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Deuterium site occupancy in YD_x by magic-angle-spinning NMR

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Magic-angle-spinning (MAS) deuterium NMR of YD_x, $x\sim 2$, yields spectrally resolved lines for D atoms in tetrahedral (T) and octahedral (O) interstitial sites. Compared to MAS line narrowing of metal hydrides, the deuterides line narrow with only modest, readily attainable spinning speeds. This is the first application of NMR to resolve inequivalent sites in these systems. For YD_x at 200 K we find only T sites occupied for $x\leqslant 2.00$, in contrast to some other reports. For $x>2.00$, the excess D atoms are accommodated in O sites. Thermally activated motions that interchange D atoms between T and O sites are detected and their rate determined, with $E_a=0.55$ eV ($=k_B\times 6390$ K). A third deuterium species, T_O, is spectrally identified: D atoms in T sites with occupied O site nearest neighbors. We expect the deuterium MAS-NMR technique to be valuable for site occupancy determination in deuterides of alloys and compounds in which there are several inequivalent occupied sites. [S0163-1829(96)03122-0]

I. INTRODUCTION

A. Measuring hydrogen site occupancies

Metal hydrides are solid-state solutions or compounds of hydrogen with various metals (Y, Sc, Ti, Pd, Nb, V, and others).[1,2] They are remarkable not only for the quantity of hydrogen that can be absorbed [e.g., up to $x=3$, in YH_x (Refs. 2–4)] but for the high mobility of the hydrogen atoms.[2,5] Applications of metal hydrides include hydrogen storage for fueling vehicles,[6] advanced electrochemical cells,[7,8] generation of ultrapure hydrogen,[2] and thermally driven pumps and heat pumps.[9]

Before any real understanding of a particular metal hydride can be obtained, one must first know where the H atoms are located in the host metal structure. In some systems, such as YH_2, the subject of the present study, symmetry suggests that H atoms are in tetrahedral interstitial sites (T sites, of which there are two per Y atom) or octahedral interstitial sites (O sites, one per Y).[10] In compounds (e.g., ZrV_2H_x, a Laves structure[11–14]) or alloys a richer variety of sites occurs. Specifically, H sites may be characterized by the numbers of nearest neighbors of each metal atom type. For example, nominally tetrahedral sites in the alloy $Nb_yV_{1-y}H_x$ can be subdivided[15,16] into Nb_4, Nb_3V, Nb_2V_2, NbV_3, and V_4.

There are existing techniques that can determine which sites are occupied by H (or D), and to what extent. First, diffraction is particularly successful in ordered or nearly ordered structures. Because of the low atomic number, hydrogen is not detected well by x-ray diffraction. But neutron diffraction, particularly of metal *deuterides*, is quite successful. Neutron vibration spectroscopy (NVS) is an inelastic scattering and distinguishes H atoms in different sites by their vibration frequencies. Proton NMR second-moment (M_2) measurements measure the proton-proton dipole interaction.[17,18] For a powder, the theoretical result is $M_2\sim\Sigma_j \mathbf{r}_{jk}^{-6}$, where $\mathbf{r}_{jk}$ is the distance from a given proton k to any of the others, j. Clearly, one cannot uniquely determine the structure from the proton M_2, but structures may be ruled out if they have the wrong M_2. The vapor pressure of H_2 in equilibrium with the metal hydride yields the hydrogen chemical potential μ of the system, as does the electrochemical cell voltage against a known reference electrode.[19,20] If the binding energies of the various sites are well separated, the graph of μ vs x ($x=\mathrm{H}/M$, the dimensionless hydrogen concentration) is expected to show separated waves, i.e., broadened steps.[16] But for modestly complex systems in which the energy of a given site depends on the occupation of other sites, these data are not easy to interpret. While a thermodynamic model can readily be solved to yield μ vs x, inverting the problem to yield the energies and numbers of sites from $\mu(x)$ data is very difficult. Thermal desorption spectroscopy[21–23] (TDS) is a temperature-ramped experiment that obtains data very closely related to $\mu(x)$.

As evidenced by the debates in the literature, none of these techniques is appropriate for all metal-hydrogen systems and none is without fault. We believe high-resolution NMR should be nearly ideal for measuring site occupancies in many nonmagnetic systems. If one can detect frequency-resolved NMR lines for H or D in inequivalent sites, it is a simple matter to determine the relative intensities (areas) to obtain quantitative site occupancies. Indeed, the single largest application of NMR is in obtaining spectrally resolved peaks from organic compounds in the solution state. Unfortunately, various line-broadening interactions are present in solids and are generally much larger than the desired frequency shifts. These solid-state broadenings need to be removed so that high-resolution NMR can successfully distinguish and quantify H (or D) atoms in different sites.

B. Magic-angle-spinning NMR

The most important broadenings in the NMR spectrum of a metal hydride or metal deuteride are nuclear spin dipole-dipole (both like spin such as proton-proton and unlike spin such as the much weaker ^{89}Y-proton), the anisotropy of the chemical and Knight shifts, the quadrupole interaction (for deuterium only, because $I=1$), and the magnetic susceptibility broadening.[17,24] This last interaction is generally substantial in metal hydrides because of the susceptibility of the d electrons (the susceptibility of Y metal is small, however). Metal hydride NMR samples are almost always powders to allow penetration of the rf fields. The odd-shaped powder particles have demagnetizing factors which are orientation dependent. Further, except for special shapes such as ellipsoids, the field inside the particle becomes nonuniform. This broadening may be accurately regarded as an unlike-''spin'' dipole-dipole interaction between the nuclear spin of interest and the magnetic moment of a volume element of the sample.

