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Magnetic Susceptibility and Low-Temperature Specific Heat of High-Purity Titanium

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Magnetic susceptibility and low-temperature specific-heat measurements have been made on several specimens of polycrystalline high-purity titanium, and in the case of the former measurement, on four single crystals. The calorimetric results are in good agreement with previously published data. A critically assessed average room-temperature susceptibility based on published magnetic susceptibility values [(3.17 ± 1)% μemu/g] is in good agreement with an average of the present results ($3.17 \pm 0.01_5$ μemu/g). The considerable scatter in the published data (3.0–3.36 μemu/g) is attributed, in part, to the influence of magnetic anisotropy and texture. The magnetic anisotropy of the best of the single crystals measured ($\chi_{\parallel} - \chi_{\perp} = 0.52_1$ μemu/g) is almost twice as large as that previously reported, and new results for the temperature dependences of $\chi_{\parallel}$ and $\chi_{\perp}$ in the range 80–400 °K are presented. The susceptibility at 0 °K is estimated to be approximately 2.9 μemu/g. Combining the calorimetric and magnetic results, and using an empirically derived electronic specific-heat enhancement factor, a value of 0.81 μemu/g was obtained for the spin paramagnetism χ_s. Finally, assuming that $\langle\chi_{\text{total}}\rangle_{\text{av}} \cong \chi_s + \chi_{\text{orb}}$ (the orbital paramagnetism), we find the latter to be the dominant component of the susceptibility of titanium and equal to 2.0_9 μemu/g.

I. INTRODUCTION

Magnetic susceptibility and low-temperature specific-heat measurements have been made as part of a study of the physical properties of titanium alloys. In order to establish reliable reference points for the alloy investigations, measurements have been made on several grades of high-purity titanium; the results of this work are reported here. Magnetic susceptibility measurements on single-crystal samples, using an original technique,[1] revealed a considerably larger magnetic anisotropy ($\chi_{\parallel} - \chi_{\perp}$) than that previously reported by Reekie and Yao.[2] If a single measurement is to yield a true value for the average susceptibility χ_{av}, an ideally polycrystalline specimen is required. Such a specimen is difficult to obtain, since the as-cast grain size is usually relatively large and cannot be assumed to possess a random orientation. Moreover, cold working (e.g., rolling) as a preliminary to recrystallization annealing introduces preferred crystallographic orientation (texture), in which the average *c*-axis direction of the hcp crystallites is normal to the rolling plane. Such texture cannot be erased by annealing in the hcp region (under 882 °C), even during recrystallization and grain growth[2,3]; the texture also survives annealing in the high-temperature bcc region.[3,4] The existence of magnetic anisotropy and the possibility of texturization require that the average susceptibility of a polycrystalline specimen be derived from the results of measurements, with the magnetic field in each of three mutually orthogonal directions using

$$\chi_{\text{av}} = \tfrac{1}{3}(\chi_1 + \chi_2 + \chi_3) \quad , \tag{1}$$

a special case of which is

$$\chi_{\text{av}} = \tfrac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) \quad . \tag{2}$$

The effect of texture is probably responsible, in part, for the wide scatter evident in the values of χ_{av} (room temperature) obtained by previous workers (Table I), of whom only Reekie and Yao[2] mentioned having made three-direction measurements. In contrast, the earlier results of low-temperature calorimetry are more consistent (Table II).

New measurements on the temperature dependences of $\chi_{\parallel}$ and $\chi_{\perp}$ have also been made in the temperature range 80–400 °K.

II. LITERATURE REVIEW

Table I presents the literature values for the susceptibilities of pure titanium. A considerable scatter is evident, the quoted susceptibilities ranging from 3.0 to 3.36 μemu/g. Measurement errors, arising chiefly in force calibration and sample positioning, have contributed uncertainties of 1 or 2%.[2,5] Sample purity is also an important consideration. In titanium, oxygen is usually the most abundant contaminant, as demonstrated by the analyses listed in Sec. III A. This has the effect of decreasing the susceptibility to the extent of 0.03_5 μemu/g per at.% of oxygen.[6] Only occasionally in the past have the oxygen concentrations been quoted.

As indicated in the Introduction, texturization is the chief source of error in a single-direction susceptibility measurement on polycrystalline hexagonal material. Of the authors listed in Table I, it appears that only Reekie and Yao[2] have made three-component measurements. For this reason, their value for average susceptibility (3.16_8 μemu/g, including both polycrystal and single-crystal data) is estimated to be the most reliable of those previously published. On the other hand, in view of the present work, it seems that the single crystal measured by these authors may have been imperfect.[7]

In Table II are listed the results of low-temperature specific-heat measurements on various specimens of pure titanium. The results are very consistent, suggesting again that the scatter in the susceptibility data of Table I is due to texturization rather than to other experimental difficulties.

TABLE I. Published values of the magnetic susceptibility of pure titanium.

χ_{av}	$\chi_{\parallel}$ (μemu/g)	$\chi_{\perp}$	Temperature (°K)	Author
3.19	...	...	293	a
3.2	...	...	300	b
3.17	3.35	3.07	298	c
3.31	...	...	296	d
3.0	...	...	293	e
3.27	...	...	293	f
3.36	...	...	293	g
3.24	...	...	293	h

[a] L. Klemm, Z. Elektrochem. 45, 354 (1939).

[b] C. Squire and A. Kaufmann, J. Chem. Phys. 9, 673 (1941).

[c] Reference 2.

