The High Temperature Magnetic Susceptibility of V, Nb, Ta, W, and Mo†‡

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The temperature range of magnetic susceptibility measurements has been extended from 1450°C to 1850°C. In the range from 25°C to the highest temperature measured, the susceptibilities of V, Nb, and Ta decrease with increasing temperature, while the susceptibilities of Mo and W increase. A periodicity in the sign of the temperature coefficient of the magnetic susceptibility of the transition elements is discussed in relation to various theories of metals.

INTRODUCTION

THE paramagnetism of the nonferromagnetic transition elements might be explained on the basis of several theoretical approaches which should give at least general predictions about the variation of magnetic susceptibility with temperature. These approaches are the collective electron picture suggested by Stoner[1] and extended by Wohlfarth[2] and the antiferromagnetic model advanced by Néel[3] and Zener.[4,5] However, comparison with experiment, especially at high temperatures, has not been possible because of the lack of data. The only data over an appreciable high temperature range were those on Ti and Zr,[6] Cr,[7] and Mn.[8–10] Much of the classic work of Honda[11] on almost all of the transition elements up to 1100°C is considered unreliable because of impurities in the samples used. The present work extends the temperature range of magnetic susceptibility measurements from 1450°C to 1850°C and furnishes data on the susceptibilities of V, Nb, Ta, Mo, and W from 25°C to about 1850°C.

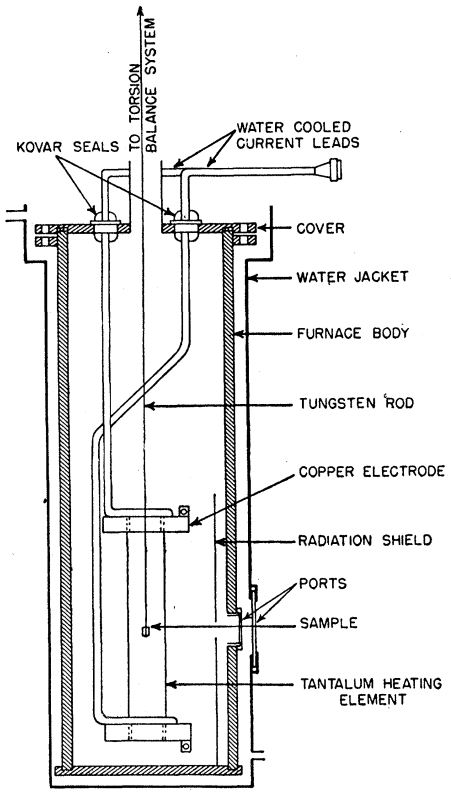

FIG. 1. Schematic drawing of the high temperature furnace.

EXPERIMENTAL METHOD

The susceptibility was measured with apparatus similar to that described by McGuire and Lane.[12] A small sample is suspended in an inhomogeneous magnetic field from one end of a torsion balance arm. The force, which is directly proportional to the suscep-

TABLE I. Purities and susceptibilities of the metals measured.

Metal	Purity, %	$\chi \cdot 10^6$ Literature	$\chi \cdot 10^6$ Present work	$\frac{10^{10}}{\chi_{Av}} \cdot \frac{\Delta\chi}{\Delta T}$
V	99.8	4.5[12]	5.00	−0.52
Nb	99.9	2.28[a]	2.20	−1.3
Ta	99.9	0.8490[b]	0.827	−1.2
W	99.99	0.284[a]	0.32	+0.87
Mo	99.95	0.949[a]	0.93	+0.88

[a] W. J. deHaas and P. M. Van Alphen, Proc. Acad. Sci. Amsterdam, **36**, 263 (1933).
[b] F. E. Hoare and J. C. Walling, Proc. Phys. Soc. (London) **64B**, 337 (1951).