All of the above broadening interactions have an angular dependence of $3\cos^2\theta-1$, where θ is the angle between the external field $\mathbf{H}_0$ and the appropriate axis of the interaction tensor (e.g., the spatial vector from one spin to the other or a principal axis of the chemical shift tensor).[17] A well-known method of removing the line broadenings is to time-average them to zero with magic-angle spinning (MAS).[25,26] MAS involves physical rotation of the sample at typical speeds of 0.5–15 kHz. The angle ϕ between the rotation axis and the external field is set to the magic angle $\phi=54.7°$; i.e., such that $3\cos^2\phi-1=0$.

To be effective in narrowing the NMR lines, the MAS speed (rotor frequency) must be sufficiently large. The minimum spinning rate required depends not only on the strength of the interaction but on the *type* of interaction. When like-spin dipole-dipole interaction (I-I) is dominant, as it is for the protons in YH_2, the resonance line is *homogeneously* broadened. In this situation, mutual spin flips (''flip-flops'') occur. To narrow the line appreciably, MAS must be at rotor frequencies greater than the I-I interaction strength, i.e., greater than the spin flip rate.[27] For YH_2 and other highly loaded metal hydrides, the proton linewidth is ~30 kHz. Spinning at this rate is beyond the current state of the art. For this reason, MAS proton NMR has not been used to distinguish H at inequivalent sites in metal hydrides.

The other interactions listed above, including unlike-spin (I-S) dipole interaction, result in inhomogeneous broadening. When these broadenings dominate, rotation at even slow speed will break the line into a forest of narrow sidebands spaced by the rotor frequency.[27] Thus rapid spinning is not required, though problems may arise from the overlap of the sidebands from different sites.

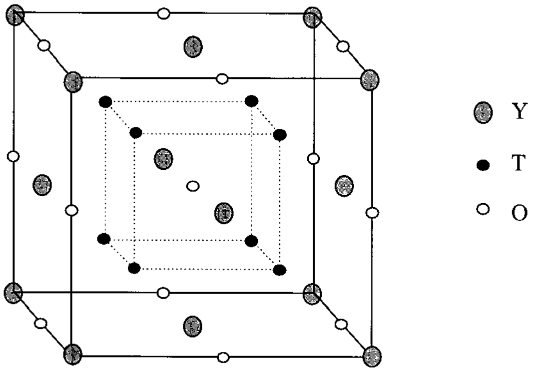

FIG. 1. The conventional cell of YD_x for $x\sim2$, the same structure as CaF_2. The Y atoms (gray) are located on a fcc lattice. The tetrahedral interstitial sites (T sites, solid symbols) form a simple cubic sublattice. The octahedral (O) sites are represented by open symbols and are at edge centers and the body center. The cell contains four Y atoms, eight T sites, and four O sites.

The magnetogyric ratio γ of the deuteron is only about 15% that of the proton. The rigid-lattice like-spin dipole-dipole linewidth is essentially the square root of the second moment and varies[17] as $[\gamma^4 I(I+1)]^{1/2}$. In a metal deuteride this linewidth will be 1/26 that of the corresponding metal hydride. Thus spinning speeds of 2–4 kHz will efficiently average to zero the deuteron-deuteron dipole couplings in metal deuterides. This is our approach here: MAS deuterium NMR of a metal deuteride. The difficult like-spin dipole interaction is reduced by deuterium substitution so that modest speed MAS efficiently averages all of the line-broadening interactions, homogeneous and inhomogeneous.[28]

For completeness, we describe an alternative approach: MAS line narrowing and detection of the residual protons ($\approx1\%$) in a nearly completely deuterided sample ($\approx99\%$). Here the difficult proton-proton dipole interaction is first reduced by isotopic dilution so that modest speed MAS yields good narrowing. We expect this approach to work, though we have not tried it. Detection of dilute protons will not present an S/N problem, because of the large magnetic moment of protons. However, with a relatively small amount of protons in the sample, all extraneous protons must be eliminated from the construction materials of the probe and MAS assembly.

C. The YH_x system

The structure of YH_x for $x\sim2$ is the CaF_2 structure[10] (Fig. 1). Thus Y atoms are arranged on a fcc lattice while the H atoms sit primarily on the simple cubic sublattice formed by the tetrahedral interstitial (T) sites. This occupancy of T sites is in good accord with the facts of hydrogen absorption in YH_x: the metal readily accepts up to two H atoms per Y atom, but the third H atom is only accepted at higher external H_2 pressure.[3,4,29–34] Thus a simple view of YH_x, $x\leqslant2.00$, is that H is accommodated only at T sites at room temperature and below. For $x>2.00$, the excess H atoms are located at O sites. (Of course, at higher temperatures one expects H atoms to be thermally promoted to the higher-energy O sites, even for $x<2$.) Because there are two T sites and one O site per Y atom, the highest loading obtained, YH_3, corresponds to all interstitial sites filled. Actually, the phase transition from nominally dihydride to nominally trihydride is accompanied by a fcc-hcp rearrangement.

