Evidence for the high-temperature spin-relaxation anomaly in metal hydrides

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Proton spin-lattice relaxation data R_1 ($1/T_1$) are reported for the solid solution $Nb_{0.5}V_{0.5}H_{0.36}$. In the region of the previously reported anomaly ($T > 700$ K), a strong frequency dependence is observed by extending the measurements to a high frequency, 341 MHz. The correlation time τ_c is determined and is found to decrease with increasing temperature. The mean-square magnetic-field fluctuation M_2 responsible for the relaxation is also determined. Surprisingly, M_2 increases rapidly with increasing temperature, suggesting an excited state with a large spin interaction, such as molecular hydrogen.

Anomalously rapid nuclear spin relaxation has been reported in several metal-hydrogen systems at high temperatures.[1–5] The spin-lattice relaxation rate R_1 ($1/T_1$) increases markedly for temperatures above 700–1000 K. The anomalous relaxation has been observed in many systems: $NbH_{0.2}$, $VH_{0.2}$, $Nb_{0.5}V_{0.5}H_{0.2}$, $TaH_{0.3}$, $YH_{1.9}$, $ScH_{1.9}$, $ZrH_{1.8}$, $YD_{1.9}$, and $ScD_{1.9}$. The effect is evident in proton and deuteron[1] relaxation as well as in the R_1 of ^{45}Sc (in $ScH_{1.9}$, for example[2]). There is at present no satisfactory understanding of the high-temperature anomaly.

An intriguing aspect of the anomaly is that nothing unusual has been reported from other measurement techniques at high temperatures. However, the effect on R_1 is large: the spin-lattice relaxation rate R_1 at 1000 K may be larger by a factor of 10 than expected from a smooth extrapolation of lower-temperature data (see Ref. 4 and present data).

What is *anomalous* about the high-temperature relaxation? Consider proton ($I = \frac{1}{2}$) relaxation, which requires a fluctuating magnetic field.[6] The only sources of such fields are the conduction electrons and nuclear spins. Conduction-electron spins give rise to the Heitler-Teller-Korringa (HTK) mechanism of nuclear-spin relaxation,[6–8] with R_1 proportional to temperature. This mechanism is observed at low temperatures ($T < 100$ K) and, in some metal-hydrogen systems, at higher temperatures. Hydrogen-hopping motions modulate the nuclear spin-spin interactions and produce relaxation as described[6,9–11] by Bloembergen, Purcell, and Pound (BPP). Typically, a BPP-type proton R_1 maximum is observed near room temperature in the dilute solutions[4] and near 700 K for the dihydrides.[1] Thus both mechanisms are observed and "accounted for." It appears there are no *additional* sources of relaxation to explain the anomalous relaxation at high temperatures. Furthermore, the anomalous relaxation is *strong*: the anomalous rate observed at the highest temperatures is approximately equal to the relaxation rate at the lower-temperature maximum of R_1 (arising from hydrogen hopping).[4] The anomaly evidently involves strong spin interactions.

Cross relaxation between protons and metal nuclei is important in some metal-hydrogen systems at low temperatures.[12,13] However, at high temperatures the dipole interaction between the species is averaged to zero by hydrogen motion, disabling this mechanism. Direct measurements[4] by pulsed-field-gradient NMR (Refs. 14–16) indicate that hydrogen diffusion follows the Arrhenius temperature variation, increasing with increasing temperature. This excludes the possibility of a reversed temperature variation of the hydrogen-hopping rate.[17] In ZrH_x ($x \sim 1.8$), the role of paramagnetic impurities at high temperatures is ruled out by measurements on samples with intentionally high paramagnetic concentrations.[5] A thorough consideration of many relaxation mechanisms, some obvious and some ingenious, has appeared;[4] those authors conclude that the source of the anomalous relaxation remains unidentified.

