Journal of ALLOYS AND COMPOUNDS

Journal of Alloys and Compounds 253–254 (1997) 441–444

Systematics of the anomalous high-temperature ^{45}Sc spin–lattice relaxation in scandium hydrides and deuterides

M. Jerosch-Herold[a], D.R. Torgeson[b], R.G. Barnes[b,*]

[a]Department of Radiology, University of Minnesota, Minneapolis, MN 55455, USA
[b]Ames Laboratory, USDOE, and Department of Physics, Iowa State University, Ames, IA 50011, USA

Abstract

The nuclear magnetic resonance of the metal nucleus ^{45}Sc shows anomalous spin–lattice relaxation at high temperatures ($T \geq 800$ K) in scandium dihydride and dideuteride. The anomalous rate R_{1A} is represented by $R_{1A} = A\exp(-U/k_BT)$, with an effective excitation enthalpy U and strength A. U increases sharply with decreasing H(D) vacancy concentration as [H(D)]/[Sc]→2.00. These new measurements and analysis support the concept of stable clusters of interacting thermally excited H(D) Frenkel interstitials and vacancies in fluorite-structure dihydrides and dideuterides.

Keywords: Scandium hydrides (deuterides); Nuclear magnetic resonance; High-temperature; Vacancy–interstitial clusters

An anomalous contribution R_{1A} to the nuclear spin–lattice relaxation rate R_1 appears at high temperatures (T~800 K) in many metal–hydrogen (M–H) systems [1]. The anomaly is that, in addition to the usual R_1 maximum that occurs at intermediate temperatures due to hydrogen diffusive motion, R_1 passes through a minimum and increases sharply again at higher temperatures instead of returning to the value R_{1e} determined by the conduction electron contribution to R_1. For protons, ^{1}H, and deuterons, ^{2}D, this is well-documented in a range of solid-solution and dihydride (dideuteride) phases, and a satisfactory explanation is presented [1]. But because of the unfavourable nuclear moment properties of nearly all metal nuclei in M–H systems, the only one for which high-temperature anomalous relaxation has been established is ^{45}Sc [2], and it is clear that the mechanism responsible for R_{1A} of ^{1}H and ^{2}D cannot explain R_{1A} of ^{45}Sc.

We report the results of further measurements of the ^{45}Sc spin-relaxation rate R_1 at high temperatures (to ~1200 K) in the fluorite-structure dihydrides and dideuterides, ScH_{2-x} and ScD_{2-x}. The temperature dependence of the anomalous rate is

$$R_{1A} = A \cdot \exp(-U/k_BT) \tag{1}$$

where U is an effective excitation enthalpy and A measures the interaction strength responsible for the relaxation. The primary objective of this work has been to characterize the dependence of the parameters A and U on H(D) concentration to assess and narrow the field of plausible mechanisms responsible for R_{1A}. The new measurements and analysis support the concept of stable clusters of interacting H(D) vacancies and interstitials [2].

In these systems the measured ^{45}Sc relaxation rate R_1 results from the sum of three independent rate contributions:

$$R_1 = R_{1e} + R_{1Q} + R_{1A} \tag{2}$$

where $R_{1e} = C_e \cdot T$ is due to the hyperfine interaction with the conduction electrons. R_{1e} typically dominates for $T \leq$ 300 K, and the factor C_e is only weakly temperature and composition dependent. R_{1Q} results from the fluctuating ^{45}Sc electric quadrupole interaction due to the random hopping of vacancies on the H(D) sublattice:

$$R_{1Q} = \frac{24\pi^2 c_v}{49 w_0}\langle \Gamma_{NN} \rangle^2 \left[\frac{\omega_0 \tau_v}{1 + \omega_0^2 \tau_v^2} + \frac{4\omega_0 \tau_v}{1 + 4\omega_0^2 \tau_v^2} \right] \tag{3}$$

$\langle \Gamma_{NN} \rangle$ is the average ^{45}Sc quadrupole coupling due to a nearest-neighbour H(D) vacancy or vacancies, ω_0 is the ^{45}Sc resonance frequency, and the factor $c_v = x/2$ is the H(D) vacancy concentration. The vacancy mean dwell time is denoted as τ_v in Eq. (3). While it is not a requirement for the validitity of Eq. (3), we assume that the vacancy jump frequency, τ_v^{-1}, follows Arrhenius behaviour, i.e. $\tau_v = \tau_v^0 \exp(H_a/k_BT)$, where $(\tau_v^0)^{-1}$ is the jump frequency prefactor, and H_a is the activation enthalpy

---

*Corresponding author.

PII S0925-8388(96)02944-1

for vacancy diffusion. R_{1Q} is most effective when $\omega_0\tau_v \approx 1$, typically in the range $400 \leq T \leq 600$ K, and is markedly less effective at lower and higher temperatures.

