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Titanium Knight shift in titanium hydride

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The titanium Knight shift was measured at room temperature as a function of hydrogen concentration in TiH_x and as a function of temperature for TiH_2. In contrast to hexagonal Ti metal, the close-lying ^{47}Ti and ^{49}Ti resonances were resolved in TiH_2 even in the tetragonal phase. The shift in TiH_2 was found to be temperature dependent, varying from $(0.252\pm0.001)\%$ at room temperature to $(0.312\pm0.001)\%$ at 180 K. It was consistent with previously measured hydrogen-spin-lattice-relaxation times and with accepted band-structure models. The accuracy of the hydrogen-concentration dependence of the Knight shift was much lower due to vacancy-induced quadrupolar interactions and the resultant inability to resolve the ^{47}Ti and ^{49}Ti resonances. The Knight shift was only slightly concentration dependent over the entire range, having a value of about 0.25%, but jumping suddenly to 0.55% at $x=1.5$. This was accompanied by a widely separated doubly peaked resonance line, We speculate on the cause of this jump and the resultant line shape.

I. INTRODUCTION

Transition-metal hydrides have been useful vehicles in the study of electronic structure and its interrelationship to physical behavior. This is especially so due to their nonstoichiometry, which allows wide variations of hydrogen concentration within a given crystallographic structure. Such a change in hydrogen concentration results in a movement of the Fermi level with concomitant variations in physical behavior. These changes are then compared with those expected from theoretical considerations.

One of the hydrides so studied is the TiH_x system. An early result is that of Trzebiatowsky and Stalinski,[1] who obtained the magnetic-susceptibility dependence as a function of temperature and hydrogen concentration. Nagel and Goretzki[2] extended this by studying the influence of V alloying. Ducastelle, Caudron, and Costa[3] measured a number of electronic-structure—related parameters in TiH_x and ZrH_x and proposed a mechanism to explain the tetragonal deformation in these systems. Bohmhammel, Wolf, Gross, and Madge[4] obtained the electronic contribution to the specific heat at low temperatures from which the density of states at the Fermi level was obtained. Weaver, Peterman, Peterson, and Franciosi[5] studied the electronic structure using photoelectron spectroscopy and synchrotron radiation, and Tanaka, Hamasaka, Yasuda, and Fukai[6] used soft-x-ray spectroscopy. We will concentrate on the nuclear-magnetic-resonance (NMR) studies related to the electronic structure of TiH_x.[7-12] Of these, only Frisch and Forman[12] investigated the more difficult to detect titanium resonance, while all the others obtained the hydrogen resonance. The factors that make the Ti resonance difficult to observe are the low values of the gyromagnetic ratios γ of the two Ti isotopes (^{47}Ti and ^{49}Ti) having nonzero magnetic moment, their low natural abundance, the close values of their γ (causing overlap of the resonance lines), and the quadrupolar interaction. Both the hydrogen and a metal resonance have been compared in titanium hydride by alloying with Nb (Ref. 13) or V (Ref. 14) and observing these nuclei. Narath[15] studied the Ti NMR in pure titanium metal.

A number of band-structure calculations of TiH_2 have been conducted for both the cubic[16-23] and tetragonal phases,[22] In addition, the influence of varying the hydrogen concentration was investigated.[22,24] Switendick[22] compared the calculated density of states as a function of hydrogen concentration with the results of the NMR hydrogen resonance[11] and found good correlation.

We report here on the Ti resonance in TiH_x using the same samples as those employed in Ref. 11, where the ^1H resonance was investigated. The temperature dependence of the Ti Knight shift was obtained for TiH_2 as well as the room-temperature hydrogen-concentration dependence of the Ti resonance in TiH_x. The latter results were more difficult to interpret due to complications resulting from quadrupolar interactions caused by hydrogen vacancies. Samples having hydrogen concentrations of x equal to 1.502, 1.548, 1.631, 1.672, 1.711, 1.734, 1.770, 1.791, 1.826, 1.884, 1.941, 1.973, and 2.00 were measured.

The hydride phase of TiH_x is nonstoichiometric, the hydrogen concentration range being $1.5\leq x\leq 2$. Hydrogen concentrations below $x=1.5$ result in a mixture of $TiH_{1.5}$ and Ti metal, and perhaps a newly discovered metastable tetragonal phase[25] having $c/a>1$. The hydride has the fcc structure for $1.5\leq x\leq 1.8$, becoming tetragonally distorted at concentrations higher than this. This distortion increases with hydrogen concentration[11,26] and decreasing temperature[27] and disappears above about 310 K. The hydrogen occupies the tetrahedral sites, forming a simple-cubic (tetragonal) sublattice with random voids in the nonstoichiometric hydride.

