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Electronic structure and magnetic susceptibility of the different structural modifications of Ti, Zr, and Hf metals

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The electronic structure of the early transition metals Ti, Zr, and Hf has been investigated for the hexagonal (ω), hcp (α), bcc (β), and fcc phases using the linear-muffin-tin-orbital method of band-structure calculation. The results of these investigations are discussed in the light of previous band-structure calculations and experimental data closely related to the electronic structure (low-temperature specific heat, superconductive properties and magnetic susceptibility). It is found from the theoretical calculations that the electronic density of states at the Fermi level increases in the phase sequence hexagonal (ω)$\rightarrow$hcp (α)$\rightarrow$fcc$\rightarrow$bcc (β) and this behavior is unambiguously reflected in all the experimental data as well. A separation of the magnetic susceptibility into its components is performed and from this, the temperature dependence of the Pauli susceptibility for Ti, Zr, and Hf is deduced.

I. INTRODUCTION

At room temperature and ambient pressure, the stable crystalline state of the early transition metals Ti, Zr, and Hf is a hexagonal close-packed (hcp) structure (α phase). At high temperatures, all three metals undergo a phase transformation into a body-centered cubic (bcc) structure (β phase). Upon applying high pressures at room or elevated temperature, the hcp phase of Ti, Zr, and Hf transforms into a hexagonal structure (ω phase). This hexagonal metastable phase can prevail around room temperature and below even after releasing the high pressure. A summary of the preparation, properties, and transformation parameters of the α, β, and ω phases of Ti, Zr, and Hf as well as their alloys was given by Sikka, Vohra, and Chidambaram.[1]

Due to these features the physical properties of these metals can be measured at low temperatures (≤ 300 K) on two different phases (α and ω). On the other hand, low-temperature values of physical properties for the β phase can be obtained by extrapolating from the β-phase region to room temperature for the pure metals and for β-phase alloys or by extrapolating low-temperature values on β-phase alloys to zero content of the alloying component. By measuring appropriate properties such as, e.g., the magnetic susceptibility (χ) and low-temperature specific heat (LTSH), we can study the influence of atomic arrangement on the electronic density of states $n(E_F)$ at the Fermi level. At the same time, the value of $n(E_F)$ can now be reliably calculated theoretically for the known crystal structures of a given element and these data can then be reconciled with the corresponding experimental results. An analysis of the magnetic-susceptibility components of α-Zr on this basis has been recently performed.[2]

The purpose of the present work is to perform such a comparison for the different structural modifications of Ti, Zr, and Hf metals by reviewing existing experimental results and band-structure calculations together with calculated electronic structure data. We shall proceed first by presenting band-structure calculation results for $n(E_F)$ from which the free-electron (χ_P^0) and Stoner-enhanced (χ_P) Pauli susceptibility data will be derived (Sec. II). Then, selected results on LTSH data and superconducting properties will be presented (Sec. III), in order to derive experimental values for $n(E_F)$ and for χ_P^0. In Sec. IV, the experimental magnetic susceptibility data will be summarized and compared to the values deduced theoretically or experimentally in the previous sections. The temperature dependence of the magnetic susceptibility will also be briefly discussed. Such a summary and analysis of electronic structure sensitive data can be helpful for clarifying the nature and origin of the phase stability and phase transformations of Ti, Zr, and Hf metals, whose questions have recently received considerable interest, from both theoretical[3-5] and experimental[6] points of view. It is also expected that this study may contribute to a better understanding of the behavior of the amorphous alloys of these metals with late transition metals such as Ni and Cu.

The main source of data for the crystal structure parameters of Ti, Zr, and Hf metals is the compilation of Villars and Calvert[7] and references therein. Additional data can be found in Ref. 8 for ω-Hf, in Refs. 1 and 9 for the $\alpha\leftrightarrow\omega$ transformation pressures at 300 K, in Ref. 10 for β-Zr and β-Hf, in Ref. 11 for β-Hf, and in Ref. 12 for a high-pressure shock-wave-stabilized β-Zr phase which was metastable at 300 K. It is noted that those data for the β phases which were obtained by extrapolating, as a function of composition, the β-phase alloy lattice parameter to the pure metals are in very good agreement with the corresponding lattice parameters obtained by extrapolating the high-temperature β-phase data of pure metals to room temperature. The $\alpha \leftrightarrow \beta$ transformation temperatures (at 1 bar) are 1153, 1135, and about 2050 K for Ti, Zr, and Hf, respectively.[7] A discussion of the relationship between the structure of the α, β, and ω phases of Ti, Zr, and Hf metals can be found in Ref. 1.

II. BAND-STRUCTURE CALCULATIONS

In Fig. 1, we present the results of self-consistent band-structure calculations for the three naturally occurring phases of Ti. These have been performed scalar relativistically using the linear-muffin-tin-orbital method[13] including the so-called combined correction terms. In addition to the results for the ω, α, and β phase, the electronic density-of-states (DOS) curve for a hypothetical fcc-Ti metal is also shown. For this latter phase a DOS curve has also been published by Moruzzi, Janak, and Williams.[14]

The corresponding curves for Zr and Hf are very similar and for this reason they are not shown here. The most important difference with respect to those in Fig. 1 is an increase in the bandwidth for the sequence Ti→Zr→Hf which is partly due to relativistic effects and partly to a stronger overlap of the d-wave functions.