Two examples of anomalous ^{45}Sc relaxation in ScD_{2-x} in Fig. 1 show clearly the exponential increase in R_1 at temperatures well above the peak due to deuterium vacancy hopping. Several features of these data should be noted: (1) As anticipated from Eq. (3), the maximum value of R_{1Q}, $R_{1Q,max}$, is markedly greater for $c_v = 0.045$ than for $c_v = 0.01$. This results from both the greater c_v and from a greater $\langle \Gamma_{NN} \rangle$ due to the more probable occurrence of multiple nn vacancies to a Sc site. (2) $R_{1Q,max}$ for $c_v = 0.01$ occurs at a substantially lower temperature than for $c_v = 0.045$ (450 K vs. 540 K), showing that the condition $\omega_0\tau_v \approx 1$ is satisfied at a lower temperature, consistent with faster deuterium diffusion at the smaller vacancy concentration, as attributed to hydrogen occupancy of octahedral (0) sites in YH_{2-x} [3]. (3) In contrast, the excitation enthalpy U increases with decreasing c_v. (4) The rate R_{1A} appears to reach a maximum value for $c_v = 0.01$, but this is not evident for $c_v = 0.045$. In addition, $R_{1A,max}$ is significantly greater than $R_{1Q,max}$ for $c_v = 0.01$.

Values of $R_1(^{45}Sc)$ in $ScD_{1.99}$, measured at two resonance frequencies, are shown in Fig. 2, where the solid curve shows the rate R_{1e} extrapolated from low temperatures. As expected from Eq. (3), $R_{1Q,max}$ is inversely proportional to ω_0. Also, on the low-temperature side of the R_{1Q} peak where $\omega_0\tau_v \gg 1$, R_{1Q} is frequency dependent, whereas on the high-temperature side where $\omega_0\tau_v \ll 1$, it is not. In sharp contrast, R_1 remains frequency-independent throughout the high-temperature region of anomalous relaxation. This means the characteristic frequency τ^{-1} of the high-temperature fluctuations responsible for R_{1A}, although slow compared to the vacancy hopping rate τ_v^{-1}, is still fast compared to ω_0.

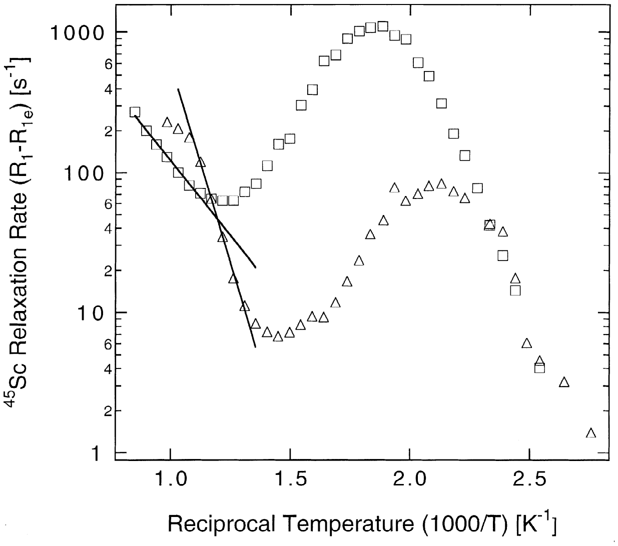

Fig. 1. ^{45}Sc spin–lattice relaxation rate, $R_1 - R_{1e}$, in $ScD_{1.91}$ (squares) and $ScD_{1.98}$ (triangles) measured at 12.2 MHz. The straight lines through the high-temperature data points are least-squares fits, yielding $U = 0.47$ eV for $x = 0.09$ and $U = 1.27$ eV for $x = 0.01$.

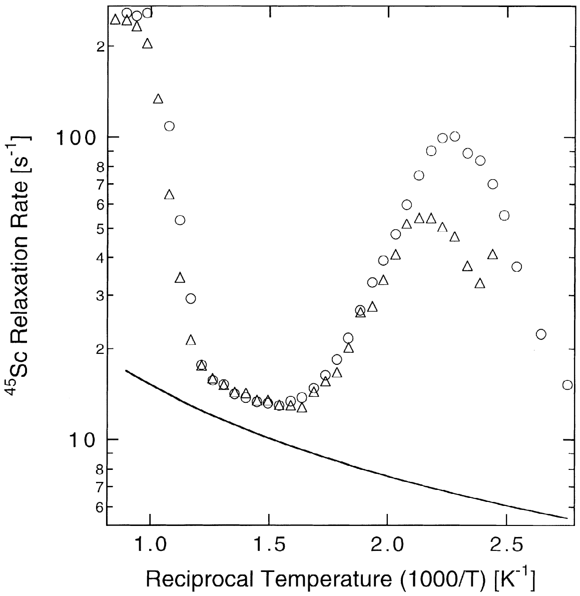

Fig. 2. The measured ^{45}Sc spin–lattice relaxation rate R_1 in $ScD_{1.99}$ measured at 12.2 MHz (circles) and 24 MHz (triangles). The solid curve shows the conduction electron contribution R_{1e} extrapolated from low-temperature measurements.