[d] J. M. Denney, Bull. Am. Phys. Soc. 30, 1640 (1955); also, California Institute of Technology Physical Metallurgy Laboratory, Sixth Technical Report to Office of Naval Research on Contract No. N6onr-24430, 1955 (unpublished).

[e] A. Münster, K. Sagel, and U. Zwicker, Acta Met. 4, 558 (1956); also, K. Sagel, E. Schulz, and U. Zwicker, Z. Metallk. 47, 529 (1956).

[f] L. F. Bates and S. J. Leach (private communication).

[g] Reference 5.

[h] Reference 14.

TABLE II. Published values of the low-tempeature specific-heat parameters of pure titanium.

Electronic specific-heat coefficient γ (mJ/mole °K^2)	Debye temperature Θ_D (°K)	Temperature range (°K)	Author
3.34	280	1.8–4.2	a
3.38	421	4–15	b
3.56	430	1.2–20	c
3.346	427	1.1–4.5	d
3.351	430	1.1–4.5	d
3.3	415	1.5–16	e
3.30	429	1.2–4.5	f
3.31	412	0.9–12	g

[a] I. Estermann, S. A. Friedberg, and J. E. Goldman, Phys. Rev. 87, 582 (1952).

[b] M. H. Aven, R. S. Craig, T. R. Waite, and W. E. Wallace, Phys. Rev. 102, 1263 (1956).

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[d] G. D. Kneip, J. O. Betterton, and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).

[e] F. Heiniger and J. Muller, Phys. Rev. 134, A1407 (1964).

[f] R. R. Hake and J. A. Cape, Phys. Rev. 135, A1151 (1964).

[g] G. Dummer, Z. Physik 186, 249 (1965).

III. EXPERIMENTAL DETAILS

A. Specimen Material

Polycrystalline specimens for magnetic susceptibility and low-temperature specific-heat measurements were cut from (i) arc-melted rods of Toho sponge, a magnesium-reduced titanium (designated TS), and high-purity electrorefined sponge, grade ELXX, from Titanium Metals Corporation of America (designated HP) and (ii) crystal bar "iodide process" titanium from the Foote Mineral

Company (designated ID). The principal impurities in these three grades of titanium, in weight percent, were (i) TS titanium: O_2 0.086, N_2 0.011, Mg 0.01, Sn 0.02, Si 0.01, Fe 0.001; (ii) HP titanium: O_2 0.037, N_2 0.004, Cl_2 0.073, Fe 0.009; (iii) ID titanium: O_2 0.040, N_2 0.003, Fe, Cr, Ni, all < 0.001.

Single-crystal specimens for the magnetic work were cut from three $\frac{1}{4}$-in.-diam rods of electron-beam-melted titanium and designated MRC-1, MRC-2, and TC-1.[8] Another specimen (TRW) was cut from a large-grain slab.[9] This material was excessively contaminated with both oxygen and dissolved iron,[10] as shown in the analysis O_2 0.23, Fe 0.14, C 0.025, N_2 0.015. From a typical analysis supplied with the MRC material the principal impurity contents, in weight percent, were C 0.0078, O_2 0.0063, Fe 0.003, Zr 0.002, Al 0.0015. The crystal TC-1 was grown from iodide titanium, whose typical analysis was summarized in the preceding paragraph. Postpreparation analysis of TC-1 gave an oxygen content of 0.0425 wt%.

The hcp titanium forms by martensitic transformation of the high-temperature bcc allotrope at 882 °C. For this reason it is extremely difficult to obtain nearly perfect single crystals. In the present work, it was necessary to cut, etch, and x ray (Laue backreflection) repeatedly until the best possible diffraction pattern was obtained. Even so, in this and similar experiments on alloys, subsequent work showed that subgrains could occasionally be missed by the x-ray beam. Laue backreflection photographs of the final TRW specimen still revealed some slight smearing of the diffraction spot pattern. Of the three high-purity specimens selected, MRC-1 was the least perfect (very faint background halos), and TC-1, an annealed crystal prepared by electron-beam melting from iodide titanium,[8] was the best. Fortunately, appreciable departures from single crystallinity can be detected by the magnetic susceptibility technique itself (Sec. III D).

B. Apparatus

Susceptibility was measured, with reference to a sample of pure platinum,[11] by the Curie technique, using a Harvey-Wells 7-in. pole diameter electromagnet and a Cahn RG electronic microbalance. The specimens weighed about 100 mg. Ferromagnetic contamination could be detected and corrected for by the Honda-Owen method[12] in which the true susceptibility is obtained by extrapolating to infinite field the measured susceptibilities plotted as functions of reciprocal field strength. Specific heats of several pure titanium samples (weighing about 30 g each) were measured between 1.5 and 6 °K in a He^4 cryostat.[13] The low-temperature thermometry was based on a precalibrated (1965 NBS Provisional Scale) CryoCal germanium resistance thermometer.

C. Polycrystalline Specimens

Low-temperature specific-heat measurements were made on rapidly cooled, as well as annealed, polycrystalline specimens of HP and ID titanium. Average magnetic susceptibility values were usually obtained by the three-direction technique [Eq. (1)], which is valid whatever the grain size or degree of texturization is. Some of the specimens were as cast, some recrystallized, and two had been cold-rolled and recrystallized for the purpose of studying texturization.