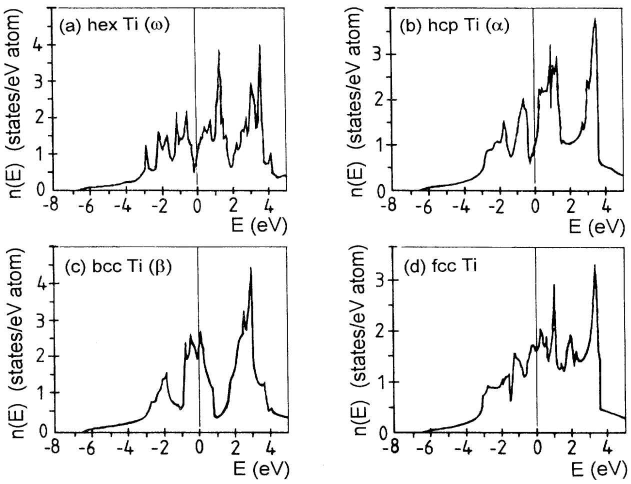

FIG. 1. Calculated electronic density-of-states curves for the different structural modifications of Ti (hexagonal, hcp, bcc, and fcc phases). The vertical dotted lines in each graph represent the position of the Fermi level.

As is seen from Fig. 1(b) for the hcp phase of Ti, the Fermi level E_F lies in a minimum of the DOS curve. This finding is in full agreement with other recent band-structure calculations.[15–18] The DOS curve for the ω phase [Fig. 1(a)] is very similar to that of the hcp phase, with a minimum around E_F that is even deeper and narrower. The band structures of the bcc and fcc phases, on the other hand, are very different in showing the corresponding features characteristic for pure transition metals of bcc or fcc structure.[14,19,20] In contrast to the ω and α phases, E_F lies in both cases in a region of high DOS. This feature is again in line with the results of previous work.[14]

The various material properties discussed below are primarily determined by the electronic structure around the Fermi level. For this reason, we summarize in Table I the results for the DOS at E_F [$n(E_F)$] of the various

TABLE I. Calculated electronic structure parameters of Ti, Zr, and Hf metals: electronic density of states $n(E_F)$ at the Fermi level obtained from the present band-structure calculations; Coulomb interaction parameter μ^* from Eq. (6); free-electron Pauli susceptibility χ_P^0 from Eq. (1); exchange-correlation integral I from the present band-structure calculations; Stoner enhancement factor S from Eq. (3); exchange-enhanced Pauli susceptibility χ_P from Eq. (2). For the crystal structure parameters used in the band-structure calculations see the text.

	Phase	$n(E_F)$ (states/eV atom)	μ^*	χ_P^0 (10^{-6} emu/mol)	I (eV)	S	χ_P (10^{-6} emu/mol)
Ti	ω (hex)	0.93	0.13	30	0.305	1.39	42
	α (hcp)	0.96	0.13	31	0.303	1.41	44
	β (bcc)	2.06	0.18	67	0.303	2.66	177
	fcc (a = 4.135 Å)	1.76	0.17	57	0.302	2.41	122
Zr	ω (hex)	0.89	0.12	29	0.278	1.33	38
	α (hcp)	0.96	0.13	31	0.271	1.35	42
	β (bcc)	1.55	0.16	50	0.275	1.75	88
	fcc (a = 4.40 Å)	1.34	0.15	43	0.279	1.60	69
Hf	ω (hex)	0.64	0.10	21	0.282	1.22	25
	α (hcp)	0.73	0.11	24	0.279	1.25	29
	β (bcc)	1.63	0.16	53	0.283	1.86	98
	fcc (a = 4.47 Å)	1.45	0.15	47	0.283	1.69	79

phases of Ti, Zr, and Hf. As one can see, in the hexagonal ω phase $n(E_F)$ is smaller than in all other phases. In accordance with the behavior to be seen in Fig. 1 $n(E_F)$ is very much larger in the cubic phases than in the ω or α phases.

The band-structure calculations from which the $n(E_F)$ data have been taken have been performed at the experimental lattice constants at 300 K for the ω and α phases and at the lattice constants extrapolated to 300 K for the β phases, while those of the fcc phases given in Table I were chosen to result in the same atomic volume as the β phases. For the d-band metals, we have approximately $n(E_F) \propto V^{5/3}$ (Ref. 21) and, therefore, $n(E_F)$ varies sensitively with the volume V. This volume dependence of $n(E_F)$ is well reflected, even quantitatively, in the values obtained for fcc-Ti at two different lattice constants.[14,19,20]