Taken together, the normal frequency dependence of R_{1Q} and the absence of such dependence for R_{1A}, seen in Figs. 1 and 2, eliminate such relaxation mechanisms as metal atom self-diffusion, diffusion of H(D) on 0-sites, the diffusion of other interstitial impurities, e.g. oxygen or iron, as seen in the high-temperature spin relaxation of ^{51}V in vanadium, for example [4], or quadrupole interactions of ^{45}Sc on particle surfaces [5]. Fixed concentrations of paramagnetic impurities are found experimentally to have no effect on the ^{45}Sc relaxation rate (e.g., 100 parts-per-million of Gd), and an electronic structure transition would affect all spins [H(D) and Sc] at the same temperature, which does not occur [1].

We now consider what can be learned from the dependence of U and A on H(D) vacancy concentration. As shown in Fig. 3, U increases sharply with decreasing c_v in ScD_{2-x}. The solid curve in this figure is a least-squares fit of the function, $U = B \cdot (2-x)^{-\beta}$, yielding $B = 0.089$ eV and $\beta = 0.54$, and suggesting that the excited entity becomes critically inhibited as $c_v \rightarrow 0$. Values of A also increase with decreasing c_v, from $4.8 \cdot 10^3$ s^{-1} to ~10^{10} s^{-1} for $0.095 \geq c_v \geq 0.005$.

Stable clusters of interacting vacancies and interstitials have been found in many nonstoichiometric compounds, including analogous fluorite-structure oxides, e.g. UO_{2+x} [6]. In the latter, clusters may involve both vacancies at regular anion sites (T-sites) and interstitials at intermediate

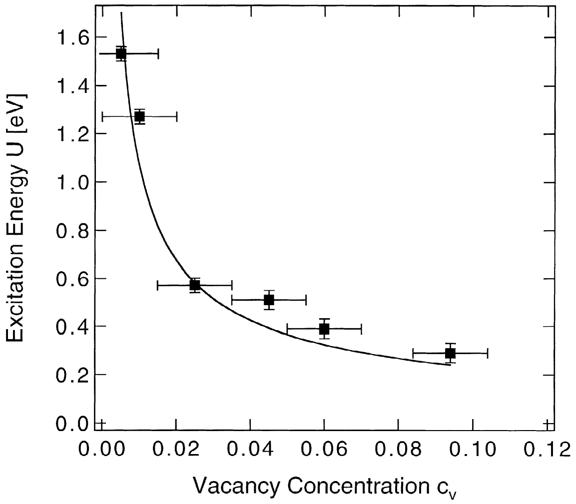

Fig. 3. Effective excitation enthalpy, U (eV), for anomalous high-temperature relaxation of ^{45}Sc in ScD_{2-x} as a function of deuterium vacancy concentration, $c_v = x/2$. The solid curve is a least-squares fit of $U = B(2-x)^{-\beta}$, with $B = 0.089$ eV and $\beta = 0.54$.

positions. It has previously been proposed that hydrides (deuterides) may display analogous effects [2], and Fig. 4 furnishes an example of a possible cluster. Because of the high vacancy mobility, the clusters very likely have a finite lifetime, although longer than the vacancy jump time, so their quadrupolar interaction with Sc nuclei will be characterized by a relatively long correlation time, $\tau_{\mathrm{cl}} > \tau_v$. Considering the clusters as remaining essentially static over their lifetime, τ_{cl} would need to remain short enough to conform to $\omega_0 \tau_{\mathrm{cl}} < 1$ in order to satisfy the observed frequency independence of $R_{1\mathrm{A}}$. The rate $R_{1\mathrm{Q,cl}}$ due to clusters will be given by Eq. (3) with c_v replaced by n_{cl}, the concentration of clusters (assuming that each cluster is associated with a single Frenkel interstitial). Since $\omega_0 \tau_{\mathrm{cl}} < 1$, the rapid increase in $R_{1\mathrm{A}}$ (i.e. $R_{1\mathrm{Q,cl}}$) with temperature arises primarily from the exponential increase in the number of Frenkel interstitials, $n_{\mathrm{cl}} = n_0 \cdot \exp(-E_{\mathrm{I}}/2k_{\mathrm{B}}T)$ [7], where E_{I} is the enthalpy needed to move an anion (H or D) from a lattice site to an interstitial site. Hence, we equate U with $E_{\mathrm{I}}/2$, and conclude that the rapid increase in U as $c_v \rightarrow \mathrm{O}$ reflects the increased energy needed to create a Frenkel interstitial–vacancy cluster as the vacancy concentration becomes very small.

