

## Dynamical evidence for a change in hydrogen-diffusion behavior in transition-metal hydrides at high temperatures

R. G. Barnes, M. Jerosch-Herold, J. Shinar, F. Borsa,\* D. R. Torgeson, and D. T. Peterson  
Ames Laboratory, Iowa State University, Ames, Iowa 50011

A. J. Lucas, G. A. Styles, and E. F. W. Seymour  
Physics Department, University of Warwick, Coventry, CV4 7AL, United Kingdom  
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The  $^{45}\text{Sc}$  nuclear spin-lattice relaxation time  $T_1$  in scandium dihydride and dideuteride measured up to 1300 K shows a second high-temperature minimum at  $\sim 1100$  K, in addition to the usual Bloembergen-Purcell-Pound minimum associated with independent motion of hydrogen vacancies among tetrahedral interstitial sites. This indicates the onset of a second mode of hydrogen motion with a relatively long associated correlation time for the hydrogen-scandium interaction. Possible origins for such long times are discussed.

Measurements of the  $^{45}\text{Sc}$  spin-lattice relaxation time in scandium dihydrides and dideuterides,  $\text{ScH}_x$  and  $\text{ScD}_x$  ( $1.8 < x < 2.0$ ) have been extended up to 1300 K and have revealed a new relaxation time "minimum," in addition to the usual Bloembergen-Purcell-Pound (BPP) minimum.<sup>1</sup> This is accompanied by a rapid reduction in  $T_1$  for  $^1\text{H}$  and  $^2\text{D}$  at the upper end of this temperature range for these hydrides and for several others<sup>2</sup> at similar temperatures indicating that this is a rather general phenomenon, though it does not occur in  $\alpha\text{-ScH}_{0.2}$ . However,  $\text{ScH}(\text{D})_x$  is the system we have investigated most fully and the only one in which we have studied the resonance of the nonmobile species. It will be argued this new minimum indicates the existence of relatively long-lived fluctuations in the local environment of the  $^{45}\text{Sc}$  nuclei compared to fluctuations associated with simple vacancy hopping on the hydrogen sublattice at these high temperatures.

The dihydrides and dideuterides of the group-III and -IV transition metals form in the  $\text{CaF}_2$  (fluorite) structure, the metal lattice being fcc and the hydrogen occupying the tetrahedral (T) interstitial sites which themselves form a simple cubic lattice.<sup>3</sup> In the cases of  $\text{TiH}_x$  and  $\text{ZrH}_x$ , as  $x$  approaches 2 the metal lattice acquires a slight tetragonal distortion, becoming fct. The scandium systems furnish the best opportunity to utilize the spin-lattice relaxation time of the metal nuclei to monitor hydrogen (deuterium) vacancy motion. Whereas other metal nuclear species ( $^{47}\text{Ti}$ ,  $^{89}\text{Y}$ , etc.) have small magnetic moments, low abundance, large electric quadrupole moments, and/or combinations of these detrimental factors,  $^{45}\text{Sc}$  (spin  $\frac{7}{2}$ ) has a substantial magnetic moment, 100% abundance, and a moderate quadrupole moment ( $Q = -0.22$  b). In addition, the conduction-electron density of states at the Fermi level,  $N(E_F)$ , in the group-III hydrides is relatively low so that the conduction-electron contribution  $T_{1e}$  to the  $^{45}\text{Sc}$   $T_1$  is weak in comparison to the vacancy-diffusion contribution.

Measurements of the  $^{45}\text{Sc}$   $T_1$  in  $\text{ScH}_x$  and  $\text{ScD}_x$  over the temperature range 77–800 K have already shown that for temperatures on the order of 500 K,  $T_1$  is dominated by quadrupolar relaxation due to the fluctuating electric

field gradient (EFG) caused by the diffusion of hydrogen (deuterium) vacancies.<sup>4</sup> The measured value of  $T_1$  is given by