D. Single Crystals

The principal susceptibility components $\chi_{\parallel}$ and $\chi_{\perp}$ were measured for four single crystals of titanium possessing various degrees of purity (Sec. III A) and perfection. It was not convenient to preorient a given crystal to enable $\chi_{\parallel}$ and $\chi_{\perp}$ to be measured directly by rotating the magnet through 90°. Moreover, such a procedure is subject to misalignment errors, which may pass undetected. Instead, a new method was used, in which $\chi_{\parallel}$ and $\chi_{\perp}$ are obtained from a pair of rotation experiments, in which initial alignment of the specimen is achieved with reference to a *single arbitrary flat surface* ground on it, the normal to which is taken as "reference direction." The principle of this technique, which has been described in detail elsewhere,[1] is briefly as follows. Imagine the magnet to be rotated through 360° about the suspended specimen. Then no matter how the specimen is hung, since any plane cuts the basal plane of a hexagonal crystal in line perpendicular to the *c* axis, all the resulting susceptibility cosine curves will have a set of common turning-point values equal to $\chi_{\perp}$. It can be shown that these will be minima if $\chi_{\parallel} > \chi_{\perp}$ (as it is for pure titanium), and conversely. If, after performing one magnet-rotation experiment, the specimen is turned 90° about its reference direction and a second rotation experiment is performed, $\chi_{\perp}$ is immediately obtained as the turning-point value common to both experiments. From the reference point (χ_1) and the "90° points" on both curves (χ_2 and χ_3, respectively), χ_{av} may be derived using Eq. (1), after which $\chi_{\parallel}$ may be obtained using Eq. (2).

With this method it is not at all necessary to know the crystallographic orientation within the specimen or to transfer this information accurately from an x-ray diffractometer to the susceptibility apparatus. On the other hand, the task of orienting the arbitrary flat face on the specimen in a direction parallel to the magnet pole face before commencing each magnet-rotation run is a simple procedure which can be carried out to a high accuracy. If the specimen contains a hidden subgrain which may have been missed after optical inspection following polishing and etching, or even after x raying, the method in general will not work; i. e., the pair of cosine curves will not possess a common set of turning points. The crystal is then reworked or rejected. Because of this property, the double-rotation technique is particularly suitable for obtaining reliable values of $\chi_{\parallel}$ and $\chi_{\perp}$ in martensitically transformed crystals or any crystal subject to internal flaws whose degree of perfection might otherwise be in doubt.

Having obtained $\chi_{\parallel}$ and $\chi_{\perp}$ in the manner outlined above, the specimen was repositioned so that these quantities could be measured directly as functions of temperature. The previously obtained values of the principal components were used as checks on the accuracy of the new sample alignment.

IV. RESULTS

A. Low-Temperature Specific Heat

The low-temperature specific-heat data ($C = \gamma T + \beta T^3$) are analyzed in the usual way by plotting C/T versus T^2 as shown in Fig. 1. The results of measurements on two specimens of ID titanium and one of HP titanium are summarized in Table III. The good agreement between this and recently published data (Table II) is to be expected, since C is independent of the detailed structure of the specimen, and material of adequate purity has been available for some years.

B. Room-Temperature Susceptibility of Polycrystalline Titanium

The results of susceptibility measurements on polycrystalline titanium specimens are summarized in Table IV. Initially, an arbitrary direction was taken in each of three specimens and susceptibility versus temperature was measured between 78 and 400 °K. The susceptibilities at 300 °K from these experiments are listed in rows 1–3 of Table IV. The agreement between the susceptibilities so obtained is fortuitous, since according to rows 4, 5, and 7 some anisotropy is encountered even in the as-cast material. Rows 4–7 are susceptibilities measured in three mutually perpendicular directions, yielding a true average susceptibility according to Eq. (1). Row 6 shows that deformation by impact in three mutually orthogonal directions followed by a prolonged recrystallization anneal (100 h at 850 °C), although successful in altering the grain structure from large acicular grains to smaller equiaxed grains, failed to improve the isotropy. Rows 8 and 9 list the results of room-temperature measurements on specimens in which considerable texturization had been induced by rolling. From this and the single-crystal work to be described, a value for χ_{av} of $3.16_5 \pm 0.01$ μemu/g (standard deviation) is obtained.