II. EXPERIMENTAL PROCEDURE

Sample preparation was described elsewhere.[11] The ^{47}Ti and ^{49}Ti resonances were obtained using a Bruker CXP-300 spectrometer at a resonance frequency of 16.925 MHz. The spectrometer recovery time was about 150 μsec. The resonance absorption curve was obtained from the Fourier transform of the average of about 10000 scans of the free-induction decay for the $TiH_{2.00}$ temperature dependence study and of the echo for the room-temperature hydrogen-concentration-dependent portion of the study. The 90° pulse was adjusted using the reference sample and the echo amplitude was optimized for the hydride by variation of the length of the second pulse. The lengths of the first and second pulses were 24 and 20 μsec, respectively. Knight shifts were measured relative to $TiCl_4$ without chemical-shift corrections for the compound or magnetic-susceptibility corrections for the powdered hydride.

III. EXPERIMENTAL RESULTS

Figure 1 shows the ^{47}Ti and ^{49}Ti absorption lines of stoichiometric $TiH_{2.00}$ at various temperatures ranging from 320 to 180 K. The two peaks are attributed to the two isotopes; the ^{49}Ti resonance (on the left) having spin of $I=\frac{7}{2}$ being more prominent than the ^{47}Ti ($I=\frac{5}{2}$) resonance. At the highest temperatures the material is cubic and should show no quadrupolar interaction. As the temperature is lowered, the crystal structure becomes tetragonally distorted. We see that the signal-to-noise ratio decreases with decreasing temperature. This is probably a result of the increasing tetragonality-induced quadrupolar interaction, leaving the $m=-\frac{1}{2}$ to $\frac{1}{2}$ transition intact to first order. The ^{47}Ti and ^{49}Ti lines are still easily resolved, while this was impossible for the pure hexagonal Ti metal.[15]

Figure 2 shows the hydrogen-concentration dependence of the Ti resonance. The effect of hydrogen vacancies causes a much larger electric field gradient at the Ti nuclear sites than does the tetragonal deformation. As a result, the free-induction decay was considerably shorter, so that the signal was lost in the receiver recovery time and the signals were detected using quadrupole echoes.

IV. DISCUSSION OF THE RESULTS

A. Temperature dependence of Ti Knight shift in TiH_2

Figure 3 shows the temperature dependence of the ^{49}Ti Knight shift in TiH_2 relative to $^{49}TiCl_4$. The ^{49}Ti resonance was chosen since it is more prominent, giving a better signal-to-noise ratio. A possible isotope effect will be discussed later.

The characteristics of the shift are that it is positive, temperature independent in the cubic phase ($T>300$ K), and *increases* with decreasing temperature. In contrast, the ^{1}H Knight shift is negative[7,9,11] and *decreases* in magnitude with decreasing temperature.[9] Furthermore, the hydrogen $(T_{1e}T)^{-1/2}$ *decreases* with decreasing temperature.[8] T_{1e} is the conduction-electron contribution to the

