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# The Relation between Hydrogen Content and Paramagnetic Susceptibility in the Vanadium–Hydrogen System

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The paramagnetic susceptibility of vanadium is decreased by the presence of dissolved hydrogen and by formation of both nonstoichiometric fcc dihydride and nonstoichiometric bct monohydride phases. The relation of $\chi$ to H/V is complex but correlates to some extent with the phase diagram. Magnetic observations of the system above the reported critical temperature show sharp discontinuities which are not observed in X-ray diffraction studies. Data are presented for the highly defective phases formed by removal of hydrogen at room temperature from $VH_{1.2}$, for equilibrium phases at 150, 200, and 300°. Magnetic anomalies are observed in vanadium, $VH_{0.47}$, $VH_{0.87}$, and $VH_{1.37}$ at low temperature. It is suggested that the anomalies for the metal are possibly due to the presence of minute traces of hydrogen or hydrogen vacancies and that the major effect of hydrogen on the magnetic susceptibility is through distension of the metal lattice.

## Introduction

This work was designed to parallel an X-ray diffraction study of the phases present in the $V-H_2$ system, carried out previously in this laboratory,[1] and to extend a concurrent study of magnetic properties, at room temperature only, carried out elsewhere.[2]

The proton magnetic resonance of $VH_{0.66}$ has been reported[3] indicating that the screening electrons around hydrogen are essentially completely spin paired. The nature of hydrogen in the metallic hydrides of vanadium is not yet clearly understood, nor is the nature of the metal–hydrogen bond.

## Experimental Section

Vanadium metal, 99.92% purity, was obtained through the courtesy of Dr. Frank Spedding, Iowa State University, Ames, Iowa. Vanadium metal having a supplier's analysis of 99.8% was obtained from Ore-Met Corp., Albany, Ore., and was used in duplicate experiments. The metal was etched briefly in aqueous 5% HF–45% $HNO_3$, rinsed in two portions each of water, isopropyl alcohol, and diethyl ether, and transferred wet with ether to the vacuum lock of an argon glove box. Subsequent handling of metal and hydride was under purified argon.

Hydrides were prepared by admitting pure hydrogen (from dissociation of $UH_3$) to the thoroughly degassed metals in a modified Sieverts apparatus. Vanadium absorbs hydrogen readily below 400° usually reaching a hydride of composition $VH_{0.75}$ to $VH_{1.0}$. The composition was ascertained either by noting the volume of hydrogen absorbed or the volume pumped off by means of two mercury diffusion pumps and a Toepler pump, into an air-jacketed gas buret.

A magnetic susceptibility apparatus of the type described previously by Norder[4] was modified for use at low temperatures and its sensitivity increased by use of improved electrical and electronic components. This apparatus permits continuous observation of susceptibility as hydrogen is added to or removed from the sample. It is well adapted to observations at constant temperature but is cumbersome when used for measurement of paramagnetic susceptibility as a function of temperature, since the electrical characteristics change somewhat with temperature. Cooling to −150° was accomplished by allowing dry nitrogen to pass through a copper coil immersed in liquid nitrogen and then into a thin-walled dewar flask surrounding the sample and secondary coils. Manual control of the nitrogen flow gave temperatures constant to ±1.25°. The temperature and voltage were recorded on a Moseley *X–Y* recorder. Instrument parameters were ascertained at several temperatures. A similar apparatus with an infrared sample heater was used for temperatures up to 350°. A Bristol Model 536 controller maintained sample temperatures constant within ±1.0°. The linear relation of voltage output to magnetic susceptibility of sample was established by use of pure metal standards and salts and solutions of known susceptibility. The reproducibility of measurement was found to be within ±0.75%. Measurements are subject to the same error as the familiar Gouy method, *viz.*, variation of bulk densities. The effect of traces of ferromagnetic impurities was minimized by use of a 60-c filter in the output circuit. This effectively removes wave-form distortions due to the presence of even 0.5% ferromagnetic nickel, added deliberately to one of the samples.

