd inner-shell moment in contrast to the relatively strong coupling evidenced for the *d*-shell moments. (In this paper the term "conduction electron" is used to denote those electrons near the Fermi surface which participate in electron transport processes.) In general, the *d*-shell impurities appear to produce effects in Ti, Zr, and Hf quite similar to those observed when they are dissovled in the noble metals.

II. EXPERIMENTAL METHOD

A. Samples and Apparatus

The experimental samples were cut from buttons arc-cast in an inert atmosphere. The finished samples were measured as-machined without annealing. No cold-rolling was used; however, it is possible that diamond-sawing and polishing may have introduced some strain in the specimens. The sample-preparation and resistance-measuring techniques have been described in detail elsewhere.[18] The previous arrangement was modified by the substitution of a Au-Co–versus–Cu thermocouple in place of the copper-constantan thermocouple. The principal source of error in the resistance measurements was the determination of the sample dimensions. Care was taken to achieve near-uniformity of cross section as practical after which the specimen dimensions were measured at nine selected positions and suitable weighted averages were taken as the final dimensions. Typical specimens were $1\times0.1\times0.01$ in. with a typical variance in the factor l/A (l is the voltage probe separation and A the cross-sectional area) of $\approx0.5\%$. Allowing for a 1% error in the measurement of the thickness, we estimated the absolute values of the resistivities to be accurate to approximately 2%. However, relative values in the range of temperature 1–30°K should be a good deal more accurate, probably 0.1%.

The magnetic susceptibilities were measured by means of a conventional Gouy technique which has been described earlier.[22]

B. Data Analysis

1. *Magnetic Susceptibility*

The magnetic moment associated with the impurity atoms is obtained if one assumes that the magnetization $\sigma_m(H,I)$ of the system of moments may be represented by the orientational paramagnetism of a system of well-defined spins j. For the weak-field magnetization, the well-known expression for the total magnetization is

$$\sigma=\sigma_m+\sigma_0=ng^2j(j+1)\mu_B{}^2H/3k(T-\theta)+\chi_0H\,, \quad (1)$$

where $\sigma_0=\chi_0H$ represents the nearly temperature-independent magnetization of the host matrix. For very strong fields the localized-moment magnetization is expected to saturate to a value

$$\sigma_m(T,\infty)=ngj\mu_B\,. \quad (2)$$

In Eqs. (1) and (2), n is the concentration of impurity atoms calculated from the measured weights of solvent and solute prior to consolidating, μ_B is the Bohr magneton, k is Boltzmann's constant, and in the following the splitting factor g is assumed to be 2. For the present alloys, Eq. (1) correctly predicts the observed inverse temperature dependence of the weak-field susceptibility $\chi=\sigma/H\approx C/T$ in those cases where χ is sensibly temperature-dependent. Consequently, the magnetic moment per atom $\mu=gj\mu_B$ may be determined from the experimentally determined value of the Curie constant C.

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2. *Resistive Anomalies*

In the analysis of the resistivity data it is assumed that ρ_a, the measured resistivity of the alloy, is simply that of the "pure" solvent ρ_p; plus a (nearly) temperature- and field-independent term ρ_V (Mattheissen's rule) arising from nonmagnetic impurity potential scattering; plus a temperature- and field-dependent contribution ρ_{mag} due to spin-dependent scattering. Accordingly,

$$\rho_a(T,H)=\rho_p(T,H)+\rho_V+\rho_{\mathrm{mag}}(T,H). \qquad (3)$$

3. *Magnetoresistivity*

If, in the same spirit as the description corresponding to Eq. (1), it is assumed that the effect of an externally applied field is to polarize the medium of otherwise nearly randomly oriented spins, and it is assumed that the scattering power of an impurity depends on the relative spin orientation of the ion and the conduction electron then it can be shown[21] that the resistivity should be decreased in proportion to the square of the localized-moment magnetization.[23] That is

$$\rho_{\mathrm{mag}}(T_0,H)-\rho_{\mathrm{mag}}(T_0,0) \equiv\delta\rho_{\mathrm{mag}}(T_0,H)\propto[\sigma_m(T_0,H)]^2, \qquad (4)$$

where T_0 refers to the constant temperature at which the experiment is performed. Combining Eq. (4) with Eqs. (1) and (2), it is easily shown (for $g=2$) that

$$j+1=[(d/dH^2)\delta\rho_{\mathrm{mag}}]^{1/2}{}_{H=0} \times[\delta\rho_{\mathrm{mag}}]^{-1/2}{}_{H=\infty}3k(T_0-\theta)/2\mu_B. \qquad (5)$$