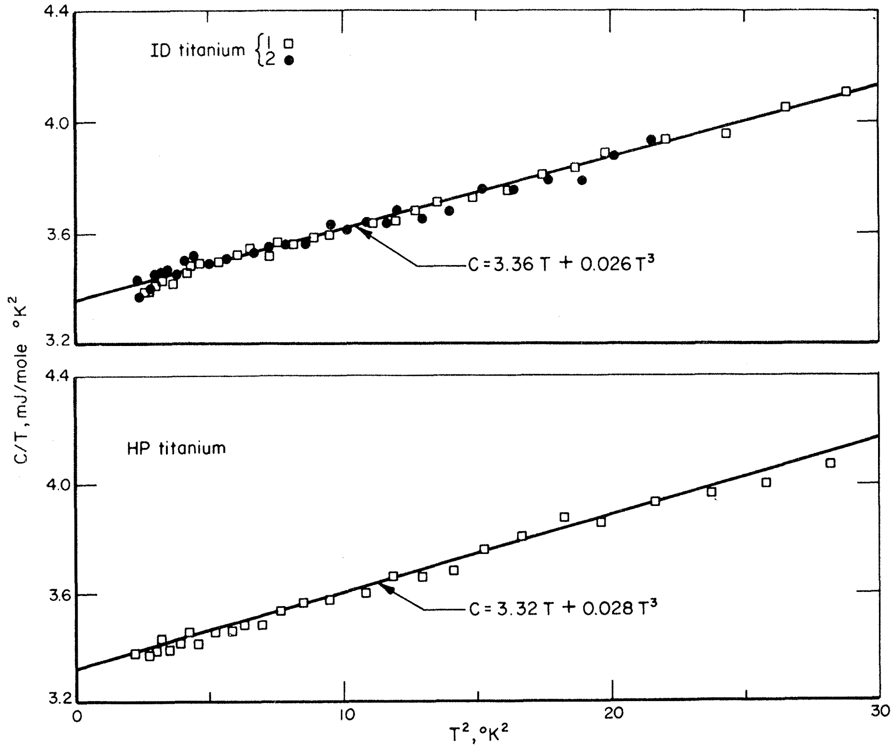

FIG. 1. Low-temperature specific heat of high-purity titanium. The ID specimens had been annealed at 850 °C and either quenched (1) or furnace-cooled (2). The HP specimen was measured in the as-cast condition.

TABLE III. Low-temperature specific heat of high-purity titanium.

Specimen	Heat treatment	Electronic specific-heat coefficient γ (mJ/mole deg^2)	Lattice specific-heat coefficient β (mJ/mole deg^4)	Debye temperature Θ_D (°K)
ID-1	850 °C, 100 h[a]	3.36	0.26	420
ID-2	850 °C, 100 h[b]	3.36	0.26	420
HP	As cast	3.32	0.28	410

[a] Quenched into iced NaCl solution.

[b] Furnace cooled.

The accuracy of the result is estimated to be about $\pm 0.01_5$ μemu/g. The influence of oxygen contamination has, for most samples, been shown to be negligible.[10]

C. Susceptibility Measurements on Single Crystals

Figure 2 shows the results of the double-rotation experiments from which the principal susceptibility components were derived as outlined in Sec. III D. The results are summarized in Table V. The magnetic anisotropy, taken as that of the best crystal (TC-1), is $\chi_{\parallel} - \chi_{\perp} = 0.52_1$ μemu/g. The only previous measurement[2] gave 0.28_0 μemu/g. This small value may have resulted from crystalline, rather than chemical, imperfection,[7] since the accompanying $\chi_{av} = 3.16_3$ μemu/g was in good agreement with the present average value.

D. Temperature Dependence of Susceptibility

The results of temperature-dependence measurements in the range 80–400 °K on the single-crystal MRC-2 are shown in Fig. 3, along with results for various polycrystalline specimens. Recently published results for χ_{av} (T),[14] after normalization to $\chi_{300\,°K} = 3.17$ μemu/g, were found to agree well with the present polycrystalline data. Various temperature coefficients are listed in Table VI. Figure 3 shows that $\chi_{\parallel}$ and $\chi_{\perp}$ increase linearly with temperature above about 120°K, but tend to flatten off below this temperature. It is instructive to compare this with the results of recent measurements on the lattice parameters of titanium, in which it has been shown[15] that $c(T)$ and $a(T)$, which also increase linearly with temperature at higher temperatures, tend to flatten off below 120 and 100 °K, respectively.

V. DISCUSSION

A. Magnetic Susceptibility and Specific Heat-Spin and Orbital Paramagnetisms

Neglecting electron correlations, the Pauli spin paramagnetism χ_s is given by

$$\chi_s \propto \mu_B^2 [2n(E_F)] \ , \tag{3}$$

where μ_B is the magnetic moment per spin (Bohr magneton), $n(E_F)$ is taken to be the density of states at the Fermi level for a *single* spin direction, and the constant of proportionality depends on the units employed. Similarly, a "band-structure" electronic specific-heat coefficient γ_{BS} may be related to the density of states through

TABLE IV. Magnetic susceptibility of polycrystalline titanium.

No.	material	Temperature (°K)	Mass of specimen (mg)	Estimated number of grains per specimen	Condition	Notes	Magnetic susceptibility χ (μemu/g)			
							χ_1	χ_2	χ_3	χ_{av}[a]
1	TS	300	81	800	As cast	b	3.16_8			
2	HP	300	84	800	As cast	b	3.16_8			
3	ID	300	84	···	As received	b	3.16_9			
4	TS	300	78	800	As cast	···	3.15_9	3.15_6	3.15_3	3.15_6
5	HP	300	73	800	As cast	···	3.19_8	3.12_9	3.12_7	3.15_1
6	HP	300	108	43 000	Recrystallized	c	3.19_3	3.14_9	3.13_3	3.15_8
7	ID	299	70	···	As received	···	3.20_9	3.12_1	3.11_0	3.14_7
8	HP	299	51	53 000	Recrystallized	d	3.25_6	3.13_5	3.10_0	3.16_3
9	HP	298	49	230 000	Recrystallized	e	3.35_3	3.08_5	3.07_8	3.17_2

[a] Equation (1).

[b] Single measurement in arbitrary direction. Based on χ (300 °K) from temperature-dependence experiment.

[c] Compressed successively in three orthogonal directions by amounts 11, 18, and 22%. Annealed for 100 h at 850 °C.

[d] Cold rolled to a reduction in thickness of 25%. Annealed 100 h at 850 °C.

[e] Cold rolled to a reduction in thickness of 50%. Annealed as above.

