

## Magnetic-Susceptibility and Low-Temperature Specific-Heat Studies of Ti, Zr, and Hf

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The results of magnetic-susceptibility and low-temperature specific-heat measurements of high-purity Zr and highest-obtainable-purity Hf are presented, together with data for high-purity Ti taken from an earlier publication by the present authors. The observed susceptibility components of the Zr single crystal ( $\chi_{11}=1.65_8$ ,  $\chi_{12}=1.09_2$   $\mu\text{emu/g}$ ) confirm the results of another recent measurement; and susceptibility data for Hf single crystals ( $\chi_{11}=0.53_1$ ;  $\chi_{12}=0.35_4$   $\mu\text{emu/g}$ ) are reported for the first time. With the aid of the calorimetric data, values of  $\chi_{\text{orb}}$  are deduced to be 125, 100, and 75  $\mu\text{emu/mole}$  for Ti, Zr, and Hf, respectively. A possible mechanism for the susceptibility temperature dependence in these metals is suggested.

## I. INTRODUCTION

In an earlier publication by the present authors<sup>1</sup> henceforth designated Ref. 1, the results of calorimetric measurements (1.5–6 K) on three polycrystalline specimens and magnetic-susceptibility measurements (78–400 K) on four single-crystal specimens of pure Ti were described. Subsequently, the measurements on one of the Ti specimens (MRC-2 of Ref. 1) were extended down to 4.2 K; and the experimental program has been repeated for samples of Zr and Hf. After the work on Zr was completed we became aware of another study by Vol'ken shteyn and co-workers,<sup>2</sup> who also measured a single crystal. To our knowledge, the susceptibility of *single-crystal* Hf has not previously been recorded. For Zr there is some small spread among the reported values of  $\chi_{\text{av}}$  which were obtained from measurements on polycrystalline specimens. This might be attributable to large grain size or texturization in association with the relatively large paramagnetic anisotropy exhibited by Zr. Conversely, for Hf there is good agreement among the reported values of  $\chi_{\text{av}}$  (polycrystal); and as the present measurements show ( $\chi_{11} - \chi_{12}$ ) is relatively small.

The results of previously reported low-temperature specific-heat measurements on Zr and Hf are summarized in Table I. Similarly, all available susceptibility values for these metals are listed in Table II.

## II. EXPERIMENTAL DETAILS

## A. Specimen Material

For the specific-heat work, specimens were cut from rods of highest-obtainable-purity<sup>3</sup> Zr and Hf supplied by the Materials Research Corporation. Short lengths of single-crystal electron-beam-melted Zr and Hf rod were also purchased from MRC. After repeatedly cutting, polishing, and x raying, small pieces of what appeared to be adequate perfection were obtained for the magnetic-susceptibility studies. The single-crystal Zr-1

(wt = 105 mg) was taken from MRC stock. Zr-2 (wt = 353 mg) was cut from a well-annealed high-purity single crystal prepared and kindly donated by Dr. T. R. Cass. As evidenced by the clarity of the Laue diffraction spots, Zr-2 was a better specimen structurally than Zr-1. After measuring the susceptibility parameters of a large Hf crystal [Hf-1 (wt = 948 mg)] it was spark cut in two and one of the pieces [Hf-2 (wt = 484 mg)] was measured as a second specimen.

## B. Experimental Procedure

Low-temperature specific-heat measurements (1.5–6 K) were made using a simple adiabatic calorimeter described elsewhere.<sup>4</sup> The susceptibility apparatus and procedures have been referred to in Ref. 1. The Honda-Owen technique was employed during the temperature-dependence measurements, to correct if necessary for the effects of possible ferromagnetic contamination. The sus-

TABLE I. Published values of the low-temperature specific-heat parameters of Zr and Hf.

Metal	Electronic specific-heat coefficient $\gamma$ (mJ/mole K <sup>2</sup> )	Debye temperature $\Theta_D$ (K)	Temperature range (K)	Year and Ref.
Zr	3.04	310	1.2–20	1956 <sup>a</sup>
	2.81	292	1.1–4.5	1963 <sup>b</sup>
	2.75	290	1.5–16	1964 <sup>c</sup>
	2.77	290	0.9–12	1965 <sup>d</sup>
Hf	2.64	261	1.2–20	1956 <sup>a</sup>
	2.159	252.3	1.1–4.5	1963 <sup>b</sup>
	2.167	251.5	1.1–4.5	1963 <sup>b</sup>
	2.146	252.2	1.1–4.2	1968 <sup>e</sup>

<sup>a</sup>N. M. Wolcott, *Phil. Mag.* **2**, 1246 (1956).<sup>b</sup>G. D. Kneip, J. O. Betterton, and J. O. Scarbrough, *Phys. Rev.* **130**, 1687 (1963).<sup>c</sup>F. Heiniger and J. Muller, *Phys. Rev.* **134**, A1407 (1964).<sup>d</sup>G. Dummer, *Z. Physik* **186**, 249 (1965).<sup>e</sup>J. O. Betterton and J. O. Scarbrough, *Phys. Rev.* **169**, 715 (1968).

TABLE II. Published values of the magnetic susceptibilities of Zr and Hf.

Metal	Magnetic susceptibility $\mu\text{emu/g}$			Temperature (K)	Year and Ref.
	$\chi_{\text{av}}$	$\chi_{\parallel}$	$\chi_{\perp}$		
Zr	1.29			Room	1941 <sup>a</sup>
	1.33			293	1961 <sup>b</sup>
	1.33			293	1962 <sup>c</sup>
	1.41			290	1965 <sup>d</sup>
	1.29	1.68	1.09	293	1968 <sup>e</sup>
Hf	0.42			Room	1955 <sup>f</sup>
	0.38			293	1961 <sup>b</sup>
	0.39			293	1964 <sup>g</sup>
	0.39			290	1965 <sup>d</sup>

<sup>a</sup>C. F. Squire and A. R. Kaufmann, *J. Chem. Phys.* **9**, 673 (1941).

<sup>b</sup>H. Kojima, R. S. Tebble, and D. E. G. Williams, *Proc. Roy. Soc. (London)* **A260**, 237 (1961).

