Magnetic susceptibility of d-band transition metals that are not magnetically ordered

É. V. Galoshina

Institute of Metal Physics, Ural Scientific Center, USSR Academy of Sciences
Usp. Fiz. Nauk **113**, 105–128 (May 1974)

Questions associated with the magnetic susceptibility of the d-band transition metals that are not magnetically ordered, i.e., that are neither ferromagnets nor antiferromagnets, are reviewed. The principal components of the magnetic susceptibility of the transition metals are discussed, theoretical estimates of these components and of the total paramagnetic susceptibility are presented for individual metals, the experimental results on the susceptibility of the transition metals and on the temperature dependence are collected, and methods used to resolve the susceptibility into its individual components are described. The results of studies of the susceptibility of single crystals with the hcp structure are analyzed. The experimental results are compared with theoretical estimates.

CONTENTS

INTRODUCTION

Those d-band transition metals[1] that do not exhibit magnetic ordering, i.e., that are neither ferromagnets nor antiferromagnets, can be somewhat arbitrarily included among the so-called "Pauli" paramagnets. This classification is customary even today, despite the fact that the spin paramagnetism accounts for only part of the observed magnetic moment of these metals.

The paramagnetism of the transition metals differs essentially from that of the normal metals that form the classic example of "Pauli" paramagnets (e.g., alkali or alkaline earth metals). First, the molar paramagnetic susceptibility is an order of magnitude larger for d-band transition metals than for normal metals ($\chi_{alk.met.} \sim 10^7$ emu/mole and $\chi_{trans.met.} \sim 10^8$ emu/mole). A certain regularity is observed in the changes of the susceptibility on going from metal to metal as the d band is being filled: metals with odd numbers of d electrons per atom have larger susceptibilities than metals with even numbers of them; this rule does not hold for metals having more than five d electrons per atom (see Table I). The temperature dependence of the susceptibility is appreciably stronger for transition metals than for normal metals. Moreover, an alternation in the signs of the temperature coefficient of the susceptibility ($d\chi/dT$) in the d-band metals of the first half of each transition series has been observed: $d\chi/dT$ is negative (positive) for metals having larger (smaller) susceptibilities. This alternation does not take place for metals having more than four d electrons per atom.

These characteristics of the magnetic susceptibility of the transition metals were discovered comparatively early[1-5] but they have still received only qualitative explanations. This is due to the fact that the observed magnetic susceptibility is actually determined by the sum of the separate magnetic moments of the conduc-

tion electrons and the ion cores, which cannot be measured independently. Recently, however, a number of papers have been published[6-9] in which attempts have been made to separate the individual components of the magnetic susceptibility by analyzing a group of diverse phenomena: electronic specific heat, magnetic susceptibility, nuclear magnetic resonance, etc. The conduction electrons, because of their spin and orbital magnetic moments, make a paramagnetic contribution to the susceptibility, while the closed shells of the ion cores make a considerably smaller diamagnetic contribution. Since the susceptibility of weakly magnetic transition metals is determined mainly by the conduction electrons, it depends strongly on the band structure. Estimates of the individual components of the magnetic susceptibility or of the total susceptibility have been made for certain d-band metal crystals on the basis of calculated electron energy spectra.

The last review article on the susceptibilities of transition metals was published in 1962 by Vonsovskiĭ and Izyumov[5]. Since then many papers have been published in which calculations of the susceptibility of individual metals on the basis of known electron energy spectra are discussed. Both theoretical and experimental evidence has been found that the orbital paramagnetism of the d electrons makes an important contribution to the susceptibility of transition metals. Studies of single-crystal specimens have revealed the anisotropy of the magnetic susceptibility of transition metals with hcp structure. It would therefore seem useful to review this field again, collecting the experimental data on the magnetic susceptibility of weakly magnetic d-band transition metals and on its temperature dependence, comparing the measured quantities with the results of theoretical calculations, discussing methods of distinguishing experimentally between the different components of the magnetic susceptibility, and pointing out the specific features of the magnetic sus-

TABLE I. Electron configuration, molar susceptibility (χ), sign of the temperature coefficient of the susceptibility ($d\chi/dT$), and the calculated susceptibility (χ_{calc}) for transition metals

Metal	Electron configuration	$\chi \cdot 10^6$, emu/mole	Sign of $d\chi/dT$ *)	$\chi_{calc} \cdot 10^6$, emu/mole**)
Scandium	$3d^1 4s^2$	264 [13]	— (4—1800 °K)	—
Titanium	$3d^2 4s^2$	155 [13]	+ (4—1800 °K)	161.4
Vanadium	$3d^3 4s^2$	300 [13]	— (4—1800 °K)	—
Yttrium	$4d^1 5s^2$	183 [14]	+ (<300 °K), — (300—800 °K)	—
Zirconium	$4d^2 5s^2$	129 [15]	+ (20—1500 °K)	171.2
Niobium	$4d^3 5s^2$	212,1 [16]	— (7—1875 °K)	182.4
Molybdenum	$4d^5 5s^1$	89,2 [16]	+ (7—1875 °K)	214.7
Technetium	$4d^5 5s^2$	270 [17]	— (7—1875 °K)	379.4
Ruthenium	$4d^7 5s^1$	39,2 [18]	+ (80—1850 °K)	276.1
Rhodium	$4d^8 5s^1$	107 [18]	+ (80—1850 °K)	290.6 287.6
Palladium	$4d^{10}$	550 [18]	+ (<80 °K), — (80—1850 °K)	143.3 205.1
Lutecium	$5d^1 6s^2$	336 [19]	— (80—1000 °K)	—
Hafnium	$5d^2 6s^2$	70 [15]	+ (20—1500 °K)	124.6
Tantalum	$5d^3 6s^2$	162 [16]	— (7—1875 °K)	147.7
Tungsten	$5d^4 6s^2$	53,3 [16]	— (7—1875 °K)	199.2
Rhenium	$5d^5 6s^2$	68,7 [16]	+ (80—1850 °K)	370.6
Osmium	$5d^6 6s^2$	13,1 [18]	— (80—1850 °K)	299.5
Iridium	$5d^7 6s^2$	24,1 [18]	— (80—1850 °K)	349.1 344.9
Platinum	$5d^9 6s^1$	192 [18]	— (80—1850 °K)	198 265

*The increase in the susceptibility observed for certain metals at low temperature (near 30–40°K) is not taken into account in the table because it is due to ferromagnetic impurities in the investigated specimens [20].

**The χ_{calc} values were taken from [66] and computed on the basis of the energy spectrum calculated by Yamashita et al. [67]. When two χ_{calc} values are given for the same metal the first was computed on the basis of the energy spectra calculated by Friedel et al. [68].

ceptibility of d-band transition metals that have not yet found their theoretical explanation.

1. PRINCIPAL COMPONENTS OF THE MAGNETIC SUSCEPTIBILITY OF TRANSITION METALS

We shall begin our consideration of the principal components to be taken into account in analyzing the magnetic susceptibility of transition metals with a discussion of the spin paramagnetism and various interactions that lead to its enhancement.

a) Spin paramagnetism of the conduction electrons. The polarization of the conduction-electron spins that takes place when the metal is placed in a magnetic field changes the free energy of the conduction electrons and gives rise to spin susceptibility ("Pauli" paramagnetism). In the band theory, the spin susceptibility of free electrons is related to the density of states at the Fermi level, $N(E)_{E=E_F}$, by the formula

$$\chi_{sp}^{band\ th.} = 2\mu_B^2 N(E)_{E=E_F}, \qquad (1.1)$$

where μ_B is the Bohr magneton and $N(E)_{E=E_F}$ is counted for one spin direction. Except for a constant factor, $N(E)_{E=E_F}$ is equal to the coefficient γ of T in the expression for the electronic specific heat:

$$\gamma = \frac{\pi^2 k^2}{3} N(E)_{E=E_F}, \qquad (1.2)$$

where k is Boltzmann's constant.

The spin susceptibility χ_{sp} is temperature independent in the first approximation, but if one takes into account the thermal broadening of the sharp Fermi distribution function, which leads to a change in the density of states $N(E)$ near the Fermi energy E_F, one finds a weak quadratic temperature dependence:

$$\chi_{sp}(T) = 2\mu_B^2 N(E)_{E=E_F} \left\{ 1 + \frac{\pi^2}{6} \left[\frac{N''(E)_{E=E_F}}{N(E)_{E=E_F}} - \left(\frac{N'(E)_{E=E_F}}{N(E)_{E=E_F}} \right)^2 \right] k^2 T^2 \right\}, \qquad (1.3)$$

where $N'(E)_{E=E_F}$ and $N''(E)_{E=E_F}$ are the first and second energy derivatives of the density of states at $E = E_F$. It is evident from (1.3) that the sign of the temperature coefficient of the susceptibility ($d\chi/dT$) for metals whose $N(E)$ curve has a complicated shape must depend on the position of the Fermi level with respect to that curve.