A large class of theories of nuclear-spin relaxation can be summarized[6] as

$$R_1 = M_2(T) J(\omega_0, T) , \quad (1)$$

where ω_0 is the spin-precession frequency and M_2 is the mean-square fluctuating field, expressed in angular frequency units. The power spectrum $J(\omega)$ of the field fluctuations is normalized to unit-integrated intensity at all temperatures: $\int_{-\infty}^{\infty} J(\omega) d\omega = 1$. The most elementary and usual assumption is that $J(\omega)$ is a Lorentzian:

$$J(\omega) = \frac{\tau_c}{1+\omega^2\tau_c^2} . \quad (2)$$

Here τ_c is the correlation time of the motion, typically dependent on the temperature.

We remark that Eq. (1) is a slight simplification. For relaxation involving dipolar-coupled spins, terms at $2\omega_0$ are present along with those at ω_0.[6,9,18] In this case, with the assumptions of isotropic motions and a Lorentzian spectral density, the relaxation rate is[18]

$$R_1 = \tfrac{10}{3} M_2 \tau_c g(\omega_0 \tau_c) . \quad (3)$$

Here the function $g(\omega_0\tau_c)$ is

$$g(\omega_0\tau_c)=\left[\frac{1}{1+(\omega_0\tau_c)^2}+\frac{4}{1+(2\omega_0\tau_c)^2}\right]\Big/5 . \quad (4)$$

We emphasize that Eqs. (1) and (2) differ from Eqs. (3) and (4) only in detail; none of our conclusions are sensitive to these differences. We shall interpret our results in terms of Eqs. (3) and (4).

The sample of $Nb_{0.5}V_{0.5}H_{0.36}$ was prepared at Ames Laboratory. The metals are of Ames' highest purity, with paramagnetic impurities at the 10-ppm level. The powder sample tended to lightly sinter at high temperatures, decreasing the penetration of the rf field H_1. To reduce this effect, the metal powder was mixed with previously baked and dried MgO powder, about 1:1 by volume. The sample was sealed into a 6-mm-outer-diameter fused-quartz tube.

The NMR measurements used two furnaces, one with an iron-core magnet (proton frequencies of 21.25 and 53.14 MHz) and the other with a superconducting solenoid (340.66 MHz). The furnaces were operated with ~35 atm of argon; the purpose was to place a larger pressure outside the quartz sample tube than the largest anticipated hydrogen-vapor pressure inside the tube, to prevent rupturing of the tube. The temperature was measured with a type-E thermocouple. The bifilar heater windings were stainless-jacketed, MgO-insulated, type-E thermocouple wire. Ceramic wool insulation was used (about 6 mm thick), and a water jacket protected the NMR magnet from heat.

The relaxation rate R_1 was measured with the saturate-wait-inspect strategy. Saturation was usually accomplished with a single $\pi/2$ pulse. At 341 MHz the available H_1 was too small, so a train (comb) of ~20 pulses was used to saturate the spins. Inspection of the recovered magnetization made use of the free induction decay (FID) following a $\pi/2$ pulse or the train of echoes from a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence.[19,20] The spin signal is available over a longer time with the CPMG sequence, yielding a narrower effective bandwidth and better signal-to-noise (S/N) ratio.

Proton relaxation data R_1 for the temperature range of interest at 21.2 and 53.1 MHz are presented in Fig. 1 (upper data set). The anomalous relaxation is evident as the rapid increase in R_1 for temperatures above 670 K ($1000/T \le 1.5$). At temperatures below 400 K ($1000/T \ge 2.5$), the principal relaxation mechanism is thermally activated hydrogen hopping. A BPP-type maximum in R_1 occurs at temperatures near 225 K, off the right side of Fig. 1 (as observed[4,21] in the similar alloy $Nb_{0.75}V_{0.25}H_{0.23}$). In the Nb-V alloys, the conventional R_1 maximum is broadened[21] by a distribution of hydrogen-hopping rates, from the random Nb-V siting. The distribution of hopping rates is also evident in the frequency dependence of R_1 on the *warm* side of the maximum, from 300 to 400 K. This frequency dependence is understood and is not the focus of the present work.