<sup>c</sup>S. Taniguchi, R. S. Tebble, and D. E. G. Williams, *Proc. Roy. Soc. (London)* **A265**, 502 (1962).

<sup>d</sup>N. V. Vol'kenshteyn and E. V. Galoshina, *Fiz. Metal. i Metalloved.* **20**, No. 3, 368 (1965).

<sup>e</sup>N. V. Vol'kenshteyn and E. V. Galoshina, and N. I. Shegolikina, *Fiz. Metal. i Metalloved.* **25**, 180 (1968).

<sup>f</sup>C. J. Kriessman and T. R. McGuire, *Phys. Rev.* **98**, 936 (1955).

<sup>g</sup>N. V. Vol'kenshteyn and E. V. Galoshina, *Fiz. Metal. i Metalloved.* **18**, 784 (1964).

ceptibility components  $\chi_{\parallel}$  and  $\chi_{\perp}$  were measured using the "double-rotation technique," whose advantages have been discussed in detail in our earlier publications.<sup>1,5</sup>

### III. RESULTS

#### A. Low-Temperature Specific Heat

Figure 1 shows the calorimetric data for Zr and Hf presented in the usual format,  $C/T$  vs  $T^2$ ; while Table III lists numerical values of the parameters  $\gamma$ ,  $\beta$ , and  $\Theta_D$  (as defined in the caption to Fig. 1).

#### B. Susceptibility Measurements on Single Crystals

Figure 2 shows the results of the double-rotation experiments on single crystals of initially undetermined axial orientations. From these measurements the principal susceptibility components  $\chi_{\parallel}$  and  $\chi_{\perp}$  were obtained. The paramagnetic anisotropy of Zr-1 ( $\chi_{\parallel} - \chi_{\perp} = 0.53_7 \mu\text{emu/g}$ ) derived from experiment (a) was slightly less than that for Zr-2 [experiment (b), ( $\chi_{\parallel} - \chi_{\perp}) = 0.56_4 \mu\text{emu/g}$ ]. This was to be expected, since x-ray examination showed the latter to be a more nearly perfect specimen than Zr-1. But in addition we attribute some of the disagreement to slight specimen-positioning error during the setting up of experiment (a), since a larger anisotropy (viz.,  $0.54_0$ ) was later obtained when Zr-1 was repositioned prior to the temperature dependence run. For these reasons, the data for Zr-1 have not been included in the final tabulations.

The two Hf experiments were in excellent agreement; the pairs of values of  $\chi_{\parallel}$  and  $\chi_{\perp}$  agreeing to  $0.001 \mu\text{emu/g}$ . The measured anisotropy was the same in both cases ( $\chi_{\parallel} - \chi_{\perp} = 0.17_7 \mu\text{emu/g}$ ). The results of the room-temperature susceptibility experiments are summarized in Table IV. Included for completeness are the previously reported data for our best Ti crystal.

The quality of the Hf-1 crystal (from which Hf-2 was later cut) was about equivalent to that of Zr-1. In addition, the best currently available Hf is actually an alloy Hf-Zr ( $\sim 3 \text{ wt}\%$ ). For these reasons, improvement on the Hf data presented here may eventually be possible.

#### C. Temperature Dependences of Susceptibility

Having determined the susceptibility components, and at the same time the direction of the  $c$  axis, by means of a "double-rotation" experiment, it is possible to reorient the crystal in preparation for measurement of  $\chi_{\parallel}(T)$  and  $\chi_{\perp}(T)$ . The susceptibility temperature dependences of Zr, Hf, and also Ti for comparison, are displayed in Fig. 3. Thicker lines have been used to connect the Zr-2 data points to indicate that we regard them as being more reliable than those for Zr-1. Even so, the two independent sets of Zr data<sup>6</sup> show quite similar trends, and the separation of the curves is within our usually claimed reproducibility ( $\pm 0.01_5 \mu\text{emu/g}$ ; cf. Ref. 1). Vol'kenshteyn and co-workers<sup>2</sup> have measured the susceptibility components of Zr over the temperature range 20–293 K. While agreeing with their results for  $\chi_{\perp}(T)$ , we found a considerably smaller average  $\partial\chi_{\parallel}/\partial T$  in the temperature range of comparison (100–300 K).

The results of our two independent experiments on the Hf crystals are in excellent agreement.

Also shown in Fig. 3, for comparison, are the susceptibility temperature dependences of a Ti crystal. Data for the interval 78–400 K were taken from Ref. 1; but more recently these measurements were extended into the He range, where as the figure shows, the susceptibility is practically independent of temperature.

Numerical values of the susceptibility temperature dependences of Ti, Zr, and Hf in the range 300–400 K are listed in Table V.

### IV. DISCUSSION

#### A. Components of the Total Magnetic Susceptibility

##### 1. Electronic Susceptibility

In discussions of electronic states in transition metals and their alloys, particularly in connection with magnetic and nuclear-magnetic-resonance (NMR) studies [e.g., Refs. (7) and (8)] the possible applicability of a two-band model is often considered as a means of distinguishing between the properties of the  $d$  and  $s$  electrons. For example, the sus-