## Results

The data obtained at room temperature by *removing* hydrogen from an original composition close to $VH_{1.8}$ are shown in Figure 1 as black circles. The higher hydrides of vanadium are sufficiently unstable to permit easy loss of hydrogen at room temperature *in vacuo*. The right-hand break in slope corresponds roughly to the $(\beta)-(\beta + \gamma)$ phase boundary reported by Maeland. The loss of hydrogen at room temperature is too slow below $H/V \cong 0.45$ to permit further change in composition by pumping at room temperature. The susceptibility of pure V metal ($5.83 \times 10^{-6}$ cgs unit) agrees well with recent published values[5,6] and is very slightly lower than and is within the experimental error of the value given by Zanowick and Wallace,[2] whose data are shown as open circles. It is not clear how Zanowick and Wallace's samples were prepared, *i.e.*, whether by removal of hydrogen from a hydrogen-rich phase or by uptake of hydrogen by metal. In any case these workers did not protect their samples from air,[7] which reacts rapidly with powdered $VH_n$ at room temperature and causes a drop in susceptibility

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(1) A. J. Maeland, *J. Phys. Chem.*, **68**, 2197 (1964).

(2) R. L. Zanowick and W. E. Wallace, *J. Chem. Phys.*, **36**, 2059 (1962).

(3) R. A. Oriani, E. McCliment, and J. F. Youngblood, *ibid.*, **27**, 330 (1957).

(4) W. A. Norder, *Rev. Sci. Instr.*, **31**, 849 (1960).

(5) B. G. Childs, W. E. Gardner, and J. Penfold, *Phil. Mag.*, **5**, 1267 (1960).

(6) S. Taniguchi, R. S. Tebble, and D. E. G. Williams, *Proc. Roy. Soc.* (London), **A265**, 502 (1962); $\chi = 5.81 \times 10^{-6}$ cgs unit.

(7) R. L. Zanowich, private communication.

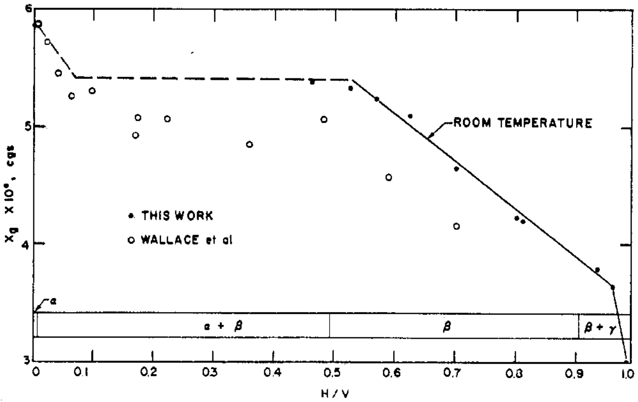

Figure 1.—Relation of paramagnetic susceptibility to atomic ratio H/V for the V–$H_2$ system at room temperature. Open circles are replotted data of Zanowick and Wallace.[2] The phase boundaries in the lower portion are from Maeland.[1]

of about the same magnitude as that reported as due to hydrogen.[8]

Figure 2 shows the peculiar behavior of the system at 150° where the bcc α phase extends, according to Maeland, to H/V $\cong$ 0.2. At this temperature it is possible to form any desired composition up to $VH_{0.75}$ by adding or pumping off hydrogen. The form of what appears to be a hysteresis loop is shown by comparison of the solid black circles representing removal of hydrogen and the other points which represent uptake of hydrogen. This type of hysteresis is also observed in dissociation pressure measurements except that the horizontal S curve in the α-phase region is new. The difference between the upper and lower portions of the loops is just outside the total error of measurement shown in the upper right-hand portion of the figure ($\pm 0.05 \times 10^{-6}$ cgs unit).

In order to explore the nature of the hysteresis more thoroughly, a sample of $VH_{0.68}$ was heated over a period of a few hours from room temperature to 310°. The susceptibility was found to fall monotonically until the temperature reached 180° when the rate of fall decreased. As the sample reached 310° the susceptibility suddenly rose from $4.8 \times 10^{-6}$ to $5 \times 10^{-6}$ cgs unit. On cooling, the susceptibility increased very slightly and linearly to its original value. This cycle could be repeated. On holding the sample at some temperature below 310°, the susceptibility would rise slowly to the upper arm of the hysteresis loop. This form of hysteresis is clearly different from that shown in the 150° isotherm (Figure 2) since the latter represents stable reproducible values that do not change over a period of days.

Curves of susceptibility *vs.* temperature are given in Figure 3 at 200 and 300°. There is no hysteresis at these temperatures, and true equilibrium is attained rapidly.