In the band theory, the peculiarities of the susceptibility of transition metals noted in the introduction are qualitatively explained by peculiarities of the spin paramagnetism associated with specific features of the band structure. The point is that in transition metals there is not only an unfilled s band, but also an unfilled d band. Since the energies of the nd and (n + 1)s levels of transition-metal atoms are close together, these bands overlap. The density of states is considerably higher in the d band than in the s band since the d band is the narrower and contains five states per atom (not counting the spin degeneracy) while the much wider s band contains only one state per atom. In transition metals the Fermi level lies below the top of the d band, so the peculiarities of the d band have their effect on such properties of the transition metals as are sensitive to the density of states at the Fermi level. This is especially evident from the fact that the transition metals have higher electronic specific heats than normal metals. The shape of the density-of-states curve $N(E)$ for metals of a single transition series can be derived from data on the electronic specific heats of the pure metals and alloys of neighboring metals in the series by analyzing those data in terms of the rigid-band model. This is a very crude approximation, but it provides a qualitative picture of the band structure that leads to an obvious explanation[4,10] of certain features of the susceptibility of transition metals.

Figures 1 and 2 show density-of-states curves $N(E)$ for the 3d-, 4d-, and 5d-band transition series as derived in[11,12] on the basis of the rigid band model from data on the electronic specific heats of the pure metals and alloys. The $N(E)$ curves consist of maxima and minima following one another. The position of the Fermi level E_F with respect to the $N(E)$ curve varies in a regular manner from metal to metal in a single transition series: for metals having an odd (even) number of d electrons, E_F lies close to a maximum (minimum) on the $N(E)$ curve. Metals having an odd number of d electrons accordingly have higher susceptibilities than metals having an even number of them.

The shape of the $N(E)$ curve near E_F also determines the sign of $d\chi/dT$, the temperature coefficient of the magnetic susceptibility. Since in the pure metals E_F lies close to an extremum of the $N(E)$ curve where the first derivative $N'(E)_{E=E_F}$ vanishes, the sign of $d\chi/dT$ will be determined by the sign of the second derivative $N''(E)_{E=E_F}$ (see Eq. (1.3)). If E_F lies close to a maximum (minimum) on the $N(E)$ curve, then $N''(E)_{E=E_F}$, and therefore also $d\chi/dT$, will be negative (positive). This explains the change in the sign of $d\chi/dT$ on going from one transition metal to its neighbor in the same series.

The values of the spin susceptibility and the temperature coefficients as estimated from the band theory differ considerably from the experimental values. For most of the metals, the spin susceptibility calculated from Eq. (1.1) using $N(E)_{E=E_F}$ values taken from
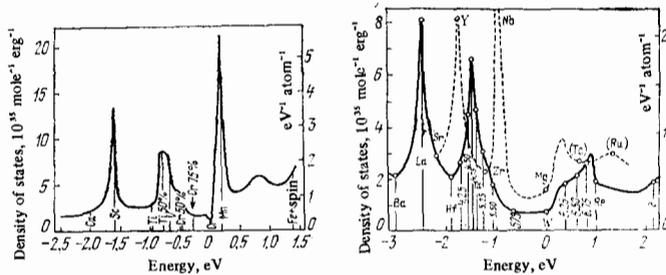
FIG. 1   FIG. 2

FIG. 1. Density of states vs energy for metals of the first transition series as derived in [11] from electronic specific heat data.

FIG. 2. Density of states vs energy for metals of the second and third transition series as derived in [12] from electronic specific heat data.

TABLE II. Electronic specific heat coefficient (γ), "band theory" susceptibility ($\chi_{sp}^{band\ th}$), and calculated spin susceptibility (χ_{sp}^{calc}) for transition metals

Metal	γ, mJ/deg² mole	$\chi_{sp}^{band\ th} \cdot 10^6$, emu/mole	$\chi_{sp}^{calc} \cdot 10^6$, emu/mole[62]**
Scandium	10.717 [21]	144	—
Titanium	3.36 [22]	45.3	79
Vanadium	9.26 [23]	125	—
Yttrium	8.75 [24]	118	—
Zirconium	2.81 [25]	38	78.7
Niobium	7.8 [26]	105	31.4
Molybdenum	2.0 [27]	28	32.5
Technetium	8.3 [28]	112	114.9
Ruthenium	3.04 [29]	41.30 *)	93.5
Rhodium	4.65 [30]	62	100 / 108.7
Palladium	9.40 [31]	127	66.8 / 111.2
Lutecium	11.27 [32]	152	—
Hafnium	2.146 [21]	29	78.2
Tantalum	5.9 [33]	80	36.4
Tungsten	0.84 [34]	11	33.9
Rhenium	2.29 [35]	31	89.7
Osmium	2.3 [36]	31.22 *)	88
Iridium	3.27 [37]	44.32 *)	99.7 / 110.2
Platinum	6.56 [38]	88	63.6 / 90.8

*Corrected for the electron-phonon enhancement of the electronic specific heat.

**See the second footnote to Table I.

electronic specific heat data is 2—3 times lower than the measured paramagnetic susceptibility (Tables I and II). Ruthenium, osmium, and iridium are exceptions; for these metals the calculated susceptibility is higher than the measured value.

The electron-phonon interaction that takes place in metals appreciably enhances the specific heat coefficient γ.[39] Hence the true value of $N(E)_{E=E_F}$, and therefore also the value of the spin susceptibility, is lower than the corresponding value calculated from γ. When the spin susceptibility calculated from γ is higher than the measured paramagnetic susceptibility one may correct for the electron-phonon enhancement of the electronic specific heat coefficient (see Table II).

The lack of quantitative agreement between the measured susceptibility and the value calculated on the band theory for free electrons can be explained on the assumption[40] that the Bohr magneton should be replaced in Eq. (1.1) for the Pauli magnetic susceptibility by a certain effective value μ^* that would take into account to a certain extent the interactions between the conduction electrons. Thus, Stoner[41] suggested that there may be a positive exchange interaction between the conduction electrons in a metal that would increase the spin susceptibility by a quantity β formally equivalent to the Weiss molecular field:

$$\frac{1}{\chi_{meas}} = \frac{1}{\chi_{sp}^{band\ th}} - \beta. \tag{1.4}$$

Estimates of the exchange interaction parameter obtained by comparing the measured and "band theory" susceptibilities give values of ~2 eV for the transition metals. This is comparable in order of magnitude with the exchange interaction in ferromagnetic metals, but the Fermi distribution of the conduction electrons prevents the establishment of magnetic ordering.

The interelectron interactions have been taken into account in calculations of the spin susceptibility only for alkali metals[42,43]; both the exchange interaction and the correlation effects (the electron-electron interaction after subtraction of the exchange interaction) were taken into account in these calculations. The exchange interaction increases the spin susceptibility, while the correlation effects act in the opposite direction. Taking these effects into account together improves considerably the agreement between the measured and calculated spin susceptibilities for lithium, sodium, and potassium. In some calculations of the susceptibilities of the transition metals[8,44] it was assumed that the exchange and correlation effects cancel one another out, while in other calculations[45] it was assumed that the exchange effects among the d electrons in the metals lying at the ends of the transition series (palladium and platinum) are large and are not cancelled out by the correlation effects. Attempts have been made[46] to establish the form of the exchange enhancement of the susceptibility of a transition metal having two conduction bands (electron and hole) without making any quantitative estimates.

The spin-orbit interaction also enhances the spin paramagnetism somewhat. The spin-orbit susceptibility χ_{sp-orb} is smaller than χ_{sp} by a factor of λ/Δ, where λ is the spin-orbit interaction parameter and Δ is the mean width of the d band. According to some calculations[47,48] χ_{sp-orb} makes significant contributions to the susceptibilities of palladium and platinum.

b) Orbital paramagnetism of the d electrons. In analyzing the magnetic susceptibility of transition metals it was formerly assumed that the orbital magnetic moment was quenched, its contribution to the susceptibility being negligible. Theoretical studies have shown[44], however, that the orbital magnetic moment of electrons in partly filled degenerate bands described by nonspherical wave functions contributes a Van Vleck term to the susceptibility, which is comparable in magnitude with the spin susceptibility.

It has been assumed[49,50] that the Van Vleck "high-frequency" orbital contribution to the paramagnetic susceptibility of transition metals is due to the reduction in the energy of the occupied electron levels by the action of the perturbation energy $-\mu_B \hat{\mathbf{L}} \cdot \mathbf{H}$, where $\hat{\mathbf{L}}$ is the orbital angular momentum operator and $\mathbf{H}$ represents the external magnetic field. If the magnetic field is parallel to the z axis the perturbation operator can be written in the form $V = -\mu_B H \hat{L}_z$.

The change in the energy of an arbitrary state i as a result mixing with state j via the perturbation V can be expressed in the form

$$\delta E_i = \frac{|\langle j|\hat{V}|i\rangle|^2}{E_i - E_j} = \frac{\mu_B^2 H^2 |\langle j|\hat{L}_z|i\rangle|^2}{E_i - E_j} \delta s_i \delta s_j; \tag{1.5}$$

here the δ symbol indicates that the interaction takes place only for electrons with opposite spins. If both the

states i and j are occupied, or if both are unoccupied, we have $\delta E_j = 0$. Hence the change in the total energy is the sum over all the occupied states i or all the unoccupied states j. In a metal at $0°K$ the states in each band are either doubly occupied or doubly empty. If the spin-orbit interaction can be neglected, the double occupation simply results in doubling the total perturbation energy, i.e., the operator $\hat{L}_z$ can couple states having the same reduced wave vector k. Then expression (1.5) for the change in the energy of the metal takes the form

$$\delta E = 2\mu_B^2 H^2 \sum_i \sum_j \int \frac{f_i(1-f_j)}{E_i-E_j} |\langle k, j|\hat{L}_z|k, i\rangle| d^3k, \qquad (1.6)$$

where the wave vector k labels the states, the numbers i and j label the bands, and $f_{i,j}$ represent the Fermi distribution function. The orbital paramagnetic susceptibility per atom has the form

$$\chi_{orb} = 4N\mu_B^2 \sum_{i,j} \overline{\frac{f_i(1-f_j)}{E_i-E_j} |\langle k, j|\hat{L}_z|k, i\rangle|^2}, \qquad (1.7)$$

where N is Avogadro's number and the bar indicates averaging in k space.