For those phases for which several independent band-structure calculations were previously performed (ω-Zr: Ref. 3; bcc-Zr: Refs. 3, 19, 20, and 22; hcp-Ti: Refs. 15–18; hcp-Zr: Refs. 16–18 and 23–25) the values of $n(E_F)$ obtained by different authors and in this work are in fairly good agreement with each other (except for the systematically lower values by Asada and Terakura[16] for hcp-Ti and hcp-Zr and the similarly low value for hcp-Zr by Chatterjee[25] as well as the evidently too high values by Iyakutti *et al.*[26] for hcp-Zr and by Vohra, Sikka, and Chidambaram[27] for ω-Ti and ω-Zr). Also, the theoretical values agree well for the hcp phase of Zr and Hf metals with the experimental $n(E_F)$ data derived from x-ray photoemission spectroscopy (XPS) measurements [0.85 and 0.84 states/eV atom for hcp-Zr (Ref. 28) and hcp-Hf,[29] respectively].

In a recent work,[30] band-structure calculations were performed for random hcp Ti-Zr alloys. It is found that the main feature of the pure hcp Ti and Zr metals (E_F lying in a deep valley of the DOS curve) is preserved for their hcp alloys as well.

For Hf metal, the only previous band-structure calculation[23] was performed for the hcp phase. The same features of the DOS curve were obtained as for Ti and Zr and E_F is again located in a sharp minimum.

From the calculated $n(E_F)$ values we have derived the free-electron Pauli susceptibility

$$\chi_P^0 = \mu_B^2 n(E_F) , \tag{1}$$

where μ_B is the Bohr magneton and χ_P^0 is also given in Table I. In order to get the enhanced Pauli susceptibility

$$\chi_P = S\chi_P^0 , \tag{2}$$

we need to know the Stoner enhancement factor

$$S = 1/[1 - n(E_F)I] , \tag{3}$$

where the exchange-correlation integral I (Ref. 20) accounts for the many-body effects (electron-electron correlation, exchange interaction of electrons).

We have calculated the integral I in a manner similar to that described by Gunnarson,[31] but included s and p in addition to the d-wave functions to approximate the induced spin polarization (see Ref. 31 for further details). The results listed in Table I have been obtained using the von Barth-Hedin parametrization for the spin-dependent exchange-correlation potential.[32] The choice of the parametrization has a surprisingly large influence on I. Using the parametrization due to Moruzzi, Janak, and Williams[14] and taking the same lattice constant as Janak,[20] we obtained for bcc-Zr a result ($I = 0.317$ eV) close to his value[20] ($I = 0.321$ eV). With the von Barth-Hedin parametrization, we find for the same lattice constant $I = 0.283$ eV. For this comparison to Janak's work, the calculations have been done nonrelativistically. A change in the lattice constant has, on the other hand, only a small effect on I. Taking $a = 4.0$ Å resulted in $I = 0.310$ eV compared to $I = 0.283$ eV for $a = 4.135$ Å in the case of fcc-Ti. This is in accordance with our finding that I changes only slightly with the crystal structure, as it is obvious from the data in Table I. The same property has been found in the case of Sc by Janak,[20] who obtained $I(\text{bcc}) = I(\text{fcc}) = 0.344$ eV. This value and that for fcc-Y [0.332 eV (Refs. 14 and 20)] are in reasonable agreement with recent results for the corresponding hcp phases [Sc: 0.369 eV and Y: 0.374 eV (Ref. 33)].

The Stoner enhancement factor S resulting from the calculated $n(E_F)$ and exchange-correlation integral I was found to lie between 1.2 and 2.7. For this reason, in parallel with $n(E_F)$, the corresponding Pauli susceptibility χ_P turns out to be smallest for the ω phase and highest for the cubic phases in the case of Ti, Zr, as well as of Hf.

Table I also contains the values of the Coulomb interaction parameter μ^* derived from the corresponding $n(E_F)$ values as will be discussed in Sec. III.

III. ELECTRONIC SPECIFIC HEAT AND SUPERCONDUCTING PROPERTIES

A straightforward way to get experimental information on $n(E_F)$ is to measure the LTSH. For temperatures below about 10 K, from the measured LTSH of metals a linearly temperature-dependent term (γT) can be clearly separated out which can be identified as a contribution by conduction electrons. The electronic specific-heat coefficient γ is directly related to the electronic DOS at the Fermi level by the expression

$$\gamma = (1/3)\pi^2 k_B^2 (1 + \lambda_{ep}) n(E_F) , \tag{4}$$

where k_B is the Boltzmann constant and the quantity λ_{ep} accounts for the enhancement of γ due to the electron-phonon interaction. For the case of superconducting metals, McMillan[34] developed a theory according to which the electron-phonon enhancement factor λ_{ep} can be directly related to the superconducting transition temperature T_c and the Debye temperature Θ_D, usually also yielded by the LTSH measurements, through the empirical formula

$$\lambda_{ep}=[\mu^*\ln(\Theta_D/1.45T_c)+1.04]/[(1-0.62\mu^*)\ln(\Theta_D/1.45T_c)-1.04]\ . \tag{5}$$

This formula is known to give reliable results as long as the calculated value of λ_{ep} does not exceed about unity. The parameter μ^* accounting for the Coulomb repulsion of the conduction electrons can be derived from the isotope shift coefficient of T_c. McMillan[34] found that for transition metals μ^* has values typically between 0.10 and 0.15 and, since λ_{ep} depends only weakly on μ^* [see Eq. (5)], he set arbitrarily $\mu^*=0.13$ for the transition metals. Another approach to μ^* is the empirical formula[35]

$$\mu^*=0.26/[1+n(E_F)^{-1}]\ , \tag{6}$$

where $n(E_F)$ should be inserted in units of (states/eV atom). Table II summarizes the above discussed parameters for the α and β phases of Ti, Zr, and Hf metals, for which a sufficient amount of experimental data are available.