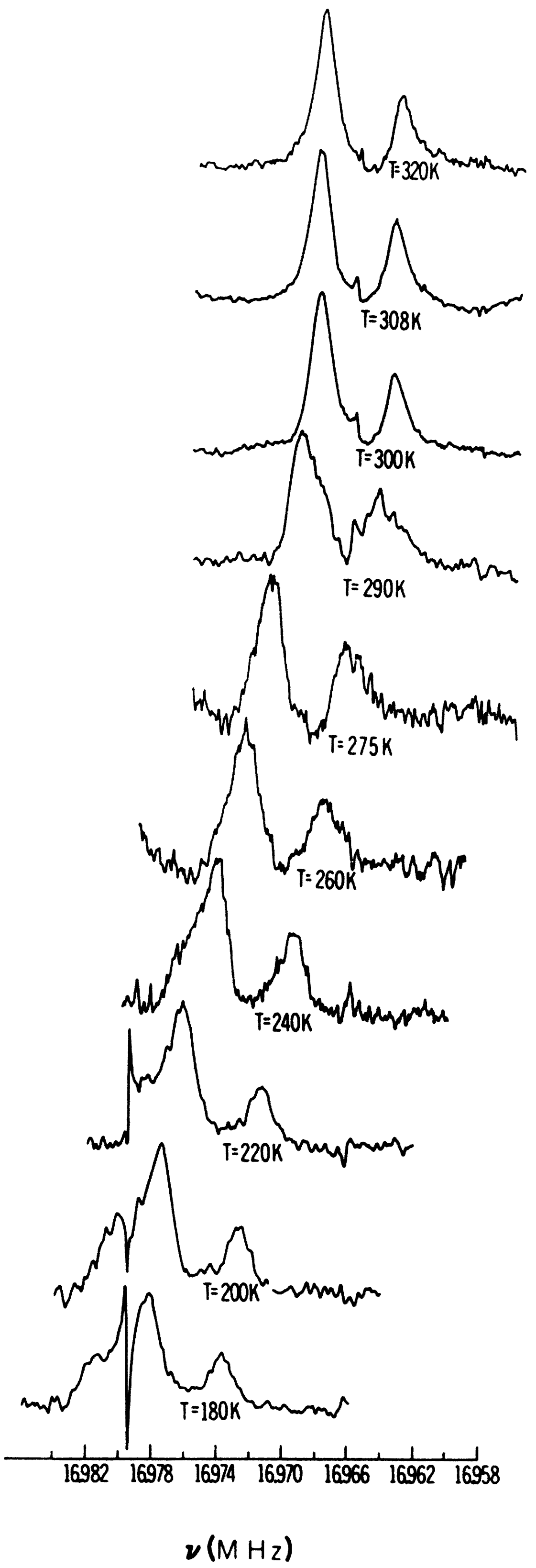

FIG. 1. Absorption traces of ^{47}Ti and ^{49}Ti in TiH_2 for various temperatures. ν increases to the left.

