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Nuclear-Magnetic-Resonance Study of Hydrogen Alloying in the Early Transition Metals (Group VB)*

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The Knight shifts and spin-lattice relaxation times of vanadium and niobium in the VH_x and NbH_x systems, respectively, have been measured. From the observed relaxation-time temperature dependence, the contribution of the conduction electrons to the nuclear relaxation was found. A comparison of the Knight shifts and the relaxation times of V and Nb in the hydrides with those in the corresponding alloys, VCr_x and $NbMo_x$, shows great similarity. We have drawn some conclusions about this similarity. Using a Korringa-type relation for Nb in the NbH_x system, we learn about the type of conduction electrons giving rise to the Knight shift and relaxation rate.

INTRODUCTION

THE transition metals of groups III, IV, and V have in common the ability to absorb relatively large amounts of hydrogen, thus forming hydrides. Nuclear-magnetic-resonance[1] and susceptibility[2] measurements led us to believe that the electronic structure of these hydrides is similar to that of ordinary alloys. The purpose of the present work is to study in detail this similarity.

The following features that are common to all the transition metals and their hydrides help us in the understanding of their electronic structure:

(a) The ability to absorb relatively large amounts of hydrogen.

(b) The correlation between the maximum amount of hydrogen absorbed and the electronic structure of the metal (its position in the periodic table).

(c) A change in the Knight shifts of the metal as a function of the amount of hydrogen absorbed.[1]

(d) The correlation between hydrogen affinity and the magnetic susceptibility.[3]

(e) The high diffusion rate (at high temperatures) of the hydrogen within the hydride.[1]

All these features can be explained if we make two assumptions. First, we assume that the hydrogen in the metal gives up its electron to the conduction band, changing in this way the density of states of the electrons near the Fermi energy. Secondly, we assume a rigid-band model.

The ability of the metal to take hydrogen atoms into its lattice is related to the density of states of the conduction electrons. They are responsible for the effectiveness of screening the positive charge of the hydrogen ion,[4] and thus for the ability to absorb more hydrogen. The screening acts here as an effective dielectric medium which reduces the ionization potential of the hydrogen. This explains the correlation between hydrogen affinity and the properties which depend on the density of states[3] (magnetic susceptibility, Knight shift, etc.).

The bare proton is responsible for the high diffusion rate of hydrogen in these metals.

Assuming a rigid-band model, the role of the hydrogen in the hydride is the same as that of the solute in ordinary alloy, namely to supply electrons to the conduction band. The validity of the rigid-band model can be tested by comparing systems with the same solvent, with hydrogen as the other constituent in one of these systems.

In the present work we have measured the Knight shifts and the spin-lattice relaxation times of vanadium and niobium in the VH_x[5] and NbH_x systems, respectively, and we have compared them with those in the VCr_x[6] and $NbMo_x$[7,8] systems. We suggest an explanation for our findings.

EXPERIMENTAL

The samples were prepared in the same way as was described previousy.[1] In both VH_x and NbH_x there exist two phasess at room temperature. Above ~100°C in both systems there exists only the metal-hydride phase. Therefore our conclusions have been based only on those data for the Knight shift and spin-lattice relaxation time which were measured at about 200°C.

The apparatus including the high-temperature probe has been described elsewhere.[1] T_1 was measured using a pulse technique. Both the 180°–90° and 90°–90° methods were employed.