Between 500 and 650 K ($2.0 > 1000/T > 1.54$), it appears that the principal relaxation mechanism is HTK,

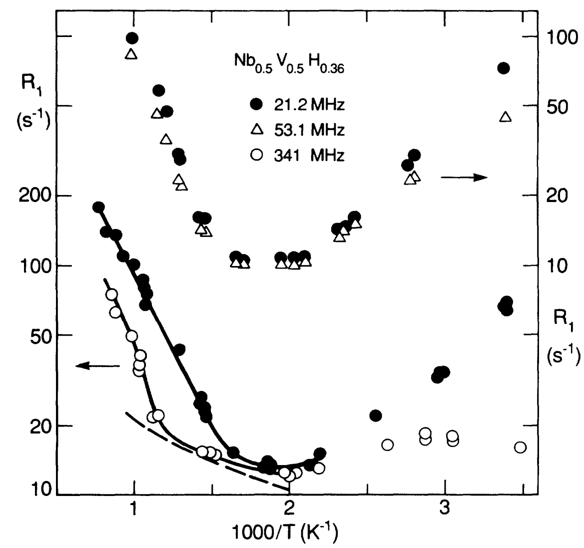

FIG. 1. Proton relaxation rate R_1 in $Nb_{0.5}V_{0.5}H_{0.36}$ as a function of reciprocal temperature at three resonance frequencies. The two sets of data have different vertical scales, offset by a factor of 10. The two sets of 21.2-MHz data are slightly different, as a result of changes in the sample under prolonged high-temperature operation. The solid curves through the data are only guides for the eyes. The dashed curve in the lower part is the estimated electronic relaxation (HTK) and is proportional to temperature.

relaxation by conduction electrons. The temperature dependence in this region is weak, in accord with the expected $R_1 \propto T$ behavior. At 625 K ($1000/T = 1.6$), the rate R_1 is 11 s^{-1}. This agrees well with the result[12] from $Nb_{0.5}V_{0.5}H_{0.23}$ between 10 and 50 K, namely, $R_1/T = 0.018\ s^{-1}K^{-1}$, which predicts a value of 11.25 s^{-1} at 625 K.

At high temperatures, where the anomalous relaxation occurs, a weak frequency dependence is evident in Fig. 1 (upper). The data were taken at 21.2 and 53.1 MHz within 30 min of each other, without changing temperature. For some temperatures the 21.2-MHz data were obtained first; at other temperatures the order was reversed. Thus the small but systematic frequency dependence is real. For almost all reasonable power spectra, $J(\omega)$ is a monotonically decreasing function of ω. Thus the observed frequency dependence is in the expected direction.

The frequency dependence is at most a 25% effect between 21.2 and 53.1 MHz. If the system were in the slow-fluctuation limit, $\omega_0\tau_c \gg 1$, a ω_0^2 dependence (factor of 6.25) would occur.[6] In the fast-fluctuation limit, $\omega_0\tau_c \ll 1$, no frequency dependence is expected. Thus the metal-hydrogen system at 900 K ($1000/T = 1.1$) is closer to the fast-fluctuation limit than the slow-fluctuation limit at frequencies of 21.2 and 53.1 MHz. Because τ_c must be small compared with ω_0^{-1} at 53 MHz, an upper limit is established at 900 K: $\tau_c \lesssim 3\times10^{-9}$ s.

The relaxation rates R_1 at 21.2 and 341 MHz are presented in Fig. 1 (lower). The 21.2-MHz data here are slightly different from the 21.2-MHz data in the upper part of the figure. Extended operation at the highest temperatures caused systematic small changes (less than 20%) in the proton R_1, most noticeably in the HTK relaxation region near $1000/T = 2.0$. We believe the hydrogen content of the sample may decrease slowly because of hydrogen permeation through the hot quartz tubes. The previously mentioned sample sintering prevents NMR from being used to measure the hydrogen content to test this hypothesis. In any event the changes in R_1 due to such sample changes are negligible compared with the frequency dependence evident in Fig. 1 (lower). The R_1 maximum at 341 MHz arising from hydrogen hopping is quite broad and is shifted to $1000/T = 3$. This maximum is very weak because it is masked by HTK relaxation and because the maximum relaxation rate from hydrogen motion should scale[6] as ω_0^{-1}.