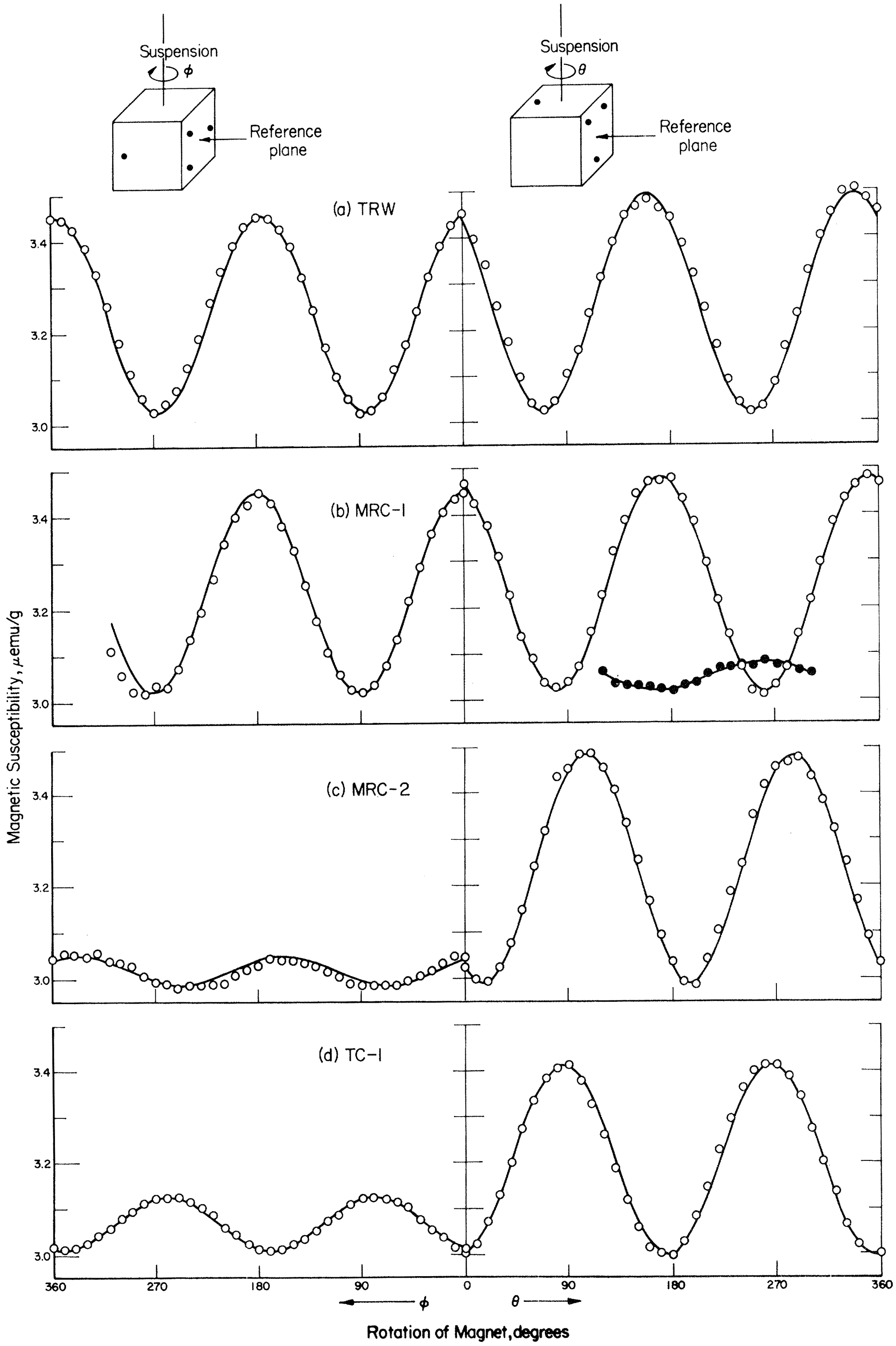

FIG. 2. Results of "double-rotation" experiments on titanium single crystals. For any crystal, the "common turning points" give $\chi_\perp$ directly. In the case of (b), in which both rotations yielded curves of similar amplitudes, a subsidiary experiment, with the crystal tilted at some arbitrary angle (about 45°), showed for this crystal (which was the first to be measured) that the relevant turning points were the minima.

TABLE V. Magnetic susceptibility of single-crystal titanium at room temperature.

Specimen	Magnetic susceptibility μemu/g			
	$\chi_\parallel$	$\chi_\perp$	$\chi_\parallel - \chi_\perp$	χ_{av}
TRW	3.50_5	3.02_3	0.48_2	3.18_4
MRC-1	3.47_3	3.02_0	0.45_3	3.17_1
MRC-2	3.49_9	2.98_8	0.51_1	3.15_8
TC-1	3.52_7	3.00_6	0.52_1	3.18_0

$$\gamma_{BS} \propto (\tfrac{1}{3})\pi^2 k^2 [2n(E_F)] \quad . \tag{4}$$

If the units of χ_s, $n(E_F)$, and γ_{BS} are, respectively, μemu/mole, (eV atom)$^{-1}$, and mJ/mole deg^2, then

$$\chi_s / 13.71 = n(E_F)/0.212 = \gamma_{BS} \quad . \tag{5}$$

γ_{BS} may in turn be connected to the measured electronic specific-heat coefficient γ through an expression of the form $\gamma_{BS} = \gamma/(1+\gamma)$. In this ex-