It is very difficult to calculate χ_{orb} for individual metals with this formula, so a simpler formula, in which χ_{orb} is expressed in terms of the width and relative filling of the d band, has been proposed[39,51,52] for estimating the orbital paramagnetism of the d electrons:

$$\chi_{orb} \approx 2\mu_B^2 \frac{n(10-n)}{5\Delta}, \qquad (1.8)$$

where n is the number of d electrons, and Δ is the mean energy separation between the vacant levels i and filled levels j for which the matrix elements of $\hat{L}_z$ do not vanish.

The calculation of the orbital susceptibility is of great theoretical interest since χ_{orb} is determined by the energy parameter Δ whose value is of the order of the width of the d band. Calculations[53,54] of the orbital susceptibility as a function of the d-electron Fermi energy for lattices of various types have shown that the orbital contribution is greatest for metals lying near the middle of the d band (Figs. 3 and 4); this corresponds to the largest values of the quantity $n(10-n)$ in Eq. (1.8). In calculating χ_{orb}, the width Δ of the d band was taken as ~ 2.67 eV for fcc metals (from the calculation of the energy spectrum of nickel[55]), and as ~ 6.3 eV for bcc metals (from the calculation of the energy spectrum of iron[56]). At equal d-electron concentrations, χ_{orb} is about twice as large for fcc metals as for bcc ones. Taking hybridization of the d band with the s and p bands into account leads to a general broadening of the $\chi_{orb}(E)$ curves and to a $\sim 25\%$ decrease in the values of χ_{orb}. The calculated values of χ_{orb} are very sensitive to the spectrum used in the calculation[6].

c) Diamagnetic susceptibility. The diamagnetic component of the susceptibility is due to the diamagnetism of the filled shells and the conduction electrons. In analyzing the magnetic susceptibility of transition metals one usually takes into account only the ionic diamagnetism by adding tabulated values of the susceptibility of the corresponding ion (Table III) to the measured susceptibility. One neglects the diamagnetism of the conduction electrons since in the transition metals it is the d electrons, which have a large effective mass,
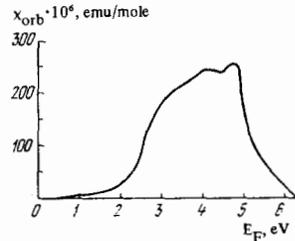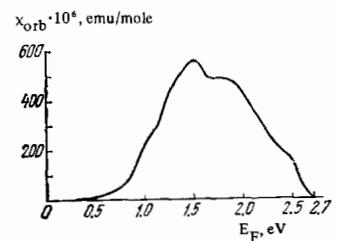

FIG. 3   FIG. 4

FIG. 3. Orbital paramagnetic susceptibility χ_{orb} vs Fermi energy for d-band metals with fcc structure. [54]
FIG. 4. Orbital paramagnetic susceptibility χ_{orb} vs Fermi energy for d-band metals with bcc structure. [54]

TABLE III. Diamagnetic susceptibility of the ion core (χ_{ion}), experimental estimates of the exchange interaction constant (α), and the calculated spin-orbit susceptibility (χ_{sp-orb}^{calc})

Metal	$\chi_{ion} \cdot 10^6$, emu/mole [57]	$\alpha \cdot 10^{-4}$, mole/emu	$\chi_{sp-orb}^{calc} \cdot 10^6$, emu/mole[62]
Scandium	6	—	—
Titanium	5	0.82 [11]	−10.8
Vanadium	4	0.52 [11]	—
Yttrium	12	—	—
Zirconium	10	0; 0.63 [58, 59]	−2.5
Niobium	9	0.21; 0.09 [59, 16]	−13.7
Molybdenum	7	0 [16, 59]	−0.5
Technetium	—	—	36.7
Ruthenium	18	—	17.0
Rhodium	18	1.33; 0.58 [58, 60]	35
			61
Palladium	18	10.85 [59]	45
			42
Hafnium	16	0; 0.876 [12]	−60
Tantalum	14	0 [12, 16]	−37.8
Tungsten	13	0; 3.06 [16, 12]	2.3
Rhenium	12	0; 1.78 [12]	59.9
Osmium	11	—	36.5
Iridium	20	—	78
			112
Platinum	28	0.62—0.66 [61]	83
			85

that play the principal part in producing the magnetic moment.

The expression for the diamagnetic susceptibility of the conduction electrons in the lattice[62] (neglecting interband transitions) contains a polynomial in the ratio of the effective masses:

$$\chi_{dia}^e = -\frac{e^2}{6} \sum_{k_1, k_2} \left[\frac{\partial^2 E}{\partial k_1^2} \frac{\partial^2 E}{\partial k_2^2} - \left(\frac{\partial^2 E}{\partial k_1 \partial k_2} \right)^2 \right] \frac{\partial f_0(E)}{\partial E} \qquad (1.9)$$

$$\approx \mu_B^2 N(E)_{E=E_F} \left[-\frac{1}{3} \left(\frac{m^0}{m^*} \right)^2 \right],$$

where e is the electron charge, $f_0(E)$ is the electron distribution function, m^0 is the mass of a free electron, and m^* is the effective mass of an electron in the lattice. For free electrons, the diamagnetic susceptibility is one-third of the paramagnetic susceptibility (Eqs. (1.1) and (1.9) with $m^* = m^0$):

$$\chi_{dia}^{free} = -\frac{1}{3} \chi_{sp}. \qquad (1.10)$$

Moreover, the paramagnetism of the s electrons is about ten times smaller than that of the d electrons ($\chi_{alk.met.} \sim 10$, $\chi_{trans.met.} \sim 100$ μemu/mole). Hence if we assume that the effective mass of an s electron is close to the mass of a free electron we may neglect the diamagnetism of the s electrons[2].

Equation (1.10) does not hold for the d electrons. The effective mass of a d electron is considerably larger than the free-electron mass ($m_d^* \gg m^0$) so the diamagnetic susceptibility of the d electrons is small and can be neglected, as in the case of the s electrons.

2. THEORETICAL ESTIMATES OF THE INDIVIDUAL COMPONENTS AND THE TOTAL PARAMAGNETIC SUSCEPTIBILITY FOR TRANSITION METALS

Now let us consider theoretical estimates of the paramagnetic susceptibility of transition metals. A number of investigators[63-69] have given expressions for the total magnetic susceptibility of free electrons, but they are so complicated that it still seems impossible to use them for estimating. Kubo and Obata[44] gave simpler expressions in the tight-binding approximation for the paramagnetic part of the susceptibility of the conduction electrons. This part of the susceptibility was expressed as the sum of three terms: the spin paramagnetism of the conduction electrons (χ_{sp}), the Van Vleck orbital paramagnetism (χ_{orb}), and the paramagnetic part of the susceptibility due to spin-orbit coupling (χ_{sp-orb}):

$$
\left.
\begin{aligned}
\chi_{sp} &= 2\mu_B^2 \sum_{n,n'} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{f(E_n(\mathbf{k})) - f(E_n(\mathbf{k}))}{E_{n'}(\mathbf{k}) - E_n(\mathbf{k})} \\
&\qquad \times \langle n\mathbf{k}|2\hat{S}|n'\mathbf{k}\rangle \langle n'\mathbf{k}|2\hat{S}|n\mathbf{k}\rangle, \\
\chi_{orb} &= 2\mu_B^2 \sum_{n,n'} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{f(E_n(\mathbf{k})) - f(E_{n'}(\mathbf{k}))}{E_{n'}(\mathbf{k}) - E_n(\mathbf{k})} \\
&\qquad \times \langle n\mathbf{k}|\hat{L}|n'\mathbf{k}\rangle \langle n'\mathbf{k}|\hat{L}|n\mathbf{k}\rangle, \\
\chi_{sp-orb} &= 2\mu_B^2 \sum_{n,n'} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{f(E_n(\mathbf{k})) - f(E_{n'}(\mathbf{k}))}{E_{n'}(\mathbf{k}) - E_n(\mathbf{k})} \\
&\qquad \times [\langle n\mathbf{k}|\hat{L}|n'\mathbf{k}\rangle \langle n'\mathbf{k}|2\hat{S}|n\mathbf{k}\rangle + \langle n\mathbf{k}|2\hat{S}|n'\mathbf{k}\rangle \langle n'\mathbf{k}|\hat{L}|n\mathbf{k}\rangle],
\end{aligned}
\right\} \quad (2.1)
$$

where μ_B is the Bohr magneton, $f(E_n(\mathbf{k}))$ and $f(E_{n'}(\mathbf{k}))$ are the Fermi distribution functions giving the probabilities for finding an electron in states with energies $E_n(\mathbf{k})$ and $E_{n'}(\mathbf{k})$, and the $\langle n\mathbf{k}|\hat{S}, \hat{L}|n'\mathbf{k}\rangle$ are the matrix elements for the spin and orbital angular momentum operators $\hat{S}$ and $\hat{L}$ between the states $n\mathbf{k}$ and $n'\mathbf{k}$.