Accordingly, if $\delta\rho_{\mathrm{mag}}(T_0,H)$ is negative and saturates at larger field values, the localized moment $\mu=gj\mu_B$ may be determined from the magnetoresistance data from the initial slope $(d\delta\rho_{\mathrm{mag}}/dH^2)_{H=0}$, and the saturation value $(\delta\rho_{\mathrm{mag}})_{H=\infty}$. From Eq. (3), $\delta\rho_{\mathrm{mag}}(T_0,H)$ is given by

$$\delta\rho_{\mathrm{mag}}(T_0,H)=[\rho_a(T_0,H)-\rho_a(T_0,0)] -[\rho_p(T_0,H)-\rho_p(T_0,0)], \qquad (6)$$

where the quantities on the right-hand side are measured directly. The relations Eqs. (3) and (6) reflect the assumption that the normal positive magnetoresistance of the solvent is unchanged by the addition of the impurities. This appears to be borne out experimentally as discussed in Sec. III B.

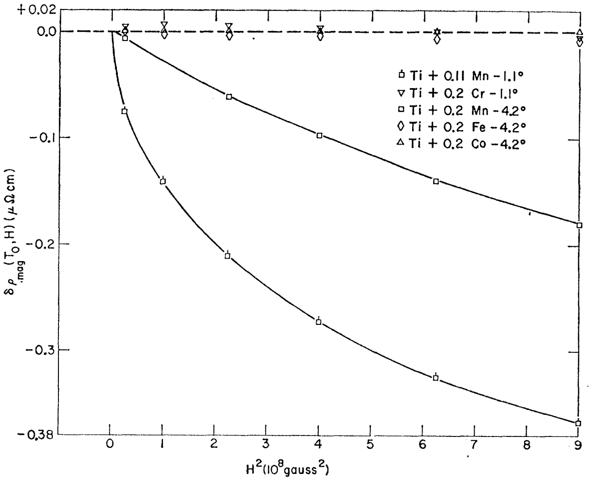

FIG. 1. The magnetoresistance data for the Ti alloys. Plotted against the square of the applied field is the change in the magnetic scattering term $\delta\rho_{\mathrm{mag}}=\rho_{\mathrm{mag}}(H)-\rho_{\mathrm{mag}}(0)$ which is given from the experimental data by Eq. (6). The dashed line is the zero line included for convenience. The indicated concentrations are in at.%.

III. EXPERIMENTAL DATA

A. Susceptibility

The magnetic susceptibilities of the alloys were measured over the temperature range 1.5–300°K. Typical measuring fields were of the order of 4 to 10 kG. When the susceptibilities were not temperature-independent the data could be fit to the Curie-Weiss equation

$$\chi-\chi_0=C/(T-\theta), \qquad (7)$$

where χ_0 and θ were determined empirically to give the best fit. At the lowest temperatures ($T\lesssim 10$°K) it was frequently observed that the susceptibilities were slightly field-dependent. In such cases only the data for $T>10$°K were used in fitting to Eq. (7). From Eq. (1), the Curie constant C is given by

$$C=ng^2j(j+1)\mu_B{}^2/3k. \qquad (8)$$

The localized moment was then calculated from Eq. (8) by assuming $g=2$ whence:

$$\mu/\mu_B=2j. \qquad (9)$$

In each case χ_0 was found to be very nearly equal to the nearly temperature-independent susceptibility of the host metal.

The observed moment values for the present alloys are given in Table I along with data from the magnetoresistance measurements. It should be noted that the localized-moment value for Mn in Ti obtained in the present work on 0.1- and 0.2-at.% Mn alloys which were arc-cast is in good agreement with that determined previously[22] for Ti-Mn alloys of comparable concentration which were annealed for eight hours at 690°C (below the bcc → hcp transition temperature). Thus it would appear that all the Mn is in solution in the hcp phase in the present quite dilute arc-cast Ti-Mn alloys.

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[23] The dependence of the negative magnetoresistance on the square of the magnetization has been observed experimentally on some Cu-Mn and Cu-Co alloys by Schmitt and Jacobs (Refs. 2–4), and on $Mo_{0.8}$-$Nb_{0.2}$ containing Fe by Sarachik (Ref. 16).

TABLE I. Localized-moment values as determined by the susceptibility μ (exp), and calculated from the magnetoresistivity μ (calc) by Eq. (5).