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[8] G. Grube and O. Winkler, Z. Electrochem. **42**, 815 (1936).
[9] A. Serres, J. phys. et radium **9**, 377 (1938).
[10] M. Isobe, Sci. Rept. Tohoku University **A3**, 78 (1951).
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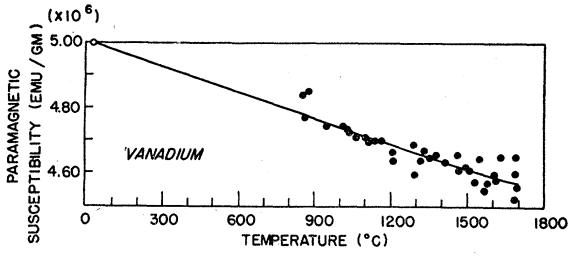

FIG. 2. The magnetic susceptibility of vanadium.

tibility according to the equation

$$F_z = m\chi H_x \frac{dH_x}{dz},$$

where χ is the magnetic susceptibility per gram, is balanced electrodynamically by passing a small current through a coil on the other end of the torsion balance arm. The balance condition is determined by a split cathode photocell method.

The high temperature furnace is shown in Fig. 1. The heating element is a cylinder of 0.003-inch sheet tantalum which is firmly clamped in heavy copper electrodes. Water-cooled copper tubes which are brought through the demountable brass furnace cover by glass-to-metal Kovar seals both support the electrodes and carry the heating current. The cover is sealed to the brass furnace body by a Neoprene gasket, and the furnace is evacuated and then filled with helium to protect the sample and heating element. The furnace body is cooled by water flowing in the outer jacket.

At 1900°C the heating current is about 500 amperes at 10 volts, which is supplied by a 208-volt step-down transformer. These large alternating currents cause vibrations in the heating element which restrict its life time to an average of three runs from 25°C to 1900°C. However, it is a relatively simple matter to remove the heating element assembly and replace the tantalum cylinder.

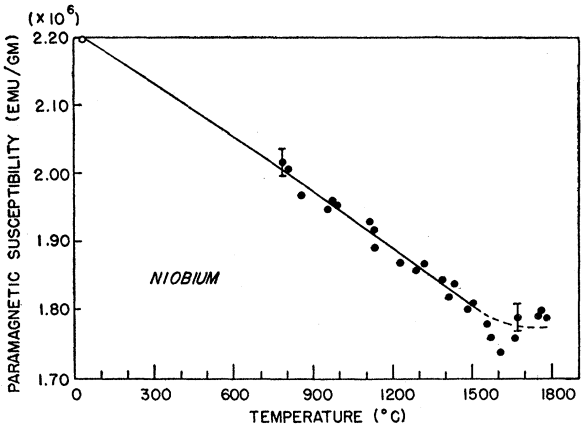

FIG. 3. The magnetic susceptibility of niobium.

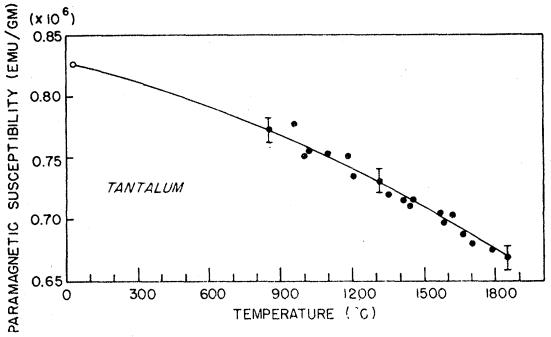

FIG. 4. The magnetic susceptibility of tantalum.

The metal to be measured, usually in the form of a small cylinder, is suspended from the torsion balance by a thin tungsten rod which passes through an axial hole in the sample. This eliminates the use of a container which might react with the metal. The small force introduced by the tungsten rod is eliminated by calibration.

The temperature is measured with a Leeds and Northrup optical pyrometer, which is sighted on the inside of the furnace through a small hole in the heating element. There are glass ports in the furnace body and the water jacket. A radiation shield protects the inner port. The optical path is calibrated for absorption by placing a standard tungsten filament blackbody source inside the furnace.

RESULTS

The Nb, Ta, Mo, and W samples were obtained in the form of spectroscopically pure rods from Johnson, Mathey, and Company, while the V sample came from the Electro Metallurgical Company. The purities of the samples as reported by the suppliers are shown in Table I. Field-dependence data at room temperature indicate that the spectroscopic samples contain only small ferromagnetic impurities requiring corrections of 0.01 to 0.02×10^{-6} susceptibility unit at 2600 gauss, the field used in the high temperature measurements.