There is some evidence that the simple view might be incorrect. Neutron vibration spectroscopy (NVS) finds a small, resolved peak at lower energy in YH_2, identified with occupied O sites.[35] Some 8% of the H atoms are believed to reside in the O sites at room temperature and below. Surprisingly, less O site occupation is measured at higher temperatures; an explanation in terms of vibrational entropy is offered. Two independent proton second-moment measurements[36,37] near 200 K arrived at the conclusion that the calculated M_2 in the ideal YH_2 structure (CaF_2-like) is 10% smaller than the experimental M_2 for $YH_{2.00}$. Thus H appears to begin to occupy O sites while some T sites are evidently still open. And neutron diffraction studies at room temperature and below likewise found that a small fraction of the O sites are occupied[35,38] at $x=2.00$. On the other hand, residual electrical resistivity measurements[34] have found a deep minimum in the resistivity at $x=2.00$. This indicates that there are no defects (no vacant T sites and no occupied O sites) at $x=2.00$. Thus the hydrogen site occupancy picture in YH_x is not clear. The present work addresses this issue with high-resolution solid-state NMR.

II. EXPERIMENT

The samples are a crucial aspect of experiments on YD_x, $x\sim 2$. There is evidence that a relatively low level of impurities can affect deuterium site occupancy by blocking a fraction of the T sites.[34,39] For this reason, samples from two different sources were examined; they yielded very similar results. Most of the experiments used samples of $YD_{1.91}$, $YD_{1.98}$, $YD_{2.04}$, and $YD_{2.08}$ prepared previously by Markert at Cornell and described elsewhere.[36] The deuterium relaxation times T_1 and $T_{1\rho}$ were measured by Markert and Cotts as well as the ^{89}Y-^{2}D cross relaxation in the rotating frame.[40] The D/Y ratios, x, are believed accurate to $\pm 1\%$ (± 0.02 out of ~ 2). Some of the experiments used YD_x samples prepared by Vajda at the Ecole Polytechnique, as described previously[34,39] and used in electrical resistivity measurements. The D content of these samples was characterized by two values: e.g., $1.95+0.09$, meaning 1.95 D atoms per Y atom in T sites (with the remaining T sites presumably blocked by strains and/or impurities) and 0.09 D atoms in O sites. These samples were small (~ 15 mg) and yielded smaller S/N. Hence experiments with the small samples were generally restricted to simple spectroscopy; selective-inversion measurements were made primarily with the larger samples from Cornell.

The air-sensitive samples were always handled in a N_2 atmosphere. The powdered samples from Cornell were mixed with carefully dried MgO powder, to keep the conducting particles apart, for better rf field penetration and less eddy-current braking during sample spinning. The samples from the Ecole Polytechnique were small strips with electrical leads attached. The leads were removed by scraping and the samples were ground under N_2; again, MgO powder was added.

The NMR probe used a magic-angle-spinning assembly intended for room temperature use from Doty Scientific, Inc. The rest of the probe was homebuilt. The samples were contained in ceramic rotor tubes with O-ring sealed end-caps. We decided not to rely on the O-ring seals to exclude air from the samples, because the O rings shrink from the ceramic rotor tubes at low temperatures. Instead, N_2 gas boiloff from a liquid N_2 vessel was used for the spinning drive and bearing gas. The probe was constructed with appropriate seals to ensure the sample would be exposed only to N_2. Between experiments, the sample was either stored in a N_2 atmosphere or left in the probe, with a steady flow of N_2 gas for protection. The angle of the MAS axis was adjusted by observing rotational echoes[41] from ^{79}Br in KBr.

The N_2 gas supplied to the MAS assembly was cooled by passing through copper coils soldered to a massive copper block. A third copper coil carried liquid N_2 to cool the block. The temperature of the gas was controlled manually by adjusting the flow rate of the liquid N_2 using a needle valve. A thermocouple recorded the temperature of the exhaust gas from the spinner assembly. This temperature is believed to be within 5 K of the sample temperature, though the relative accuracy of our measurements is ± 2 K (i.e., we expect a nearly constant offset between sample and thermocouple). For the bearing and drive gas pressures, manually adjusted regulators were used. Spinning below 190 K was difficult because of the contraction of the end-cap seals. Overall, the spinning and temperature-control arrangements and stability were only adequate. In particular, long-term signal averaging was not feasible. We note that better designs for low-temperature spinners are in the literature[42–44] and some good designs are commercially available.

The NMR experiments were performed with a Chemagnetics CMX-360 spectrometer with an 8.4 T superconducting magnet from Cryomagnet Systems, Inc. Typically, $\pi/2$ pulses were 5.5 μs at a deuterium frequency of 54.36 MHz. Spectra were obtained by Fourier transformation of the free induction decay (FID). Because of the receiver recovery, some baseline distortion is present. Nevertheless, we prefer the use of FID's over spin echoes: for properly phased spinning sidebands from spin echoes, the rotor period and the pulse separation τ should be matched.[45] With our equipment, this was difficult. The spinning speed was typically 3000 Hz and was measured by an electrostatic pickup and frequency counter. The homogeneity of $\mathbf{H}_0$ was measured with D_2O and was much better than the narrowest lines reported here.

III. RESULTS AND DISCUSSION

Magic-angle-spinning deuterium NMR spectra of YD_x at 194 K are presented in Figs. 2 and 3, for $x=2.08$ and 1.98, respectively. The dominant spectral feature is the large line near zero frequency; this is assigned to T site deuterium atoms, in accord with the previously cited evidence. For $x=2.08$, an additional, weak line is present at 1470 Hz up frequency (all frequencies reported here are measured from the center of the T site resonance). Because this line is absent for all the samples with $x<2$ (see Fig. 3), it is assigned to O site deuterium atoms. In addition, sidebands are prominent in Fig. 3 and especially in Fig. 2 and are denoted by stars. Modulation of the anisotropic interactions at the MAS rotor frequency results in sidebands, separated from the true reso-