Base metal	Solute at. %	$(d[\delta\rho_{\mathrm{mag}}(T_0,H)]/dH^2)_{H=0}$ ($\mu\Omega$ cm G^{-2})	$\delta\rho_{\mathrm{mag}}$ (T_0,∞) ($\mu\Omega$ cm)	μ/μ_B (calc)	μ/μ_B (exp)
Ti	0.2 Cr	≈ 0	...	...	...
Ti	0.1 Mn	-0.7×10^{-5}	-0.5	3.2	3.5
Ti	0.2 Mn	-1.7×10^{-5}[a]	-0.3[a]	3.8[a]	3.5
Ti	0.2 Fe	[b]	[b]	[b]	0
Ti	0.2 Co	≈ 0	...	...	...
Zr	0.2 Cr	-1.7×10^{-5}	[b]	...	0.2
Zr	0.2 Mn	-6.7×10^{-5}	-0.45	3.2	3.5
Zr	0.2 Co	≈ 0	...	...	0
Zr	0.2 Gd	[b]	[b]	[b]	7.0
Hf	0.2 Cr	-3.2×10^{-5}	-0.35	0.8	1.7
Hf	0.2 Mn	-8.7×10^{-5}	-0.60	3.8	3.8
Hf	0.2 Fe	-7.0×10^{-6}	-0.06	0.5	0.7
Hf	0.2 Co	≈ 0	...	...	0
Hf	0.2 Gd	[b]	[b]	[b]	6.1

[a] At 4.2°K. Others at 1.1°K.

[b] Negative; but $\delta\rho_{\mathrm{mag}}$ is very small at 30 kG. See Figs. 1, 2, and 3.

We assume in this paper that all the 0.2-at. % alloying concentrations are in hcp solid solution in Ti, Zr, and Hf.

B. Magnetoresistivities

In the present study magnetoresistivity data were taken at $T_0=1.1$ or 4.2°K from 0 to 30 kG. On Figs. 1, 2, and 3 we have plotted the quantity $\delta\rho_{\mathrm{mag}}(T_0,H)$ [defined by Eq. (6)] against the square of the applied magnetic field. This procedure is based on the assumption that the normal positive magnetoresistivity of the host metal is negligibly affected by the dilute addition of the solutes. Consequently, the quantity $\delta\rho_{\mathrm{mag}}(T,H)$ may be expected to represent the anomalous negative contribution arising from localized magnetic states. This assumption appears to be borne out insofar as those alloys displaying little or no localized moment likewise exhibit very small $\delta\rho_{\mathrm{mag}}(T_0,H)$. Conversely, it may be noted that for those alloys for which $\mu/\mu_B>0.1$, the magnetoresistivities are commensurately large and negative. Where $\delta\rho_{\mathrm{mag}}(T_0,H)$ is appreciable, one is able to estimate the initial slope $[d(\delta\rho_{\mathrm{mag}})/dH^2]_{H=0}$ and the saturation value at high magnetic fields. With these values, the quantity j and hence the moment $gj\mu_B$ may be calculated by means of Eq. (5). On Table I, we have listed the values of the initial slope and the saturation value of $\delta\rho_{\mathrm{mag}}$ as estimated from the graphs of Figs. 1, 2, and 3. These estimated values are clearly quite inaccurate. For example, one may estimate the saturation value of $\delta\rho_{\mathrm{mag}}$ for Ti+0.1-at. % Mn (Fig. 1) to be anywhere from 0.4 to 0.6 $\mu\Omega$ cm. Similarly, the initial slope may be in error by perhaps 20%. The estimated values however, go under the square-root sign in Eq. (5) for the evaluation of j so that the error in j is reduced accordingly. More important is the value of the temperature θ of Eq. (1) which could not be obtained accurately from the data. For these 0.2-at. % alloys, the fit of the data to a Curie-Weiss line indicated θ values between 0 and -1°K and not conclusively different from zero in contrast to the situation

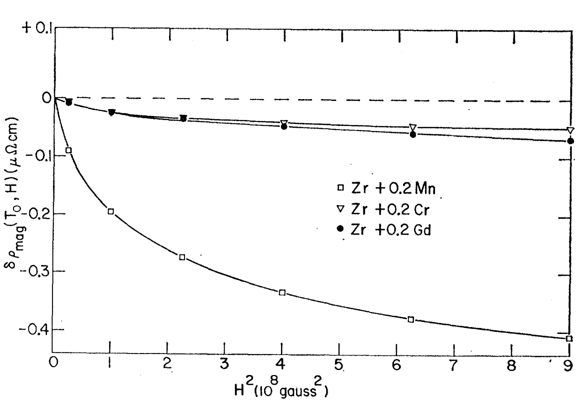

FIG. 2. The magnetoresistance data for the Zr alloys. Refer to the caption of Fig. 1 for pertinent remarks.

