Rapid Low-Temperature Hopping of Hydrogen in a Pure Metal: The ScH_x System

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The localized motion of hydrogen in scandium has been studied by quasielastic neutron scattering. The results reveal that the quasielastic linewidth has a pronounced minimum near 100 K and rises at lower temperature with approximate T^{-1} dependence, indicative of nonadiabatic behavior that can be associated with weak coupling of hydrogen to the metal conduction electrons. This is the first such observation in a pure-metal–hydrogen system. The simultaneous determination of the elastic incoherent structure factor is interpreted in terms of labile and nonlabile hydrogen configurations in a manner consistent with recent estimates of pairing and activation energies in the rare-earth–hydrogen systems.

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We report the results of a neutron-scattering study of α-ScH_x which reveals a striking *increase* in proton "hopping" rates between near-neighbor H sites along the c axis at low temperatures, with the apparent rate reaching 10^{12} s^{-1} at 10 K, comparable to the rate measured at room temperature. An approximate T^{-1} dependence observed for the quasielastic linewidth points to nonadiabatic behavior associated with weak coupling of a quantum two-state system to the conduction electrons. This is the first such observation for a pure-metal–hydrogen system.

Hydrogen dissolved in hcp rare-earth metals is known to exhibit unusual short-ranged ordering, which apparently stabilizes the α phase to much higher concentration at low temperatures than in other metal-hydrogen systems, and which leads to a variety of interesting physical properties.[1] Neutron-diffraction[2,3] and diffuse-scattering[4,5] studies show that the hydrogen atoms are in tetrahedral (T) sites and are arranged in next-nearest-neighbor pairs bridging the metal atoms, and a recent quantum-chemical cluster calculation[6] has demonstrated the stability of such pairs in YH_x. These H-M-H pairs in turn exhibit temperature-dependent cooperative structure along the c direction.[7,8] Recently, these systems also have been shown to exhibit anomalous dynamical behavior. Quasielastic-neutron-scattering experiments[9,10] on $YH_{0.2}$ and NMR studies of several rare-earth–hydrogen systems[11] show that long-range diffusion of H in the rare earth is rather slow but at the same time suggest a more rapid proton diffusion, presumably related to near-neighbor jumps along the c axis. Moreover, neutron spectroscopy of H and D in yttrium[12,13] reveals a much softer vibrational potential along the c axis than in the a-b plane, and a subsequent neutron-scattering study finds an even more anisotropic potential in the ScH_x system.[14] Since ScH_x also has a smaller near-neighbor H distance than the other rare earths (1.0 Å, cf. 1.3 Å for Y), it seems a good candidate for probing the influence of local structure on proton motion between these T sites.

We present here direct quasielastic-neutron-scattering measurements of the localized motion of hydrogen in scandium. Our experiments were carried out between 2 and 300 K on a single-crystal slab of scandium prepared from high-purity Ames Laboratory scandium metal (total metallic impurities $\approx 0.01\%$, oxygen $< 0.01\%$). Samples were loaded with hydrogen from the gas phase in a high-vacuum system with base pressure of 2×10^{-6} Pa to minimize introduction of other gas impurities (traps). Hydrogen concentrations were determined both volumetrically and gravimetrically. Measurements were performed at H concentrations between 5 and 20 at.% on the IN-5 Spectrometer at the Institut Laue-Langevin with energy resolution of 70 μeV at momentum transfers $1.05 < Q < 2.05$ Å^{-1}. The H scattering was determined by subtraction from the ScH_x spectra of the absorption-corrected scattering from an identical scandium crystal.

The resulting spectra were fitted with an empirical two-component function comprising an elastic term described by the resolution function of the spectrometer and a resolution-broadened Lorentzian quasielastic term. Figure 1 shows the results of such a fit to the data from $ScHO_{0.16}$ at various temperatures and indicates the adequacy of the model in describing the observed spectra. The observed Q independence of the measured Lorentzian linewidth (not shown here) can be taken as proof of the localized nature of the motion responsible for the quasielastic scattering. Our analysis of the Q depen-