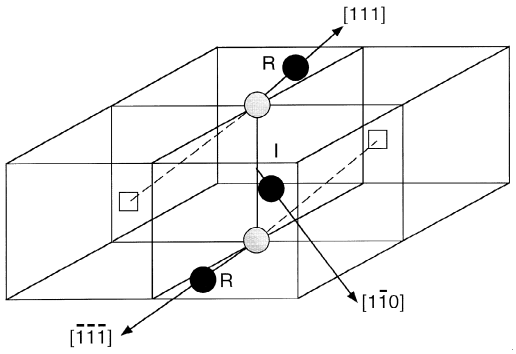

Fig. 4. Example of a cluster formed from one Frenkel interstitial anion (I), two relaxed anions (R), and two vacancies (open circles). Regular anion sites are at cube corners. Cations (Sc) are indicated by open squares. The Frenkel vacancy may not be closely associated with the cluster and is not shown. (From Ref. [2], with permission).

Calculations show the electric field gradient (EFG) at a Sc site due to a relaxed ion is very nearly compensated by that of the vacated T-site. However, the Frenkel interstitial yields an EFG greater than that due to an ion or vacancy at a regular T-site. On this basis, we find that $\langle \Gamma \rangle^2_{\mathrm{cl}} / \langle \Gamma_{\mathrm{NN}} \rangle^2 \cong 2.5$. Thus the cluster mechanism furnishes a possibility for $R_{1\mathrm{A}}$ to exceed $R_{1\mathrm{Q,max}}$, as is evident for $\mathrm{ScD}_{1.98}$ in Fig. 1 and for $\mathrm{ScD}_{1.99}$ in Fig. 2. At the temperature of $R_{1\mathrm{A,max}}$, $\omega_0 \tau_v \sim 10^{-3}$ so one needs $\omega_0 \tau_{\mathrm{cl}} > 10^{-3}$ to satisfy $\tau_{\mathrm{cl}} > \tau_v$. Taking $\omega_0 \tau_v \approx 0.1$ so that $\omega_0 \tau_{\mathrm{cl}} < 1$ for frequency independence, then yields $n_{\mathrm{cl}} \approx 0.25$ for the examples in Fig. 1.

Little other experimental evidence exists to support or deny the cluster hypothesis for the dihydrides. A neutron diffraction study of $\mathrm{PuD}_{2.25}$ [8] showed a fluorite structure with substantial numbers of vacancies at regular T-sites together with interstitial deuterium ions, and the results were best fitted by postulating vacancy–interstitial clusters. Nevertheless, the cluster picture provides the only explanation for the anomalous high-temperature ^{45}Sc relaxation rate behaviour consistent with all the experimental NMR evidence.

Acknowledgments

The authors are indebted to B.J. Beaudry and A. Johnson for their careful preparation of the samples studied. This research was performed in part by R.G.B., at the Max-Planck-Institut für Metallforschung, Institut für Physik, Stuttgart, Germany, and travel support provided by the North Atlantic Treaty Organization through Grant No. 910179 is gratefully acknowledged. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

References

[1] R.G. Barnes, J.W. Han, D.R. Torgeson, D.B. Baker, M.S. Conradi and R.E. Norberg, *Phys. Rev., B51* (1995) 3503, and references therein.

[2] R.G. Barnes, M. Jerosch-Herold, J. Shinar, F. Borsa, D.R. Torgeson, D.T. Peterson, A.J. Lucas, G.A. Styles and E.F.W. Seymour, *Phys. Rev., B35* (1987) 890.

[3] U. Stuhr, D. Steinbinder, H. Wipf and B. Frick, *Europhys. Lett., 20* (1992) 117.
[4] B. Günther and O. Kanert, *Acta. Metall., 31* (1983) 909.
[5] S.R. Rabbani and D.T. Edwards, *Phys. Rev., B50* (1994) 6184.
[6] O. Toft Sørensen, (ed.), *Nonstoichiometric Oxides,* Academic Press, New York, 1981.
[7] Charles Kittel, *Introduction to Solid State Physics, third edn.,* John Wiley and Sons, New York, 1966, p. 564.
[8] W. Bartscher, A. Boeuf, R. Caciuffo, J.M. Fournier, J.M. Haschke, L. Manes, J. Rebizant, F. Rutichelli, and J.W. Ward, Solid State Commun. 52 (1984) 619.