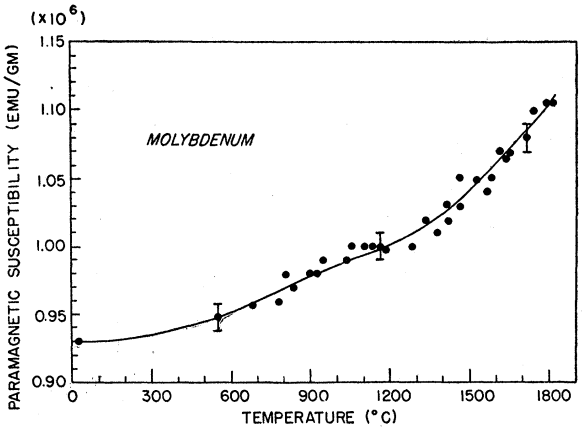

FIG. 5. The magnetic susceptibility of molybdenum.

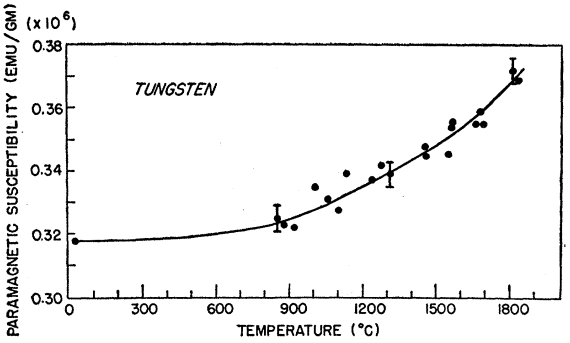

FIG. 6. The magnetic susceptibility of tungsten.

The same type of correction for V amounts to 0.25×10^{-6} unit. The experimental results are shown in Figs. 2 to 6. Data have also been taken between room temperature and 800°C with another furnace,[7] and these results are indicated by solid lines.

The susceptibility of V decreases from 5.00×10^{-6} at 25°C to 4.57×10^{-6} at 1700°C, although this high temperature value is in doubt because there is a large scattering of the data as the melting point is approached. The temperature dependence observed here for V is different from that of Honda,[11] who reported that the susceptibility of V increased with temperature. However, the data of Klemm[13] from −195°C to room temperature indicate a slight decrease in susceptibility with increasing temperature, and Klemm's room temperature value of 4.5×10^{-6} is much closer to the present value than Honda's 1.50×10^{-6}. Klemm suggests that the temperature dependence he observed for V is due to a small amount of iron present in a paramagnetic form, but this would not account for the continued decrease in susceptibility at high temperatures.

The susceptibility of Nb decreases from 2.20×10^{-6} at 25°C to 1.79×10^{-6} at 1575°C, at which point it appears to level off. A crystal structure change might explain this behavior, but recent x-ray studies[14] reveal no such transition in Nb.

The susceptibility of Ta decreases uniformly from 0.827×10^{-6} at 25°C to 0.668×10^{-6} at 1850°C.

Unlike the preceding metals, W and Mo show an increasing susceptibility with increasing temperature. The susceptibility of W increases from 0.32×10^{-6} at 25°C to 0.37×10^{-6} at 1850°C, while that of Mo increases from 0.93×10^{-6} at 25°C to 1.11×10^{-6} at 1825°C.

Table I shows a comparison between the best room temperature susceptibility values available in the literature for these metals and the values found in this work. If the difficulties in the preparation of these metals are considered, agreement is good except in the case of W, where the value 0.32×10^{-6} is closer to Honda's old data. The last column in Table I gives a rough measure of the relative change in susceptibility over the entire temperature range.

[13] L. Klemm, Z. Electrochem. 45, 354 (1939).
[14] Edwards, Speiser, and Johnston, J. Appl. Phys. 22, 424 (1951).

DISCUSSION

The most notable feature of the experimental results is that the temperature coefficient of the magnetic susceptibility of the transition elements alternates in sign with the columns in the periodic table. V, Nb, and Ta, all in the fifth column of the periodic table, have a negative temperature coefficient, while W and Mo, in the sixth column of the periodic table, have a positive temperature coefficient. When the data on Ti, Zr, Cr, and Mn are added, as shown in Table II, this periodicity becomes more evident. The ability of existing theories to qualitatively account for this effect will be discussed.