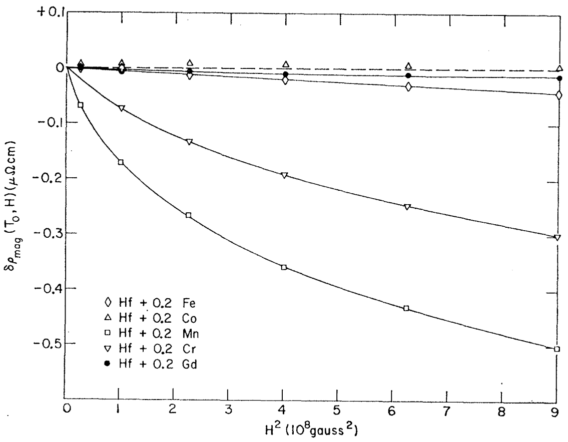

FIG. 3. The magnetoresistance data for the Hf alloys. Refer to caption of Fig. 1 for pertinent remarks.

for 1–4-at.% alloys[22] where the θ values are clearly more like -1 to -3°K. Accordingly, the μ values listed as μ(calc) on Table I were obtained by taking $\theta=0$ and using an initial and unprejudiced estimate of the slope and saturation value of $\delta\rho_{\text{mag}}$. As one may note in those cases where μ is large, e.g., for the case of Mn in each solvent, this crude procedure yields values quite close to those determined by the susceptibility. It would seem that the agreement between μ(calc) and μ(exp), for the Mn alloys, though obviously somewhat fortuitous, constitutes material evidence that the observed negative magnetoresistivity of these alloys is indeed caused by localized magnetic moments on the Mn impurity ions. It should be noted, at this point, that Eq. (5), by which the susceptibility data and magnetoresistance data appear to be correlated, is derivable from the *s-d* theories of Yosida[8] and Kasuya.[9] However, since Eq. (5) is obtained by combining the $H=0$ and $H=\infty$ limits of the theory, the detailed dependence of the resistance on the field and on the *s-d* interaction J has been removed. Consequently, the apparent correlation indicated by the results on Table I cannot be regarded as substantiating evidence for the applicability of the *s-d* interaction model to these transition-metal solvents.

C. Resistivities

Figures 4, 5, and 6 illustrate the temperature dependence of the resistivities (in zero field) of the alloys of the present study. On Fig. 4 we have plotted the resistivities of Ti containing 0.2 at.% of the various solutes (excepting Gd) as indicated. We have arbitrarily plotted $\rho(T)-\rho(4.2°\text{K})$ to illustrate the differences between the various alloys in the region where the resistivity minimum appears. One notes that minima occur for "pure[24]" Ti as well as Ti-Fe, Ti-Mn, and Ti-Cr, as was observed earlier.[18] In the inset of Fig. 4 we have plotted $\rho_a(T)-\rho_p(T)$, i.e., the difference between the resistivity of the alloy and that of the "pure" solvent. According to the assumption expressed by Eq. (3) this difference is expected to correspond to a temperature-independent contribution ρ_V, plus the anomalous low-temperature contribution ρ_{mag} attributed to magnetic scattering by the localized moments. Thus, since the total resistivity ρ_a has a minimum, and ideally ρ_p increases monotonically with increasing temperature while ρ_V is temperature-independent, one would expect $\rho_a-\rho_p$ to be largest at the lowest temperatures and tend to a constant value at higher temperatures.[25] This is in accord with the theory of Kondo[11] which predicts that $\rho_a-\rho_p$ should go as $A-B\ln T$ (A and B are constants for a given alloy), a function that increases with decreasing temperature. As one may note from Fig. 4 however, this does not appear to be the case for these Ti alloys. Moreover, the interesting result is that the curves for $\rho_a-\rho_p$ have a minimum in each case for which there is a minimum for ρ_a. The error flags shown in Fig. 4 for Ti+0.2-at.% Cr are representative of each of the curves and are based on the estimate that the absolute resistivities are measured to an accuracy of approximately 2%. Thus at the lowest temperatures where the differential resistivity is the difference between smaller numbers, the corresponding error is smaller. On this basis, the unusual behavior of these $\rho_a-\rho_p$ curves below about 40°K cannot be ascribed to experimental error. It appears, at this point, that Kondo's calculation in its present form, i.e., an additive $\ln T$ term, is not sufficient to explain the resistivities of these dilute Ti alloys.