To calculate the paramagnetic susceptibility one must also know the dispersion law $E(\mathbf{k})$ and the electron wave functions.

The formulas of Kubo and Obata have been used[47,48] to calculate the paramagnetic susceptibilities of many transition metals and transition-metal alloys having various crystal structures. The energy spectra of nickel, chromium, and cobalt, altered in the rigid band model in conformity with the particular metal, were used in the calculations. It is characteristic that for all the metals the calculated spin and orbital parts of the paramagnetic susceptibility were of the same order of magnitude, the orbital susceptibility of the d electrons being somewhat larger, as a rule, than the spin susceptibility of the conduction electrons (see Tables II and IV). The component of the paramagnetic susceptibility due to spin-orbit coupling was negligible as compared with χ_{sp} and χ_{orb} for all the metals except for five of the d-band transition metals, for which χ_{sp-orb} was considerable (see Table III). The calculations indicated a weak temperature dependence for all the components of the paramagnetic susceptibility (Figs. 5 and 6).

The calculated values of the spin and total paramagnetic susceptibilities of the transition metals are given in Tables I and II. The calculated spin susceptibility (Table II) differs from the band-model estimate, the calculated value being usually higher than the band estimate. In some cases (Mo, Tc, Pd, and Pt) the two values are virtually the same. The total paramagnetic susceptibilities calculated for metals close to the beginnings of the transition series (Ti, Zr, Nb, and Ta)

TABLE IV. Orbital paramagnetic susceptibilities: experimental values obtained by different methods, and theoretical estimates

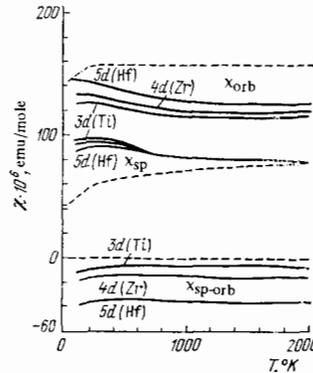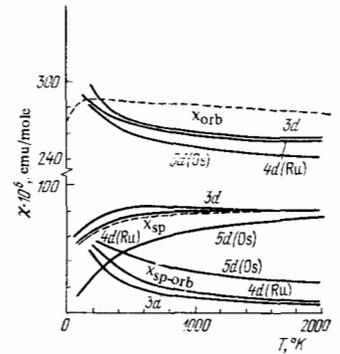| Metal	$\chi_{orb} \cdot 10^6$, emu/mole (Shimizu's method)	$\chi_{orb} \cdot 10^6$, emu/mole (Clogston's method)	$\chi_{orb} \cdot 10^6$, emu/mole (Theory)
Scandium	95 [52]	—	145 [62], 93 [62]
Titanium	73 [11], 113 [70]	—	—
Vanadium	178 [11]	200 [51]	183 [69], 146 [62], 75 [6]
Yttrium	75 [71]	—	—
Zirconium	110 [58], 69 [59]	—	95 [62]
Niobium	98 [72], 123 [16]	—	128 [69]
Molybdenum	60 [72], 82 [16]	110 [74]	182 [62]
Technetium	—	—	228 [62]
Ruthenium	18. 29 *) [73]	—	165 [62]
Rhodium	30 [16]	30 [60]	130, 144 [62]
Palladium	30 [16]	25 [75]	46 [6], 34, 48 [62]
Luttecium	41. 58 [12]	—	106 [62]
Hafnium	98 [12], 117 [16]	—	139 [62], 102 [6]
Tantalum	71 [16], 58. 67 [12]	96 [74]	163 [62], 113 [6]
Tungsten	4.69 [12]	—	221 [62]
Rhenium	—	—	175 [62]
Osmium	—	—	100, 110 [62]
Iridium	42. 28 [61]	30 [8]	63 [62]

FIG. 5   FIG. 6

FIG. 5. Calculated [48] temperature dependences of χ_{sp}, χ_{sp-orb}, and χ_{orb} for 3d-, 4d-, and 5d-band transition metals with the fcc structure and two d electrons per atom (Ti, Zr, and Hf). The dashed curves show the temperature dependences of χ_{sp} and χ_{orb} without correction for spin-orbit coupling.

(see Table I) are in satisfactory agreement with the experimental values. For the other metals, the calculated paramagnetic susceptibilities are considerably higher than the experimental values. This difference should be compensated to some extent by the diamagnetic contributions from the ion cores and the conduction electrons themselves.

Modern electron structure calculations are not so accurate as to lead one to expect quantitative agreement between the observed and calculated values of the susceptibility. It is very important, however, that the calculations give the correct order of magnitude for the paramagnetic susceptibility, for this would be evidence that the principal contributions to the susceptibility have been taken into account and correctly evaluated.

3. EXPERIMENTAL RESULTS

Now we shall consider the experimental data on the magnetic susceptibilities, and in Sec. 4 we shall also discuss the methods used to resolve the measured susceptibility into its individual components for comparison with the theoretical estimates discussed above.

The results of various measurements of the molar magnetic susceptibility and its temperature dependence for the transition metals are presented in Table I and Figs. 7—13.[3] As is evident from the figures, the general behavior of the susceptibility as a function of the temperature is about the same for the several metals

of a single group, although there are some discrepancies among the data from different sources on the magnitude of the molar susceptibility and the details of the $\chi(T)$ curves. These discrepancies are probably due to inadequate purity of the investigated specimens.

Now let us examine the experimental results for the several groups of transition metals in somewhat more detail:
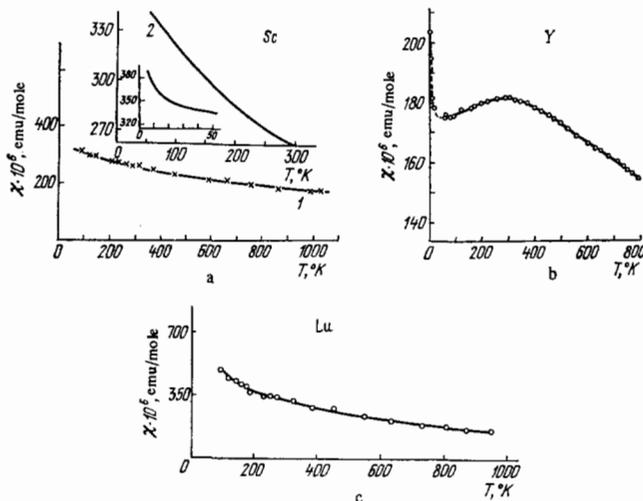

FIG. 7. Temperature dependence of the magnetic susceptibility of scandium (a) (curves 1 and 2 are from [76] and [13], respectively), yttrium [14] (b), and lutetium [19] (c).
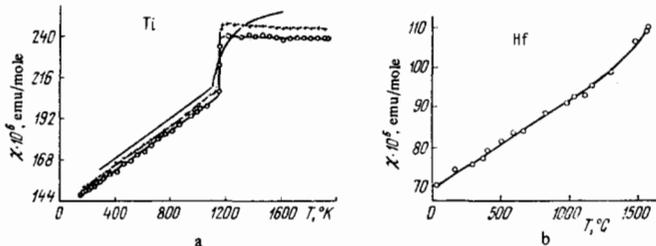

FIG. 8. Temperature dependence of the magnetic susceptibility of titanium (a) (according to data from various sources reported in [77]) and hafnium [78] (b).
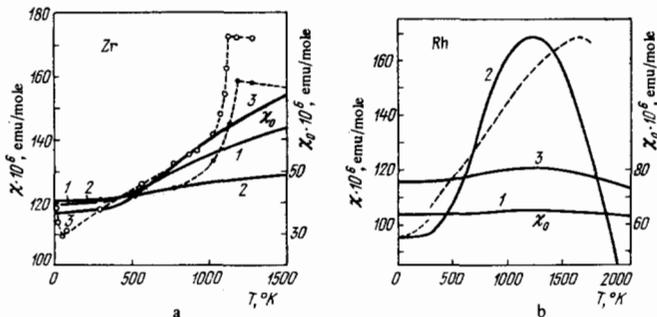

FIG. 9. Mangetic susceptibility of zirconium [79] (a) (1—calculated temperature dependence of the spin susceptibility $\chi_0(T)$, 2—total susceptibility calculated for $\alpha = -1.37 \times 10^4$ mole/emu and $\chi_c = 0.95 \times 10^{-4}$ emu/mole, 3—the same as curve 2 but for $\alpha = 0.37 \times 10^4$ mole/emu and $\chi_c = 0.71 \times 10^{-4}$ emu/mole; the other curves represent experimental data from different souces) and rhodium [79] (b) (1—calculated temperature dependence of the spin susceptibility $\chi_0(T)$, 2—total susceptibility calculated for $\alpha = 1.33 \times 10^4$ mole/emu and $\chi_c = 3.22 \times 10^{-4}$ emu/mole, 3—the same as curve 2 but for $\alpha = 0.7 \times 10^4$ mole/emu; the other curves represent experimental data from different sources).