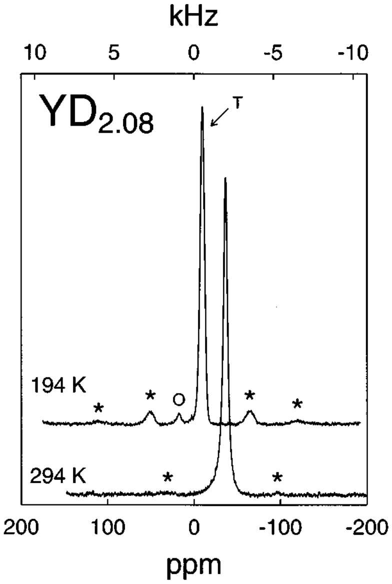

FIG. 2. Deuterium NMR of $YD_{2.08}$ under magic-angle spinning (MAS). The strong line is from T sites and is near zero frequency; the 294 K spectrum has been shifted horizontally for display purposes. At 194 K, a weak line at +1470 Hz appears from occupied O sites. Upon warming, the O site line disappears and the sidebands become much weaker. Both changes are due to T-O interchanges. Sidebands are denoted by stars. The MAS speeds are 3.15 and 3.46 kHz at 194 and 294 K, respectively. Zero frequency corresponds to the resonance of D_2O at room temperature.

nance frequency (centerband) by integer multiples (here, primarily ±1) of the spinning frequency.[27]

For the $x = 2.08$ Cornell sample, the ratio of the spectral intensity (area) of the O site resonance to the T site line together with its two spinning sidebands (see Fig. 2) is 0.033 $(= 0.066/2)$, ±0.005. This result is consistent with the above assignment of the lines for a deuterium concentration $x = 2.066$ (assuming all T sites are occupied), in good agreement with the specified composition of $x = 2.08 \pm 0.02$. For the nominally $x = 2.04$ Cornell sample, the relative intensity of the O site resonance is 0.023 ± 0.005 indicating an actual deuterium concentration of 2.046. Thus the absence of the line at +1470 Hz for $x < 2$ and the values of the relative spectral intensities for $x > 2$ are fully consistent with the simple view of deuterium site occupancy in YD_x: for $x < 2$, no O sites are occupied, while for $x > 2$ all T sites are occupied. Similar results were obtained with samples from the Ecole Polytechnique. The ratio of the O site and T site resonance intensities agreed better with $(x_O + x_T - 2)/2$ than with x_O/x_T, where x_O and x_T were the separately specified D concentrations from the sample loading procedure.[34,39] The value $(x_O + x_T - 2)/2$ would be expected to be the ratio of resonance intensities only if the *true* occupation of tetrahedral sites per metal atom is 2, and not x_T. However, this distinction is at the limit of our confidence in the NMR data analysis.

The shift of +1470 Hz of the O site line relative to the T line is +27 ppm. Given that proton (or deuteron) chemical shifts generally lie in a 10 ppm interval,[46] it is clear that the shift is at least partially a Knight shift.[17] Knight shifts (from interaction with electron spins) and chemical shifts (from electronic orbital motion) are difficult to separate, in general.

The Knight shifts of H (or D) in metals are small, because of the low atomic number. Although there are not many data, the Knight shift is often negative (down frequency).[47–51] This is in qualitative agreement with the shifts measured here, with the more metallic T sites (closer to the metal atoms and lower in energy than the O sites) being towards lower frequency. The shift of the T site line relative to D_2O in a ceramic rotor tube in the same spinner assembly is −12 ppm (down frequency). Because of the magnetic susceptibilities of the probe and sample tubes, we believe this absolute shift is only accurate to ±3 ppm.

At higher temperatures, the O site resonance for $x = 2.08$ disappears and the spinning sidebands of the T sites become much weaker, as presented in Fig. 2. By comparison, there are at most only minor changes in the $x = 1.98$ spectrum upon heating to room temperature (Fig. 3). We believe exchange of deuterium atoms between T sites and O sites is responsible for the collapse of the O resonance *and* the T site sidebands. Slow T-O interchanges, that is, with a rate slow compared to the 1470 Hz separation, will result in lifetime broadening of the O line;[46] presumably, when the weak O line is broadened it becomes undetectable in our experiment. Faster T-O interchanges (rate faster than the 1470 Hz separation) will cause the T and O lines to coalesce. However, because of the much larger number of deuterium atoms on T sites than on O sites, any frequency shift and broadening of the T line will be comparatively small.

T-O interchanges are revealed most clearly with a selective-inversion pulse sequence [Fig. 4(a)].[52] The first two pulses serve to invert the T resonance while not perturbing the O resonance. The T line is placed on resonance with the spectrometer carrier frequency, so the two $\pi/2$ pulses effect a net nutation of π. The O line is off resonance by

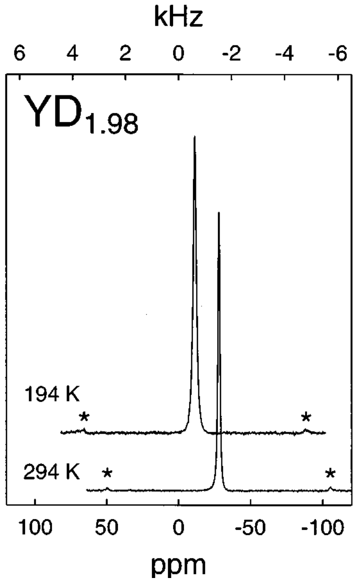

FIG. 3. Deuterium MAS NMR of $YD_{1.98}$. The O site resonance is not apparent (compare to Fig. 2). The 294 K spectrum is nearly identical to the 194 K result, but has been shifted horizontally for display. The MAS speeds are 4.22 kHz. Zero frequency corresponds to the D_2O resonance at room temperature.