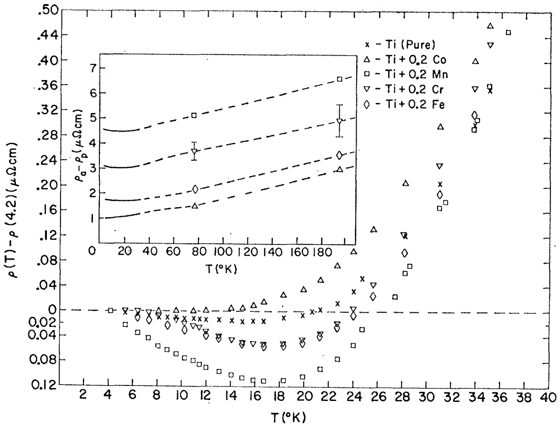

FIG. 4. The resistivity versus temperature of the Ti alloys in zero field. In the main portion of the graph the data points represent the difference between the resistivity at temperature T and the resistivity at 4.2°K. Note how "pure" (arc-cast, iodide-process) Ti has a resistance minimum. In the inset is plotted the difference between the resistivity of the alloy and that of the solvent Ti. The concentrations are in at.%. The solid portions of the curves represent continuous data points, while the dashed portions are extrapolated through the 77° and 194.6° (dry-ice) data points. The error flags are based on the estimate of 2% accuracy for the absolute values of the resistivities. Note that for each alloy which exhibits a resistivity minimum, a minimum appears in $\rho_a-\rho_I$ (inset).

Figures 5 and 6 show the corresponding resistivity data for the Hf and Zr alloys. In Zr, Fig. 5, the resistivity-minimum effect appears to be much weaker—only Mn gives a minimum, and it lies at a good deal lower temperature, approximately 8°K, than the minima for the Ti alloys (about 17°K). Moreover, whereas in Ti only Mn exhibited a measurable localized moment while minima were found for Ti, Ti-Fe, and Ti-Mn, in Zr both Mn and Cr carry measurable moments yet only Mn produces a detectable minimum. The $\rho_a-\rho_p$ curves for the Zr alloys (inset of Fig. 6) again show marked deviations from Matthiessen's rule. However, the anomalous minimum in $\rho_a-\rho_p$ was not evident in any of these, in particular Zr-Mn.

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[24] Iodide-process Ti supplied by the Foote Mineral Company and arc-cast in an inert atmosphere. For further details on the purity of the starting material see Ref. 18.

[25] This behavior has been frequently observed. See, for example, the work of Sarachik *et al.* (Refs. 15, 16) on some Nb-Mo alloys containing Fe.

In the Hf alloys (Fig. 6), on the other hand, minima were observed for each alloy which exhibited a localized moment from the susceptibility measurements. In addition, the Hf alloys are more like the Ti alloys in that those with a localized moment (Mn and Cr) exhibit the anomalous minima in $\rho_a-\rho_p$ (inset of Fig. 6) and $\rho_a-\rho_p$ is larger at higher temperatures. Again as for Ti, the minima for 0.2-at.% Mn and Cr in Hf are observed at the same temperature, ≈ 12°K. For Hf-Fe, $\rho_a-\rho_p$ showed a clearly discernible inflection at approximately 12.5°K—the curvature tends upward at this point, but then continues downward at higher temperatures. The inflection point is perhaps a vestige of the anomalous minimum in $\rho_a-\rho_p$. As with Ti and Zr, no localized moment (susceptibility or magnetoresistivity) or resistivity minimum is detectable for Co impurity.

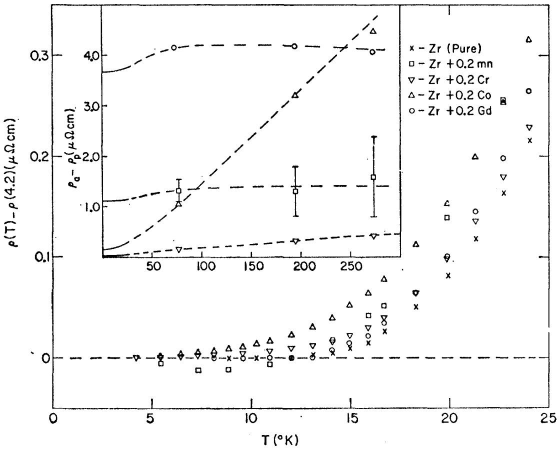

FIG. 5. The resistivities of the Zr alloys. Refer to the caption of Fig. 4 for remarks pertinent to this figure and to Fig. 6. Note that only Zr-Mn shows a resistivity minimum. The error flags shown on the curve for Zr+0.2 Mn are representative of all the curves in the inset and are based on the estimate that the absolute values of the resistivity are accurate to ±2%. This applies also to the error flags in Figs. 4 and 6. Isolated points in the inset are for 77, 194.6, and 273.2°K, respectively.