For the experimental values of γ and Θ_D of hcp Ti, we have selected those of Collings and Ho[37] which can be considered a good representative of other published data as well[40] and for this phase, the scatter of available T_c values is also small.[36] The use of these Θ_D and T_c values yields closely McMillan's μ^* and λ_{ep} value, leading to the $n(E_F)$ value in Table II. With the help of Eq. (6) and using this $n(E_F)$ value, the McMillan value $\mu^*=0.13$ is fairly well reproduced. This analysis yields an $n(E_F)$ value which is in close agreement with our theoretical result in Table I. It should also be noted that using the same γ value for hcp Ti, Collings and Ho[38] derived $n(E_F)=1.20$ states/eV atom which deviates much more from the theoretical data. The reason for their too high value is the choice of $\lambda_{ep}=0.185$ which was based on the application of the BCS-Morel equation.[41] However, this equation is valid for the weak-coupling limit of superconductivity only, i.e., for $\lambda_{ep} \ll 1$ which is evidently not the case here and, therefore, the McMillan theory [Eq. (5)] should be applied.

For bcc Ti, we have selected the γ, Θ_D, and T_c values obtained by using the reliable experimental data of Collings and Ho[38] on $Ti_{1-x}Mo_x$ alloys and extrapolating to zero Mo content (these authors have shown that in Ti-rich alloys the sudden change in the values of various physical properties is due to the appearance of an ω phase and, therefore, this mixed β region was omitted when extrapolating to pure bcc Ti). Other available experimental data for γ,[40] Θ_D,[40] and T_c (Refs. 36 and 42) support further the results and conclusions of Collings and Ho[38] in that the bcc phase of Ti should have a significantly different electronic structure than hcp Ti. An evaluation based on Eqs. (4)–(6) leads to λ_{ep} and $n(E_F)$ values about a factor of 2 higher than those for hcp Ti. This is again in good quantitative agreement with our theoretical $n(E_F)$ value of bcc Ti (Table I). Finally, we note that applying the hcp value of λ_{ep} (Ref. 34) with the *experimental* bcc γ value in Eq. (4) yields an $n(E_F)$ value for which the deviation would be rather large.

TABLE II. Low-temperature specific heat and superconductive parameters for the α and β phases of Ti, Zr, and Hf metals: electronic specific-heat coefficient γ; Debye temperature Θ_D; superconducting transition temperature T_c; Coulomb interaction parameter μ^*; electron-phonon coupling parameter λ_{ep} from Eq. (5); electron density of states $n(E_F)$ at the Fermi level from Eq. (4); free-electron Pauli susceptibility χ_P^0 from Eq. (1). The values of the parameters μ^*, λ_{ep}, and $n(E_F)$ were chosen so as to be consistent with the experimental values of γ, Θ_D and T_c in the same row through Eqs. (4), (5), and (6) (for μ^*, we allowed a deviation of about ±0.02). The figures for χ_P^0 were derived from the values of $n(E_F)$ in the previous column.

	Phase	γ (mJ/mol K^2)	Θ_D (K)	T_c (K)	μ^* (eV)	λ_{ep}	$n(E_F)$ (states/eV atom)	χ_P^0 (10^{-6} emu/mol)
Ti	α (hcp)	3.36[b]	420[b]	0.4[a]	0.13[c]	0.38[c]	1.03	33
	β (bcc)	8.5±1[d]	250±20[d]	5.5±1[d]	0.17	0.80	2.00	65
Zr	α (hcp)	2.80[e]	291[e]	0.8±0.3[a]	0.13[c]	0.41[c]	0.84	27
	β (bcc)	≈9[f]	200[f]	5.8[g]	0.17	0.88	2.03	66
Hf	α (hcp)	2.15[e]	248[e]	0.1[a]	0.13[c]	0.34[c]	0.68	22
	β (bcc)			6.0±1.5[h]				

[a] Reference 36.

[b] Reference 37.

[c] Reference 34.

[d] Reference 38.

[e] Reference 39.

[f] Our estimate from the data of Ref. 40.

[g] Reference 10.

[h] Average of data from Refs. 10 and 36.