RESULTS

A. Knight Shift

In Figs. 1 and 2 are plotted the Knight shifts as a function of the electron-to-atom ratio, assuming that

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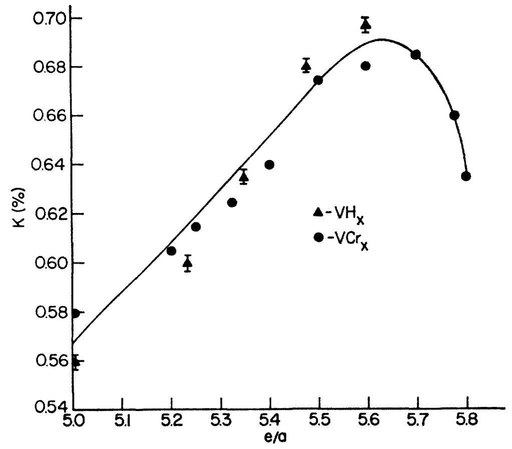

FIG. 1. V Knight shift as a function of e/a in the VH$_x$ and VCr$_x$ (Ref. 6) systems. ▲—VH$_x$, ●—VCr$_x$.

hydrogen contributes its electron to the conduction band.

Figure 1 depicts the vanadium Knight shift in the VH$_x$[5] system. For comparison we have included the vanadium Knight shift in the VCr$_x$ system as measured by Butterworth.[6] The similarity in behavior in the two systems is easily seen.

Figure 2 depicts the Nb Knight shifts in the NbH$_x$ and NbMo$_x$ systems (the latter taken from Refs. 7 and 8). The two systems behave quite similarly.

B. Spin-Lattice Relaxation Time

In general there is more than one mechanism responsible for the nuclear-spin-lattice relaxation. The problem was to determine that part of the relaxation which comes through the conduction electrons as this is the only interaction in which we are interested in the present work.

There is a very effective mechanism for relaxation competing with that due to the conduction electrons. It is caused by the diffusion of the hydrogen within the lattice.[1] Both the dipole-dipole interaction of the Nb with the hydrogen, and the quadrupole interaction of the Nb with its noncubic environment (caused by the presence of the hydrogen) become time-dependent when the hydrogen diffuses, and can thus cause spin-lattice relaxation.

The diffusion is a thermally activated process, and T_1 as a function of temperature has a known behavior. The activation energy for diffusion has been calculated using T_1 of the hydrogen.[1] This knowledge helps us to eliminate the contribution of the conduction electrons to the spin-lattice relaxation.

The diffusion becomes most effective for relaxation when the hydrogen jump frequency is about the same as the nuclei Larmor frequency. In the present case it occurs around room temperature; above and below this temperature, diffusion becomes less and less effective in causing relaxation.

Because of the large static-quadrupole interaction, it is difficult to see the Nb resonance at low temperatures. On the other hand, at high temperatures the diffusion averages out this interaction and the resonance is observable. It can be shown that at high enough temperatures, the diffusion is very ineffective for relaxation, and the T_1 that we measure is essentially that which comes from the interaction of the nuclei with the conduction electrons.

$(T_1)_d$ is the spin lattice relaxation time caused by diffusion. Its temperature dependence has the form (at the high-temperature side)

$$(T_1^{-1})_d=\nu_0 e^{E/kT}, \tag{1}$$

where ν_0 is the attempt frequency and E the activation energy of the diffusion. It was found[1] that the activation energy for hydrogen diffusion in NbH$_x$ is

$$E=3.7\pm0.3 \text{ kcal/mole}, \quad T>50°\text{C}. \tag{2}$$

We can write

$$(T_1^{-1})_m=(T_1^{-1})_d+(T_1^{-1})_e, \tag{3}$$

where $(T_1)_m$ is the measured value of the spin-lattice relaxation time. $(T_1)_d$ and $(T_1)_e$ are the relaxation times due to diffusion and conduction electrons, respectively. We now want to find out at what temperature

$$(T_1^{-1})_d \ll (T_1^{-1})_e.$$

Using the value $E=4$ kcal/mole, we can write for the ratio of T_1 in two temperatures, T' and T''

$$(T_1)_{T'}/(T_1)_{T''}=e^{E/k(1/T''-1/T')}. \tag{4}$$

For $T'=350°$K and $T''=650°$K, we get

$$(T_1)_{350}/(T_1)_{650}\sim e^8 \sim 3000.$$

We have found that the ratio of the measured T_1's at these two temperatures is about 5. Therefore, $(T_1^{-1})_d$ at