a) **Group III metals** (Sc, Y, and Lu) (Fig. 7). For scandium and lutecium, $d\chi/dT < 0$ over the entire investigated temperature range. The magnetic susceptibility of yttrium passes through a maximum near $T = 300°$K; the nature of this maximum has not yet been established. Above $300°$K, $d\chi/dT < 0$ for yttrium, as for the other two metals of this group.

b) **Group IV metals** (Ti, Hf (Fig. 8), and Zr (Fig. 9)). For all these metals, $d\chi/dT > 0$. The $\chi(T)$ curves for titanium and zirconium each has a break at the temperature (1150 and 1130°K, respectively) of the phase transition from the hcp to the bcc structure. We note that there are some discrepancies between the values of the susceptibilities and the details of the $\chi(T)$ curves obtained for titanium and zirconium by different investigators. This is due to differences in the purity
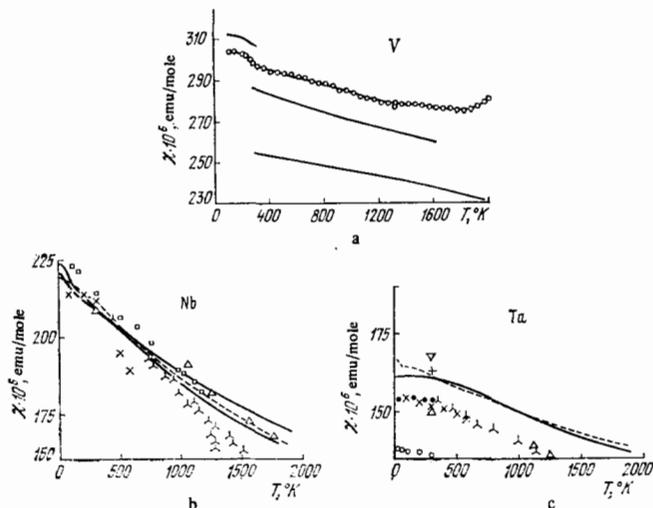

FIG. 10. Temperature dependence of the magnetic susceptibility of vanadium (a), niobium (b), and tantalum (c) according to data from various sources reported in [16].
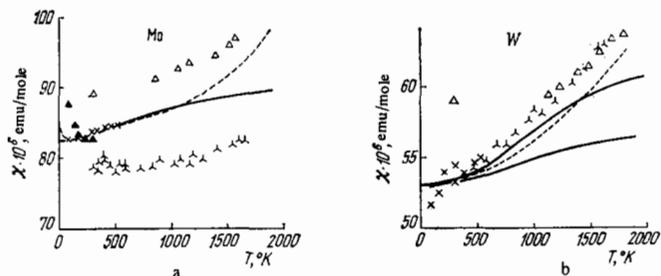

FIG. 11. Temperature dependence of the magnetic susceptibility of molybdenum (a) and tungsten (b) according to data from various sources reported in [16].
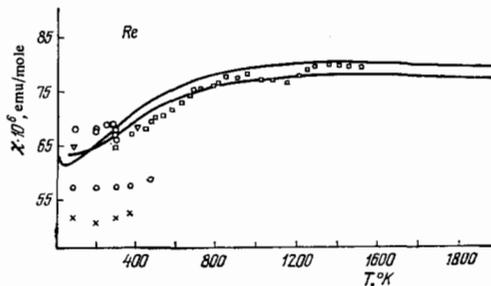

FIG. 12. Temperature dependence of the magnetic susceptibility of rhenium according to data from various sources reported in [16].
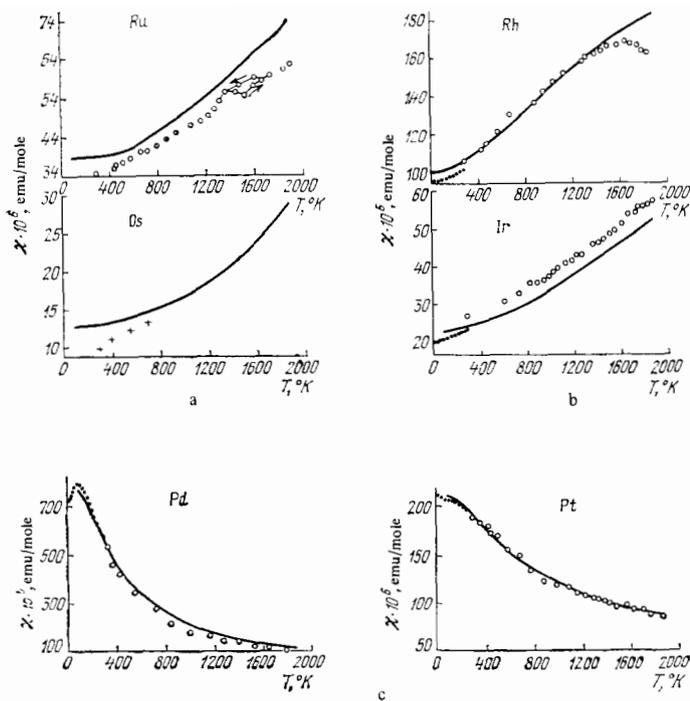
FIG. 13. Temperature dependence of the magnetic susceptibility of ruthenium and osmium (a), rhodium and iridium (b), and palladium and platinum (c) according to data from various sources reported in [18].

of the investigated metals and also, possibly, to texture of the specimens, since considerable anisotropy has been observed in the magnetic susceptibilities of transition metals with the hcp structure (see Sec. 5).

c) Group V metals (V, Nb, and Ta) (Fig. 10). For these metals $d\chi/dT$ is always negative and the $\chi(T)$ curves have no anomalies. However, the considerable discrepancies among the molar susceptibility data for vanadium and tantalum from different sources are striking. A considerable effect of the presence of oxygen in the specimens on the observed susceptibility of vanadium has been noted[9].

d) Group VI metals (Mo and W) (Fig. 11). These metals resemble the group IV metals in having $d\chi/dT$ > 0. For molybdenum and tungsten, as for the group V metals, there are considerable discrepancies between the measured molar susceptibility values from different sources.

e) Group VII metals (Tc and Re) (Fig. 12). Up to now, results on the temperature dependence of the susceptibility have been published only for rhenium; $d\chi/dT$ is positive. The results of different studies on the $\chi(T)$ curves are somewhat contradictory: some investigators[78] report a susceptibility minimum at high temperatures, while others[16] report a monotonic increase in the susceptibility.

f) Group VIII metals (Ru, Os, Rh, Ir, Pd, and Pt) (Fig. 13). For ruthenium, osmium, rhodium, and iridium, $d\chi/dT$ is positive in the investigated temperature range. However, the data from the several sources differ as regards the magnitude of the susceptibility and there are some differences in the shape of the $\chi(T)$ curve: for rhodium, at high temperatures, and for osmium, at low temperatures. According to some data[78] ruthenium exhibits hysteresis of the magnetic susceptibility, while according to other data[18] it does not.

For palladium and platinum $d\chi/dT$ is negative. The susceptibility of palladium has a maximum in the low-temperature region; this maximum has been attributed to peculiarities of the energy structure of the conduction band[7] and to peculiarities of the exchange interaction[80].

4. EXPERIMENTAL METHODS FOR SEPARATING THE SUSCEPTIBILITY COMPONENTS

The following contributions are usually taken into account in analyzing the magnetic susceptibility measurements: 1) the spin paramagnetism of the conduction electrons as enhanced by the exchange interaction, 2) the orbital paramagnetism of the d electrons, and 3) the diamagnetism of the ion cores. To establish the magnitudes of these individual contributions one must make use of the results of studies of other physical properties of the metals.

Shimizu[7] proposed a method for resolving the susceptibility into components on the basis of a joint study of the susceptibility and the electronic specific heat. This method is based on the assumption that for the transition metals, the observed temperature dependence of the susceptibility is entirely due to that of the spin susceptibility of the conduction electrons. Accordingly, one considers two terms in the susceptibility:

$$\chi_{meas}(T) = \chi_{const} + \chi_{sp}(T), \qquad (4.1)$$

where χ_{const} is the temperature independent part of the susceptibility, which is due to the orbital paramagnetism of the d electrons, and the ionic diamagnetism

$$\chi_{const} = \chi_{orb} + \chi_{ion}, \qquad (4.2)$$

and $\chi_{sp}(T)$ is the temperature dependent part of the susceptibility:

$$\chi_{sp}^{-1}(T) = \chi_0^{-1}(T) - \alpha,$$

where $\chi_0(T)$ is the spin paramagnetic susceptibility of the conduction electrons and α is the exchange interaction constant.