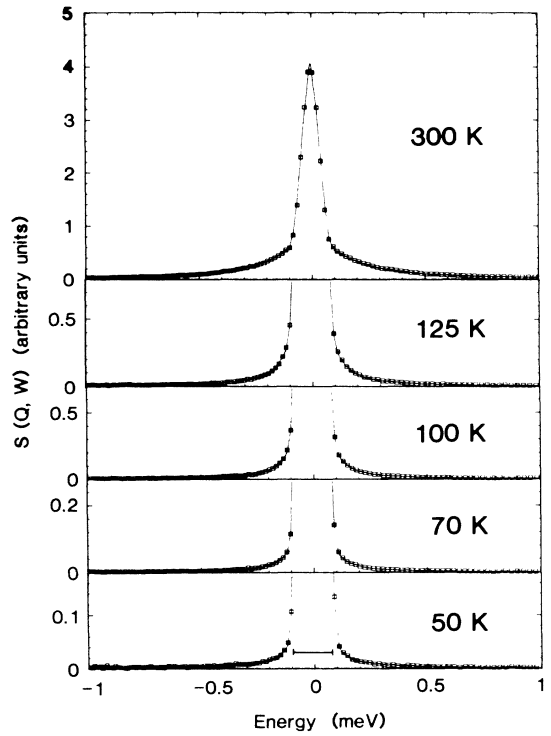

FIG. 1. Quasielastic neutron spectra for $ScH_{0.16}$ at several temperatures. The solid lines are the results of least-squares fits to the data by the two-component model described early in the text; the dotted lines represent the Lorentzian quasielastic component. The increase of the quasielastic linewidth at low temperature is illustrated in the 50-K spectrum, where the length of the included horizontal line is equal to the width of the 70-K Lorentzian component.

dence of the elastic incoherent structure factor (EISF) gave a hopping distance ≈ 1.0 Å, in agreement with the near-neighbor T-site distance in $ScD_{0.33}$.[3]

Figure 2 shows the quasielastic linewidth Γ versus temperature for $ScH_{0.16}$. Less extensive data sets for $ScH_{0.05}$ and $ScH_{0.25}$ show behavior consistent with the 0.16 results and will be discussed in a more complete description of this work. For each case the data show a hopping rate exceeding $\sim 7\times 10^{10}$ s^{-1}, indicative of very rapid motion compared to the bulk diffusion in these systems. Indeed these rates are at least 100 times faster than the hydrogen hopping rates inferred by recent NMR measurements by Lichty *et al.*,[11] which were also attributed to jumps between neighboring T sites. The remarkable upturn of Γ below the minimum is approximately T^{-1} in the range shown, and is similar in appearance to the observations by Steinbinder *et al.*[15] of quasielastic scattering from hydrogen trapped by oxygen impurities in Nb. These were explained in terms of Kondo's predictions[16] of nonadiabatic effects of the coupling of the metal conduction electrons to the proton, which in that system is trapped on a pair of equivalent T sites in the bcc lattice. We believe that ScH_x presents a

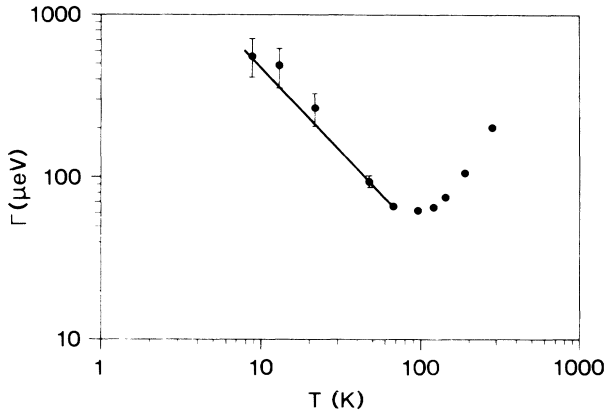

FIG. 2. Fitted Lorentzian linewidths (FWHM) for $ScH_{0.16}$. The solid line is the fit to the data below 100 K discussed in the text.

novel situation in which the effects of such coupling are also amplified by the effective restriction of the proton to a pair of sites: in this case the near-neighbor T sites between metal atoms along the c axis in the pure-metal-hydrogen system. In this picture the linewidth is the sum of the width from the interaction of the proton with the lattice, which falls monotonically with decreasing T, and the electronically induced broadening which increases with decreasing T.