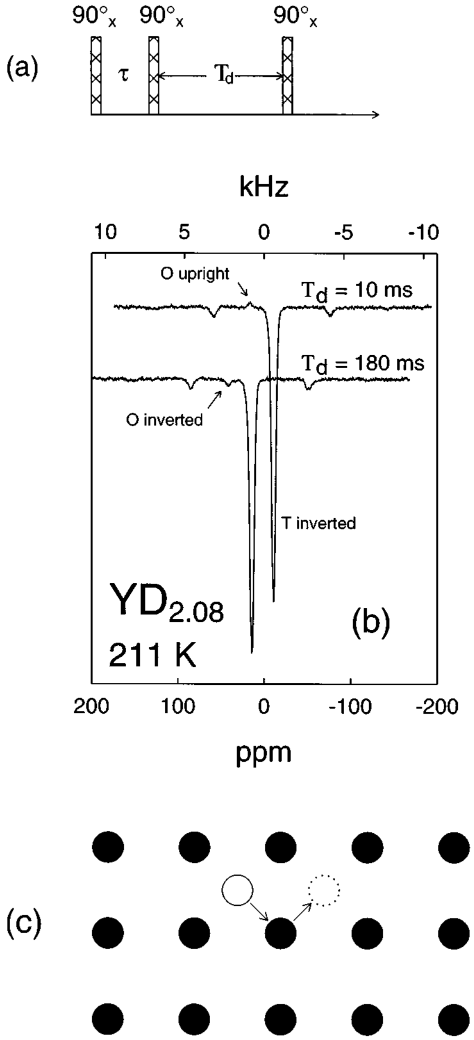

FIG. 4. (a) rf pulse sequence for selective inversion/magnetization transfer. The effect of the sequence is to invert the *T* site NMR line (at exact resonance) without perturbing the *O* site line. (b) Spectra of YD_x at 211 K and MAS at 3.68 kHz. In the spectrum inspected 10 ms after selective inversion of the *T* line, the *O* site intensity is still positive. But 180 ms after selective inversion, the *O* site intensity has become negative, through physical exchange of deuterium atoms between *T* and *O* sites. The 180 ms spectrum is shifted horizontally for display. (c) Schematic representation of *T*-*O* interchange. A deuterium on an *O* site (open symbol) moves onto a neighboring *T* site, just as the previous occupant (solid symbol) moves to a vacant *O* site (dotted). In the actual three-dimensional lattice of YD_x, each *O* has eight nearest *T* neighbors (see Fig. 1). *T* sites with an occupied *O* site nearest neighbor are termed T_O sites.

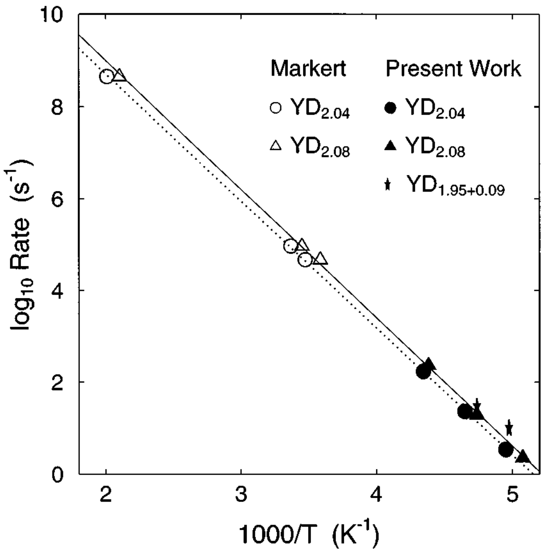

FIG. 5. Rate of motion in YD_x for $x>2$, as a function of reciprocal temperature. The solid symbols are taken from selective inversion/magnetization transfer data such as in Fig. 4(b). Previous measurements (Ref. 36) of T_1^{-1} and $T_{1\rho}^{-1}$ on the same samples yielded peaks at the temperatures shown by the open symbols. The straight lines are good fits to the data, with $E_a/k_B=0.55$ eV.

$\Delta\omega=2\pi\times1470\ \mathrm{s}^{-1}$; the interval τ is chosen so that $\Delta\omega\tau=\pi$. Hence the first $\pi/2$ pulse brings *O* site magnetization into the transverse plane, it precesses by π during τ, and the second pulse returns the magnetization to its initial orientation.

After selective inversion, exchange of atoms between *T* and *O* sites, as schematically represented in Fig. 4(c), will result in magnetization transfer[52] between the two resonance lines. The spectrum is then inspected at delay time T_d after selective inversion, using a $\pi/2$ pulse to produce a free induction decay. Data from the $x=2.08$ sample at 211 K are presented in Fig. 4(b). The spectrum observed at $T_d=10$ ms after selective inversion reveals an inverted *T* resonance and sidebands (because the *same spins* produce the centerband and sidebands, they must invert together). The *O* resonance is still positive, indicating that the pulse sequence had the intended effect. But at $T_d=180$ ms [Fig. 4(b)], the *T* line is negative, showing that *T*-*O* interchanges have equalized the spin polarizations of the two species. The exchange process was followed by recording spectra at several values of T_d to find the value T_d^* where the *O* site intensity is zero, by interpolation.