The temperature dependence of the conduction-electron spin susceptibility is calculated theoretically. For this calculation one first constructs the density of states curves $N(E)$ for the metals of all the transition periods from the electronic specific heat data (see Figs. 1 and 2). Then, in the context of the rigid band model one determines the change in energy with temperature and calculates the $\chi^{calc}(T)$ curves for the individual metals from formula (1.3). Figure 9 shows such calculated $\chi_0(T)$ curves[79] for zirconium and rhodium. The calculated $\chi_0(T)$ curves differ considerably from the experimental $\chi(T)$ curves both in the magnitude of the susceptibility and in the temperature trend itself. The curves are brought into conformity by selecting suitable values for χ_{orb} and α. Tables III and IV give the values of χ_{orb} and α that lead to calculated curves showing the total susceptibility as a function of temperature which agree most closely with the experimental $\chi(T)$ curves. The orbital paramagnetism of the d electrons is found to be greatest for the metals lying close to the middle of their respective transition series.

Clogston et al.[8,51] proposed another method for resolving the susceptibility into components. This method is based on joint study of the temperature dependences of the susceptibility and the Knight shift. The Knight shift is the difference between the NMR frequency for the metal and the resonance frequency for the same

nucleus in a nonmetallic compound; it arises because in the metal there appear additional fields at the nucleus owing to the indirect or contact interaction of the nuclear spins with the conduction electrons.

Just as the net susceptibility of the metal is determined by both diamagnetic and paramagnetic moments acting jointly, so the Knight shift is the sum of a number of negative and positive contributions, each of which is associated with a corresponding contribution to the susceptibility. For the transition metals, the Knight shift K (in percent) is usually regarded as the sum of the following terms:

$$K = K_s + K_d + K_{orb} + \delta K_{dia}. \quad (4.3)$$

Here K_s arises from the contact interaction of the nuclear spins with the fields of the unfilled s shells; K_d arises from the contact interaction of the nuclear spins with the fields of the filled s shells whose spins are polarized as a result of the exchange interaction with the spin moments of the d electrons; K_{orb} arises from the contact interaction of the nuclear spins with the fields of the filled s shells whose spins are polarized as a result of the exchange interaction with the orbital magnetic moment of the d electrons; and δK_{dia} is the diamagnetic contribution to the Knight shift.

The spin paramagnetic contributions from the s and d electrons are treated separately in the expression for the magnetic susceptibility:

$$\chi = 2\chi_s + \chi_d(T) + \chi_{orb} + \chi_{dia}.$$

Each component of the Knight shift in Eq. (4.3) is associated with a corresponding contribution to the susceptibility:

$$K_s = \alpha_s \chi_s, \quad K_d = \alpha_d \chi_d, \quad K_{orb} = \beta F_J \chi_{orb}$$

The coefficients α_s, α_d, and β, the relativistic correction factor F_j, and the quantity δK_{dia} can be calculated by making certain approximations that we shall not discuss here.

On comparing the temperature dependences of the Knight shift and the susceptibility for the transition metals it was found that the K vs T plot for any given transition metal is a straight line (Fig. 14). As in Shimizu's method, it is further assumed that the temperature dependence of the susceptibility (and in the present method, also that of the Knight shift) is entirely due to the temperature dependence of the d-electron spin susceptibility.

Now let us see how the $K(\chi)$ plot for separating the spin and orbital components is constructed, using platinum as an example. The heavy line segment on the
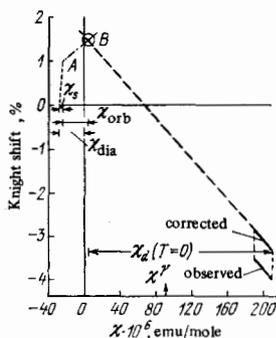
lower right in Fig. 14 represents the experimental part of the $K(\chi)$ plot; its slope is assumed to be α_d. The quantity χ_{dia} is laid off leftward from zero along the abscissa axis; for platinum, its contribution δK_{dia} to the Knight shift is negligible. Then the quantity χ_s is laid off along the abscissa axis from the point B, and a line is drawn with slope α_s and continued until it intersects the vertical erected at the end of the χ_s segment. A line with slope β is drawn from the point A and is extended until it intersects the extension of the experimental line. Projection of the intersection point onto the abscissa axis yields segments corresponding to the values of χ_d and χ_{orb}. The orbital susceptibilities of a number of metals have been evaluated in this way (see Table IV); the results are in satisfactory agreement with the values of χ_{orb} obtained by Shimizu's method.

It is also possible to obtain information about the magnetic moment by a method that does not involve investigating the magnetic susceptibility—namely, by measuring the magnetomechanical ratio. Such measurements for the weakly magnetic transition metals are very difficult since, for example, to evaluate the Einstein-de Haas effect for these metals one must measure very small ($\sim 10^{-5}$ rad) angles of rotation-angles that are two orders of magnitude smaller than those encountered in similar measurements on ferromagnets. An improved resonance technique has made it possible to make such measurements for a number of transition metals. The results of these measurements[81,82] are presented in Table V. The fact that the magnetomechanical ratios differ from two shows that the orbital magnetic moment does not vanish in these metals[4].

The experimental values of the orbital paramagnetic susceptibilities of the transition metals as obtained by the two different methods are collected, together with their theoretical estimates, in Table IV. In some cases the agreement is not bad, although no particular significance should be attached to precise agreement since the experimental values and theoretical estimates are equally inaccurate. However, the agreement in order of magnitude between the theoretical estimates and the experimental values of the orbital paramagnetic susceptibility definitely shows that in the weakly magnetic-transition metals the orbital magnetic moment is responsible for a considerable part of the net paramagnetic moment.

5. MAGNETIC ANISOTROPY

Studies of the magnetic susceptibility of single crystals of weakly magnetic transition metals[29,76,83-91] have shown that the susceptibility of the metals with the hcp structure depends on the direction of the magnetic field with respect to the crystallographic axes, i.e., these metals exhibit magnetic anisotropy. Anisotropy of the magnetic susceptibility with a period of 180° is observed in a plane containing the hexagonal axis c (Fig. 15). For some of the metals (titanium, zirconium, hafnium) the greatest susceptibility is measured with

FIG. 14. Knight shift of the Pt[195] NMR in platinum metal vs the susceptibility. The heavy line marked "observed" represents the experimental data; the line above it marked "corrected" represents the same data corrected for the positive NMR shift in the chloroplatinic acid reference solution; and χ^γ is the spin susceptibility calculated from the electronic specific heat data.

TABLE V. Magnetomechanical ratio for transition metals as determined from the Einstein-de Haas effect

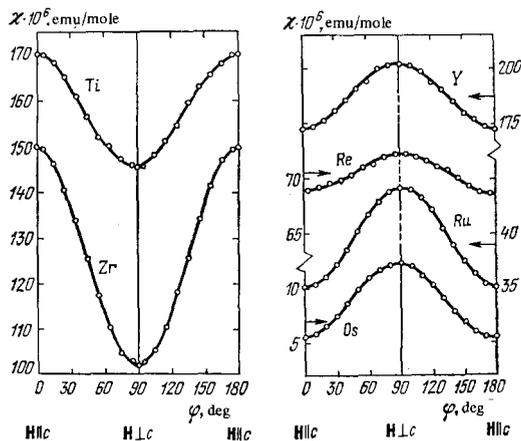| Metal	Vanadium	Niobium	Tantalum	Palladium	Platinum
g'	1.18	1.05	1.02	1.77	1.62

FIG. 15. Magnetic susceptibility of single crystals of transition metals with the hcp structure vs the angle between the magnetic field vector **H** and the hexagonal axis c.

structure. The trouble is that the observed susceptibility is the sum of a number of components and it is impossible to determine experimentally whether the anisotropy is associated with the diamagnetic part of the susceptibility, or with the paramagnetic part of it.

TABLE VI. Molar susceptibilities of hcp metals for the magnetic field parallel ($\chi_\parallel$, **H** $\parallel$ c) and perpendicular ($\chi_\perp$, **H** $\perp$ c) to the c axis, and the values of $\chi_{poly} = (\chi_\parallel + 2\chi_\perp)/3$

Metal	$\chi_\parallel \cdot 10^6$, emu/mole	$\chi_\perp \cdot 10^6$, emu/mole	$\chi_{poly} \cdot 10^6$, emu/mole	Refs.
Scandium	294, 281	232, 298	253, 294	76, 85
Yttrium	174, 270	220, 445	191, 387	20, 83
Titanium	169; 164; 168,7	144.5; 143; 145.3	152; 147; 153	87-89
Zirconium	147; 151	86; 100	110; 117	84, 86
Hafnium	95	63	73	86
Rhenium	68.3	73.0	69.8	20
Ruthenium	35.2	44.2	41.2	88
Osmium	5.40	12.65	10.23	91

the field parallel to the c axis $(\chi_\parallel)$, while for others (scandium, yttrium, rhenium, ruthenium, and osmium) the maximum susceptibility is measured with the field perpendicular to the c axis $(\chi_\perp)$. In the basal plane, the susceptibility is independent of the direction of the magnetic field with respect to the crystal axes within the accuracy of the measurements.

As Table VI shows, the experimental data are not numerous and require confirmation. There is considerable spread of the $\chi_\parallel$ and $\chi_\perp$ values for scandium and yttrium. The values of χ obtained in[76,83,90] are perhaps much enhanced with respect to the other data because of the presence of rare-earth metal impurities (~0.3%) in the investigated specimens. Except for the data of[76,83], the susceptibilities of the polycrystalline specimens are correctly given for all the metals by the usual averaging formula: $\chi_{poly} = (\chi_\parallel + 2\chi_\perp)/3$.