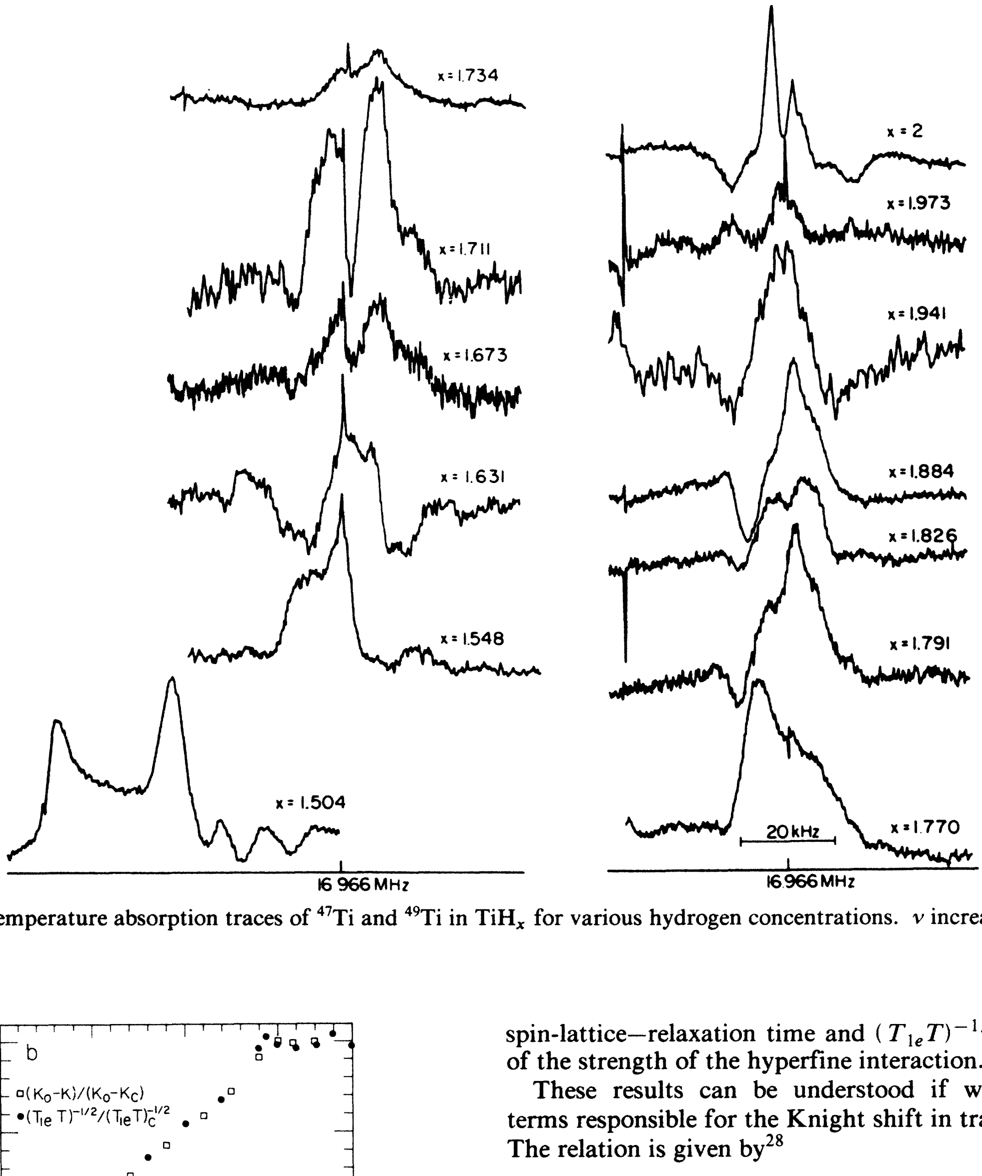

FIG. 2. Room-temperature absorption traces of ^{47}Ti and ^{49}Ti in TiH$_x$ for various hydrogen concentrations. ν increases to the left.

spin-lattice—relaxation time and $(T_{1e}T)^{-1/2}$ is a measure of the strength of the hyperfine interaction.

These results can be understood if we consider the terms responsible for the Knight shift in transition metals. The relation is given by[28]

$$K = 2\mu_B[H_{\rm hf}^{(s)}N_s(E_F) + H_{\rm hf}^{(d)}N_d(E_F)] + \frac{1}{A\mu_B}H_{\rm hf}^{(o)}\chi_o \ , \tag{1}$$

where $H_{\rm hf}^{(s)}$, $H_{\rm hf}^{(d)}$, and $H_{\rm hf}^{(o)}$ are the s contact, d-spin core polarization, and orbital hyperfine fields at the nucleus, and where we have approximated the susceptibilities χ_s and χ_d by $2A\mu_B^2N_s(E_F)$ and $2A\mu_B^2N_d(E_F)$, respectively. $N_s(E_F)$ and $N_d(E_F)$ are the s- and d-band densities of states at the Fermi level E_F. χ_o is the orbital contribution to the magnetic susceptibility, A is Avogadro's number and μ_B is the Bohr magneton. All terms are generally positive, except for the core-polarization interaction $H_{\rm hf}^{(d)}$, which is usually negative. Both band calculations[19,22] and NMR measurements[10,11] support the theory that the tetragonal deformation of TiH$_2$ is accompanied by a splitting of the d band near the Fermi level which causes $N_d(E_F)$ to decrease with increasing tetragonality.

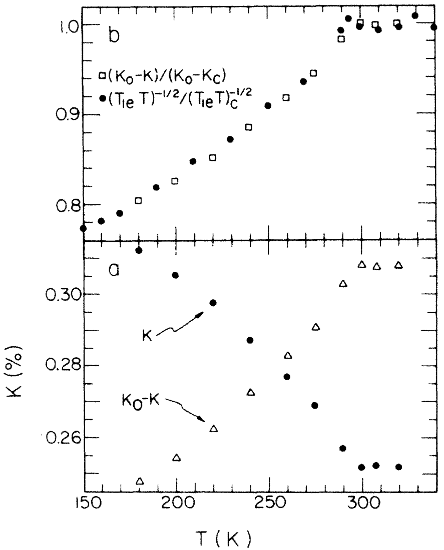

FIG. 3. (a) Temperature dependence of ^{49}Ti Knight shift K in TiH$_2$ and temperature dependence of K_0-K. The curve K_0-K is similar to the hydrogen $(T_{1e}T)^{-1/2}$ in Ref. 8 since both are proportional to the density of states at the Fermi level. This is verified in (b), wherein both the titanium K_0-K and hydrogen $(T_{1e}T)^{-1/2}$ are normalized with respect to their values in the cubic phase. If the assumptions in the text are correct, they should lie on one curve.

This is explicitly shown in Fig. 4 of Ref. 8, comparing $(T_{1e}T)^{-1/2}$ of H to the temperature-dependent tetragonality. We can thus write the Ti Knight shift in the form

$$K = K_0 - \beta N_d(E_F) , \tag{2}$$

where the first term is positive and independent of $N_d(E_F)$, and the minus sign is used since the core polarization is negative. Only the second term will be temperature dependent via the temperature-dependent tetragonality. The negative value of the ^{1}H Knight shift,[7,9,11] and the identical hydrogen-concentration variation of the hydrogen Knight shift and hydrogen $(T_{1e}T)^{-1/2}$,[7,9] show that the dominant H hyperfine interaction is core polarization.[7–9] We can thus write the hydrogen $(T_{1e}T)^{-1/2}$ in the form