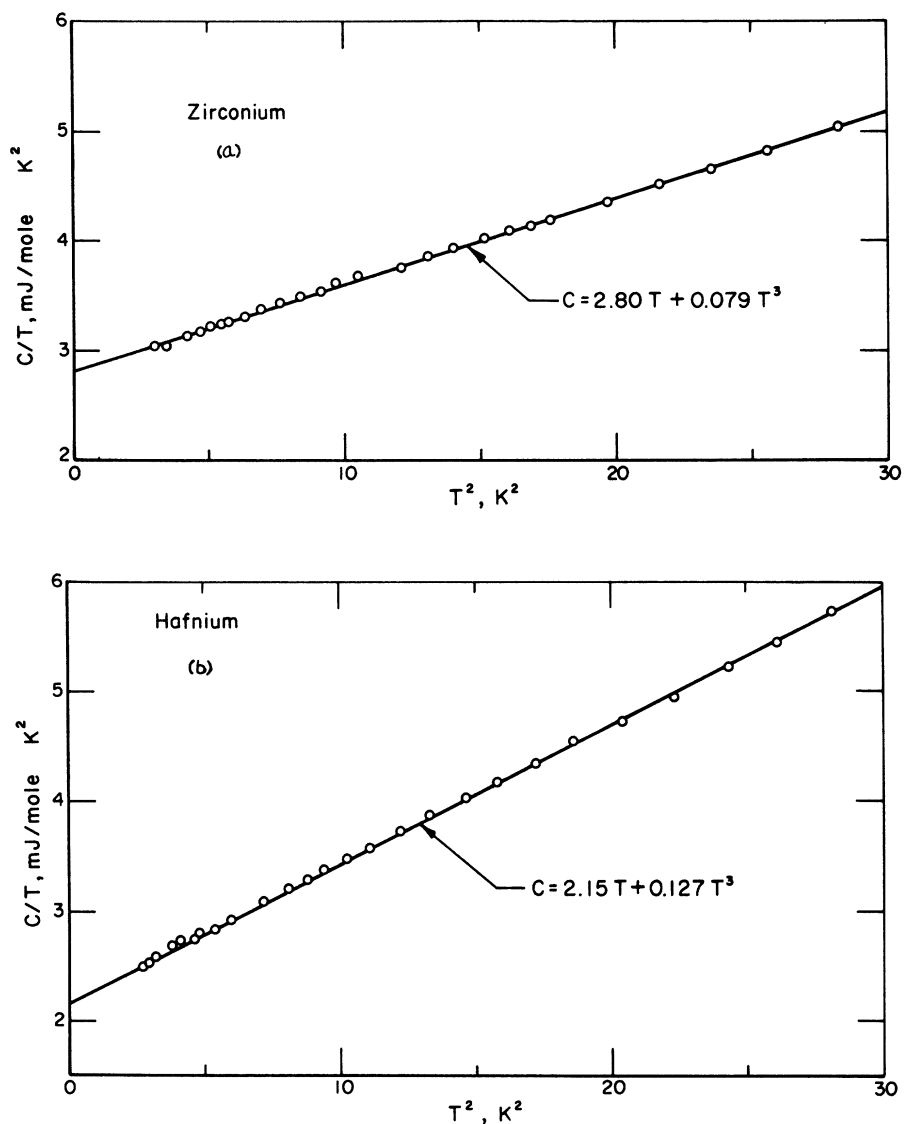


FIG. 1. Low-temperature specific-heat data for Zr and Hf. In the low-temperature regime, specific heat  $C = \gamma T + \beta T^3$ , where  $\gamma$  is the electronic-specific-heat coefficient and  $\beta = \frac{12}{5} \pi^4 R (T/\Theta_D)^3$ .

TABLE III. Low-temperature specific-heat parameters of Ti, Zr, and Hf.

Metal	Condition	Electronic specific-heat coefficient $\gamma$ (mJ/mole K <sup>2</sup> )	Lattice specific-heat coefficient $\beta$ (mJ/mole K <sup>4</sup> )	Debye temperature $\Theta_D$ (K)
Ti <sup>a</sup>	Annealed and either quenched or slow-cooled	3.36	0.026	420
Zr	As-received (electron-beam refined)	2.80	0.079	291
Hf	As-received (electron-beam refined)	2.15	0.127	248

<sup>a</sup> Crystal-bar iodide Ti—results from Ref. 1.