A very similar analysis can be performed for Zr as well, by using the data summarized in Table II and the trends are again very similar to those obtained for Ti. For hcp Zr, the $n(E_F)$ value derived from LTSH and the superconducting data shows very good agreement with the theoretical and XPS values. The γ, Θ_D, and T_c values extrapolated for bcc Zr are less reliable than those for bcc Ti (although further experimental data[36,43–45] for T_c are also as high as 5 to 7 K); nevertheless they yield an $n(E_F)$ value well above that for hcp Zr. However, the agreement with the theoretical values is less satisfactory as was in the case of bcc Ti. It is noted furthermore that the experimental values of T_c on *disordered* or *amorphous* samples of Zr (Refs. 36, 46, and 47) also show a significant increase with respect to the T_c of hcp Zr.

For the hcp phase of Hf, the LTSH and superconductive data (Table II) again yield an $n(E_F)$ value in good agreement with our band-structure calculations and comparable to the XPS result. Also, the rather limited data for bcc Hf seem to indicate a tendency similar to that observed for Ti and Zr, namely, that $n(E_F)$ of the bcc phase is higher than that for the hcp phase. This trend is again in full agreement with our band-structure calculations.

IV. MAGNETIC SUSCEPTIBILITY

The total magnetic susceptibility of metals with no spontaneous magnetization can be generally written as

$$\chi=\chi_P+\chi_{so}+\chi_{orb} \ . \tag{7}$$

Here, χ_P is the Pauli susceptibility due to the electron spin, χ_{orb} is the susceptibility due to the orbital motion of electrons, and χ_{so} represents the susceptibility contribution due to the spin-orbit coupling. It was shown by relativistic calculations[48] that χ_{so} is a higher-order term in comparison with χ_P and χ_{orb} and, numerically, its value for V metal was, indeed, found to be much smaller than the other two terms. This justifies the neglect of χ_{so} for Ti. Although the relativistic effects may be more important for the heavier elements, we neglect this term also for Zr and Hf. Conventionally, the orbital susceptibility is split into three contributions[49]

$$\chi_{orb}=\chi_{VV}+\chi_L+\chi_{dia} \ . \tag{8}$$

These terms correspond to the generalization of the van Vleck paramagnetism, the Landau diamagnetism of conduction electrons, and the Langevin diamagnetism, respectively.

For these susceptibility contributions, we always have $\chi_{VV}>0$ and $\chi_{dia}<0$ whereas for transition metals χ_L may be[49] either positive or negative and may be of the same order of magnitude as χ_{dia} (the Landau result $\chi_L=-\chi_P/3$ is valid for a free-electron gas only[50]). Furthermore, it is also found[49] that since all occupied electronic states within the Wigner-Seitz cell must be included when accounting for χ_{dia}, this term contains contributions not only from core electrons but also from conduction electrons

$$\chi_{dia}=\chi_{dia}^{core}+\chi_{dia}^{cond} \ . \tag{9}$$

The susceptibility χ_{dia} has recently been calculated by Banhart *et al.*[51] for pure metals with $Z\leq 49$. The values of χ_{dia} derived in this way are between the free-atom and free-ion diamagnetic susceptibilities and may differ from those by as much as 20×10^{-6} emu/mol. In this work, we shall use the χ_{dia} values of Banhart *et al.*[51] for Ti (-23×10^{-6} emu/mol) and for Zr (-36×10^{-6} emu/mol) obtained for the fcc and bcc structure, respectively. By applying a simple extrapolation from the Ti and Zr data, we take a value $\chi_{dia}\approx -49\times10^{-6}$ emu/mol for Hf metal. In this manner, the total susceptibility can now be written as

$$\chi=\chi_P+\chi_{VV}+\chi_L+\chi_{dia} \ . \tag{10}$$

The experimental values of the magnetic susceptibility (χ_{exp}) are shown in Fig. 2 for the α and the β phases of Ti, Zr, and Hf metals above $T=100$ K. A general feature for all these metals is a linear increase of χ_{exp} in the α phase and an almost temperature-independent susceptibility in the β phase. The results of most of the studies are in reasonable agreement with each other. The value of χ_{exp} decreases, in both the α and the β phases, in the sequence Ti→Zr→Hf. The β-phase data can be linearly extrapolated to $T=0$ K, to get a low-temperature value of χ_{exp} for the bcc phase of these metals. The re-