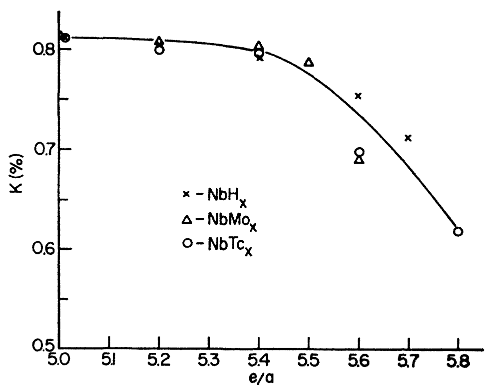

FIG. 2. Nb Knight shift as a function of e/a in the NbH$_x$ (Ref. 1a), NbMo$_x$ (Refs. 7, 8) and NbTc$_x$ (Ref. 8) systems. ×—NbH$_x$ △—NbMo$_x$, ○—NbTc$_x$.

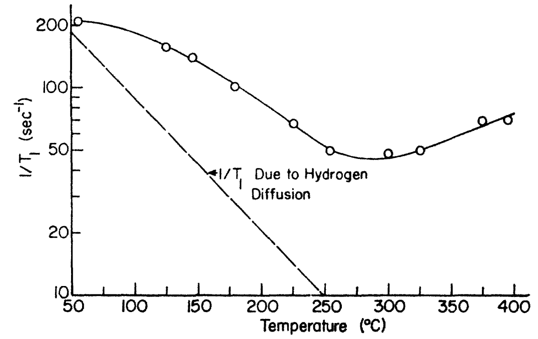

FIG. 3. $1/T_1$ of Nb in $NbH_{0.7}$ as a function of temperature. The broken line represents the calculated value of $(T_1^{-1})_d$ assuming $(T_1)_m \sim (T_1)_d$ at room temperature and $E=4$ kcal/mole.

650°K is negligible in comparison with $(T_1^{-1})_m$, that is, the main contribution to $(T_1^{-1})_m$ comes from $(T_1^{-1})_e$.

In the above argument we have assumed that these are the only two mechanisms for relaxation. Actually there is another possible mechanism: through paramagnetic impurities; however, their small concentration and the high temperature exclude this possibility.

Figure 3 shows the temperature dependence of the measured $1/T_1$ of Nb in $NbH_{0.7}$. We can see that T_1^{-1} becomes smaller as the temperature increases, reaching a minimum beyond which the main mechanism is the conduction electrons. In the figure is also plotted the calculated value of $(T_1^{-1})_d$, assuming $(T_1)_m \sim (T_1)_d$ at about room temperature and $E=4$ kcal/mole.

In the VH_x system the narrowing temperature of the hydrogen line is about room temperature and the activation energy for diffusion is similar to that in the NbH_x system. We can thus use the same consideration in the VH_x system and take $(T_1)_m$ at high temperatures to be the $(T_1)_e$ we are interested in. Following Butterworth[6] and in order to compare our results with his, we plot $(T_1T)^{-1/2}$ (which is proportional to the density of state around Fermi energy) as a function of hydrogen concentration (which is assumed equal to electron/atom). Figure 4 is such a plot of V in the VH_x system. For comparison, Butterworth's data for V in the VCr_x system are included in the figure. The similarity in behavior is easily seen.

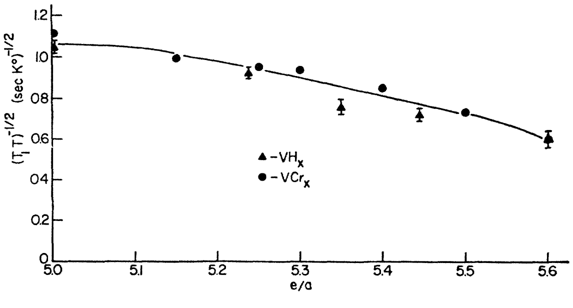

FIG. 4. $(T_1T)^{-1/2}$ as a function of e/a where T_1 is the spin lattice relaxation time of V in the VH_x system taken at 300°C. The circles represent Butterworth's data (Ref. 6) for V in the VCr_x system. ▲—VH_x, ○—VCr_x.