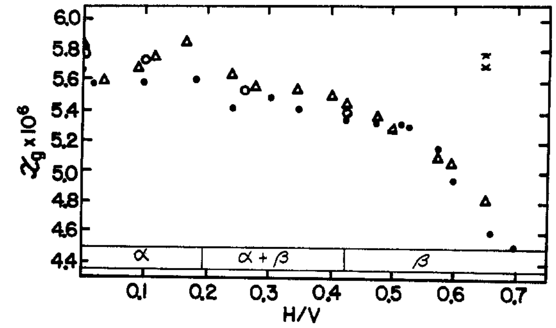

Figure 2.—Magnetic susceptibility *vs.* H/V at 150°. Black circles indicate removal of hydrogen and an equilibrium time of 24–48 hr. Other points indicate uptake of hydrogen. The open circles represent equilibration times of approximately 1 week at temperature; the triangles represent equilibration times of 18–24 hr. Experimental error is indicated at upper right.

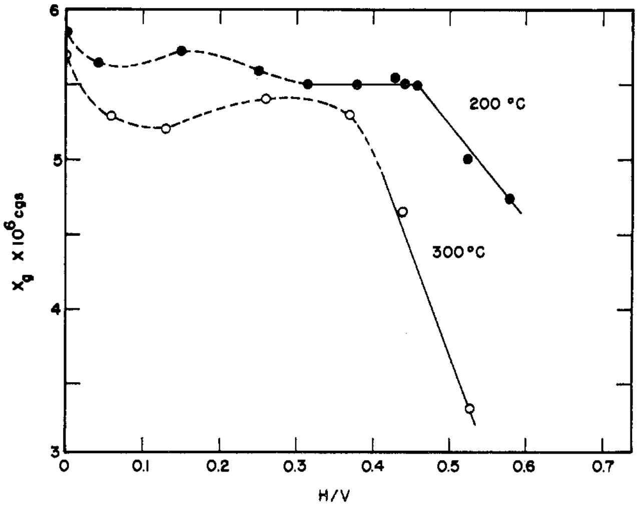

Figure 3.—Magnetic susceptibility *vs.* H/V at 200 and 300°. Points represent equilibration at temperature over 24–48 hr. Compositions were attained only by removal of hydrogen.

The various compositions were obtained by progressively pumping off hydrogen from a hydrogen-rich sample in order to avoid the formation of gross inhomogeneities in hydrogen distribution. According to Maeland's phase diagram,[1] both temperatures are above the critical temperature so that only α phase is present. The sharp change in slope at approximately $VH_{0.4}$ and $VH_{0.5}$ is therefore not correlated with any phase change discernible by X-ray observations. The line between several points is dashed because there is no theoretical reason for drawing either a horizontal or a sloping straight line. The general form of the curve is confirmed by continuous visual observations of the susceptibility over short times, and the lower susceptibilities at H/V $\cong$ 0.1 are unequivocal.

Figure 4 shows the difference between room temperature susceptibility and the susceptibility at lower temperatures plotted *vs.* temperature. The magnetic anomaly at 250°K observed by Burger and Taylor[9] is confirmed, and a second anomaly is shown at 185°K. The trend of the peaks with increasing hydrogen content suggests a relationship between the observed peaks in vanadium metal and the presence of hydrogen or hydrogen-induced dislocations, etc.

## Discussion

The data shown in Figures 1–3 indicate a very small decline in paramagnetic susceptibility with increasing

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(8) R. J. Roy, private communication.

(9) J. P. Burger and M. A. Taylor, *Phys. Rev. Letters*, **6**, 185 (1961).

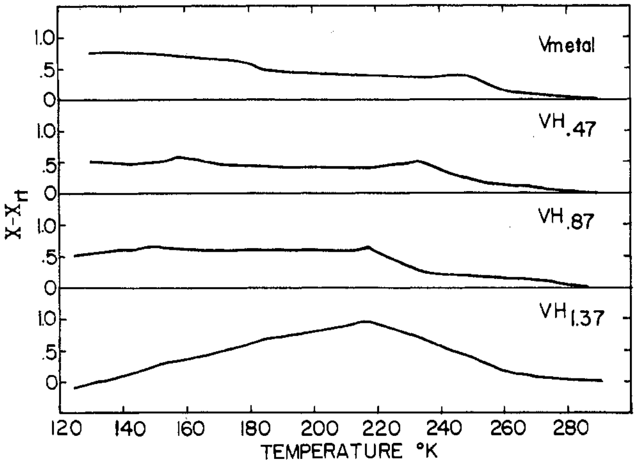

Figure 4.—The difference ($\chi - \chi_{rt}$) × $10^{-6}$ cgs unit *vs.* *T* for vanadium metal and three compositions of the V–$H_2$ system.