$$(T_1)^{-1} = (T_{1Q})^{-1} + (T_{1e})^{-1}, \quad (1)$$

with the quadrupolar relaxation rate given by<sup>5</sup>

$$(T_{1Q})^{-1} = \frac{24\pi^2 c_v}{49\omega_0} \left( \frac{e^2 q Q}{h} \right)^2 \left[ \frac{\omega_0 \tau_v}{1 + \omega_0^2 \tau_v^2} + \frac{4\omega_0 \tau_v}{1 + 4\omega_0^2 \tau_v^2} \right], \quad (2)$$

where  $c_v$  is the vacancy concentration,  $Q$  the quadrupole moment,  $\omega_0$  the  $^{45}\text{Sc}$  Zeeman frequency,  $\tau_v$  the correlation time for single vacancy hopping,  $h$  is Planck's constant, and the numerical factor includes a factor of 8 for the number of nearest-neighbor T sites. The usual simple exponential correlation function form for the electric-field-gradient fluctuations responsible for the quadrupolar relaxation is used, and the EFG,  $eq = \partial^2 V / \partial z^2$ , is for a single vacancy at a nearest-neighbor metal site and is considered to be axially symmetric.

Representative  $^{45}\text{Sc}$   $T_1$  data are shown in Fig. 1 for the temperature range of interest (solid points) for  $\text{ScH}_{1.83}$  [Fig. 1(a)] and  $\text{ScD}_{1.99}$  [Fig. 1(b)] at two resonance frequencies, 12.2 and 24 MHz. In each figure, the solid curve shows the conduction-electron contribution  $T_{1e}$  extrapolated from low-temperature measurements, where  $T_{1e}T = 62$  sK for  $\text{ScH}_{1.83}$  and 66 sK for  $\text{ScD}_{1.99}$ .<sup>4</sup> In Fig. 1(a) the dashed line shows the extension of  $T_{1Q}$  behavior to high temperatures, and in both figures the open circle points show the expected path of  $T_1$  as it returns to  $T_{1e}T = \text{const}$  behavior. Instead, a new minimum appears which is deepest relative to the normal, vacancy-diffusion-induced ( $T_{1Q}$ ) minimum for small vacancy concentrations, as in  $\text{ScD}_{1.99}$  [Fig. 1(b)], where the newly observed minimum is actually deeper than the lower-temperature minima at the frequencies employed. The highest temperature reached ( $\sim 1300$  K) was determined by the high hydrogen pressure generated in the quartz sample containers which caused several samples to explode and limited the amount of data on the high-temperature side of the

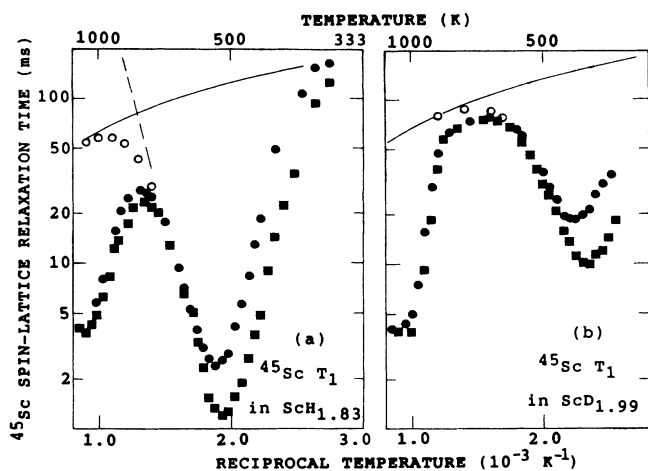


FIG. 1. Temperature dependence of  $^{45}\text{Sc } T_1$  in (a)  $\text{ScH}_{1.83}$  and (b)  $\text{ScD}_{1.99}$  at 12.2 and 24 MHz ( $\blacksquare$  and  $\bullet$ , respectively). The solid curve shows the conduction-electron contribution  $T_{1e}$  extrapolated from low temperatures, and the dashed line continues the quadrupolar contribution  $T_{1Q}$  to higher temperatures. The open circles show the expected behavior of  $T_1$  resulting from the combined effects of  $T_{1e}$  and  $T_{1Q}$ . Some data points have been omitted for clarity.