Figure 5 is the same plot for Nb in the NbH_x system. Unfortunately there are no data available on T_1 in the $NbMo_x$ system, mainly because the lines of Nb in the Nb-rich side alloys are too broad.

DISCUSSION

In the present work we want to indicate primarily the striking similarity in the NMR data (Knight shift and relaxation rate) for the transition-metal alloy and the transition-metal hydride. The electronic structure of the transition metal alloys, as reflected in the NMR data, does not depend on the type of solute (we define here the solvent as the nuclei on which the NMR measurements are taken). It depends only on the number of electrons contributed by the solute to the conduction band.

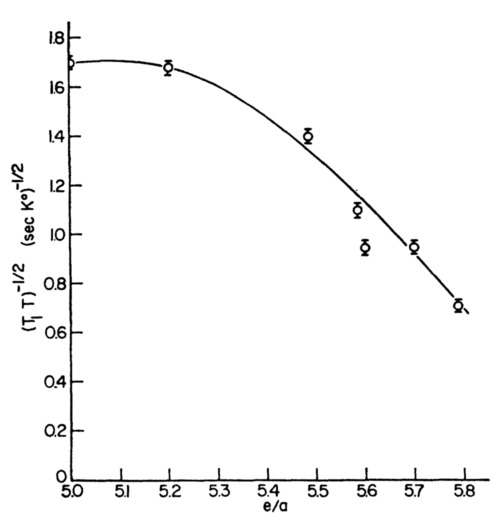

FIG. 5. $(T_1T)^{-1/2}$ as a function of e/a where T_1 is the spin-lattice relaxation time of Nb in the NbH_x system taken at 300°C.

The usual approach[6] in analyzing the Knight-shift and relaxation-rate data in transition-metal alloys is to assume that there are three kinds of interactions which are the principal contributors to the Knight shift and to the relaxation. This is expressed in the form:

$$K=K_s+K_d+K_o$$

$$T_1^{-1}=(T_1^{-1})_s+(T_1^{-1})_d+(T_1^{-1})_o, \qquad (5)$$

where K and T_1 are the observed Knight shift and relaxation time, respectively; s indicates the s electron's contact hyperfine interaction, d the induced core polarization[9] and o the orbital interaction.[10]

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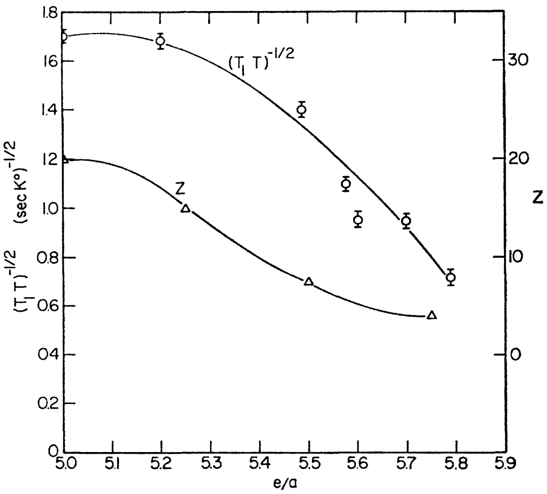

FIG. 6. $(T_1T)^{-1/2}$ where T_1 is the spin-lattice relaxation time of Nb in the NbH_x system, and Z the density of states of the conduction electrons in the $NbMo_x$ system as reflected in specific-heat data (Ref. 8)—both as functions of e/a.

The same considerations used in the analysis of the VCr_x data[6] can be applied to the VH_x. This means that the Knight shift and the relaxation rate have the same origin in both systems.