$$(T_{1e}T)^{-1/2} = \alpha N_d(E_F) . \tag{3}$$

In order to obtain K_0 we consider two widely separated values of K, namely K_c and $K_{180\,\mathrm{K}}$, where K_c is the Ti Knight shift in the cubic phase and $K_{180\,\mathrm{K}}$ is the Knight shift at 180 K. Equations (2) and (3) then give

$$K = \frac{K_{180\,\mathrm{K}} - K_c (T_{1e}T)^{-1/2}_{180\,\mathrm{K}} / (T_{1e}T)_c^{-1/2}}{1 - (T_{1e}T)^{-1/2}_{180\,\mathrm{K}} / (T_{1e}T_c)^{-1/2}} .$$

Using the experimental values of $K_{180\,\mathrm{K}} = 31.22 \times 10^{-4}$ and $K_c = 25.21 \times 10^{-4}$ from this study, and $(T_{1e}T)^{-1/2}_{180\,\mathrm{K}} = 111.3$ $(\sec \mathrm{K})^{-1/2}$ and $(T_{1e}T)_c^{-1/2} = 138.3$ $(\mathrm{Sec\,K})^{-1/2}$ from Ref. 8 yields $K_0 = 56.0 \times 10^{-4}$. We thus see that the reason K decreases with increasing temperature despite the increasing hyperfine interaction lies in the fact that we have a constant value of K_0 from which an increasingly larger value (core polarization) is subtracted. If we subtract this constant value out and plot $K_0 - K$ as a function of T, we find behavior very similar to that of the hydrogen $(T_{1e}T)^{-1/2}$. If our analysis is correct, then Eqs. (2) and (3) indicate that both $(K_0 - K)/(K_0 - K_c)$ and $(T_{1e}T)^{-1/2}/(T_{1e}T)_c^{-1/2}$ should equal $N_d(E_F)/N_d(E_F)_c$. Plotting these as a function of temperature (Fig. 3), we see that the points do indeed lie along the same curve. This lends further verification that changes recorded in $(T_{1e}T)^{-1/2}$ as a function of hydrogen concentration do indeed reflect changes in the density of states at the Fermi level.

Our room-temperature value of $K = (0.252 \pm 0.001)\%$ for the Ti Knight shift agrees within experimental error with that of Frisch and Forman,[12] who obtained $(0.26 \pm 0.04)\%$. They did not resolve the separate ^{49}Ti and ^{47}Ti lines, nor did they observe the increase of the Knight shift from 0.252% to 0.312% as the temperature was lowered from ambient temperature to 180 K, but this change is about equal to the experimental error they report.

1. Hyperfine field $H_{\mathrm{hf}}^{(d)}$ at Ti nucleus

We can use our results to get a rough indication of the magnitude of the core-polarization contribution $H_{\mathrm{hf}}^{(d)}$ to the hyperfine field at the Ti nucleus. If we identify

$$2\mu_B H_{\mathrm{hf}}^{(s)} N_s(E_F) + \frac{1}{A\mu_B} H_{\mathrm{hf}}^{(o)} \chi_o$$

with K_0, we obtain

$$H_{\mathrm{hf}}^{(d)} = (K - K_0)/2\mu_B N_d(E_F) .$$

Thus, to obtain $H_{\mathrm{hf}}^{(d)}$ we must know $N_d(E_F)$ and K. A number of calculations of $N_d(E_F)$ have been made for the cubic phase. These give, variously, values of 5.31×10^{11} (Ref. 22), 5.96×10^{11} (Ref. 18), 8.77×10^{11} (Ref. 21), and 10.8×10^{11} (Ref. 19) states of one spin/erg cell. Using our value of $K_0 = 56.0 \times 10^{-4}$ and $K_c = 25.2 \times 10^{-4}$ for the cubic phase, we obtain, respectively, $H_{\mathrm{hf}}^{(d)} = -313$, -278, -189, and -154 kG. Narath[15] estimated $H_{\mathrm{hf}}^{(d)} = -100$ kG for the case of Ti metal. We note that these values are more than an order of magnitude larger than $H_{\mathrm{hf}}^{(d)} = -13.4$ kG estimated for the hyperfine field at the hydrogen nucleus.[11]

When the above values of $N_d(E_F)$ are substituted into $\chi_p = 2A\mu_B^2 N_d(E_F)$, one obtain 55.1×10^{-6}, 61.9×10^{-6}, 91.1×10^{-6}, and 112×10^{-6} emu/mol. This compares with the experimental value of Trzebiatowsky *et al.*,[1] 210×10^{-6} emu/mol, and $\chi = 280 \times 10^{-6}$ emu/mol obtained by Frisch *et al.*[12] Hence we see that there is probably a very large orbital contribution to the susceptibility.