minimum. The temperature  $T_C$ , at which the relaxation rates due to normal vacancy diffusive hopping and the high-temperature mechanism are approximately equal, occurs when the vacancy hopping rate deduced from the  $^{45}\text{Sc } T_1$  data reaches  $\sim 10^{10} \text{ s}^{-1}$ . The minimum  $^{45}\text{Sc } T_1$  value reached at high temperatures is essentially independent of  $x$ , showing the new relaxation mechanism is not determined by the compositional vacancy concentration, whereas the lower-temperature  $T_{1Q}$  minimum is strongly sensitive to  $x$ . In addition, the entire high-temperature  $T_1$  behavior is independent of the resonance frequency within experimental uncertainty.

At the high-temperature minimum the value of  $T_1$  is smaller than expected from Eq. (2) by a factor of 100–1000. Such a change is too great to be accommodated wholly by changes in any of the parameters of Eq. (2) except the effective correlation time  $\tau$  of the quadrupolar interaction. The frequency independence of  $T_1$  means the characteristic frequency  $\tau^{-1}$  of the high-temperature fluctuations which cause the observed relaxation, although slow compared to the frequency of a hopping vacancy or hydrogen, is, nevertheless, fast compared to the resonance frequency.

Several possible sources of the increased relaxation rate at high temperatures can be ruled out. In particular, measurements made on samples containing controlled low levels of Gd (<100 ppm) show the high-temperature  $^{45}\text{Sc } T_1$  behavior is independent of the Gd content. Scandium self-diffusion or diffusion of other interstitials such as O or N would yield a strongly-frequency-dependent  $T_1$  minimum, which is not observed and would not appreciably affect the  $^1\text{H}$  or  $^2\text{D}$  relaxation times, which also show indications of high-temperature minima.<sup>2</sup> An electronic structure transition, causing a sudden marked change in the

density of states, and hence in  $T_{1e}$ , would be frequency independent, but would also change the  $^{45}\text{Sc}$  Knight shift ( $K$ ). In fact,  $K$  shows only a smooth linear increase from 0.045% at 300 K to 0.097% at 1100 K, and based on the usual interpretation of  $K$  and  $(T_{1e})^{-1}$  in transition metals,<sup>6</sup> this increase implies a decrease of the  $d$ -band density of states at the Fermi level,  $N_d(E_F)$ , with increasing temperature and therefore a decrease of  $(T_{1e}T)^{-1}$ .  $T_{1e}$  would therefore increase above the value extrapolated from low temperatures, as is the case in vanadium,<sup>7</sup> and could not be responsible for the sharp decrease in  $T_1$  observed.

Octahedral (O) sites might be populated above  $T_C$  by a rapid transfer of a substantial fraction of hydrogen from the regular T sites to the normally empty O sites. The hydrogen randomly occupying O sites would have to diffuse much more slowly than hydrogen on T sites in order to provide the larger value of  $\tau$  required. This possibility cannot be entirely ruled out. However, there is now good evidence<sup>8</sup> that O sites are unfavorable at high temperature; it is not easy to imagine why the long value of  $\tau$  would occur, and we have not succeeded in adjusting the parameters of such a model to the  $^1\text{H}$  and  $^2\text{D}$  data.<sup>2</sup>

The simplest interpretation of the change in the correlation time is a corresponding change in the T-site vacancy hopping rate, which means the motion must become slower with increasing temperature above  $T_C$  until the minimum is reached, when it begins to speed up again. A reason for such unusual behavior has been suggested by Richards<sup>9</sup> based on the now well-authenticated strong reduction in O-site occupation by hydrogen in dihydrides with the fluorite structure at high temperatures.<sup>8</sup> This is brought about by the large amplitude anharmonic vibrations of hydrogen at tetrahedral sites for the  $\langle 111 \rangle$  directions towards O sites. At moderate temperatures the repulsion thus exerted on any ion attempting occupation of an O site is not great and the dominant diffusive jump path between T sites is through a neighbor O site ( $T$ -O- $T$  jumps). At higher temperatures this path is progressively inhibited, leaving mainly direct  $T$ - $T$  jumps along  $\langle 100 \rangle$  directions, which are characterized by an intrinsically higher activation energy, and which provide a relatively slow residual diffusive motion. By suitable choices of parameters such a model could fit most aspects of the data, but some additional feature would be needed to explain the observations that the highest temperature  $T_1$  value is independent of the hydrogen concentration  $x$  and sometimes significantly less than the normal minimum. The model provides a natural explanation of the absence of the high-temperature minimum in  $\alpha$ - $\text{ScH}_{0.2}$ , where the low hydrogen concentration would result in less significant repulsion effects.