The time constant T_d^* was found to depend markedly on temperature, as a thermally activated quantity. In Fig. 5, the *rate* of motion $(T_d^*)^{-1}$ is presented. T_1^{-1} and $T_{1\rho}^{-1}$ were measured previously on the same $x=2.08$ sample and passed through peaks as a function of temperature.[36] These relaxation peaks also appear in Fig. 5, with the rate of motion taken as $2\omega_0$ and $2\omega_1$ for T_1^{-1} and $\mathrm{T}_{1\rho}^{-1}$ peaks, respectively. Clearly, all of the data over $8\frac{1}{2}$ decades are well described by a single, thermally activated process. The activation energy is $E_a=0.55$ eV $(=k_B\times6390$ K) and the rate prefactor is $3.8\times10^{14}\ \mathrm{s}^{-1}$. The identity of the motion, *T*-*O* interchanges, is clear from the selective inversion/magnetization transfer experiments; it would be much harder to identify the motion from the spin-relaxation data alone. The data for $x=2.04$ also appear in Fig. 5; again, the MAS magnetization transfer data at low temperatures agree with the T_1 and $T_{1\rho}$ data. In fact, Markert[36] found $E_a=0.54$ eV on the basis of the T_1 and $T_{1\rho}$ data alone. The $x=2.04$ data in Fig. 5 are well described by the same 0.55 eV activation energy and a smaller prefactor, $1.7\times10^{14}\ \mathrm{s}^{-1}$. Measurements on the 1.95+0.09 sample from the Ecole Polytechnique have substantially smaller *S*/*N* but are still in good agreement with the data from the two Cornell samples. The selective inversion/magnetization transfer experiments are restricted to relatively long exchange time constants. The typical O site deuterium must not exchange during the time required for selective inversion [Fig. 4(a)] and for any inadvertently created transverse coherences to decay; a typical lower limit is 5 ms.

The ability to make magnetization transfer measurements is a real strength of the MAS deuterium NMR technique. In systems of two sites, the interchange rate can be determined. In systems of three or more sites, richer possibilities open up. In particular, the rate ω_{ij} of jumping from sites i to sites j may be determined. Thus, the entire ω_{ij} jump-rate matrix $(i \neq j)$ can be measured, yielding more information on the diffusive pathway. Of course, short-lived intermediate states are not accessible this way because their occupations are too small to yield detectable, distinct signals. Related measurements without MAS have been reported in other solid systems by Gullion and Conradi[53] and by Kanert, Kolem, and Gunther.[54]

We now consider and exclude an alternative explanation for the line at +1470 Hz in the $x>2$ samples of YH_x. For $x>2.095$ and temperatures at or below room temperature, a two-phase coexistence region separates the nominally dihydride and nominally trihydride compositions.[2–4,34] Thus it is reasonable to ask whether the +1470 Hz, low-intensity line arises from small grains of nominally YH_3 in a background of $x=2.095$ material. The selective-inversion/magnetization transfer experiments demonstrate that the species responsible for the two resonances are intimately mixed on a short length scale, so that diffusion at these low temperatures leads to magnetization transfer. This virtually rules out segregated phases. Further, the good agreement in Fig. 5 of our rate data with previous T_1 and $T_{1\rho}$ results confirms the O site origin of the +1470 Hz line. Additionally, we note that it is unlikely to cross the phase boundary as temperature is decreased, because the phase boundary is nearly vertical (parallel to the temperature axis).

It was argued above that thermally activated T-O interchanges lead to the disappearance of the O site resonance above 240 K. Now we show that the decrease in sideband intensity with increasing temperature (see Fig. 2 for $x=2.08$) is also a result of this motion. The T and O sites have sufficiently high symmetry that the electric field gradient (EFG) vanishes at both. Thus the quadrupole interaction should be zero at these sites. However, T sites with one or more occupied O site nearest neighbors [termed T_O sites; see Fig. 4(c)] have a distorted environment and thus a nonzero EFG and static quadrupole interaction. Because the T_O sites have a large anisotropic interaction, most of the spinning sideband intensity comes from T_O sites. Indeed, in Fig. 3 the sidebands of the $x=1.98$ sample at 194 K are substantially weaker than for the $x=2.08$ sample (Fig. 2), because the 1.98 sample has no O site occupation and thus no T_O sites. Furthermore, at elevated temperatures where T-O interchange is rapid, the lifetime of a T_O site is quite short [see the motion proposed in Fig. 4(c)]. For sufficiently rapid T-O exchange, each T site in the sample will have time-averaged tetrahedral symmetry. Hence the sidebands from the quadrupole interaction at T_O sites should first broaden with increasing temperature and eventually disappear altogether.[55,56] Thus the T-O interchanges explain the temperature dependence of the sideband intensity for $x=2.08$ (Fig. 2).

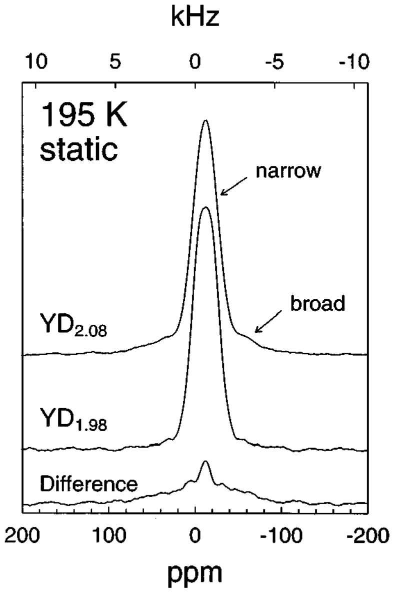

FIG. 6. Static spectra S of YD_x at 195 K. A broad tail, present for $x=2.08$ but absent for $x=1.98$, arises from T_O sites (T sites with one or more occupied O site nearest neighbors). The spectra are gain normalized to yield the same intensity per D atom concentration. The difference spectrum D, $D=S_{2.08}-(0.79)S_{1.98}$, is presented with the constant chosen for the best cancellation of the narrow, central spectral line. The difference shows primarily the quadrupole-broadened resonance from the T_O sites of the $x=2.08$ sample.