Although we do not have T_1 data for Nb in the $NbMo_x$ system to compare with that in the NbH_x system, the similarity of the Knight shifts in the two systems leads us to assume that what has been said above for the VH_x, VCr_x systems can also be applied to the NbH_x, $NbMo_x$ systems. Following Butterworth[6] we can write

$$(T_1T)^{-1}=C_sZ_s^2+C_dZ_d^2\,, \tag{6}$$

where Z is the electronic density of states at Fermi level, C_s, C_d, are constants that characterize the interactions caused by s and d electrons, respectively. In Fig. 6 is plotted $(T_1T)^{-1/2}$ as a function of e/a for Nb in NbH_x and Z as a function of e/a (Z is based on specific-heat data taken from Ref. 8). The similarity of the two curves leads to the same conclusions that were reached for the VCr_x system, namely that (a) $Z_d \gg Z_s$ and (b) C_d does not depend on hydrogen concentration. However, the last conclusion does not hold very well for high hydrogen concentrations, which means that C_d decreases for high e/a. We shall return to this point later.

Van Ostenberg *et al.*[8] reached a similar conclusion: that the main contribution to the Knight shift comes from the d electrons through orbital-type interaction.

We can now use the Knight-shift analysis[8] and our T_1 data to learn more about the NbH_x and $NbMo_x$ systems.

For the s-type electrons thate is a simple relation (Korringa relation) between T_1 and K written in the form

$$(T_1T)^{-1}AK^2\,, \tag{7}$$

where A is a constant.

On can write a Korringa-type relation for the two other types of interactions—core polarization and orbital[10]:

$$((T_1T)^{-1})_d=AK_d^2a_1\,, \tag{8}$$

$$((T_1T)^{-1})_0=A\alpha K_0^2a_2\,. \tag{9}$$

The observed T_1 is related to the observed K by

$$((T_1T)^{-1})=A\,(K_s^2+a_1K_d^2+\alpha a_2K_0^2)\,, \tag{10}$$

where a_1 and a_2 measure the degree of admixture of Γ_3 and Γ_5 type wave functions in the d electrons. α stands for the ratio of the $\langle r^{-3}\rangle$ that appears in the T_1T formula to that which appears in the K formula. In the latter, r^{-3} is to be averaged over all occupied states of the band, whereas in the former r^{-3} is averaged only over states at the Fermi surface. It has been shown[11] that

$$\tfrac{1}{5}<a_1<\tfrac{1}{2} \quad \text{and} \quad 0\leqq a_2\leqq 10\,. \tag{11}$$

As the main contribution to the Knight shift comes from orbital interaction and $a_1<1$,

$$a_2K_0^2\gg a_1K_d^2, K_s^2 \tag{12}$$

so that

$$(T_1T)^{-1}=A\alpha K_0a_2^2\,. \tag{13}$$

We also assume that α does not change with e/a. We can calculate for example the ratio of the T_1T's of Nb metal and $NbH_{0.7}$:

$$(T_1T)_{Nb}^{-1}/(T_1T)_{NbH_{0.7}}=(a_2K_0^2)_{Nb}/(a_2K_0^2)_{NbH_{0.7}}\,. \tag{14}$$

From our data, the left-hand side of Eq. (14) is 3.6, using Table 1 of Ref. 8 for the orbital contribution to K_0, we get $((a_2)_{Nb}\times 0.85)/((a_2)_{NbH_{0.7}}\times 0.42)=3.6$. Therefore

$$(a_2)_{Nb}=1.8(a_2)_{NbH_{0.7}}\,. \tag{15}$$

This result means that upon alloying, the amount of Γ_3-type wave function increases. This is not surprising as it is known that the Γ_3-type electrons are higher in energy than the Γ_5-type (at least at the upper half of the band).[12] By alloying we fill up the band and in this way increase the number of higher energy electrons. It also explains the deviation from the similarity of the curves $(T_1T)^{-1/2}$ and Z as functions of e/a discussed before.

ACKNOWLEDGMENTS

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