At the highest temperatures, a large variation in R_1 occurs from 21.2 to 341 MHz (Fig. 1, lower). Because the HTK mechanism is frequency independent, the frequency dependence of the observed, total relaxation rate R_1 is smaller than the frequency dependence of the anomalous contribution itself. The large frequency dependence observed at 900 K indicates that the correlation time τ_c is at least as large as ω_0^{-1} at 341 MHz: $\tau_c \gtrsim 5\times10^{-10}$ s. Together with the upper limit imposed on τ_c above, τ_c is thus restricted to the range $5\times10^{-10} \lesssim \tau_c \lesssim 3\times10^{-9}$ s.

Equations (3) and (4) can be used to determine τ_c more accurately. The function $g(\omega_0\tau_c)$ is plotted in Fig. 2 on a logarithmic frequency scale. The three arrows in the figure are *separated* by distances according to the *ratios* of the three resonance frequencies: 21.2, 53.1, and 341 MHz. The *absolute location* of the arrows (which determines τ_c) was established by the following criteria, appropriate for 900 K: The relaxation rate R_1 at 53.1 MHz is about 0.8 that at 21.2 MHz, and the relaxation rate at 341 MHz is no larger than 0.25 times the rate at 21.2 MHz. Without accurate knowledge of the HTK rate to be subtracted from the observed rate, we cannot place a narrower restriction on the 341-MHz rate. The location of the arrows in Fig. 2 satisfies the above criteria and corresponds to $\tau_c = 7.5\times10^{-10}$ s, with a factor of 2 uncertainty.

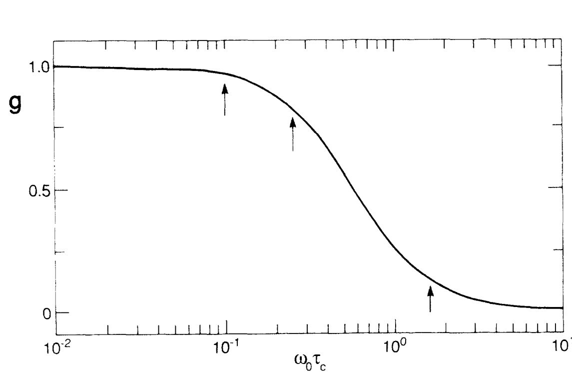

FIG. 2. Spectral density function $g(\omega_0\tau_c)$ from Eq. (4). This function expresses the frequency dependence of the relaxation rate R_1 in Eq. (3). The three arrows correspond to the frequencies $\omega_0/2\pi$ of 21.2, 53.1, and 341 MHz from left to right, with $\tau_c = 7.5\times10^{-10}$ s. With the arrow locations shown, the frequency dependence of R_1 agrees with the 900-K data.

This value of the correlation time τ_c, which characterizes the motion responsible for the high-temperature relaxation anomaly, is surprisingly long. By comparison, the correlation time τ_d for single-particle hopping derived from the measured rate of diffusion is about 3×10^{-13} s at the same temperature.[4] Thus τ_c and τ_d refer to very different motions. These disparate correlation times strongly suggest that two species of hydrogen are present at high temperatures, one rapidly mobile and one less mobile. These two populations must be in rapid exchange, since two-component signals are not observed.

The above value of τ_c, combined with the observed relaxation rate R_1 at 900 K and 21.2 MHz, yields the second moment M_2 through Eqs. (3) and (4): $M_2 = 2.9\times10^{10}$ s^{-2}, with a factor of 2 uncertainty from τ_c. This large second moment is a direct indication that the anomalous relaxation involves very strong spin interactions.