2. Isotope effect

Since the two isotopes ^{47}Ti and ^{49}Ti have practically the same gyromagnetic ratio, the frequency difference between the two lines should be about the same in the hydride and the reference material $TiCl_4$. It was found that this difference was somewhat greater in the hydride, the change being about of the same order as the uncertainty, but consistently in one direction. Carter, Bennet, and Kahan[29] discuss the causes of an expected isotope effect. When Δ is defined by

$$\Delta \equiv (K_{\mathrm{light}} - K_{\mathrm{heavy}})/K_{\mathrm{heavy}} ,$$

We obtain $\Delta = (-35 \pm 7) \times 10^{-4}$, where Δ is the mean obtained from the ten measurements at the different temperatures and the error is the standard deviation of the mean.

B. Concentration dependence of room-temperature Ti resonance in TiH_x

1. Shape of traces

We have seen in the preceding section that while the tetragonal distortion introduces a quadrupole interaction, it is relatively weak and the two lines from the two isotopes remain resolved at all the temperatures. The electric field gradients set up by the hydrogen-site voids is much more severe and the presence of two lines that interfere makes the interpretation of the results much more difficult. It is seen from Fig. 2 that most of the traces show two maxima, but at lower hydrogen concentrations these maxima are too far apart (note change in frequency scale between Figs. 1 and 2) to be attributable to the two isotopes. We assume instead that a second-order shift of the $m = \pm\frac{1}{2}$ transition giving a double-peaked powder pattern is the primary contribution to the double maxima, and that the distance between the two isotope lines due to their different gyromagnetic ratios is small compared to the breadth of the experimental traces at low hydrogen concentrations. There are many complications. While the traces for the TiH_2 sample were obtained from a Fourier transform of the free-induction decay, here they were derived from the echo, and we have to keep in mind that the Fourier transform of the echo cannot be compared directly with the one of the induction decay. Furthermore, the tetragonal deformation leaves the asymmetry parameter η equal to zero, in contrast to quadrupolar interactions due to voids. The quadrupolar moments of ^{47}Ti and ^{49}Ti are not well established, so it is difficult to say how the second-order shift would influence the shape of the two overlapping isotope traces. Even if they were essentially the same and we would consider the two unshifted central lines close enough, they still would not be expected to form a simple double maximum since the distance between the maxima for ^{49}Ti having a spin $I=\frac{7}{2}$ would be about half that of ^{47}Ti, which has a spin of $I=\frac{5}{2}$. We would thus expect to see more than two peaks. Also, the voids are random without translational symmetry, so that Friedel oscillations may complicate the interaction. In stoichiometric titanium hydride each titanium atom is located at the center of a cube formed by eight hydrogen atoms. Figure 4 shows the probability $P_n(x)$ of a titanium atom having n nearest-neighbor hydrogen voids as a function of the hydrogen concentration x. The probability that a titanium atom has one nearest-neighbor hydrogen vacancy rises steeply as x drops from 2 to 1.9. At $x=1.9$ some 30% of the Ti have nearby vacancies. This broadens the lines sufficiently to be unable to distinguish the two isotopes.

Despite the aforementioned difficulties, a number of results can be inferred from the data. Table I gives the approximate separation δ between the two peaks in descending order of the hydrogen concentration. When the traces had no clearly resolvable peaks, bumps in the traces were used. The separation of the unperturbed peaks due to the two isotopes is of the order 4 kHz. The separation increases steadily beyond this value as x decreases below $x=1.83$ up to about a factor of 2 until the lowest concentration of $x=1.502$ is reached. For this sample two widely spaced peaks are discerned and the separation suddenly jumps to 26 kHz.