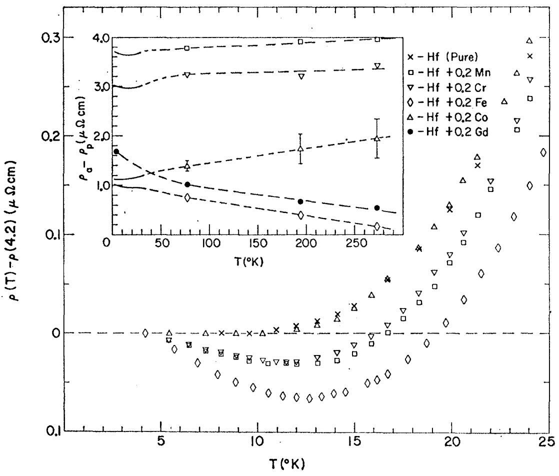

FIG. 6. The resistivities of the Hf alloys. Refer to the captions of Figs. 4 and 5 for remarks also pertinent to this figure. Note that Hf-Fe has the most pronounced minimum, yet displays the weakest moment in the susceptibility measurements (Table I).

Table II lists, for each of the alloys, the 4.2-°K resistivities, the temperatures at which the minima occurred ($T_{\min}$), and the position of the minimum in the $\rho_a-\rho_p$ curves ($T_{\min}{}^*$). The experimental localized-moment values (susceptibility) are shown in the third column, and in the last column, the depth of the minimum $\Delta\rho\equiv\rho(H=0,\ T=4.2)-\rho(H=0,\ T=T_{\min})$ is given for each of the alloys. Values are also given of ρ(4.2°K) and $\Delta\rho$ from earlier data on different specimens by Hake *et al.*[18] The earlier data and the present results are in reasonable agreement. Saturation effects in ρ and $\Delta\rho$ at concentrations above 0.2 at.% are indicated for Fe and Cr in Ti as was noted previously[18] for Ti-Mn. These saturation effects are possibly due to segregation as discussed earlier.[18,22] A moderate discrepancy appears between the earlier ($\Delta\rho=0.09$) and present ($\Delta\rho=0.11$) data for Ti-0.2-at.% Mn. Such a discrepancy is probably due to the uncertainties in the actual solute concentration caused primarily by weight loss during arc-melting (particularly evident in the case of Ti-Mn[18]).

From the values of $T_{\min}$ in Table II, one may note that as long as the impurity concentration is the same, $T_{\min}$ appears to be virtually constant for a given solvent, e.g., 16.7°K for 0.2-at.% solution in Ti, and 12–12.5°K for the same concentration in Hf. Following Kondo,[11] if one assumes that for $H=0$, ρ_p is predominantly a lattice resistance term and takes Kondo's result for ρ_{mag}, one may expect the alloy's resistivity to be describable by

$$\rho_a=\rho_L(T)+c[\rho_V+C_1-C_2J^3j(j+1)\ln T],\qquad(10)$$

where ρ_L is the lattice resistivity, c the concentration, C_1 and C_2 are constants, J is the s-d exchange energy, and j is the localized spin as in Eqs. (1) and (2). Thus, if ρ_V, J, and j are temperature-independent, one finds

$$T_{\min}(d\rho_L/dT)_{T_{\min}}\propto cJ^3j(j+1)\,,\qquad(11)$$

that is, $T_{\min}$ will depend on the s-d integral J and the localized spin j. The present data on the other hand appear to indicate that $T_{\min}$ is independent of j, in disagreement with Eq. (11). Considering this, and the fact that minima appear in the $\rho_a-\rho_p$ curves, it appears that an expression of the form Eq. (10) cannot account for the resistivity of the present alloys unless (a) ρ_V is not temperature-independent, as assumed for Eq. (11) or (b) the magnetic impurities introduce a minimum into the lattice resistance term of the alloy $\rho_L(T)$. The discrepancy between Eq. (10) and the present data can be removed without invalidating Kondo's $\ln T$ term, if

TABLE II. Resistivities at 4.2°K, localized-moment values and temperatures at which minima were observed in the resistivity curves for the various alloys.