The frequency variation of R_1 between 21.2 and 341 MHz (Fig. 1, lower) becomes smaller with increasing temperature. Because the 341-MHz R_1 data near $1000/T = 1.5$ are almost entirely from the HTK mechanism, it is important to compare rates after the HTK contributions are removed (see dashed curve in Fig. 1). The result is that the anomalous rate has a weaker frequency dependence at the highest temperatures ($1000/T \approx 0.9$). Thus τ_c *decreases,* though weakly, with increasing temperature.

Despite the decrease in τ_c, the anomalous relaxation rate at 21.2 MHz in the vicinity of 1000 K *increases* with increasing temperature. Since the limit $\omega_0\tau_c \ll 1$ applies here (so $g \simeq 1$), the second moment M_2 *must increase* more *rapidly with temperature* than τ_c decreases [see Eq. (3)]. In other words, the increasing second moment results in a relaxation rate R_1 which increases with temperature, even though the system is in the fast-fluctuation limit (at 21 MHz). This suggests that an excited state with a large second moment is present. At higher temperatures the thermal equilibrium (Boltzmann) population of the state increases, rapidly increasing the average mean-square interaction, M_2.

One possible excited state would be H_2 *molecules,* stabilized in the metal structure. Compared with the usual situation of isolated hydrogen nuclei in the metal, separated by at least 2.1 Å (the Switendick criterion[22]), molecular H_2 has protons separated by 0.745 Å. Because the second moment involves this distance to the minus sixth power,[6,18] a very large second moment results. In the extreme case in which all the proton nuclei occurred in molecules with the random (3:1) ratio of ortho-H_2 to para-H_2, the dipolar M_2 would be 1.4×10^{12} s^{-2}, much larger than the experimental value determined above. Even if partially averaged by rapid uniaxial rotation (reducing[6] M_2 by a factor of 4), a small fraction (several percent) of the nuclei pairing into molecules would be sufficient to account for the observed anomalous relaxation. Presumably, the pairing would be a dynamic process with a relatively short lifetime equal to the measured correlation time τ_c. Of course, it is not necessary to postulate the existence of H_2-like configurations. Similar effects will occur whenever proton-proton distances become substantially shorter than at low temperatures.[4]

There is a precedent for H_2 molecules as an excited state in metals. Certain chemical clusters with single metal atoms (W, for example) are capable of binding hydrogen molecules.[23] The bonds are strong; in at least one case, the H_2 is bound as strongly as two separate H atoms.[24] The experimental evidence[23] for H_2 in these clusters includes NMR T_1 data,[25] diffraction by x rays and neutrons, and a J coupling (indirect spin-spin interaction, mediated by electrons) nearly equal to the free molecule. Cotts has considered in detail the possibility of H_2 molecules in metals in a summary of a discussion at a recent conference.[26] He concludes that the mechanism can only explain the data for correlation times τ_c near 3×10^{-9} s, close to the value experimentally determined here.

An exactly similar argument based on the strong deuteron electric quadrupole interaction in the D_2 molecule could be expected to account for the similar anomalous relaxation of deuterons observed in transition metal-deuterides, for example.[1,26] Likewise, it is not unreasonable to expect that the presence of a H_2 (or D_2) molecule would give rise to a substantial electric-field gradient at neighboring Sc sites, resulting in anomalous relaxation of the ^{45}Sc nuclei, as observed in scandium hydrides and deuterides.[2,26] However, it is not yet clear why the anomalous relaxation of ^{45}Sc should occur at a significantly lower temperature than that of protons in the same dihydride.[26]

In summary, by extending the measurements to a high frequency, a substantial frequency dependence has been found in the anomalous relaxation rate R_1 of protons in a metal-hydrogen system. The correlation time τ_c and second moment M_2 of the fluctuations responsible for the relaxation have been determined. To explain the increase in R_1 with increasing temperature, the second moment M_2 must also increase with temperature. The possibility of an excited state in the metal, such as molecular hydrogen or other configuration with protons in close proximity, has been considered.

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