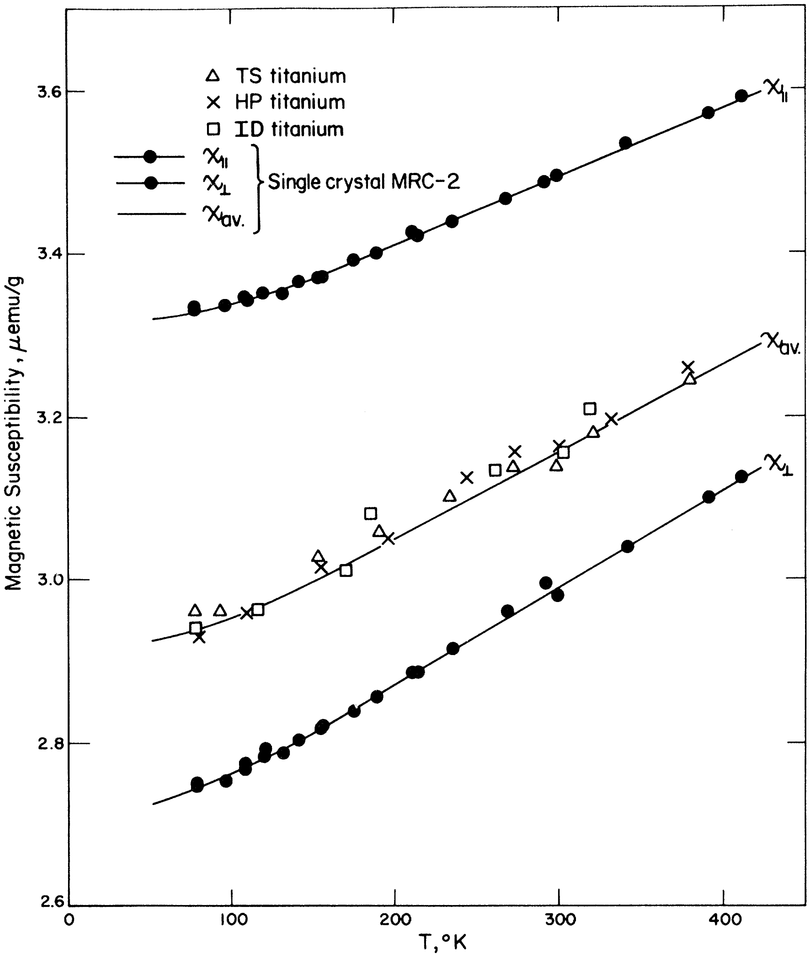

FIG. 3. Temperature dependences of susceptibility for polycrystalline titanium specimens, and the single-crystal MRC-2.

pression $\lambda \cong Vn(E_F)$ represents the influence of electron-electron and electron-phonon interactions,[16] where V is the pairing potential of the BCS[17] theory. Using an empirical technique described elsewhere,[18] based on calorimetric measurements of a series of titanium-alloy superconductors, an estimate of $\lambda = 0.18_5$ for pure hcp titanium has been derived. Equation (5) then yields a value for the spin paramagnetism $\chi_s = 39$ μemu/mole $= 0.81$ μemu/g.

As pointed out explicitly by Kubo and Obata[19] and by Mori,[20,21] the total susceptibility of a transition metal consists chiefly of the spin and orbital paramagnetic components. In fact, the latter, which is of magnitude $\chi_{orb} \sim (E_F/\Delta)\chi_s$, where Δ is the mean separation of levels connected by the orbital angular momentum, may, in general, be comparable to or even exceed χ_s. Taking $\chi_{av} = 139$ μemu/mole $= 2.9_0$ μemu/g for the total susceptibility at 0 °K (Fig. 3), we find $\langle \chi_{orb} \rangle_{av} = 100$ μemu/mole $= 2.0_9$ μemu/g, i.e., for hcp titanium $\langle \chi_{orb} \rangle_{av} = 2.5\chi_s$.

TABLE VI. Temperature coefficient of susceptibility of titanium.

Specimen	Temperature range (°K)	$\frac{d\chi_{av}}{dT}$	$\frac{d\chi_{\parallel}}{dT}$ (μemu/g °K)	$\frac{d\chi_{\perp}}{dT}$
MRC-2	150–400	$+1.07\times10^{-3}$	$+0.84\times10^{-3}$	$+1.17\times10^{-3}$
a	150–400	$+1.07\times10^{-3}$		
b	300–600	$+1.1\ \times10^{-3}$		

[a] Slope common to the following: (i) $\chi(T)$ for the three specimens of polycrystalline titanium (TS, HP, and ID); (ii) $\chi_{av}(T)$ for MRC-2; (iii) the normalized data of Kohlhaas and Weiss (Ref. 14) in this temperature interval.

[b] Reference 2.

The results of calculations of χ_{orb}, for bcc and fcc transition metals, show considerable scatter, attributable to variations between the energy bands employed.[21] For vanadium, for example, theoretical values of χ_{orb} of 160–260 μemu/mole have been quoted.[20–22] Calculations for hcp metals are obviously even more difficult, and no theoretical values of χ_{orb} for hcp titanium appear to be available with which to compare the present results. Qualitatively, it is clear that $\chi_{\mathrm{orb}}(\mathrm{Ti}_{\mathrm{hcp}})$ will be sensitive to band structure and anisotropy.