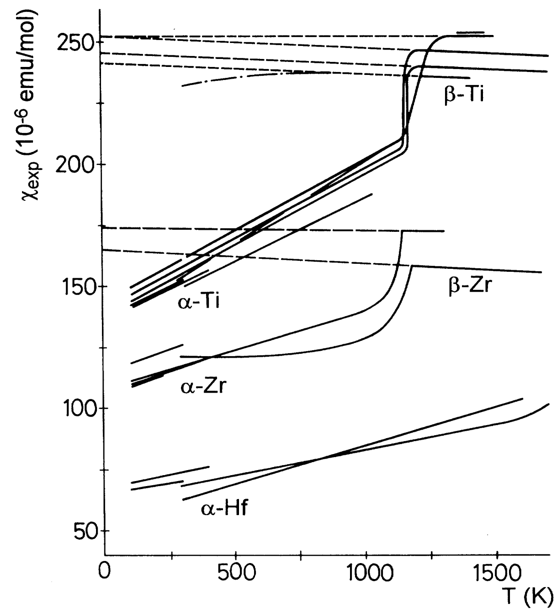

FIG. 2. Temperature dependence of the measured magnetic susceptibility χ_{exp} (solid lines) of Ti (Refs. 37, 38, and 52–57), Zr (Refs. 39, 55, 56, 58, and 59) and Hf (Refs. 39, 57, 60, and 61) metals above 100 K in the α and β phases obtained either on polycrystalline samples or on hcp single-crystals [in this latter case, the average $\chi_{av}=(\chi_c+2\chi_a)/3$ is displayed where χ_c and χ_a are the measured susceptibilities with the magnetic field oriented along the c axis and perpendicular to it, respectively]. The dashed lines represent the linear extrapolations of the β-phase data to low temperatures, the dashed-dotted line is a nonlinear extrapolation of Collings and Ho (Ref. 38) for their data.

sults of susceptibility measurements in the α and ω phases from 4.2 to 300 K are shown in Fig. 3 for Ti metal. The data on sufficiently high-purity samples unambiguously demonstrate that, in both phases, the linear temperature dependence of χ_{exp} above about 100 to 200 K goes over smoothly into a practically temperature-independent behavior below about 100 K and the same was found for ω-Zr,[56] α-Zr,[39,56,58] and α-Hf.[39] As for Ti, it was observed[56] also for Zr that although the temperature dependence of χ_{exp} is practically the same for the ω and the α phases, the magnitude of the susceptibility is definitely smaller for the ω phase.

The zero-temperature values of the measured susceptibility [$\chi_{\text{exp}}(0\text{ K})$, see Table III] were corrected for diamagnetism and these corrected values [$\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}$] are also given in Table III for Ti, Zr, and Hf. For bcc Ti and bcc Zr, data are included also which were derived from measuring the temperature and composition dependence of χ_{exp} for binary bcc alloys of Ti and Zr with other early transition metals.

We shall now make a comparison with the susceptibility values derived from DOS calculations (Sec. II) and from other experimental data (Sec. III). First, it is noted that the values of χ_P^0 in the α phase of each metals, as obtained from our theoretically calculated $n(E_F)$ values (Table I), agree reasonably well (within at least 15%) with the corresponding χ_P^0 values derived from the LTSH and superconductive data (Table II). The agreement between these data for the β phase of Ti is also good but less satisfying for bcc Zr. This is probably a consequence of the uncertainty of the bcc Zr experimental values due to the extrapolation procedure from above 1000 to 0 K or from binary alloys to the pure metals. Because of the satisfying agreement in the case of the α-phase data, we consider, therefore the χ_P^0 values from DOS calculations as fairly reliable for all the phases and the χ_P values from our DOS data are also given in Table III.

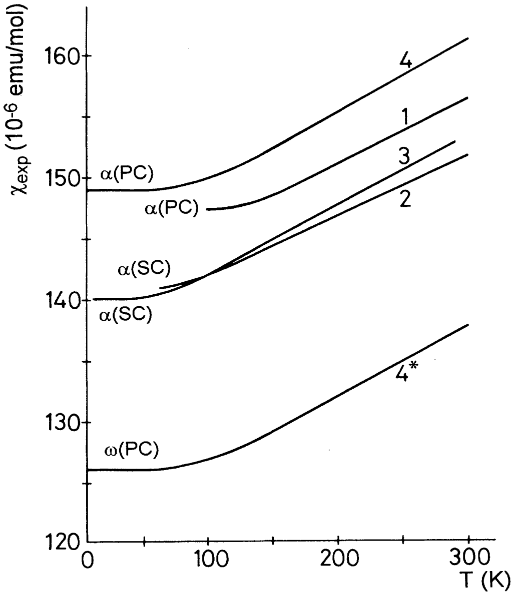

FIG. 3. Temperature dependence of the measured magnetic susceptibility χ_{exp} of α-Ti and ω-Ti for $T \leq 300$ K [PC: polycrystalline sample; SC: single-crystal, $\chi_{\text{av}}=(\chi_c+2\chi_a)/3$]. Data sources: curve 1 (Ref. 52, average of data on two PC samples); curve 2 (Ref. 37); curve 3 (Ref. 54); curves 4 and 4* [Ref. 56, data obtained on the same PC sample, first in the α phase (4) and, then, after transforming it into the ω phase (4*)].

In the absence of other estimates for the van Vleck paramagnetic and Landau diamagnetic susceptibilities, we may proceed as follows. According to Eq. (10), the quantity $\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}-\chi_P(0\text{ K})$ yields just $\chi_{VV}+\chi_L$. Thus, by subtracting the susceptibility data in the third row from those of the second row in Table III for each phase, we get values of $\chi_{VV}+\chi_L$ which are given in the fourth row of Table III.