TABLE I. Distance δ between peaks.

x	δ (kHz)	x	δ (kHz)
2.000	4.6±0.3	1.734	7.5±2
1.973	3.6±2	1.711	9.6±2
1.941	3.3±2	1.672	8.1±2
1.884	4.5±3	1.631	7.2±3
1.826	5.9±2	1.548	8.3±2
1.791	6.8±2	1.502	26 ±2
1.770	7.3±2		

2. Resonance shift

We now discuss the resonance shift with respect to $TiCl_4$. Since resolution of the peaks was not always possible, and the probability that the high-concentration peaks are due to the two Ti isotopes while the low-concentration peaks are traceable to second-order quadrupolar interaction, the shifts were measured by taking the midpoints between the peaks. This gives the trend of the resonance shift as a function of hydrogen concentration and is shown in Fig. 5. Going from higher to lower concentrations, the shift is essentially constant in the tetragonal phase, rising slightly in the cubic region down to $x=1.77$, where it cusps and then drops again. A small break in the curvature is also found in the hydrogen $(T_{1e}T)^{-1/2}$ curve at $x=1.77$.[11] As the concentration is lowered further, the shift goes through a small trough. The most outstanding feature is the sudden rise in the shift to 0.548%

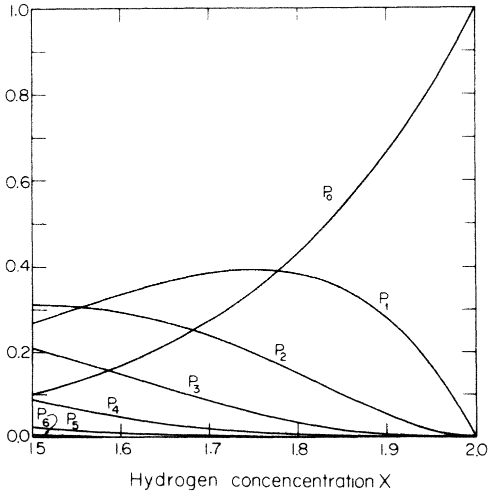

FIG. 4. The probability $P_n(x)$ that a titanium atom in TiH_x has n nearest-neighbor vacancies.

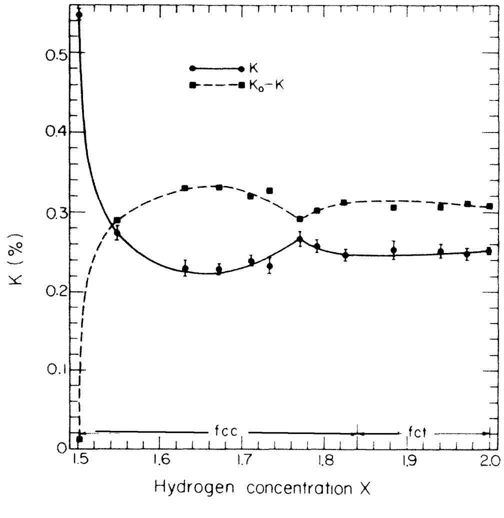

FIG. 5. Room-temperature Knight shift of Ti and TiH_x as a function of hydrogen concentration.

when x reaches 1.50. This is also the sample for which there is a sudden rise in the quadrupolar interaction. Nothing comparable is observed in the hydrogen Knight shift or the hydrogen $(T_{1e}T)^{-1/2}$.[11] Figure 5 also shows the K_0-K dependence on the hydrogen concentration, where K_0 is the previously obtained value of 0.56%. We should not expect this to give us the same dependence on x as the hydrogen $(T_{1e}T)^{-1/2}$, since one would expect K_0 to be hydrogen-concentration dependent. Nevertheless, this representation does give us some of the generally convex curvatures found for the hydrogen K and $(T_{1e}T)^{-1/2}$ rather than the troughlike appearance of the shift curve.

3. *Discussion of sample $TiH_{1.502}$*

The resonance of sample $TiH_{1.502}$ shows two well-defined peaks. There are two features that change radically in contrast to the continuous changes of the other samples; there is a sudden jump in both the peak separation and the resonance shift when compared to the adjacent sample of $TiH_{1.548}$. There are no comparable jumps in other parameters near $x=1.5$. The hydrogen Knight shift and the hydrogen $(T_{1e}T)^{-1/2}$ is almost constant in this region.[11] There are no radical changes in the crystallographic structure[11] nor have any other parameters, such as magnetic susceptibility, shown unusual behavior near this concentration. We have no single convincing explanation. We shall speculate on a number of possibilities.

We first discuss the origin of the two peaks. They cannot be attributed to the two isotopes where the quadrupole interaction is effective only to first order. In first-order perturbation the $m=\pm\frac{1}{2}$ transition is unshifted, but the unshifted resonances of the two isotopes are separated by 4.5 kHz, while the separation of the two peaks is 26 kHz. Hence second-order quadrupole interaction must be invoked. The pattern of the two peaks is similar to that which one would expect from a single second-order perturbation powder pattern with the higher shoulder on the low-frequency side. Since we have two isotopes, one should expect to see four peaks. The fact that only two peaks are observed leads us to surmise that either (a) the two peaks represent the more prominent shoulder of the two isotopes, the less prominent shoulder being unresolved, or (b) the two peaks represent the two shoulders of the more prominent resonance (^{49}Ti), the weaker resonance (^{47}Ti) being unresolved. If the latter holds, we can estimate e^2qQ/h for ^{49}Ti, from the relation[29]

$$(e^2qQ/h)^2=10.24\nu_0\Delta\nu I^2(2I-1)/(2I+3)\ ,$$

where $\Delta\nu$ is the peak separation, giving $e^2qQ/h=5.7$ MHz. This is only approximate since the relation assumes $\eta=0$, a condition not necessarily fulfilled in our case of randomly distributed hydrogen voids.