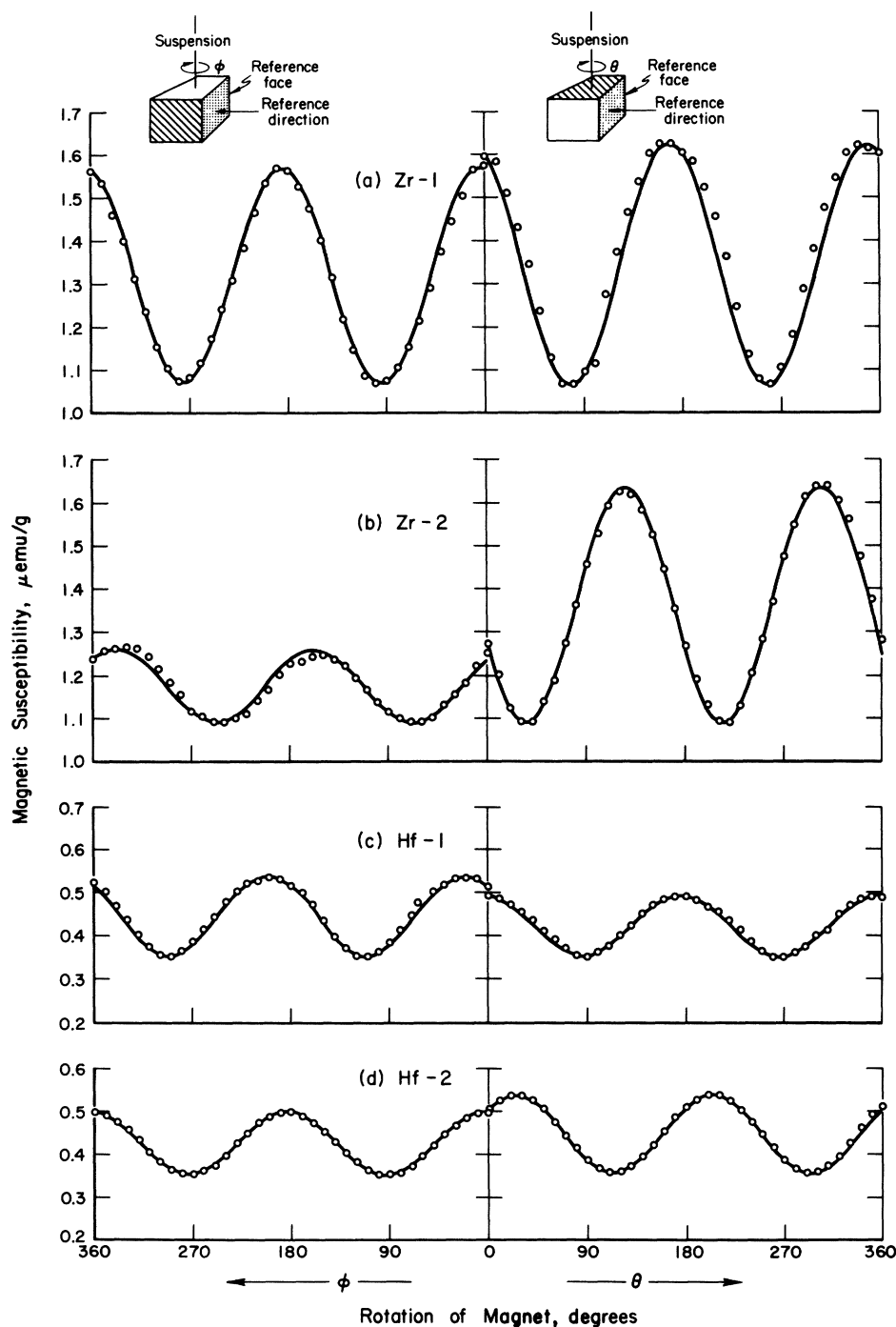


FIG. 2. Results of "double-rotation" experiments on Zr and Hf. The method (described in Ref. 1) is suitable for use with a single crystal of unknown crystallographic orientation. The curves yield  $\chi_{\perp} = \chi_{\min}$ ,  $3\chi_{\text{av}} = \chi_{\text{ref}} + \chi(\phi=90) + \chi(\phi=270)$ ; hence  $\chi_{\parallel} = 3\chi_{\text{av}} - 2\chi_{\perp}$ .

ceptibility of the conduction electrons may be expressed as

$$\chi_{\text{cond el}} = \chi_P^s + \chi_P^d + \chi_L^s + \chi_L^d, \quad (1)$$

where subscripts  $P$  and  $L$  refer to the Pauli paramagnetism and Landau diamagnetism, respectively, which are related such that

$$\chi_L^{s,d} = -\frac{1}{3}(m/m^*)^2 \chi_P^{s,d}. \quad (2)$$

Appropriate approximations are then made depending on the particular metal under consideration. For Pt for example, Clogston *et al.*<sup>8</sup> have assumed a high density of states for  $d$  holes near the top of the band. In this case,  $n^d(E_F) \gg n^s(E_F)$ , and  $(m^*/m)^d \gg 1$ . Assuming in addition that for the  $s$

TABLE IV. Magnetic susceptibilities of single-crystal Ti, Zr, and Hf at room temperature.

Metal	Magnetic susceptibility		$\mu\text{emu/g}$ ( $\mu\text{emu/mole}$ )	
	$\chi_{\parallel}$	$\chi_{\perp}$	$\chi_{\parallel} - \chi_{\perp}$	$\chi_{\text{av}}$
Ti <sup>a</sup>	3.52 <sub>7</sub> (169)	3.00 <sub>6</sub> (144)	0.52 <sub>1</sub> (25)	3.18 <sub>0</sub> (152)
Zr-2	1.65 <sub>6</sub> (151)	1.09 <sub>2</sub> (100)	0.56 <sub>4</sub> (51)	1.28 <sub>0</sub> (117)
Hf-1, 2	0.53 <sub>1</sub> (95)	0.35 <sub>4</sub> (63)	0.17 <sub>7</sub> (32)	0.41 <sub>3</sub> (74)

<sup>a</sup>Specimen TC-1 of Ref. 1.

electrons  $(m^*/m)^s = 1$ , Eq. (1) reduces to

$$\chi_{\text{cond e1}} \approx \frac{2}{3} \chi_P^s + \chi_P^d \quad (3)$$

For the group-IV metals, Ti, Zr, and Hf, we again start out with a modified two-band model, with a relatively high density of  $d$ -electron states at the Fermi level. The calculated widths of the  $d$  bands for Ti and Zr (6.5 and 3.9 eV, respectively<sup>9</sup>) together with the de Haas-van Alphen data of Thorsen and Joseph<sup>10</sup> indicate that  $(m^*/m)^{s,d} \approx 1$  is a reasonable assumption for the group-IV transition metals. This condition is then satisfied by a single-band model for which

$$\chi_{\text{cond e1}} \approx \chi_P + \chi_L, \quad (4)$$

with

$$\chi_L = -\frac{1}{3} \chi_P.$$

These relationships are applied in Table VI.