Not only do the T_O sites have a different EFG than the undistorted T sites, they have a slightly different shift (chemical and/or Knight). The sidebands in Fig. 2 for $x=2.08$ at 194 K are displaced about +140 Hz (2.5 ppm) from the expected symmetrical location about the main resonance. Our interpretation is that the main resonance at zero frequency is primarily from undistorted T sites, while the sidebands are primarily from T_O sites, whose centerband (unresolved) is shifted from the main line, by somewhat less than the linewidth. Thus MAS deuterium NMR identifies three distinct deuterium sites in Y. It is reasonable that the T vs T_O shift is much smaller than the T vs O shift.

Static (nonspinning) deuterium NMR experiments confirm the picture of T_O sites advanced above. The spectra of $x=2.08$ and $x=1.98$, at 195 K, are presented in Fig. 6 with equal effective gains. That is, the spectral intensities (areas) are in the ratio 2.08:1.98, corresponding to equal signals for equal deuterium concentrations. The $x=2.08$ spectrum has more substantial tails that correspond to the quadrupolar-broadened T_O sites. The rest of the 2.08 spectrum looks quite similar to the 1.98 spectrum. Also presented in Fig. 6 is the difference spectrum D, $D=S_{2.08}-(0.79)S_{1.98}$, where the constant 0.79 was chosen empirically to yield the best cancellation of the central feature of the spectrum. Values between 0.82 and 0.76 all yield satisfactory results. The difference spectrum shows primarily the broad feature (from the T_O, we assert), most of the central line is absent, and a small (in area) sharp pip remains (i.e., sharper than the main resonance for $x=1.98$). We do not understand the sharp pip in the difference spectrum. We have repeated the spectra of Fig. 6 using the $x=2.04$ and 1.91 samples of YD_x from Cornell. The tails of the spectra (not shown) are larger for $x>2$, consistent with most of the intensity in the tails being from T_O sites.

We now turn to the expected *number* of T_O sites. In the nominally $x=2.08$ sample, the O site relative NMR intensity indicated an actual composition $x=2.066$. Each T site has four nearest neighbor O sites (see Fig. 1) and each O site is vacant with probability $1-0.066$. The probability of a T site having no occupied O site nearest neighbors is thus $(1-0.066)^4=0.761$, assuming random O site occupation. Hence the nominally 2.08 sample should have an occupation of 1.522 undistorted T sites and 0.478 T_O sites. Only T_O sites have large quadrupole interactions, so one expects that the component of the $x=2.08$ spectrum from the undistorted T sites and O sites is very similar to the spectrum of the $x=1.98$ sample (all undistorted T sites, neglecting the unknown effect of the few T site vacancies). Hence, to obtain the component of the $x=2.08$ spectrum from T_O sites, we should subtract from the 2.08 spectrum the 1.98 spectrum scaled by the ratio

$$\frac{(\text{No. undistorted } T \text{ sites} + \text{No. } O \text{ sites})_{2.08}}{(\text{No. undistorted } T \text{ sites})_{1.98}}.$$

This last ratio is 0.80, in good agreement with the empirical choice of 0.79 used in subtracting the spectra in Fig. 6. Hence, the static sample measurements not only display the expected tails from the quadrupole-broadened (T_O) sites, but their fractional concentration is quantitatively correct.

The motion responsible for the broadening/disappearance of the O site resonance and sidebands of the T_O sites is an interchange of D atoms between T sites and O sites. We note that direct hops of D atoms from one O site to the next would not lead to the T-O interchange evident in the magnetization transfer experiments. If such direct O-O hops occurred more frequently than the T-O interchanges, the sidebands from the T_O sites would disappear at a lower temperature than the O site line at $+1470$ Hz, but this is not observed. The T-O interchanges may be a concerted motion with two atoms moving simultaneously, as depicted in Fig. 4(c), or the motions may be separated in time. However, motion of a T site vacancy cannot be the rate-controlling step, since motion is much more rapid[36] for $x>2$ than for $x<2$.

We note that a T-O interchange event [Fig. 4(c)] has nearly the same effect as a direct O-O jump, in contributing to the rate of diffusion. Both processes have the same net atomic displacement and both lead to no net changes in T site and O site occupations. (However, because different atoms are moved in the two processes, the values of mean-squared displacement are numerically slightly different.) Recently, models of diffusion in the nearly dihydrides have been described,[57,58] involving hops from occupied T sites to vacant O sites (quite distinct from the *T-O interchanges* here), from occupied O sites to vacant O sites (O-O hops, for short), and from occupied T sites to vacant T sites. In those treatments, the O-O hops are believed to be crucial in determining the rate of diffusion (these are called X-X hops in Ref. 57; X sites are actually O sites there, though the language is kept non-specific). From our results and the above considerations, we believe that the O-O (or X-X) hops in the models actually refer to T-O interchanges. Although two different metals are involved, we compare the 0.55 eV activation energy for T-O interchanges reported here in YD_x to the 0.40 eV for O-O hops obtained[57] by fitting all the data in ZrH_x as a function of x and T. We note that the fitting procedure used there does not yield unique values of all the several parameters.