Some features of the susceptibilities of transition-metal single crystals with the hcp structure can be traced in their temperature dependences (Fig. 16). Although the general behavior of the susceptibility as a function of temperature remains the same as for polycrystalline materials, i.e., the sign of the derivative $d\chi/dT$ is the same for single-crystal and polycrystalline specimens, the magnitude of the temperature coefficient is different for $\chi_\parallel$ and $\chi_\perp$: specifically, the smaller of the two susceptibilities has the larger temperature coefficient. Hence the absolute value of the susceptibility anisotropy (i.e., of the difference $\Delta_\chi = \chi_\parallel - \chi_\perp$) falls with increasing temperature.

For convenience in the subsequent discussion we arbitrarily introduce the notion of the "sign of the magnetic anisotropy," by which we shall mean the sign of the susceptibility difference $\chi_\parallel - \chi_\perp$. As Table VII shows, the sign of the anisotropy is not the same for all the metals. If we trace the filling of the d-band energy levels, we find a definite regularity: metals having an even number of d electrons have positive anisotropy, while metals having an odd number of d electrons have negative anisotropy, i.e. metals of the same group have anisotropies of the same sign. Osmium is an exception: it has six 5d electrons but negative anisotropy.

At present we have no unambiguous explanation for the anisotropy of the magnetic susceptibility observed for the weakly magnetic transition metals with the hcp

TABLE VII. Electron configuration, magnitude and sign of the susceptibility anisotropy, and the relative anisotropy for hcp transition metals

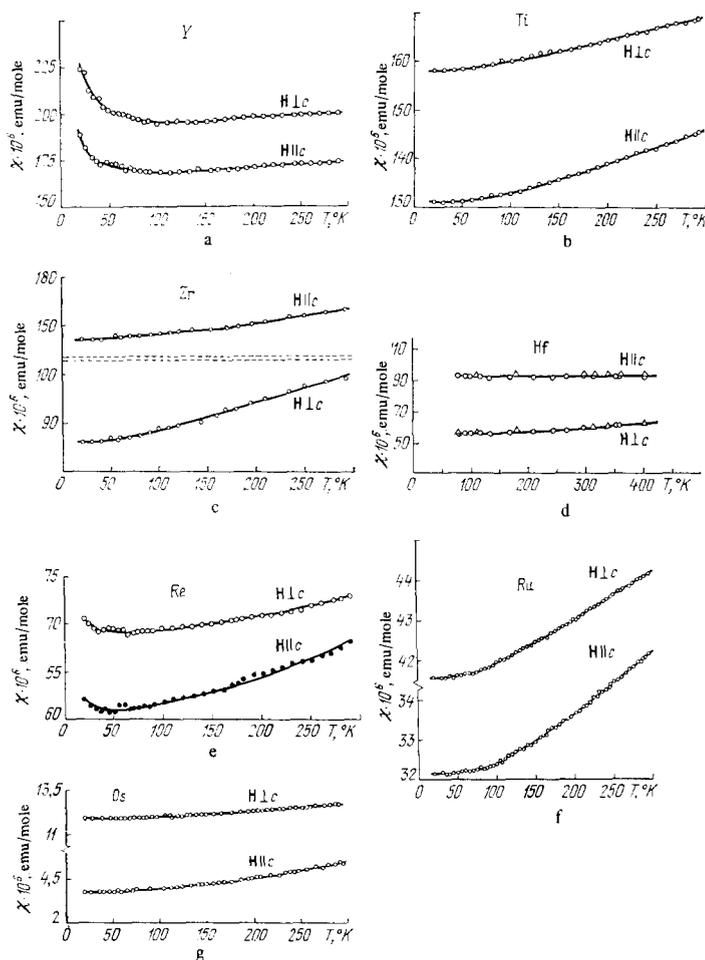| Metals	No. of d electrons	$\Delta\chi \cdot 10^6$, emu/mole	$\Delta\chi/\chi_{orb}$	Metals	No. of d electrons	$\Delta\chi \cdot 10^6$, emu/mole	$\Delta\chi/\chi_{orb}$
Scandium	1	−11	−0.11	Hafnium	2	32	0.43
Yttrium	1	−26	−0.43	Rhenium	5	−4.7	−0.12
Titanium	2	21—25	0.22—0.26	Osmium	6	−7.25	—
Zirconium	2	51—61	0.64—0.73	Ruthenium	7	−9.0	−0.5

FIG. 16. Temperature dependence of the magnetic susceptibilities of yttrium [20] (a), titanium [88] (b), zirconium [84] (c), hafnium [86] (d), rhenium [20] (e), ruthenium [88] (f), and osmium [91] (g) single crystals with the magnetic field parallel and perpendicular to the c axis (**H** $\parallel$ c and **H** $\parallel$ c, respectively).

Authors usually limit themselves to more or less well founded assumptions concerning the nature of the susceptibility anisotropy.

It is well known that the energy characteristics of the conduction electrons in hcp crystals depend to a considerable extent on the crystallographic axis ratio c/a. The hypothesis has been advanced[90] that the anisotropy of the susceptibility is due to the anisotropy of the charge density of the electron cloud consisting of collectivized s and d electrons. In hcp crystals this distribution is axially symmetric and could lead to anisotropy of the diamagnetic part of the susceptibility. Estimates[90] of the isotropic and anisotropic parts of the diamagnetic susceptibility of the conduction electrons in scandium and yttrium based on the Bloembergen-Rowland[92] formula for the mean density of the electron cloud gave very large values for the isotropic diamagnetic part. There is no foundation for the presence of considerable diamagnetism in these metals and no attempts have been made to reconcile such diamagnetism with the shape of the Fermi surface. The view that the anisotropy of the magnetic susceptibility of the weakly magnetic transition metals is associated with the orbital paramagnetic contribution has received better theoretical foundation. Ducastelle and Cyrot-Lackmann[93], using a method proposed by them involving a moment expansion of the density of states, showed that when calculating the orbital paramagnetism in the tight binding approximation anisotropy appears in the fourth order of perturbation theory provided the axial ratio c/a differs from its ideal value of 1.633. One also finds that the orbital paramagnetic susceptibility of an ideal close packed lattice is anisotropic, but in this case the anisotropy appears in the sixth order of perturbation theory. It is the overlap integrals in the expression for χ_{orb} that are responsible for the directional dependence of the latter. It was shown that the anisotropy changes sign at least twice in each series as the d band is being filled, and that the magnitude of the susceptibility anisotropy depends on the deviation of c/a from its ideal value. Preliminary estimates of the relative anisotropy of the susceptibility as defined by the formula $\Delta\chi/\chi_{orb} = (\chi_{\parallel} - \chi_{\perp})/[(\chi_{\parallel} + 2\chi_{\perp})/3]$ give values of the order of 0.02, whereas the experimental values are much larger: ~0.1—0.5.

6. CONCLUSION

The establishment of correlations between the theoretical estimates and observed values of the orbital contribution to the paramagnetic susceptibility and of the total paramagnetic susceptibility for the weakly magnetic transition metals strongly supports the assumption that the theory does take the principal components of the susceptibility into account and that those components can be calculated provided the electron structure of the metal is known. Nevertheless, there are a number of problems of fundamental importance that remain unsolved and that cannot be solved on the basis of studies of the static susceptibility alone. Among these problems is that of determining the part played by the exchange interaction and the diamagnetism of the free electrons in forming the net magnetic moment of the transition metals. The observed temperature dependence of the susceptibility of the transition metals has not been explained; it is essentially attributed entirely to the spin paramagnetism, but discrepancies between the theoretical and experimental $\chi(T)$ curves clearly

indicate that this explanation is inadequate. Further studies of the anisotropy of the magnetic susceptibility of the d-band metals with the hcp structure will also be necessary before its nature can be satisfactorily explained.

In concluding I wish to express my sincere gratitude to N. V. Volkenshteĭn for suggesting that this review be written, for his interest in the work, and for discussions during the course of the work, and to S. V. Vonsovskiĭ for reading the manuscript and for critical remarks.

---

[1] K. Honda, Ann. d. Phys. (Lpz) 32, 1003 (1910).

[2] H. Z. Bommer, Zs. Electrochem. 45, 357 (1939).

[3] C. J. Kriessman and H. B. Callen, Phys. Rev. 94, 837 (1954).

[4] M. Shimizu and T. Takahashi, J. Phys. Soc. Japan 15, 2236 (1960).

[5] S. V. Vonsovskiĭ and Yu. A. Izyumov, Usp. Fiz. Nauk 77, 377 (1962) [Sov. Phys.-Usp. 5, 547 (1963)].

[6] M. Shimizu, J. Phys. Soc. Japan 31, 378 (1971).

[7] M. Shimizu, T. Takahashi, and A. Katsuki, ibid. 18, 240 (1963).

[8] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. A134, 650 (1964).

[9] B. J. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. 4, 1126 (1959).

[10] S. A. Nemnonov, Fiz. Met. Metalloved. 19, 4 (1965).

[11] M. Shimizu, T. Takahashi, and A. Katzuki, J. Phys. Soc. Japan 18, 1192 (1963).