## 2. Ion-Core Diamagnetism

The diamagnetic contributions from the ion cores

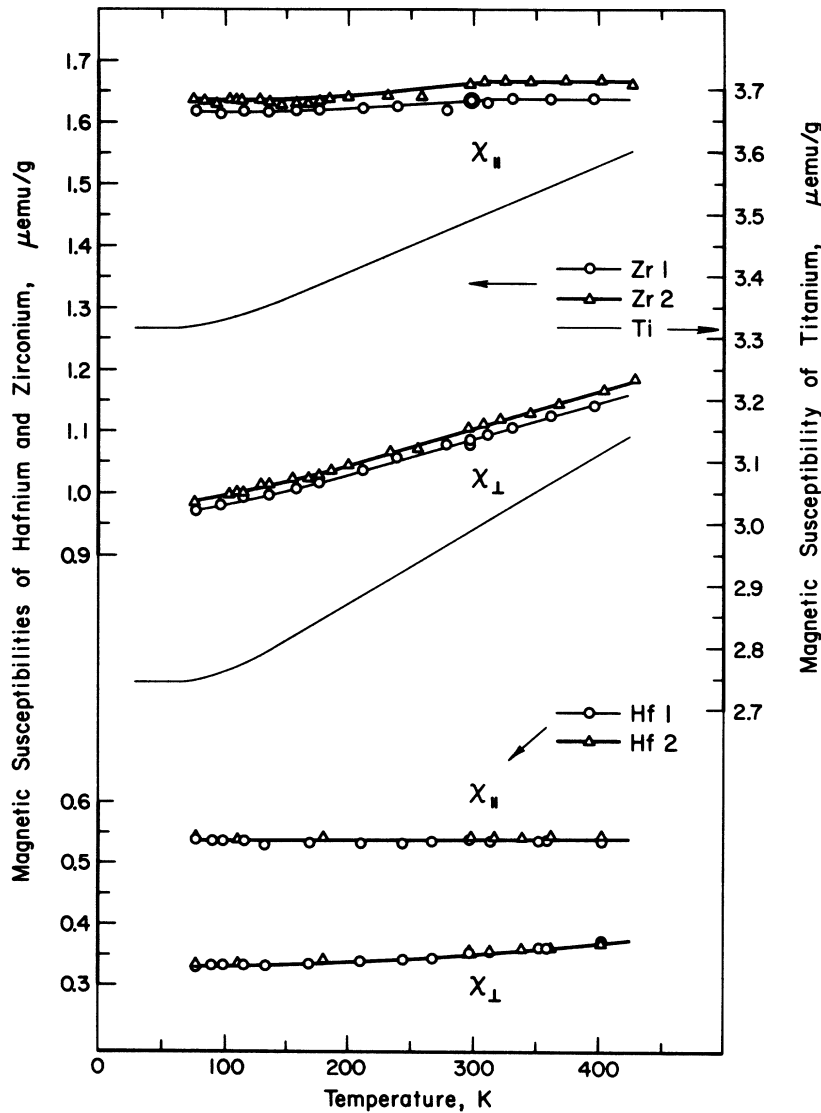


FIG. 3. Susceptibility temperature dependences of Zr and Hf. The experiments on the two different Zr specimens, performed at widely differing times, agree within the nominal reproducibility of the experiment ( $\pm 0.015 \mu\text{emu/mole}$ , in this susceptibility range). Old data for a Ti crystal (Ref. 1) have been extended to the helium temperature range, where  $\partial\chi/\partial T \sim 0$ .

TABLE V. Temperature coefficients of susceptibility of Ti, Zr, and Hf in the temperature range 300–400 K.

Metal	Temperature coefficient $\mu\text{emu/g K} (\mu\text{emu/mole K})$		
	$10^3 \partial\chi_{11}/\partial T$	$10^3 \partial\chi_L/\partial T$	$10^3 \partial\chi_{av}/\partial T$
Ti <sup>a</sup>	0.34 (40)	1.17 (56)	1.07 (51)
Zr 1, 2	0.0 (0)	0.59 (54)	0.39 (36)
Hf 1, 2	0.0 (0)	0.20 (36)	0.13 (23)

<sup>a</sup>Specimen MRC-2 of Ref. 1.

Ti<sup>4+</sup>, Zr<sup>4+</sup>, and Hf<sup>4+</sup>, as listed by Angus<sup>11</sup> and Selwood,<sup>12</sup> are also shown in Table VI.

### 3. Orbital Paramagnetism

Kubo and Obata<sup>13</sup> seem to have been the first to point out in a general discussion of paramagnetism in metals that for partly filled non-s bands the Pauli spin susceptibility is augmented by a term comparable to it in magnitude resulting from a type of van Vleck magnetic polarization. In general, the band paramagnetism is  $\chi_P + \chi_{so} + \chi_{orb}$ ; in which according to Kubo and Obata,  $\chi_{so}$  (the spin-orbit component) is usually negligible compared to  $\chi_P = 2\mu_B^2 n(E_F)$ ; and  $\chi_{orb} \sim \mu_B^2/\Delta$  (where  $\Delta$  refers to the mean separation of energy levels connected by the orbital angular momentum operator). That  $\chi_{orb}$  should be an important contributor to the paramag-

netism of transition metals was later independently suggested by Orgel<sup>14</sup> who estimated that its magnitude would be typically about 125  $\mu\text{emu/mole}$ . Numerical estimates of  $\chi_{orb}$  for specific metals were subsequently made by Clogston *et al.*<sup>15</sup> [ $\chi_{orb}(\text{V}) \sim 210 \mu\text{emu/mole}$ ], Denbigh and Lomer<sup>16</sup> [ $\chi_{orb}(\text{Cr}) \sim 100 \mu\text{emu/mole}$ ], Butterworth<sup>7</sup> (V-Cr), Clogston *et al.*<sup>8</sup> (Pt), Mori<sup>17,18</sup> (several transition metals), Gardner and Penfold<sup>19</sup> (Sc), and others.

Following Kubo and Obata<sup>13</sup> we will assume  $\chi_{so}$  to be negligible, and will take for  $\chi_{orb}$  the difference between  $\chi_{total}$  and the sum of the other "known" susceptibility components, as listed in Table VI.

### B. Evaluation of the Pauli Spin Susceptibilities from the Calorimetric Data

#### 1. Bare-Spin Paramagnetism and Electronic Specific-Heat Coefficient

The Pauli spin susceptibility for free noninteracting electrons is

$$\chi^0 \propto 2\mu_B^2 n^0(E_F), \quad (5)$$

where  $\mu_B$  is the magnetic moment per spin (1 Bohr magneton) and  $n^0(E_F)$ , the corresponding bare density of states, is understood to refer to a single-spin direction. The constant of proportionality will depend on the units employed.

Similarly, the bare electronic specific-heat coefficient  $\gamma^0$  may be written

$$\gamma^0 \propto \frac{2}{3} \pi^2 k^2 n^0(E_F). \quad (6)$$

Expressing the above quantities in the units

TABLE VI. Components of the magnetic susceptibilities of Ti, Zr, and Hf. All susceptibilities are in  $\mu\text{emu/mole}$  except for the bracketed values, which are ( $\mu\text{emu/g}$ ).