The theoretical elaboration of the line shape in nonadiabatic systems has received much attention[17-21] and remains unsettled in important respects, even for coupling to relatively simple two-site defect potentials. (Within these approaches, the defect potential ultimately is defined by the renormalized tunneling matrix element Δ and the double-well asymmetry energy ϵ.) A central issue in these developments is that the most tractable analytical scheme, the so-called *dilute-bounce-gas approximation* (DBGA), is justified at small-to-intermediate times, while the line shape near $\omega=0$ is determined by long-time behavior, which turns out to be especially sensitive to the asymmetry ϵ.[21] As Weiss and Wollensack[21] have recently shown, behavior at $\omega=0$ can be regularized by low-order corrections to DBGA but these in turn can lead to unphysical results near $\omega=\epsilon$.[22] Such difficulties, however, are concentrated on the low-temperature regime, $T<T_1=\Delta/2\pi K k_B$, where K is the proton-electron coupling constant. As shown in Ref. 20, the DBGA is a consistent scheme at $T>T_0=\epsilon_b=(\Delta^2+\epsilon^2)^{1/2}$, which encompasses $T>T_1$ if $T_1>T_0$ —i.e., if ϵ is not too large. Therefore, our approach is to accept the quasielastic linewidth formula from the DBGA, which in the relevant T domain is[20,21]

$$\Gamma=K\Delta^3(2\pi k_B T/\Delta)^{2K+1}/[(2\pi k_B TK)^2+\epsilon^2], \qquad (1)$$

which also assumes $K\ll 1$. This becomes $\Gamma=K^{-1}\Delta(2\pi\times k_B T/\Delta)^{2K-1}$ for $k_B T\gg\epsilon/2\pi K$. We have applied (1) to the $ScH_{0.16}$ data in Fig. 2 for $T<T_{\min}$ using error-weighted least-squares fitting. Since three parameters

are involved, we first determined that no fit was possible for ϵ greater than a few tenths meV. Then taking $\epsilon=0$ and using the power-law limit of (1) we obtained $K=0.039$ and $\Delta=0.32$ meV. This gives $T_1=4.4$ K, consistent with $T>T_1$ over most of the measured range. The fitted K and Δ are sensitive to the errors, which are fairly large at low temperatures, and thus not sharply defined by these measurements. Nonetheless, they lie near the values reported for H in Nb-O,[15] where the relevant T-site separation is close to that in ScH_x. Furthermore, the small value of K is in contrast to the substantially stronger coupling found for muons in Cu and Al.[23] Thus the Kondo mechanism for the low-temperature upturn provides a reasonable explanation of the observed rapid motion for labile protons in nearly symmetric double wells between the metal atoms. The data do not support the much steeper power laws that have been discussed recently in association with nonlinear polaron effects for mobile defects in insulators.[24] Recently, Svare[25] has questioned the application of the nonadiabatic theory to the quasielastic data of Steinbinder *et al.*[15] as being inconclusive evidence of the Kondo mechanism, arguing that the $\sim T^{-1}$ dependence observed there is, in essence, an artifact. Svare's alternative depends on a broad distribution of site asymmetries, which do not describe the environment of the fast-moving protons in ScH_x.

Our interpretation of the linewidth data is consistent with the simultaneously measured EISF, shown as a function of T in Fig. 3. Specifically, we assume all of the measured hydrogen atoms are in two populations, which we designate as labile (l) and nonlabile (nl), with relative occupations c_l and c_{nl}, respectively, and with $c_l+c_{nl}=1$. We attribute the labile defects to configurations in which H-M-H pairing cannot occur because of the unavailability of nearby protons to form such bridged pairs along the c axis; examples of such configurations can be visualized by removing an H from every H-M-H pair to a neighboring, unoccupied chain. The scattering function $S(\mathbf{Q},\omega)$ is then the population average,

$$S(\mathbf{Q},\omega)=\sum c_i\{f_i(\mathbf{Q})\delta(\omega)+[1-f_i(\mathbf{Q})]L_i(\omega)\}\,, \qquad (2)$$

where $f_i(\mathbf{Q})$ is the EISF for the ith member ($i=$l,nl) and $L_i(\omega)$ is the corresponding normalized quasielastic-scattering function. We identify the nonlabile species as being slow moving on the resolvable time scale of the measurement, which corresponds to a hopping rate of $\Gamma\approx 3\times 10^{10}\ \mathrm{s}^{-1}$. Thus in the model $L_{nl}(\omega)\approx\delta(\omega)$, and (2) can eventually be rewritten as