B. Temperature Dependence of Susceptibility

Susceptibility temperature dependence was first considered theoretically by Stoner[23] and has subsequently been discussed by the Sheffield[5,24] and Nagoya[25] groups, and by others. The temperature dependence has frequently been attributed to an intrinsic thermal variation of the spin paramagnetism according to the relationship

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

first introduced by Stoner,[26] where n refers to $n(E)$. This equation expresses the influence of temperature on χ_s through the variation of both the Fermi energy and the width of the Fermi distribution, taking into consideration the shape of $n(E)$ in the vicinity of E_F. As confirmation of this approach, correlations between the signs of $\partial\chi/\partial T$ and the signs of $[(\partial^2 n(E)/\partial E^2)]_{E_F}$, derived from a rigid-band interpretation of electronic specific-heat data for sequences of transition-metal binary alloys, have frequently been cited. However a simple calculation will demonstrate that the curvatures present in such a rigid-band $n(E)$ profile are about two orders of magnitude too small to explain the observed values of $\partial\chi/\partial T$ through Eq. (6). But this particular difficulty is removed in going to a calculated $n(E)$ curve in which sufficiently narrow[27] minima and maxima seem to be available.[28]

Studies of susceptibility temperature dependences of transition-metal binary alloys, such as those referred to above (e.g., Ref. 24) and others,[29] show that $\partial\chi/\partial T$ is only slightly affected by alloying. But if we assume an electronic mean free path in a typical alloy of 100 Å and a Fermi velocity of 10^8 cm/sec, Heisenberg's principle predicts an uncertainty in electron-state energy of about $2\,kT$ at 400 °K.[30] But it is obvious that Eq. (6) is effective in the present context only if significant variations in $n(E)$ occur within a few kT of E_F, i.e., within the Fermi tail. Consequently, if the structure in $n(E)$ is itself smoothed out through the effect of alloying on the electronic mean free path, we must look to other mechanisms for an explanation of the observed susceptibility temperature dependence.

As pointed out in Sec. V A, the total paramagnetic susceptibility of hcp titanium contains a component $\chi_{\mathrm{orb}} > 2\chi_s$, which cannot be ignored as a possible contributor to susceptibility temperature dependence. The orbital paramagnetism $\chi_{\mathrm{orb}} \sim (E_F/\Delta)\chi_s$ represents a magnetic-field-induced polarization effect between energy states separated by $\Delta \gg kT$. χ_{orb} will not therefore be intrinsically temperature dependent. By the same token Δ, although it may be perturbed, is too large to be smeared out by alloying, which is an important requirement in the light of the experimental results for alloys. The results of the theoretical calculations of χ_{orb} for various cubic transition metals have shown it to be sensitive to the choice of band structure. For a given metal this in turn depends on, among other quantities, the lattice parameters. Accordingly, we make the suggestion that χ_{orb} contributes significantly to the temperature dependence of susceptibility of titanium through the influence of lattice thermal expansion on the band structure.

VI. SUMMARY

Low-temperature calorimetric experiments on pure polycrystalline titanium have yielded values of the electronic specific-heat coefficient ($\gamma = 3.36$ mJ/mole deg^2) and Debye temperature ($\Theta_D = 420$ °K) in accord with published data. Magnetic susceptibility measurements gave $\chi_{\mathrm{av}} = 3.17 \pm 0.01_5$ μemu/g which is in good agreement with an average of the relatively widely scattered published data. Room-temperature measurements by an original technique on practically perfect single crystals yielded $\chi_{\parallel} = 3.52_7$ and $\chi_{\perp} = 3.00_6$ μemu/g; the temperature dependence of χ_{av} in the range 150–400 °K was 1.07×10^{-3} μemu/g °K. The susceptibility at 0 °K is estimated, by extrapolation, to be approximately 2.9 μemu/g.

Using the measured γ, and an empirical estimate of 1.18_5 for $(1+\lambda)$, the electronic specific-heat enhancement factor discussed elsewhere,[18] a value was obtained for the spin paramagnetic susceptibility $\chi_s = 0.81$ μemu/g. Making the usual assumption that for transition metals the dominant components of the total susceptibility are χ_s and the orbital paramagnetism χ_{orb} we find $\langle\chi_{\mathrm{orb}}\rangle_{\mathrm{av}} \sim 100$ μemu/mole $= 2.0_9$ μemu/g.

In considering the temperature dependence of susceptibility, we drew attention to the frequently discussed correlation [with reference to a sequence of transition-metal binary alloys with monotonically increasing electron-to-atom ($\mathfrak{z}$) ratios] between the sign of $\partial\chi/\partial T$ and the sign of the curvature of γ versus $\mathfrak{z}$. If the specific-heat data are interpreted as representing a rigid-band density-of-states curve, the association of positive $\partial\chi/\partial T$'s with minimum values of γ (and the converse of this) has traditionally been accepted as confirmation of the equation

$$\chi_s = 2\mu_B^2 n(E_F)\left\{1+\tfrac{1}{6}\pi^2(kT)^2\left[\frac{1}{n}\frac{\partial^2 n}{\partial E^2}-\left(\frac{1}{n}\frac{\partial n}{\partial E}\right)^2\right]_{E_F}\right\}, \qquad n\equiv n(E)$$

with the temperature dependence ascribed to χ_s. We point out, however, that for Ti, and possibly for other transition metals, the curvature required to achieve the measured temperature dependence is several orders of magnitude greater than that provided by the rigid-band $n(E)$ curve. A calculated $n(E)$ curve may in principle provide the necessary structure – a minimum of width $\sim 5\times 10^{-3}$ Ry, with E_F situated within it, thus satisfying the conditions implicit in the above equation – but even so, such fine structure would not survive alloying, with its smearing effect on the energies of the electron states. It was concluded, therefore, that the temperature dependence of susceptibilities observed in Ti, as well as some of its alloys, must be associated with energy intervals large compared to kT. Consequently, a mechanism other than direct thermal excitation of electron states must be sought to explain the temperature dependence. For titanium in particular, the largest contribution to the total susceptibility is the orbital paramagnetism $\chi_{\text{orb}} \sim N\mu_B^2/\Delta$, where $\Delta \gg kT$ is a band gap. χ_{orb} is obviously not intrinsically temperature dependent. However we suggest that, relying as it does on band structure and consequently on the crystal lattice, χ_{orb} is responsible (a) for the paramagnetic anisotropy of hcp Ti and (b) for the susceptibility temperature dependence through the influence of lattice expansion.