Stable clusters of interacting vacancies and interstitials have been found in many nonstoichiometric compounds. Such clustering<sup>10</sup> is particularly well documented for oxygen-excess ionic fluorite-structure oxides  $\text{UO}_{2+x}$  at high temperatures ("Willis clusters"), but has been shown to occur also for oxygen-deficient oxides with this structure, such as yttria-stabilized zirconia, and for oxides with other structures, both ionic and metallic. In the fluorite-structure oxides, clusters may involve both vacancies at regular anion sites (T sites) and interstitials at intermedi-

ate positions (Fig. 2). The nonstoichiometric hydrides might display analogous effects. In view of the high hydrogen-ion mobility the clusters would be likely to have a finite lifetime, though most probably longer than the individual jump time for a free ion, and so their interaction with scandium nuclei and with other hydrogen nuclei within the same cluster would be characterized by a relatively long correlation time  $\tau_{cl} > \tau_v$ . Moreover, the cluster mechanism provides a possibility for a  $T_1$  value at high temperature, which is less than the lower-temperature minimum. Considering the clusters as remaining essentially static over their lifetime,  $\tau_{cl}$  would have to remain short enough to conform to the requirement  $\omega_0 \tau_{cl} < 1$ , to satisfy the observed frequency independence of  $T_1$ . The rate  $(T_{1Q})_{cl}^{-1}$  due to clusters would be given by Eq. (2) with  $c_v$  replaced by  $n_{cl}$ , the concentration of clusters (assuming that each cluster is associated with a single Frenkel interstitial). However, since  $\omega_0 \tau_{cl} < 1$ , the rapid decrease in  $T_1$  would result from a rapid increase of  $n_{cl}$  in this temperature range, although in this critical region there might also be some increase in  $\tau_{cl}$ . The high-temperature  $T_1$  minimum would occur when  $n_{cl}$  reached its maximum value. Thereafter,  $T_1$  would increase slowly again as  $\tau_{cl}$  decreased.

To test the reasonableness of the cluster model, Eq. (2) may be used to compare the relaxation rates at the high- and low-temperature  $^{45}\text{Sc}$   $T_1$  minima, taking as an example clusters of the type shown in Fig. 2. Since  $\omega_0 \tau_v \approx 1$  at the vacancy-induced (lower-temperature) minimum, and  $\omega_0 \tau_{cl} < 1$  at the cluster-induced (higher-temperature) minimum, we have from Eq. (2), approximately,

$$\frac{(T_{1Q})_{cl}^{-1}}{(T_{1Q})_v^{-1}} \approx \frac{(e^2 q Q)_{cl}^2 n_{cl} \tau_{cl}}{(e^2 q Q)_v^2 c_v (4\omega_0)^{-1}} \quad (3)$$

For  $\text{ScH}_x$  an average value for the vacancy concentration  $c_v$  is 0.05 ( $x = 1.9$ ). Calculation shows the EFG produced at a metal nucleus by a relaxed ion is very nearly compensated by the T-site vacancy left behind. However, the Frenkel interstitial ion produces an EFG which is larger than that due to an ion at a regular T site or to a vacancy. On this basis, and neglecting screening and antishielding effects which do not influence ratios of EFG's greatly, we