$$S(\mathbf{Q},\omega)=F_{\mathrm{EISF}}(\mathbf{Q})\delta(\omega)+[1-F_{\mathrm{EISF}}(\mathbf{Q})]L_l(\omega)\,, \qquad (3)$$

where

$$F_{\mathrm{EISF}}(\mathbf{Q})=1-c_l s_l\sin^2(\mathbf{Q}\cdot\mathbf{d}/2)\,, \qquad (4)$$

with $s_l=1-\bar{z}^2$, $\bar{z}=(\epsilon/\epsilon_b)\tanh(\epsilon_b/2k_BT)$, and $\epsilon_b=(\epsilon^2+\Delta^2)^{1/2}$. Thus $s_l=1$ for a symmetric well, while $s_l\to 0$ for a strongly asymmetric well at $k_BT<\epsilon$.

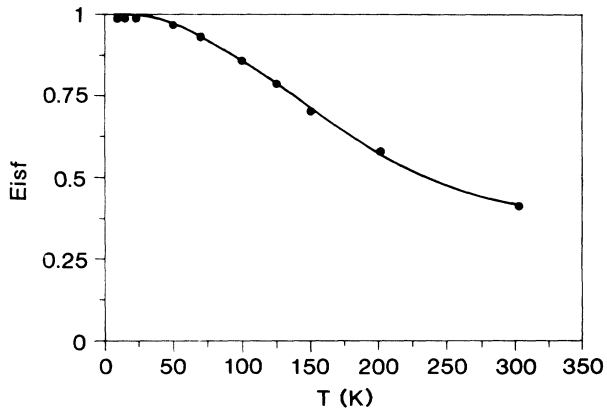

FIG. 3. Temperature dependence of the elastic incoherent structure factor (EISF) for $ScH_{0.16}$. The solid line is a fit to the data using (4) with $s_l=1$. The T dependence of c_l is obtained by assuming Boltzmann occupations of labile and nonlabile configurations; as a convenient fitting model we approximated a continuum density of labile states by two unequally weighted δ functions separated from the nonlabile state by (fitted) energies of 17 and 78 meV and with almost all the weight at the higher energy.

At $T=300$ K, the Q dependence of the measured EISF is well described by (4) with $c_l s_l=0.89$, indicating that most of the scattering protons at room temperature are labile. The distinction between labile and nonlabile is not completely unambiguous at high temperatures, of course, and we can expect some contribution to the EISF from "paired" protons moving in a presumably very asymmetric potential. However, since the quasielastic linewidth measurements at low temperatures appear to require close to symmetric T sites within the labile population, we assume that the potential seen by the labile protons does not depend strongly on temperature, except possibly at the highest temperatures. Thus we note that with $s_l(T)=1$, the measured T dependence of the EISF is, within the model, an empirical measure of $c_{nl}(T)$, the fraction of nonlabile configurations. As the curve in Fig. 3 shows, at low temperatures only a small fraction of the protons are labile, but in our scheme these labile species are responsible for the anomalous hopping. A quantitative fit to the data in Fig. 3 requires knowing how to account for metastable hydrogen configurations which certainly are important at the lower temperatures. Preliminary analysis, assuming equilibrium statistics, indicates that the occupational density of states for the labile protons are separated from the nonlabile configurations by energies in the range of 15–80 meV. The lower end of this broad band may reflect the influence of metastable configurations on the measured EISF at low T, while the upper portion suggests the magnitude of the T-site potential asymmetries due to short-ranged order of paired nonlabile protons along the c axis. Resistivity anom-

alies[26] in the rare-earth–hydrogen systems also have been linked to energies in the 50-75-meV range. Liu *et al.*[6] predict a binding energy of 110 meV for H-Y-H pairs in YH_x.

In summary, our quasielastic-neutron-scattering studies show the existence of fast-moving protons in ScH_x, whose apparent hopping rate increases to 10^{12} s^{-1} at 10 K after passing through a minimum at ≈ 100 K. Thus we identify a labile population of interstitial hydrogens, i.e., hydrogens not involved in short-ranged H-*M*-H pairing order at low temperatures, and whose remarkable low-temperature dynamical behavior is determined by weak coupling to the conduction electrons, as described by Kondo's analysis.

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