Base metal	Solute at. %	ρ ($H=0$, $T=4.2$°K) ($\mu\Omega$ cm)	μ (exp) (μ_B/atom)	$T_{\min}$ (°K)	$T_{\min}^*$ (°K)	Δ^a ($\mu\Omega$ cm)
Ti	"Pure"	1.40	...	14.5	...	0.016
Ti	"Pure"[a]	1.44	...	14.1	...	0.012
Ti	0.2 Cr	3.990	0	16.7	19	0.051
Ti	1.15 Cr[b]	7.36	...	16.8	...	0.061
Ti	0.1 Mn	2.845	3.5	15.0	17	0.047
Ti	0.114 Mn[b]	2.88	...	16.2	...	0.047
Ti	0.2 Mn	5.497	3.5	16.7	19	0.11
Ti	0.212 Mn[b]	5.47	...	18.3	...	0.090
Ti	1.06 Mn[b]	8.22	...	17.0	...	0.097
Ti	0.2 Fe	2.648	0	16.7	19	0.054
Ti	0.96 Fe[b]	3.44	...	17.3	...	0.057
Ti	0.2 Co	1.911	0	[c]	[c]	
Ti	1.29 Co[b]	3.43	...	12	...	0.004
Zr	"Pure"	1.522	...	[c]	[c]	
Zr	0.2 Cr	1.557	0.2	[c]	[c]	
Zr	0.2Mn	2.632	3.5	8	[c]	
Zr	0.2 Co	1.704	0	[c]	[c]	
Zr	0.2 Gd	5.205	7.0	[c]	[c]	
Hf	"Pure"	2.496	...	[c]	[c]	
Hf	0.2 Cr	5.606	1.7	12.0	19	
Hf	0.2 Mn	6.189	3.8	12.0	19	
Hf	0.2 Fe	3.508	0.7	12.5	19	
Hf	0.2 Co	3.615	0	[c]	[c]	
Hf	0.2 Gd	4.172	6.1	[c]	[c]	

[a] $\Delta\rho \equiv \rho(H=0,\ T=4.2°\text{K}) - \rho(H=0,\ T=T_{\min})$.
[b] Earlier data on different specimens from Ref. 18.
[c] No minimum observed.

one assumes that ρ_V increases with temperature in the low-temperature region (say 0–50°K). If so, $\rho_a - \rho_p$ could have a minimum. The $\rho_a - \rho_p$ curves for Ti and Hf appear to support this speculation inasmuch as those curves which show a $T_{\min}^*$ tend to higher values with increasing temperature. In view of the fact that those localized states which are magnetized are expected to lie very close to the Fermi energy[26] it might well be that the impurity potential scattering ρ_V can have a substantial temperature dependence.

IV. SUMMARY AND DISCUSSION

In this paper we have reported on a survey of transport anomalies arising from magnetic impurities in the transition elements of the IVth column. It is found that of the "*d*-shell" impurities Cr, Mn, Fe, and Co, only Mn induces a Curie-Weiss-like susceptibility in each of the solvents Ti, Zr, and Hf with indicated localized-moment values of $\approx 3.5\ \mu_B$/Mn atom. Localized moments are formed on Cr in Zr ($0.2\ \mu_B$/atom), and Hf ($1.7\ \mu_B$/atom), but not in Ti. Iron forms a localized moment only in Hf ($0.7\ \mu_B$/atom), and Co produces no indication of moment localization in any of the IVth column transition metal solvents. It thus appears that the predilection towards localized-moment formation increases in the sequence of solvents Ti-Zr-Hf. From the theoretical point of view,[26] the extent of polarization of a localized state increases as the width of the state decreases. The width of the state is on the other hand proportional to the density of electronic states at the Fermi surface. On Table III we show the experimentally observed moment values and the densities of states of the solvent metals to illustrate how the theoretical picture is borne out qualitatively for the present alloys. One notes that in the sequence Ti-Zr-Hf, the density of states decreases markedly, while localized-moment formation becomes more prevalent.

As regards the magnetoresistance in each case where the susceptibility indicates a localized moment, the resistance decreases with applied magnetic field by an amount commensurate with the magnitude of the localized moment. At very weak fields the change in the resistance is found to be proportional to the square of the magnetization associated with the localized moments. The relation Eq. (5) by which the magnetoresistance and the susceptibility of the present alloys appear to be correlated can be deduced from: (1) A combination of the molecular-field model, Eq. (1), and some elementary phenomenological arguments[21] about the scattering power of the magnetic moments leading

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[26] P. de Faget de Casteljau and J. Friedel, J. Phys. Radium **17**, 27 (1956); J. Friedel, Can. J. Phys. **34**, 1190 (1956); J. Phys. Radium **19**, 573 (1958); Nuovo Cimento Suppl. VII, 287 (1958); A. Blandin and J. Friedel, J. Phys. Radium **19**, 573 (1958). P. W. Anderson, Phys. Rev. **124**, 41 (1961); P. A. Wolff, *ibid.* **124**, 1030 (1961); A. M. Clogston, *ibid.* **125**, 439 (1962). For a review of the theoretical picture of localized magnetic states see P. W. Anderson in Proceedings of the International Conference on Magnetism (Institute of Physics and the Physical Society, London, 1965, to be published).

to Eq. (4); or (2) the $H=0$ and $H=\infty$ limits of the s-d model theories.[8,9] Consequently, Eq. (5) does not contain the detailed predictions of the s-d theories. The present results, therefore, cannot be regarded as substantial evidence for the general applicability of the s-d model to transition-metal solvents. To examine further the applicability of the s-d model to the present alloys, one may attempt comparison of the experimental magnetoresistance data at higher fields with the detailed predictions of the s-d theories. Other measurements, for example the thermopowers (also calculated by Kasuya[9]), would be needed to evaluate the parameters of the theory.