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[7] The presence of a cluster of randomly oriented subgrains, for example, in an otherwise perfect crystal, would reduce $\chi_\parallel$ (apparent), increase $\chi_\perp$ (apparent), so as to leave $\chi_{\text{av}} = \frac{1}{3}[\chi_{\parallel(\text{app.})} + 2\chi_{\perp(\text{app.})}]$ unchanged.

[8] The MRC material was purchased from Materials Research Corporation. MRC-2 was a more nearly perfect crystal than MRC-1, as evidenced by Laue back-reflection photography and the susceptibility results themselves (Table V). TC-1 was grown and kindly given by T. R. Cass, Martin-Marietta Corporation, Fla.

[9] This material was kindly supplied, through P. C. Gehlen, by M. F. Amateau, Materials Research and Development Equipment Group Laboratories, TRW, Inc.

[10] Honda-Owen plots (susceptibility versus $1/H$, Ref. 11) showed TRW to be free of detectible ferromagnetic contamination. Assuming the analyzed Fe to be uniformly distributed and therefore present in the actual specimen measured, it must have been in solution. Dissolved iron has not been definitely shown to support a local moment in titanium [e.g., R. R. Hake, D. M. Leslie, and T. G. Berlincourt, Phys. Rev. 127, 170 (1962)], but could possibly have the effect of increasing the electron-to-atom ratio, and hence increasing the resultant susceptibility. The average susceptibility value indicates that this effect more than offsets any decrease in susceptibility due to dissolved oxygen. As for the oxygen itself, on the basis of Ref. 6, 0.2-wt% oxygen would decrease the susceptibility by 0.02 μemu/g. The more usual oxygen concentrations of 0.04–0.08 wt% (see analyses for ID and TS titanium) would have a negligible effect.

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[27] To account for the measured average $\partial\chi/\partial T$ for pure titanium using Eq. (6), E_F must be situated at a minimum in $n(E)$ of "width" of the order 5×10^{-3} Ry.

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[30] With mean free path ~ 100 Å and a Fermi velocity of 10^8 cm/sec we find $\tau\sim10^{-14}$ sec, leading to $\Delta E\sim\hbar/\tau\sim5\times10^{-3}$ Ry.

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New Potential Function for Atomic and Solid-State Calculations*

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An expression for the potential energy of an isolated atom or a solid as a functional of the electron density is proposed. A one-electron potential function is derived from it by means of the variational principle. It has the correct asymptotic form at large radii in the case of atoms and ions. It also gives the correct total energy of the low-density electron gas. Calculations of binding energies of electrons in negative ions and of the bulk properties of some simple solids are given as examples of applications.

INTRODUCTION

The free-electron approximation for exchange[1-4] has been much used in recent years for atomic and band-structure calculations. The variational formulation,[2] which we want to consider here, consists in approximating the potential energy of the interelectron interaction with the classical Coulomb energy of the electron charge distribution and an exchange term based on the Hartree-Fock theory of the degenerate electron gas:

$$\frac{e^2}{2}\int|\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)|^2\sum_{i\neq j}\frac{1}{r_{ij}}\,d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_N$$
$$\to\frac{e^2}{2}\iint\frac{\rho(\vec{x}_1)\rho(\vec{x}_2)}{|\vec{x}_1-\vec{x}_2|}\,d\vec{x}_1d\vec{x}_2$$
$$-\frac{3e^2}{4\pi}\int\rho(\vec{x})\,[3\pi^2\rho(\vec{x})]^{1/3}d\vec{x},\tag{1}$$

where
$$\rho(\vec{x})=\int|\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)|^2\times\sum_i\delta(\vec{x}-\vec{r}_i)\,d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_N\tag{2}$$

is the electron density. Then variation of the (approximate) total energy, subject to the usual normalization condition, gives an equation for the wave function

$$\sum_i h(\vec{r}_i)\psi=E\psi,\tag{3}$$

with
$$h(\vec{r})=-\hbar^2\nabla^2/2m-Ze^2/r+e^2\int\rho(\vec{r}\,')/|\vec{r}-\vec{r}\,'|\,d\vec{r}\,'-e^2[3\pi^2\rho(\vec{r})]^{1/3}/\pi,\tag{4}$$

which may be solved by separation of variables. By this means, a set of one-electron equations,

$$h(r)\varphi_n(\vec{r})=\epsilon_n\varphi_n(\vec{r}),\tag{5}$$

is obtained. One recognizes in $h(\vec{r})$ the potential of the nucleus (for the moment we consider only the isolated atom), the potential of the electron charge distribution, and the free-electron exchange potential.

For the ground states of neutral atoms this prescription works very well[4,5] giving orbital functions very close to those obtained by the much more complicated Hartree-Fock method. It is clear, however, that cases will arise in which the same good results will not be obtained as the potential function has the wrong asymptotic form at large radii, going to zero exponentially rather than as $1/r$ as it should. To remedy this situation, the