In either case we are left with a jump in the Knight shift and an accompanying jump in the strength of the quadrupole interaction for this sample. We speculate on three different possibilities, with the last one connected directly to the calculated band structure.

It has been established[30,31] that the Fermi-level electrons are prime sources of the electric field gradient at the nucleus of a metal. Thus the large K shift and the large peak separation probably have their origin in the same source. One may argue that K For this sample is practically equal to the K_0 we obtained for TiH_2. As the hydrogen concentration is decreased from its maximum value $x=2$, where the Fermi level lies at a peak in the density of states derived primarily from Ti d states, the Fermi level drops relative to the band.[16,20,22] Since the negative core-polarization contribution to K is due to d electrons at the Fermi level, one may infer that when $x=1.502$ the Fermi level drops below this band, leaving only the K_0 contribution. If this were the case, however, one would expect it to be reflected in the hydrogen NMR parameters. Both the hydrogen Knight shift and $(T_{1e}T)^{-1/2}$ remain smooth near $x=1.5$. Furthermore, the H Knight shift is negative, showing core-polarization d-electron influence at the Fermi level. Also, the hydrogen $(T_{1e}T)^{-1/2}$ was attributed to this band,[11] and the term does not vanish at $x=1.5$. This assumption would also not explain why there is such a large increase in the peak separation.

At $x=1.5$ the hydrogen concentration is given by the ratio of two small integers 3:2, so that an ordering of the H sites may be suspected. This could perhaps explain an increased electric-field-gradient effect, but it is difficult to see why it should give a large increase in the Ti Knight shift and why it should differentiate between the Ti and H NMR parameters. There has been no evidence of an order-disorder transition reported for this concentration.

We speculate on another possibility. Switendick has shown[20,32] that an additional band composed of the hydrogen antibonding states (Γ_2') is formed just below the Γ_{25}' d states. The Fermi level lies within Γ_{25}' and the energy difference $E_F-\Gamma_2'$ is an important factor in Switendick's theory of the stability of the hydrides. The deeper Γ_2' lies below E_F, the more stable the hydride. All the reported band calculations[19–22] (except that of Kulikov[18]) place Γ_2' just below E_F. As x decreases, the Fermi level is lowered so that it approaches Γ_2'. In addition, the lattice constant decreases, raising the Γ_2' level.[20,32] The drastic change in the NMR parameters may be due to Γ_2' intersecting E_F. Γ_2' is composed of hydrogen orbitals surrounding the titanium atom and is f-like at Γ. This change in orbital character at the Fermi level may be what induces a change in the vacancy-induced quadrupolar interaction and may also be the cause of a new contribution to the Knight shift. Since the state is not s-like at the Ti nucleus, and the Knight shift becomes strongly positive, the contribution would have to be orbital. It may further be speculated (although this is not a necessary condition for the above to hold) that since the stability of the hydride depends on bringing Γ_2' down below the Fermi level, the minimum x possible is that for which Γ_2' intersects E_F. It would then not be surprising that the above phenomenon occurs at the minimum x. This hypothesis of where the minimum x occurs differs from an explanation offered in Ref. 11. Also, if it were true, one would expect the minimum x for ZrH_x to be lower since Γ_2' for this hydride, having a larger lattice constant, lies deeper below E_F.[20,22] However, $x_{\min}$ for ZrH_x is not below 1.5.

V. CONCLUSIONS

We have shown that the Ti resonance complements results obtained from the hydrogen resonance. In particular, it was shown that the Ti Knight shift is the sum of a dominant positive term and a negative core-polarization contribution that changes with the density of states at the Fermi level. While there is only a small hydrogen-concentration dependence of the Ti Knight shift, there is a radical positive jump at $x = 1.5$ which has yet to be satisfactorily explained. This large shift is accompanied by a huge increase in the separation of the two peaks. Measurements at different frequencies would be useful in separating second-order quadrupolar shifts from the Knight shift.

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