Metal	$\gamma$ (mJ/mole K <sup>2</sup> )	$\lambda$ McMillan <sup>a</sup>	"Expt" <sup>b</sup>	$\chi_P \cong \chi^0$ $= \frac{13.71\gamma}{(1+\lambda)}$	$\chi_{total}$ at 70 K <sup>c</sup>			$\chi_i$ Ref. d	$\chi_i$ Ref. e	$\langle \chi_i \rangle_{av}$	$\chi_L = -\frac{1}{3}\chi_P$	$\chi_{orb}^f$	$\Delta^g$ (eV)
					$\chi_{11}$	$\chi_L$	$\langle \chi \rangle_{av}$						
Ti	3.36 <sup>b</sup>	0.38	0.18 <sub>5</sub>	36 ± 3	159 (3.31 <sub>g</sub> )	131 (2.74 <sub>g</sub> )	141	-7	-5	-6 ± 1	-12	125	1.7
Zr	2.80	0.41	0.20	30 ± 3	149 (1.63 <sub>g</sub> )	90 (0.98 <sub>g</sub> )	109	-15	-10	-12 ± 2	-10	100	2.1
Hf	2.15	0.34	0.17	24 ± 2	96 (0.53 <sub>g</sub> )	59 (0.33 <sub>g</sub> )	71	-22	-16	-19 ± 3	-8	75	2.8

<sup>a</sup>Reference 24.

<sup>b</sup>From an alternative experimental approach [Ref. 1],  $\lambda_{Ti} = 0.18_5$ . The subsequent values for Zr and Hf were obtained by applying the factor 0.185/0.38 to McMillan's values. The influence of this uncertainty in  $\lambda$  is expressed in the  $\chi_P$  column as an average with an associated error.

<sup>c</sup> $\chi_{Ti}(T)$  is independent of temperature below about 70 K. Because of this behavior, and also since the  $\chi_{av}$ 's of Zr and Hf are much less temperature dependent than those of Ti (Table V), we will assume that the zero-degree susceptibilities of those metals are equal to the respective values extrapolated to 70 K.

<sup>d</sup>Ionic diamagnetic susceptibilities of the 4+ ions, after W. R. Angus, Proc. Roy. Soc. (London) **A136**, 569 (1932); Hf was not listed, but we made an estimate for  $\chi_i$  based on equal intervals in the sequence Ba(32), La(27), Hf(x) [cf. Sr(20), Y(17), Zr(15)].

<sup>e</sup>Susceptibilities of Ti<sup>4+</sup>, Zr<sup>4+</sup>, and Hf<sup>4+</sup> cited by P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956).

<sup>f</sup>Neglecting  $\chi_{so}$  (spin-orbit),  $\chi_{orb} \cong \langle \chi_{tot} \rangle_{av} - (\chi_P + \chi_i + \chi_L)$ . Values are taken to the nearest 5  $\mu\text{emu/mole}$ .

<sup>g</sup> $\Delta \equiv$  mean separation of  $d$  bands contributing to  $\chi_{orb}$ .

<sup>h</sup>Data from Ref. 1.

$\mu\text{emu/mole}$ ,  $\text{states/eV atom}$ , and  $\text{mJ/mole K}^2$ , respectively, we have

$$\chi^0/13.71 = n^0(E_F)/0.212 = \gamma^0. \quad (7)$$

## 2. Influence of Many-Body Effects

*a. Magnetic Susceptibility.* Through the influence of exchange and correlation, the "observed" spin susceptibility  $\chi_P$  is larger than the value expected from Eq. (5) according to the well-known expression due to Seitz (see also Gardner *et al.*<sup>19,20</sup>),

$$\chi_P = \chi^0/(1 - \alpha), \quad (8)$$

where  $\alpha = 2n^0(E_F)\phi$ ,<sup>21,22</sup>  $\phi$  being an interaction energy. As an example of the expected magnitude of this correction, we cite the work of Gardner *et al.*<sup>20</sup> who concluded that for Sc and Y,  $\phi$  assumed the values 0.091 and 0.029, respectively. These are consistent with the observation [Gardner (Ref. 19)] that  $0.03 < \phi < 0.30$  eV for all the paramagnetic transition elements. [The alkali metals yield considerably larger values for  $\phi$ , viz., 0.4–1.5 eV (Ref. 21)]. Using the simply calculated calorimetric  $n(E_F)$  values ( $\gamma_{\text{Sc, Y}} \cong 10$  mJ/mole K<sup>2</sup>) the correction terms ( $\alpha \cong 0.424\gamma\phi$ ) for Sc and Y are, respectively, about 0.4 and 0.1. In order to obtain crude estimates of  $\alpha$  for Zr and Hf we take into consideration (a) the trend  $\alpha_{\text{Sc}} \rightarrow \alpha_{\text{Y}}$ ; (b) the positions of Zr and Hf with respect to those of Sc and Y in the Periodic Table, bearing in mind that  $\phi$  increases somehow in going towards the Pd, Pt corner of the transition-metal block; (c) that the  $\gamma^0$ 's for Zr and Hf ( $\sim 2$ – $3$  mJ/mole K<sup>2</sup>) are much smaller than those for Sc and Y. Accordingly, we suggest that  $\alpha$  for Zr and Hf might be in the vicinity of 0.05, and as such would represent a negligible correction to the magnetic density-of-states expression [Eqs. (5) and (7)]. In other words, we make the approximation in Table VI that  $\chi_P \cong \chi^0$ .

*b. Electronic Specific Heat.* Although corrections for electron-electron correlation and exchange interactions may be regarded as negligible,<sup>23</sup> the calorimetrically measured  $\gamma$  is enhanced with respect to  $\gamma^0$  due to the effect of electron-phonon interaction. In case the metal is a superconductor, an expression due to McMillan,<sup>24</sup> viz.,

$$\gamma = \gamma^0(1 + \lambda),$$

$$\lambda = \frac{0.10 \ln(\Theta_D/1.45 T_c) + 1.04}{0.94 \ln(\Theta_D/1.45 T_c) - 1.04}, \quad (9)$$

enables an electron-phonon correction to be applied to the measured electronic specific-heat coefficient, using the parameters  $\Theta_D$  and  $T_c$  generally obtainable (provided  $T_c$  is not too low) from the same specific-heat measurement. For the transition metals Ti, Zr, and Hf, McMillan has quoted  $\lambda$  values of 0.38, 0.41, and 0.34, respectively. As pointed out in

an earlier publication,<sup>25</sup> we have obtained  $\lambda = 0.18_5$  for pure hcp Ti, based on calorimetric studies of a sequence of Ti-Mo superconductors. The calorimetrically derived spin susceptibilities for Ti, Zr, and Hf, respectively, based on Eqs. (7) and (9) are listed in Table VI.