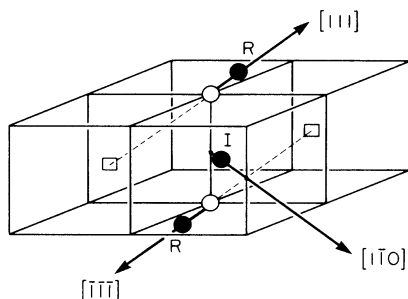


FIG. 2. Example of a cluster formed from one Frenkel interstitial anion ( $I$ ), two relaxed anions ( $R$ ), and two vacancies (open circles). Regular anion sites are at cube corners. Cations are indicated by open squares. The Frenkel vacancy may not be closely associated with the cluster and is not shown in this figure. Larger clusters may also occur.

find  $(e^2 q Q)_{cl}^2 / (e^2 q Q)_v^2 \approx 2.5$ . Incorporating these various values in Eq. (3) yields

$$\frac{(T_{1Q})_{cl}^{-1}}{(T_{1Q})_v^{-1}} \approx 100 n_{cl} \omega_0 \tau_{cl} \quad (4)$$

To be meaningful, two limits must be placed on  $\tau_{cl}$ : (a)  $\tau_{cl} > \tau_v$ , and (b)  $\omega_0 \tau_{cl} < 1$ . At the temperature of the cluster-induced minimum,  $\omega_0 \tau_v \approx 10^{-3}$ , so we need to have  $\omega_0 \tau_{cl} > 10^{-3}$ . Thus both limits are satisfied if  $10^{-2} \lesssim \omega_0 \tau_{cl} \lesssim 10^{-1}$ . To match the observed ratios of minimum  $T_1$  values at 12.2 MHz (Fig. 1) of 0.3 for  $\text{ScH}_{1.83}$  and 2 for  $\text{ScH}_{1.98}$ , we conclude  $n_{cl} \approx 0.2$  from Eq. (4). This indicates a possible and substantial degree of clustering, essentially independent of hydrogen concentration  $x$ .

There is little additional evidence at present to support or deny this cluster hypothesis for the dihydrides. A neutron diffraction study of  $\text{PuD}_{2.25}$  (Ref. 11) shows a fluorite structure with substantial numbers of vacancies at regular T sites accompanied by interstitial deuterium ions, and the results are best fitted by postulating vacancy-interstitial clusters. However, a recent neutron diffraction study of  $\text{ScD}_{1.8}$  (Ref. 12) at high temperature shows anion mean square displacements which exhibit no unusual behavior which would provide evidence of substantial anion sublattice disordering. Indeed, the relatively small  $^{2D}$  mean square displacements found do not provide support for the first possibility, the inhibition of O-site occupation.

Order-disorder transitions are exhibited in many essentially stoichiometric fluorite-structure compounds containing relatively light anions, e.g.,  $\text{CaF}_2$ ,  $\text{PbF}_2$ . At higher temperatures they become (type-II) fast ion conductors ("superionics"). Measurements of the  $^{19}\text{F}$  resonance in  $\text{PbF}_2$  as it enters the superionic phase<sup>13</sup> show somewhat similar behavior to the  $^1\text{H}$  and  $^2\text{D}$  high-temperature relaxation in  $\text{YH}_x$ ,  $\text{LaH}_x$ ,  $\text{TiH}_x$ , and  $\text{ZrH}_x$  ( $x \approx 2$ ),<sup>2</sup> where we have observed a decrease in  $T_1$  with increasing temperature, though in the case of  $\text{PbF}_2$  the interpretation is clouded by the possible effect of paramagnetic impurities. For these materials there is some disagreement between pictures which emerge from neutron scattering<sup>14</sup> and molecular-dynamics studies.<sup>15,16</sup> On the one hand, neutron data have been interpreted in terms of the thermal generation of anion clusters similar to those found in nonstoichiometric oxides, eventually resulting in about one-half of the regular anion sites becoming unoccupied. Again, O sites play no part in this high-temperature process, and diffusion occurs predominantly by direct  $T$ - $T$  jumps along  $\langle 100 \rangle$  paths. However, while the  $\text{F}^-$  clusters are deduced to be almost stationary over their lifetimes, the lifetime is only about  $10^{-12}$  s in these ionic materials. It seems unlikely that the replacement of the ionic potential by a metallic potential would drastically increase this time, if at all, and thus provide the long correlation time needed. Moreover, the most recent molecular-dynamics studies<sup>16</sup> suggest a different interpretation in which vacancies and doubly occupied regular anion sites have similar jump rates and occur with much lower number densities than is suggested by the neutron data. To reconcile these two pictures, it would be essential that the cluster configuration last no longer than the mean jump time of individu-