Stoner[1] has investigated the temperature coefficient of the magnetic susceptibility by using

$$\chi=\chi_0(1+c\gamma T^2);\quad \gamma=\left[\frac{\partial^2 \ln N(E)}{\partial E^2}\right]_{E_0},$$

where $N(E)$ is the number of energy states per energy interval and χ_0 and c are constants. The sign of the temperature coefficient γ depends critically on the shape of the curve for the distribution of energy states at E_0, the Fermi limit. For the usual forms assumed for $N(E)$ at E_0, e.g., $E^{\frac{1}{2}}$ or E^n, γ is negative. However, if E_0 is very close to a minimum in the $N(E)$ curve as shown in Fig. 7(a) then γ can be positive and the magnetic susceptibility can increase with temperature. Now if we assume that the main contribution to the paramagnetism of the transition elements is from electrons in the d band, then the Fermi limit of an element like Cr, which has a positive γ, should occur at a minimum in the $N(E)$ curve for the $3d$ band. No actual calculation for the curve of the distribution of states for Cr has been made, but it should qualitatively resemble the $N(E)$ curves for Ni and Cu. The $N(E)$

TABLE II. The temperature coefficient of the magnetic susceptibility, the electronic specific heat constant, and the antiferromagnetic ordering μ_n (in Bohr magnetons) found by neutron diffraction.

	Ti	V	Cr	Mn
Temperature coefficient	+	−	+	−
$a\cdot10^4$	8.3	14	3.7	42
μ_n		0	0.4	(≃0.3)
	Zr	Nb	Mo	Tc
Temperature coefficient	+	−	+	
$a\cdot10^4$	6.9	60		
μ_n		0		
	Hf	Ta	W	Re
Temperature coefficient		−	+	
$a\cdot10^4$		19.4	5.1	
μ_n			0	

curve for the 3*d* band in Cu given by Krutter and Slater[15] and a more exact calculation for the 3*d* band in Ni by Fletcher[16] are shown in Fig. 7(b) on arbitrary scales. Although these curves differ in some important details, both indicate a minimum where the 3*d* band would be approximately half filled with electrons. This minimum occurs, then, about where one would expect the Fermi limit of Cr with its five to six 3*d* electrons.

Another property which depends on the distribution of states at E_0 is the electronic specific heat. Recently, Friedberg, Estermann, and Goldman[17] have suggested that the surprisingly low electronic specific heat of Cr may be explained by a minimum in the 3*d* $N(E)$ curve for Cr. Values for the constant a (often called γ in the literature), which is a measure of the magnitude of the electronic specific heat, are shown in Table II. Here too, a periodicity is evident. Elements in the Ti and Cr columns have lower electronic specific heats than their neighbors. Therefore, reasoning as in the Cr case, one might expect minima in the *d* band $N(E)$ curves of Ti, Zr, Mo, and W, and a resulting increase of susceptibility with temperature, just the behavior which is observed. The basic feature, then, of the *d* band in the transition metals would be its division into two parts, the upper part having a very high density of states. In the case of the Ti and Cr type of elements an increase in temperature will cause a movement of electrons to the high density portion of the band, resulting in an increase in susceptibility. The $N(E)$ curve and Fermi limit calculated for W by Manning and Chodorow[18] is shown in Fig. 7(c). Here again the Fermi limit occurs at a minimum in the $N(E)$ curve, and here again the susceptibility increases with temperature as in the case of Cr.

Another approach which may also give a qualitative explanation of the periodicity in the sign of γ is the assumption of Néel and Zener that the *d* shells of the transition elements are antiferromagnetic. The metals with a positive γ would have a high antiferromagnetic Curie point, i.e., the observed susceptibility curve is rising toward a maximum while the metals with a negative γ would have a low antiferromagnetic Curie point, i.e., the observed susceptibility curve is decreasing from a maximum. No Curie point in the susceptibility of the transition metals has been observed except the apparent one found at low temperatures in crystalline Mn by Serres[9] and more recently by McGuire and Kriessman;[19] however, in the same temperature range Bates and Pantalu[20] have observed no such Curie