## C. Susceptibility Temperature Dependence

### 1. Spin Susceptibility

Because of the appreciable  $d$ -band width  $\chi_P$  is practically insensitive to thermal change in Fermi energy, which introduces a factor  $[1 - (\pi^2/12) \times (T/T_0)^2]$  into Eq. (5). Also, by virtue of the arguments outlined in Ref. 1,  $\chi_P$  when expressed in the "band-curvature" form

$$\chi_P = 2\mu_B^2 n(E_F) \left\{ 1 + \frac{1}{6} \pi^2 (kT)^2 \left[ \frac{1}{n} \frac{\partial^2 n}{\partial E^2} - \left( \frac{1}{n} \frac{\partial n}{\partial E} \right)^2 \right]_{E_F} \right\}, \quad (10)$$

is practically independent of temperature.

### 2. Orbital Paramagnetism

The experimentally derived orbital susceptibilities of Ti, Zr, and Hf are listed in Table VI. In particular, the estimate of 125  $\mu\text{emu/mole}$  for hcp Ti is consistent with the values previously quoted for Sc<sup>19</sup> (95  $\mu\text{emu/mole}$ ) and V<sup>15</sup> (210  $\mu\text{emu/mole}$ ).

Denbigh and Lomer<sup>16</sup> have derived an expression for  $\chi_{\text{orb}}$ , an exact evaluation of which requires a detailed knowledge of the band structure. In view of the approximations involved, it is satisfactory to use the frequently quoted simplified expression<sup>2,19</sup>

$$\chi_{\text{orb}} \sim 4\mathfrak{N} \mu_B^2 N_0 N_u / 10\Delta, \quad (11)$$

where  $\mathfrak{N}$  is Avogadro's number;  $N_0$ ,  $N_u$  are the number of occupied and unoccupied states, respectively, in the  $d$  band subject to  $N_0 + N_u = 10/\text{atom}^3$ ;  $\Delta$  is a mean separation of the occupied and unoccupied  $3d$  subbands. Assuming a spectroscopic state  $[Ar] 3d^2 4s^2$  for Ti, we find  $\Delta \cong 1.7$  eV. The other  $\Delta$  values are listed in Table VI.

With  $\Delta \gg kT$ , all quantities in Eq. (10) are practically temperature independent. In other words, the orbital susceptibilities of Ti, Zr, and Hf have no intrinsic temperature dependences. It follows then that the intrinsic temperature dependence of  $\chi_{\text{total}}$  must be practically zero. A clue to a possible mechanism for the *observed* temperature dependence is provided by the fact that the susceptibilities are anisotropic. Of the various susceptibility components considered above, since we have neglected  $\chi_{\text{so}}$ , only  $\chi_{\text{orb}}$  can be anisotropic. This anisotropy arises through the dependence of  $\chi_{\text{orb}}$  on the band structure and consequently the crystal lattice. Accordingly, we suggest that it is this lattice-

coupled susceptibility component that is responsible for the susceptibility temperature dependence through lattice expansion. In some alloys of Ti, the observation that changes in slope of  $\chi(T)$  tend to occur at about the same temperatures as changes in the lattice-parameter thermal-expansion coefficients gives some support to this postulate. However, a good experimental test of the influence of lattice expansion on magnetic susceptibility (in particular,  $\chi_{\text{orb}}^{28}$ ) would be to compare  $(\partial\chi/\partial T)_P$

with either  $(\partial\chi/\partial T)_V$  or  $(\partial\chi/\partial V)_T$ .

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<sup>1</sup>E. W. Collings and J. C. Ho, Phys. Rev. B **2**, 235 (1970).

<sup>2</sup>N. V. Vol'kenshteyn, E. V. Galoshina, and N. I. Shchegolikina, Fiz. Metal. i Metalloved. **25**, 180 (1968).

<sup>3</sup>MARZ-grade material was purchased. The nominal purity of the Zr was 99.99%. That of the Hf was 99.97% for all elements except Zr, which was stated to be present to a nominal concentration of about 3 wt%. All the usual suppliers quote this level of Zr contamination in "high-purity" Hf.

<sup>4</sup>J. C. Ho and R. Viswanathan, Phys. Rev. **172**, 705 (1968).

<sup>5</sup>E. W. Collings and R. D. Smith, J. Appl. Phys. **39**, 4463 (1968).

<sup>6</sup>Zr-1 was measured in June, 1968 (as were Hf-1 and Hf-2); Zr-2 was measured in January, 1971.

<sup>7</sup>J. Butterworth, Proc. Phys. Soc. (London) **83**, 71 (1964).

<sup>8</sup>A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

<sup>9</sup>S. L. Altmann and C. J. Bradley, Proc. Phys. Soc. (London) **92**, 764 (1967).

<sup>10</sup>A. C. Thorsen and A. S. Joseph, Phys. Rev. **131**, 2078 (1963).

<sup>11</sup>W. R. Angus, Proc. Roy. Soc. (London) **A136**, 569 (1932).

<sup>12</sup>P. W. Selwood, *Magnetochemistry* (Interscience, New

York, 1956), p. 78.

<sup>13</sup>R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

<sup>14</sup>L. E. Orgel, J. Phys. Chem. Solids **21**, 123 (1961).

<sup>15</sup>A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

<sup>16</sup>J. S. Denbigh and W. M. Lomer, Proc. Phys. Soc. (London) **82**, 156 (1963).

<sup>17</sup>N. Mori, J. Phys. Soc. Japan **20**, 1383 (1965).

<sup>18</sup>N. Mori, J. Phys. Soc. Japan **26**, 926 (1969).

<sup>19</sup>W. E. Gardner and J. Penfold, Phil. Mag. **11**, 549 (1965).

<sup>20</sup>W. E. Gardner, J. Penfold, and M. A. Taylor, Proc. Phys. Soc. (London) **85**, 963 (1965).

<sup>21</sup>In Gardner (Refs. 19, 20) [but not 22],  $n(E_F)$  is the total Fermi density of states, so that  $\alpha_G = n(E_F) \phi$ .

<sup>22</sup>W. M. Lomer and W. E. Gardner, Progr. Mater. Sci. **14**, 145 (1969).