[12] A. Katzuki and M. Shimizu, ibid. 21, 279 (1966).

[13] R. Kohlhaas and W. D. Weiss, Zs. angew. Phys. 28, 16 (1969).

[14] W. E. Gardner and J. Penfold, Phys. Lett. A26, 204 (1968).

[15] N. V. Volkenshteĭn and É. V. Galoshina, Fiz. Met. Metalloved. 20, 368 (1965).

[16] R. Kohlhaas and K. M. Wunsch, Zs. angew. Phys. 32, 158 (1971).

[17] C. M. Nelson, Ph. D. Thesis (Tennessy Univ., 1952).

[18] W. D. Weiss and R. Kohlhaas, Zs. angew. Phys. 23, 175 (1967).

[19] V. I. Chechernikov and Iuliu Pop, Zh. Eksp. Teor. Fiz. 46, 1226 (1964) [Sov. Phys.-JETP 19, 831 (1964)].

[20] N. V. Volkenshteĭn, É. V. Galoshina, and N. I. Shchegolikhina, Zh. Eksp. Teor. Fiz. 56, 139 (1969) [Sov. Phys.-JETP 29, 79 (1969)].

[21] J. O. Betterton, Jr. and J. O. Scarbrough, Phys. Rev. 168, 715 (1968).

[22] E. W. Collings and J. C. Ho, Phys. Rev. B2, 235 (1970).

[23] W. S. Corak, V. V. Goodman, C. B. Satterthwaite, and A. Wexler, Phys. Rev. 102, 656 (1956).

[24] T. C. Cetas, J. C. Holste, and C. A. Swenson, Phys. Rev. 182, 679 (1969).

[25] M. A. Jensen and J. P. Maita, ibid. 149, 409 (1966); R. P. Gupta, Phys. Stat. Sol. 20, 291 (1967).

[26] B. J. C. van der Hoeven Jr. and P. H. Keesom, Phys. Rev. **134**, 1320 (1964).

[27] F. J. Morin and J. P. Maita, ibid. **129**, 1115 (1963).

[28] J. G. Daunt and J. W. Cobble, Phys. Rev. **92**, 507 (1953).

[29] M. Horowitz and J. G. Daunt, ibid. **91**, 1099.

[30] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. **A257**, 250 (1960).

[31] G. Chouteau, R. Fourneaux, K. Gobrech, and R. Tourniex, Phys. Rev. Lett. **20**, 253 (1968).

[32] O. V. Lounasmaa, Phys. Rev. **A133**, 219 (1964).

[33] E. Bucher, F. Heiniger, and J. Muller, Proc. of the 9th Intern. Conference on Low Temperature Physics (LT-9), Ohio, 1964, p. 1059.

[34] T. H. Geballe, Rev. Mod. Phys. **36**, 134 (1964).

[35] D. R. Smith and P. H. Keesom, Phys. Rev. **B1**, 188 (1970).

[36] D. H. Parkinson, Rept. Progr. Phys. **21**, 226 (1958).

[37] M. Dixon, F. E. Hoare, and T. M. Holder, Proc. Phys. Soc. **20**, 253 (1967).

[38] G. E. Shoemake and J. A. Rayne, Phys. Lett. **A26**, 222 (1968).

[39] A. M. Clogston, Phys. Rev. **A136**, 8 (1964).

[40] S. V. Vonsovskiĭ, Magnetizm (Magnetism), Nauka, 1971, Chapter II.

[41] E. C. Stoner, Proc. Roy. Soc. **A154**, 656 (1936).

[42] J. B. Sampson and F. Seitz, Phys. Rev. **58**, 633 (1940).

[43] D. Pines, Sol. State Phys. **1**, 368 (1955).

[44] R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

[45] F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdin, Phys. Rev. **B1**, 4617 (1970).

[46] J. R. Cullen and E. Callen, Phys. Lett. **A28**, 20 (1968).

[47] N. Mori, J. Phys. Soc. Japan **20**, 1383 (1965).

[48] N. Mori, ibid. **29**, 366 (1970).

[49] J. S. Denbigh and W. L. Lomer, Proc. Phys. Soc. **82**, 156 (1963).

[50] J. Butterworth, ibid. **83**, 71 (1964).

[51] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Lett. **9**, 262 (1962).

[52] W. E. Gardner and J. Penfold, Phil. Mag. **11**, 549 (1965).

[53] L. E. Orgel, J. Phys. Chem. Sol. **21**, 123 (1961).

[54] C. M. Place and P. Rhodes, J. Appl. Phys. **39**, 1282 (1968); Phys. Stat. Sol. **b47**, 475 (1971).

[55] G. C. Fletcher, Proc. Phys. Soc. **A65**, 192 (1952).

[56] J. H. Wood, Phys. Rev. **126**, 517 (1962).

[57] P. W. Selwood, Magnetochemistry, Interscience, N. Y., 1956 (Russ. Transl., IL, 1958).

[58] M. Shimizu and A. Katsuki, J. Phys. Soc. Japan **19**, 1856 (1964).

[59] M. Shimizu, A. Katzuki, and K. Ohmori, ibid. **21**, 1922 (1966).

[60] J. A. Seitchik, V. Jaccarino, and J. H. Wernick, Phys. Rev. **A138**, 150 (1965).

[61] M. Shimizu, A. Katzuki, and T. Takahashi, J. Phys. Soc. Japan **19**, 614, 1134 (1964).

[62] R. E. Peierls, Zs. Phys. **80**, 763 (1933).

[63] J. E. Hebborn, J. M. Luttinger, E. H. Sondheimer, and P. J. Stile, J. Phys. Chem. Sol. **25**, 741 (1964).

[64] E. I. Blount, Phys. Rev. **126**, 1636 (1962).

[65] L. M. Roth, J. Phys. Chem. Sol. **23**, 433 (1964).

[66] N. Mori, J. Phys. Soc. Japan **31**, 359 (1971).

[67] J. Yamashita, M. Fucuchi, and S. Wakoh, ibid. **18**, 999 (1963).

[68] J. Friedel, P. Lenglert, and G. J. Leman, J. Phys. Chem. Sol. **25**, 781 (1964).

[69] C. M. Place and P. Rhodes, Phys. Stat. Sol. **b47**, 475 (1971).

[70] E. W. Collings and J. C. Ho, Phys. Lett. **A31**, 193 (1970).

[71] W. E. Gardner, J. Penfold, and M. D. Taylor, Proc. Phys. Soc. **85**, 963 (1965).

[72] D. O. Van Ostenburg, D. J. Lam, M. Shimizu, and A. Katsuki, J. Phys. Soc. Japan **18**, 1744 (1963).

[73] M. Bernasson, P. Descouts, P. Donze, and A. Trayvand, J. Phys. Chem. Sol. **30**, 2453 (1969).

[74] A. Narath and D. Alderman, Phys. Rev. **143**, 328 (1966).

[75] J. A. Seitchik, A. C. Gossard, and V. Jaccarino, Phys. Rev. **A136**, 1119 (1964).

[76] V. I. Chechernikov et al., Zh. Eksp. Teor. Fiz. **44**, 387, 1868 (1963) [Sov. Phys.-JETP **17**, 265, 1228 (1973)].

[77] R. Kohlhaas and W. D. Weiss, Zs. Naturforsch. **20a**, 1227 (1965).

[78] H. Kojima et al., Proc. Roy. Soc. **A260**, 27 (1961).

[79] M. Shimizu et al., J. Phys. Soc. Japan **19**, 1856 (1964).

[80] S. Misawa, Phys. Lett. **A32**, 541 (1970).

[81] R. Huguenin and D. Baldock, Phys. Rev. Lett. **16**, 795 (1966).

[82] R. Huguenin, G. P. Bells and D. N. Baldock, J. Phys. F **1**, 281 (1971).

[83] V. I. Chechernikov, Iuliu Pop, V. F. Terekhova, and V. E. Kolesnichenko, Zh. Eksp. Teor. Fiz. **46**, 444 (1964) [Sov. Phys.-JETP **19**, 298 (1964)].

[84] N. V. Volkenshtein, É. V. Galoshina, and N. I. Shchegolikhina, Fiz. Met. Metalloved. **25**, 180 (1968).

[85] J. W. Ross, F. Y. Fradin, L. L. Isaacs, and D. J. Lam, Phys. Rev. **183**, 645 (1969).

[86] E. W. Collings and J. C. Ho, Phys. Rev. **B4**, 349 (1971).

[87] E. W. Collings and J. C. Ho, Phys. Rev. **B2**, 235 (1970).

[88] N. V. Volkenshteĭn, E. V. Galoshina, and N. I. Shchegolikhina, Zh. Eksp. Teor. Fiz. **61**, 1506 (1971) [Sov. Phys.-JETP **34**, 802 (1972)].

[89] R. J. Wasilewski, J. Appl. Phys. **40**, 2677 (1969).

[90] V. I. Chechernikov et al., Fiz. Met. Metalloved. **24**, 174 (1967).

[91] E. V. Galoshina, et al., Phys. Stat. Sol. **b58**, K45 (1973).

[92] N. Bloembergen and T. J. Rowland, Acta. Metall. **1**, 731 (1953).

[93] F. Ducastelle and F. Cyrot-Lackmann, J. de Phys. **32**, CI-534 (1971).