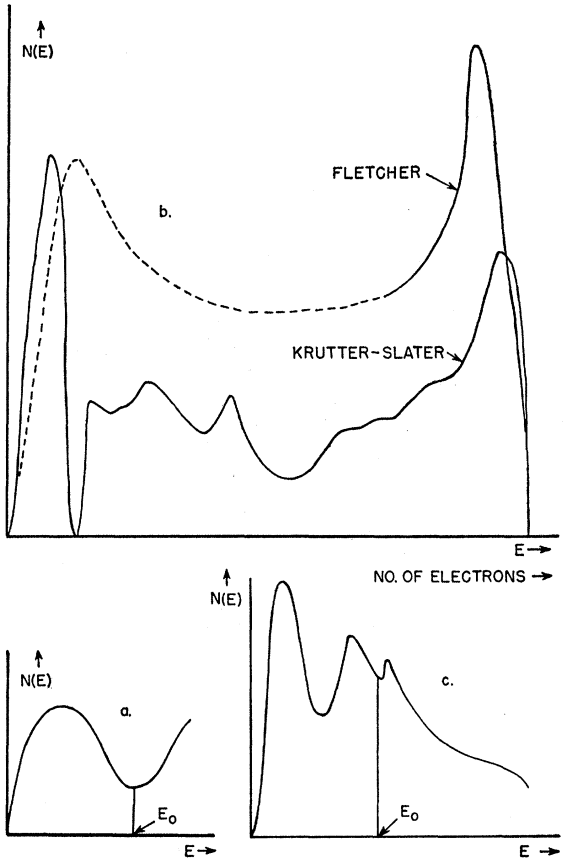

FIG. 7. (a) Idealized $N(E)$ curve with a minimum occurring at E_0. (b) Two calculations for the 3d band distribution of states curve. The Krutter-Slater curve for Cu is based on the cellular approximation. The Fletcher curve for Ni is based on a tight binding approximation. Both curves are qualitatively reproduced here, and only the solid portion of the Fletcher curve represents the actual calculation. The dotted portion has been added according to a suggestion in the original paper by Fletcher. (c) The $N(E)$ curve and Fermi limit for W calculated by Manning and Chodorow.

point in amorphous Mn. This would seem to indicate that the maximum observed depends on the crystalline ordering, and this is consistent with the requirements for antiferromagnetism. The absence of Curie points in the other metals is not contradictory at the present time since their susceptibilities have not yet been measured at the highest or the lowest temperatures.

Antiferromagnetism can be detected directly by neutron diffraction.[21] Therefore, one should find a high temperature antiferromagnetic ordering for the positive γ-metals like Ti and Cr and a low temperature antiferromagnetic ordering for the negative γ-metals like V and Mn. The data of Shull[22] on some of the transition metals are shown in Table II. Antiferromagnetic ordering is found in Cr corresponding to about 0.4 of a Bohr magneton with a Curie point of about 150°C. However, it is difficult to see how this antiferro-

[15] H. M. Krutter, Phys. Rev. 48, 664 (1935); J. C. Slater, Phys. Rev. 49, 537 (1936).
[16] G. C. Fletcher, Proc. Phys. Soc. (London) 65, 192 (1952).
[17] Friedberg, Estermann, and Goldman, Phys. Rev. 85, 375 (1952).
[18] M. F. Manning and M. I. Chodorow, Phys. Rev. 56, 787 (1939).
[19] T. R. McGuire and C. J. Kriessman (unpublished results).
[20] L. F. Bates and D. V. Pantalu, Proc. Phys. Soc. (London) 47, 197 (1935).
[21] C. G. Shull and J. S. Smart, Phys. Rev. 76, 1256 (1949).
[22] C. G. Shull, Phys. Rev. 86, 599 (1952).

magnetism which disappears at 150°C can account for the susceptibility which is still slowly increasing at 1400°C, unless in keeping with a suggestion by Zener,[5] the polarity of the atoms begins to fluctuate rapidly enough at 150°C to make detection of antiferromagnetic ordering by neutrons impossible. No ordering in W is found, but its moment might be expected to be undetectable since the susceptibility of W is only one tenth that of Cr. Now Mn, which has a negative γ, should show antiferromagnetic ordering at low temperatures. Shull[23] does find antiferromagnetic ordering in Mn at low temperatures, although at the present time the type of ordering is uncertain. In the case of V and Nb no magnetic ordering is found, and unless the moments are too small to detect or fluctuate too rapidly, this weakens the argument that antiferromagnetism is responsible for the periodicity in γ. Neutron diffraction data on Ti would be enlightening, since they should show antiferromagnetic ordering similar to that in Cr if antiferromagnetism actually is responsible for the periodicity in γ.

[23] C. G. Shull (private communication).

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