As regards the resistivities and the resistivity minima observed in the present alloys, the salient result seems to be that there is *not* an evident correlation between the appearance of a minimum and the presence of the localized magnetic states as manifested by the magnetic susceptibility and the magnetoresistance. Moreover, even in those (preponderant) cases where the minimum and a localized moment are both observed, the temperature dependence of the resistivity is not explicable by Kondo's theory. In this connection we conjecture that a possible substantial temperature dependence of the impurity potential scattering may account for much of the discrepancy without impugning the correctness of Kondo's calculations. Until a better understanding of electronic transport processes in transition-metal alloys is achieved, it would seem inadvisable to assess the degree of moment localization on a given solute solely from an examination of the zero-field low-temperature resistivity. Thus an earlier suggestion by Hake *et al.*,[18] based on the appearance of resistivity minima, that Cr and Fe possessed localized moments in Ti must now be regarded as somewhat doubtful, although further work will be required to clarify this point.

In attempting any comparison with theory one must consider, of course, that the purity of the starting material of the present alloys leaves much to be desired. One may conjecture, for example, that the minimum in the "pure" (iodide process) Ti results from primitive Mn impurity. However, if this is the explanation of the minimum in iodide process Ti, the concentration dependence of $T_{\min}$ is difficult to explain[27] on the basis of the Kondo theory. For example, for the iodide Ti, where the Mn impurity concentration is of the order of 0.001–0.01 at.%,[18,28] the minimum is at 14.5°K. In the present case, on the other hand, when the concentration is 0.2 at.% the minimum is only up to 16.7°K. This reflects a concentration dependence of something like $c^{1/20}$ (c is the concentration); far from anything like $c^{1/5}$ as predicted by Kondo under the assumption that the lattice resistivity varies as T^5. Allowing for Fe or Cr impurities in the iodide Ti (perhaps 0.03 at.% all together) to participate does not appreciably reduce the great discrepancy.

TABLE III. Localized-moment values (susceptibility) and the electronic density of states for the group IV B solvents.

	Ti	Zr	Hf
$N(E_F)$	0.71[a]	0.59[a]	0.46[a]
μ/μ_B for Cr	0	0.2	1.7
μ/μ_B for Mn	3.5	3.5	3.8
μ/μ_B for Fe	0	0	0.7
μ/μ_B for Co	0	0	0
μ/μ_B for Gd	···	7.0	6.1

[a] In units of states of one spin direction per eV per atom. Derived from the specific-heat measurements of G. K. Kneip, Jr., J. O. Betterton, Jr., and J. O. Scarbrough, Phys. Rev. **130**, 1687 (1963).

As regards the rare-earth impurity Gd, one expects a very limited range of solid solubility in Ti, Zr, or Hf. In the present case at 0.2 at.%, the susceptibility data were found to fit a Curie-Weiss line down to below 10°K. Using the slope of the line thus obtained and taking the concentration of contributing moments to be the concentration of Gd atoms, one obtains μ values reasonably close to the free-atom moments. We believe this to be evidence in favor of reasonable solid solution in the present alloys inasmuch as clusters with larger moments would be expected to introduce considerable curvature in the Curie-Weiss line at low temperatures ($\mu H/kT\approx 1$). Metallographic examination did not reveal any evidence of inhomogeneity. The salient results, therefore, appear to be that (1) the susceptibility indicates large (nearly free-atom value) localized moments associated with these ions, and (2) the data evidence no resistivity minima and negligible changes in magnetoresistance. These results probably indicate that the conduction-electron interaction with the Gd f-shell moment is a good deal weaker than the interaction with the localized d states of Mn, Cr, and Fe. One may conjecture that these localized f-shell levels are substantially removed from the Fermi level to account for the much weaker interaction.

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[27] It has previously been pointed out (Ref. 18) that if the Mn impurity alone in iodide-process Ti were responsible for the resistivity minimum, then substantially greater deviations from Kohler's rule than those observed should have been seen.

[28] R. Falge, Jr., Phys. Rev. Letters **11**, 248 (1963).