al ions. This suggests hydrogen clusters with a long enough lifetime to explain our results cannot be argued by direct analogy with stoichiometric fluorite fast ion conductors. Of course, the thermal generation of additional vacancies and doubly occupied hydrogen sites would increase both quadrupolar relaxation rates of  $^{45}\text{Sc}$  and  $^2\text{D}$  and the dipolar relaxation rate of  $^1\text{H}$ , but insufficiently to match the observations without a lengthening of the correlation times.

Molecular dynamics applied to these fast ion conductors<sup>15</sup> shows the ions begin to move in a correlated manner. The correlated motion of a sufficient number of hydrogen ions could provide, in principle, the required long correlation time. However, for a quantitative fit to the data, it would be necessary to envisage columns of 100–1000 hydrogen ions all following one another with a jump rate  $\tau_v^{-1}$ , and maintaining fixed mutual separations both as regards magnitude and direction. [Of course, jumps of successive ions would likely be separated by one or two vibrational periods, but such a small interval is of no consequence for nuclear magnetic resonance (NMR).] This seems most unlikely (see, for example, the simulated trajectories computed by Gillan<sup>15</sup>), and we consider the correlated nature of the motion can provide only a relatively small part of the observed increase in relaxation rate. We note, however, in addition to the extra  $T_1$  minimum which occurs for  $^{19}\text{F}$  in  $\text{PbF}_2$ , a similar minimum has been observed for  $^7\text{Li}$  in the metallic, fast ion conductor  $\text{Li}_x\text{Al}_{1-x}$  ( $x \leq 0.5$ ) (Ref. 17), which has the bcc NaTl structure. This has not received a satisfactory explanation. It is tempting to suggest a common cause for all these high-temperature minima in materials containing highly mobile ions.

If the present observations are characteristic of fluorite-structure compounds one must expect similar phenomena will occur in other fcc dihydrides. Unfortunately, there are rather few suitable NMR metal nuclei among the dihydrides; however, we are turning attention to observation of the  $^{91}\text{Zr}$  resonance in  $\text{ZrH}_2$ . It would be particu-

larly valuable to measure  $T_1$  for a spin- $\frac{1}{2}$  metal nucleus since it would be relaxed by dipolar interaction alone. It would sample the long correlation time in the case of a transition to direct  $\langle 100 \rangle$  jumps or static clusters but would sample the short, individual hydrogen jump time in the case of correlated motion. Unfortunately, even the best candidate,  $^{89}\text{Y}$ , for this experiment is not favorable from an NMR point of view because of its small nuclear moment.

In addition to  $\text{ScH}_x$  and  $\text{ScD}_x$ , we have observed similar  $^1\text{H}$  and  $^2\text{D}$  high-temperature relaxation behavior in  $\text{YH}_x$ ,  $\text{LaH}_x$ ,  $\text{TiH}_x$ , and  $\text{ZrH}_x$ ,<sup>2</sup> and in  $\alpha\text{-Nb(V)H}_{0.2}$  (Ref. 18), indicating the phenomenon may be typical of, but not confined to, hydrides with the fluorite structure. The predicted high-temperature bulk diffusion rate which emerges from the data of Goldstone, Eckert, Richards, and Venturini<sup>8</sup> and Richards<sup>9</sup> differs markedly from the rates expected by analogy with nonstoichiometric oxides or stoichiometric fluorite fast ion conductors. For the former, the rate should decrease anomalously for  $T > T_c$ , whereas for the latter the rate should increase faster than extrapolation from lower temperatures. Moreover, the latter suggests the appearance of an order-disorder specific-heat anomaly (as in the fast ion conductors). Both these properties are currently under investigation.

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\*Permanent address: Istituto di Fisica, Università di Pavia, Pavia, Italy.

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