This analysis yields $\chi_{VV}+\chi_L$ values that are very similar for Ti, Zr, and Hf. In all three cases the data do not differ very much for the three different phases. This corresponds to expectation in that the orbital susceptibility contribution (at least its van Vleck part) is not sensitively dependent on the crystal structure, but is primarily determined by the width of the d band and the number of electrons.[48,49] The major sources of uncertainty for the data in Table III are: (i) the probably large error of the extrapolated low-temperature data for the β phases, and (ii) eventually, for Zr and Hf the neglect of relativistic effects beyond our scalar-relativistic approach in accounting for χ_P and χ_{so}.

By assuming that the orbital susceptibility contributions (χ_{VV}, χ_L, and χ_{dia}) are independent of temperature, we can now deduce the temperature dependence of the Pauli susceptibility $\chi_P(T)$ if we subtract the values of $\chi_{VV}+\chi_L$ and χ_{dia} as given in Table III from the averaged experimental susceptibility data presented in Fig. 2. In getting the average $\chi_{\text{exp}}(T)$ values for the α phase, we preferred, also as in the case of Table III, the data of Collings and Ho[37,39] obtained for $T<400$ K, the extrapolation of which up to the $\alpha\leftrightarrow\beta$ transformation temperature conforms well with the data of other investigators in this temperature range (since for all three metals the observed temperature dependence shows a very similar, approximately linear behavior, it is felt that the data of Taniguchi, Tebble, and Williams[59] do not properly represent, due to the strongly flat behavior below about 1000 K, the actual temperature dependence of the magnetic susceptibility of α-Zr and, therefore, they were left out of consideration). For the β phase, we simply took an average of the available data. The temperature dependence of the Pauli susceptibility $\chi_P(T)$ derived in this manner is shown in Fig. 4 (around the $\alpha\leftrightarrow\beta$ transformation temperature, we have neglected an eventual rounding off of the susceptibility curve; however, the data of Kohlhaas and Weiss,[52] also included in Fig. 2, on two different Ti samples demonstrate that the transition can, indeed, be very sharp). Due to the way of deducing the values of $\chi_{VV}+\chi_L$, the $\chi_P(0\text{ K})$ values in Fig. 4 equal the Pauli susceptibilities obtained from our band-structure calculations, $\chi_P^{\text{DOS}}(0\text{ K})$.

Finally, it is mentioned that Shimizu[62] has attempted to derive the temperature dependence of the magnetic susceptibility of these metals, based on an empirical DOS curve obtained from the variation of γ with the electron-atom (e/a) ratio. Since the DOS curves are significantly different in the α phase and in the β phase (Fig. 1) and the γ versus e/a curves were obtained on alloys having different structures, this rigid-band model consideration could not properly describe the variation of χ_P in the whole temperature range of experimental investigations.

V. SUMMARY

In this paper, we have analyzed the influence of crystal structure on the electronic band structure of Ti, Zr, and Hf metals. Theoretical electronic DOS curves were presented for the ω, α, β, and fcc phases of Ti. For the α phase, for which several band-structure calculations have been performed before, our DOS curve agrees well with previous ones. The main features of the DOS curves are that E_F lies in a deep valley of the DOS for the ω and α phases. This is not the case for the bcc and fcc phases. Furthermore, it was found that the value of the DOS at the Fermi level, $n(E_F)$, significantly increases in the sequence $\omega \rightarrow \alpha \rightarrow \text{fcc} \rightarrow \beta$. The calculated band-structure curves for Zr and Hf show a strong similarity to the DOS curves of the corresponding phases of Ti. We have also calculated the exchange-correlation integral I which was found to depend only slightly on the crystal structure, in agreement with the results of the few previous calculations. From the theoretical $n(E_F)$ and I values we have

TABLE III. Magnetic-susceptibility data (in units of 10^{-6} emu/mol) for Ti, Zr, and Hf metals. For each phase, the first row gives the experimental values at 0 K, $\chi_{\text{exp}}(0\text{ K})$ (for data sources, see remarks below), the second row the experimental values after applying the diamagnetic correction, $\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}$, the third row the exchange-enhanced Pauli susceptibility, $\chi_P^{\text{DOS}}(0\text{ K})$, from our DOS calculations as given in Table I, and the fourth row the sum of the van Vleck and Landau susceptibility contributions, $\chi_{VV}+\chi_L$, obtained from the data in the second and third rows according to Eq. (10).

Phase	Susceptibility	Ti	Zr	Hf
	χ_{dia}	−23	−36	≈−49
ω (hex)	$\chi_{\text{exp}}(0\text{ K})$	118[a]	96[d]	≈65[f]
	$\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}$	141	132	115
	$\chi_P^{\text{DOS}}(0\text{ K})$	42	38	25
	$\chi_{VV}+\chi_L$	90	94	90
α (hcp)	$\chi_{\text{exp}}(0\text{ K})$	140[b]	108[e]	71[g]
	$\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}$	163	144	120
	$\chi_P^{\text{DOS}}(0\text{ K})$	44	42	29
	$\chi_{VV}+\chi_L$	119	102	91
β (bcc)	$\chi_{\text{exp}}(0\text{ K})$	250[c,i]	170[c]	≈130[h]
		220[j]	165[k]	
	$\chi_{\text{exp}}(0\text{ K})-\chi_{\text{dia}}$	273	206	180
		243	201	
	$\chi_P^{\text{DOS}}(0\text{ K})$	177	88	98
	$\chi_{VV}+\chi_L$	96	118	82
		66	113	
fcc	$\chi_{\text{exp}}(0\text{ K})$	≈200[l]	≈150[l]	≈110[l]
	$\chi_P^{\text{DOS}}(0\text{ K})$	122	69	79

[a] From Fig. 3 [the measured $\chi_{\text{exp}}(0\text{ K})$ value for the ω-phase was scaled down by a factor chosen to bring curve 4 in coincidence with the average of curves 2 and 3 at 0 K].