H/V in this metallic system. It is evident that hydrogen is contributing no net spin, *i.e.*, that it is not present as trapped free atoms. The gross effect of hydrogen is, in fact, about what one would expect from isotropic expansion of the bcc lattice of the metal throughout the $\alpha$-phase region. This is strikingly illustrated by the sharp drop in susceptibility between V metal and $VH_{\sim 0.1}$ which closely parallels a sharp increase in unit cell volume recently observed in X-ray diffraction studies over this composition region.[10] Presumably this increase in volume is due both to hydrogen and to formation of dislocations accompanying its introduction into the metal lattice. The right-hand portion of the curves shown in Figures 1–3 may most simply be interpreted as due to distension of the metal. The central portions may represent an almost horizontal relation of susceptibility to hydrogen content over regions where the unit cell volume is not changing rapidly with H/V (compare spacing of lines in ref 1, Figure 3). In Figure 1 the region H/V $\cong$ 0.05 to H/V $\cong$ 0.48 is composed of mixtures of hydrogen-saturated cubic metal ($\alpha$ phase) and tetragonal hydride ($\beta$ phase). If these two solid phases are in equilibrium, a linear relation between $\chi$ and H/V is obviously expected. Neither Zanowick and Wallace's data nor ours are in agreement with this expectation. Our samples which were obtained by pumping off hydrogen at room temperature are highly defective unannealed solid phases containing many vacant H sites. The dashed line is drawn simply to relate the two sets of data. This region is not accessible to experiment for reasons mentioned above, but we expect the defective $\beta$ phase to have a susceptibility which is nearly independent of H/V as the latter diminishes down to the point where the metastable lattice reverts to the $\alpha$ phase, *i.e.*, at H/V $\cong$ 0.05.

The sharp changes in slope shown in Figure 1 at H/V = 0.5 and 0.9 correlate reasonably well with the ($\alpha + \beta$)–($\beta$) and ($\beta$)–($\beta + \gamma$) phase boundaries given by Maeland (ref 1, Figure 1) at room temperature. A similar relationship between the susceptibility and the phase boundaries is shown in Figure 2. The correlation between susceptibility and the lattice parameter $c_0$ of the tetragonal arrangement of V atoms in the $\beta$ phase is plausible since $c_0$ increases sharply with H/V beyond the ($\alpha + \beta$)–($\beta$) boundary. The decrease in susceptibility between H/V = 0.2 and 0.7 does *not* correlate very well with the monotonic increase in molar volume over this region since no break in the susceptibility slope at H/V = 0.43 would be expected.

The results at 200 and 300° shown in the right-hand portions of Figure 3 are not explicable by reference to Maeland's phase diagram where only the $\alpha$ phase is shown above 200°. It is possible that the magnetic susceptibility measurement is sensitive to ordering or disordering of hydrogen atoms, *e.g.*, formation or decay of a superlattice or microphases which are not detectable by X-ray observations (which "see" only vanadium atom positions). It is also possible that since the bcc vanadium unit cell is progressively distended by increasing hydrogen content, one sees some fine structure in the plots of $\chi$ *vs.* H/V due to movement of the Fermi level along the density of states curve. Jones[11] has suggested the latter possibility.

Zanowick and Wallace have argued that their result is expected if one postulates that hydrogen donates its electron to the d band of vanadium as is generally supposed and have cited the fact that chromium, which has one more electron than vanadium, behaves similarly in vanadium–chromium alloys. Unfortunately, for this argument, either addition or removal of an electron may result in a lowering of the susceptibility in the case of vanadium alloys. Thus in ref 6, Figure 3, pure vanadium is shown to be at or near a peak in a graph of susceptibility *vs.* number of (outer) electrons per atom. (This peak is actually at 4.95 electrons rather than 5.00 according to ref 12.) A decreased magnetic susceptibility cannot therefore be taken by itself as an argument in favor of an increased population in the d band of vanadium, particularly since a considerable and, later, an anisotropic expansion of the metal–metal distance occurs as hydrogen is absorbed.

The question of whether the hydrogen is protonic or hydridic has been considered recently in the case of the closely related Ta–$H_2$ system[13] and the question is still not resolved. It is the purpose of this paper to suggest that the most important contribution of hydrogen, irrespective of electronic considerations, is its effect on the metal–metal interactions and, further, that for the most part these interactions are just what one would expect from distension of the metal lattice.

This conclusion is borne out by preliminary results from a study of the Pd–$H_2$ system.[14]

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