<sup>23</sup>D. Pines, Solid State Phys. **1**, 367 (1955).

<sup>24</sup>W. L. McMillan, Phys. Rev. **167**, 331 (1968).

<sup>25</sup>E. W. Collings and J. C. Ho, in *Proceedings of the Third IMR Symposium on Electronic Density of States* (U. S. GPO, Washington, D. C., 1970), Natl. Bur. Std. U. S. Spec. Publ. 323.

<sup>26</sup>The intrinsic volume dependence of  $\chi_P$  is negligible in this context.

## Raman Spectra and Lattice Dynamics of Tellurium<sup>†</sup>

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The Raman spectrum of trigonal tellurium has been obtained at 295 and 90 °K. The Raman-active  $A_1$  singlet and two  $E$  doublets are identified by the scattering polarization selection rules, and the  $E$ -mode LO-TO splittings and linear wave-vector shifts are observed. The natural linewidths of the phonons are resolved and some weak second-order structure is evident. A spectrum of amorphous tellurium is also presented. The data on trigonal tellurium, together with neutron-scattering and infrared reflectivity measurements, are used to construct a lattice-dynamical model based on a symmetrized Fourier-expansion scheme incorporating generalized noncentral forces.

### I. INTRODUCTION

The lattice vibrations of trigonal tellurium have been studied recently by neutron scattering,<sup>1</sup> infrared reflectivity,<sup>2</sup> and Raman scattering.<sup>3,4</sup> The principal Raman modes of  $A_1 + 2E$  symmetry have

been identified by Pinczuk, Lucovsky, and Burstein<sup>3</sup> and by Torrie.<sup>4</sup> The latter work, however, contains some spurious lines and somewhat inconclusive polarization data. Complementary Raman data are presented here together with a lattice-dynamics calculation of the phonon spectrum. New results



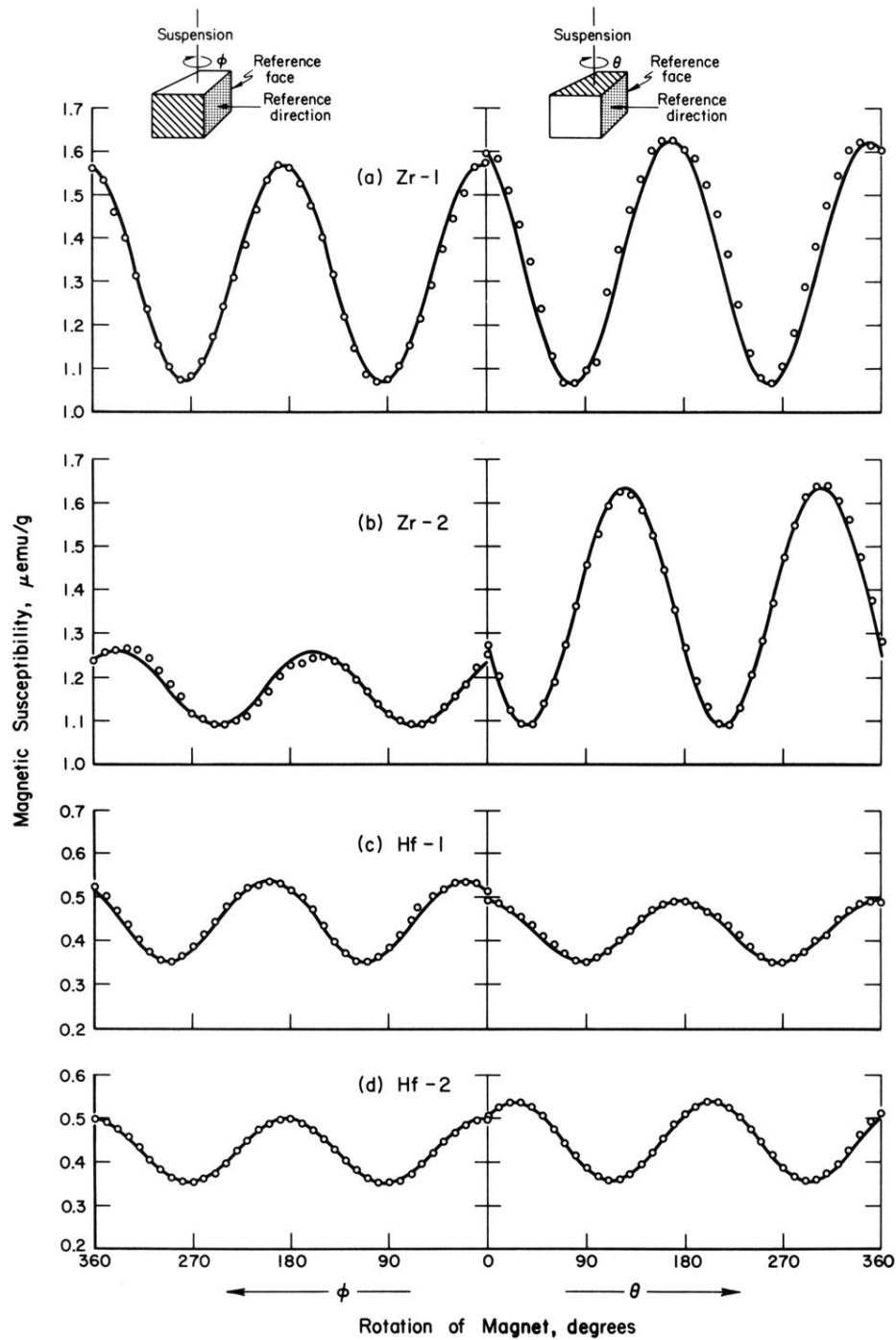


FIG. 2. Results of "double-rotation" experiments on Zr and Hf. The method (described in Ref. 1) is suitable for use with a single crystal of unknown crystallographic orientation. The curves yield  $\chi_L = \chi_{\min}$ ,  $3\chi_{\text{av}} = \chi_{\text{ref}} + \chi(\phi=90) + \chi(\phi=0)$ ; hence  $\chi_{11} = 3\chi_{\text{av}} - 2\chi_L$ .