[b] From Fig. 3 (average of curves 2 and 3 at 0 K).

[c] From Fig. 2 (average of extrapolated values from the β-phase region to 0 K, see dashed lines).

[d] The data of Ref. 56 by scaling down as for Ti.

[e] Average of data of Refs. 39 and 58.

[f] Rough estimate based on the other measured susceptibility values for Ti, Zr, and Hf.

[g] From Ref. 39.

[h] Rough estimate based on the β-phase data of Ti and Zr (Fig. 2).

[i] Data obtained from χ_{exp} of bcc Ti-V (Ref. 59) alloys extrapolated from the β-phase region at high temperatures to 0 K and then extrapolating to pure bcc-Ti and bcc-Zr.

[j] Data obtained from χ_{exp} of bcc Ti-Mo (Ref. 38) alloys extrapolated from the β-phase region at high temperatures to 0 K and then extrapolating to pure bcc-Ti and bcc-Zr.

[k] Data obtained from χ_{exp} of Zr-Nb (Ref. 59) alloys extrapolated from the β-phase region at high temperatures to 0 K and then extrapolating to pure bcc-Ti and bcc-Zr.

[l] Rough estimate for the hypothetical fcc phase with the help of Eq. (10), by using an average of the values of the ω, α, and β phases for $\chi_{VV}+\chi_L$.

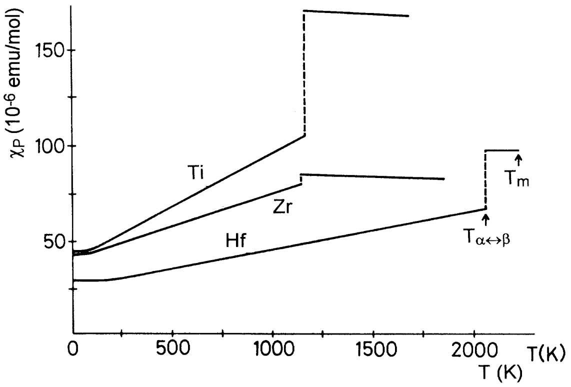

FIG. 4. Temperature dependence of the Pauli susceptibility χ_P of Ti, Zr, and Hf metals in the α and β phases up to the melting point T_m. For a given metal, χ_P was obtained, according to Eq. (10), by subtracting from the average of the experimental susceptibility $\chi_{\rm exp}$ given in Fig. 2 the susceptibility contributions χ_{VV}, χ_L, and $\chi_{\rm dia}$ which were assumed to be temperature independent and the values of which were taken from Table III. The temperature of the $\alpha\leftrightarrow\beta$ phase transition is marked by the vertical dashed lines. The value of χ_P(0 K) for each phase and each metal equals the corresponding value in Table I from our theoretical band-structure calculations.

derived the Stoner-enhanced Pauli susceptibility for the different structural modifications of these metals.

From an analysis of previously reported LTSH and superconductive data, we have obtained experimental values for $n(E_F)$ of the different phases which were in reasonable agreement with $n(E_F)$ values from our band-structure calculations. This justifies the extrapolation procedure in getting experimental values for the bcc phase of these metals by using data on their bcc alloys. The variation of the magnetic susceptibility with crystal structure also corresponds to the same trend as revealed by the theoretical $n(E_F)$ values and, therefore, it can be ascribed to the corresponding variation of the Pauli susceptibility. Finally, we have decomposed the magnetic susceptibility into its contributions for the ω, α, and β phases of Ti, Zr, and Hf and derived the temperature dependence of the Pauli susceptibility for the α and β phases, by assuming the temperature independence of the orbital contributions. For the α phase, χ_P(0 K) has very similar values for all three metals and it remains practically constant up to about $T=100$ K. Above this temperature, χ_P increases linearly for each metal, with a slope decreasing in the sequence Ti$\rightarrow$Zr$\rightarrow$Hf, up to the $\alpha\leftrightarrow\beta$ transformation. In the β phase, χ_P is practically constant and has almost the same value for Zr and Hf whereas for Ti its value is higher by about a factor of 2 (see Fig. 4). It might be tempting to say that the sizable variation of χ_P for both the ω and α phase are probably connected with the fact that E_F is located on the flank of a deep valley of the DOS curve and the weak temperature dependence of χ_P for the β phase is due to the location of E_F on top of a DOS peak. However, an understanding of the temperature dependence of χ_P in these metals evidently requires further theoretical work.

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