IV. CONCLUSIONS

We have demonstrated that magic-angle-spinning deuterium NMR of a metal deuteride yields spectrally resolved lines for D atoms at inequivalent sites. While MAS has long been known as a robust method of line narrowing for solid-state NMR, the large (~30 kHz) proton-proton dipole coupling in metal *hydrides* requires unreasonably high spinning speeds for efficient line narrowing. Because of the smaller magnetic moment of ^{2}D, lower spinning speeds give good linewidth reduction in metal deuterides. The quadrupole interaction present for ^{2}D is also averaged by magic-angle spinning.

For YD_x with $x\sim 2$, only T site occupation is found for $x\leqslant 2.00$ at 200 K. For $x>2.00$, only the excess D atoms are accommodated in O sites with a resonance line 27 ppm up frequency from the T site resonance. These results disagree with conclusions from proton NMR second-moment measurements, neutron diffraction, and inelastic neutron scattering (neutron vibrational spectroscopy): these works found that O sites are occupied even for $x<2.00$. For $x=2.0$, the proton NMR found 15–19 % of occupied O sites,[36,37] with 8% according to inelastic neutron scattering.[35] On the other hand, the present conclusions are in good accord with measurements of the residual electrical resistivity of both YH_x and YD_x.[34] A very deep minimum in resistivity occurs at $x=2.00$, indicating fully occupied T sites and empty O sites. It is believed that impurity of the Y metal is a major source of the disagreement, with impurities blocking some of the available T sites. This leads to ''pure'' dihydride concentrations of $YH_{2-\Delta}$ with Δ values reaching up to 0.2 (see the review by Vajda[59] on deviations from ideal stoichiometry in the dihydrides). This may explain the small value of the room temperature lattice parameter reported for $YH_{2.0}$ in Ref. 35, $a=5.2037$ Å. By comparison, a pure dihydride, $YH_{2.00}$ (no octahedral occupation), gave[34] $a=5.2085$ Å; this decreased to 5.2056 Å with increasing octahedral occupation, $YH_{2.10}$. Thus it seems likely that the $YH_{2.0}$ of Ref. 35 had substantial octahedral occupation, perhaps by virtue of blocked T sites. Very recent neutron diffraction measurements of $YD_{2.00}$ find 100% occupation of T sites and no occupation of O sites, to within 1%.[60] The sample was one of the samples used in Ref. 61. The neutron diffraction is further support for the site occupancies measured here by deuterium MAS NMR.

For YD_x, $x>2$, and above 240 K, the weak O site resonance and the spinning sidebands of the T line disappear due to T-O interchanges. Selective inversion and subsequent magnetization transfer were used to measure the rate and activation energy ($E_a = 0.55$ eV) of T-O interchanges. The sidebands are principally from D atoms at T_O sites: T sites with one or more occupied nearest neighbor O sites (disrupting the local cubic symmetry). Thus diffusion via T-O interchanges results in a reduced lifetime of the T_O, broadening the spinning sidebands. The frequency shift of the sidebands shows a slight difference in Knight/chemical shift between T_O and T sites, confirming the distinction between these species.

In the present case of YD$_x$, there are only three inequivalent deuterium sites (T, O, and T_O). But in deuterides of alloys and compounds, there are typically several occupied inequivalent sites. The MAS deuterium NMR technique is expected to be valuable in determining site occupancies and diffusion pathways in the alloys and compounds.

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[1] T. Graham, Philos. Trans. R. Soc. London **156**, 399 (1866).

[2] *Metal Hydrides*, edited by W. M. Mueller, J. P. Blackledge, and G. G. Libowitz (Academic Press, New York, 1968).

[3] C. E. Lundin and J. P. Blackledge, J. Electrochem. Soc. **109**, 838 (1962).

[4] L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, J. Phys. Chem. **69**, 2510 (1965).

[5] *Hydrogen in Metals I: Basic Properties*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), Chap. 1.

[6] *Hydrogen in Metals II: Application-Oriented Properties*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), Chap. 5.

[7] S. R. Ovshinsky, M. A. Fetcenko, and J. Ross, Science **260**, 176 (1993).

[8] J. J. G. Willems, Philips Tech. Rev. **43**, 22 (1986).

[9] *Hydrogen in Intermetallic Compounds II: Surface and Dynamic Properties, Applications*, edited by L. Schlapbach (Springer-Verlag, Berlin, 1992), Chap. 5.

[10] A. Pebler and W. E. Wallace, J. Phys. Chem. **66**, 148 (1962).

[11] R. Hempelmann, D. Richter, O. Hartmann, E. Karlsson, and R. Wäppling, J. Chem. Phys. **90**, 1935 (1989).

[12] A. V. Irodova, V. P. Glazkov, V. A. Somenkov, and S. Sh. Shil'shtein, Sov. Phys. Solid State **22**, 45 (1980).

[13] J.-J. Didisheim, K. Yvon, P. Fischer, and P. Tissot, Solid State Commun. **38**, 637 (1981).

[14] A. V. Skripov, M. Yu. Belyaev, S. V. Rychkova, and A. P. Stepanov, J. Phys. Condens. Matter **3**, 6277 (1991).

[15] R. Hempelmann, D. Richter, J. J. Rush, and J. M. Rowe, J. Less-Common Met. **172**, 281 (1991).

[16] R. Feenstra, R. Brouwer, and R. Griessen, Europhys. Lett. **7**, 425 (1988).

[17] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1978).

[18] R. M. Cotts, in *Hydrogen in Metals I: Basic Properties*, (Ref. 5).

[19] J. H. Harris, W. A. Curtin, and M. S. Tenhover, Phys. Rev. B **36**, 5784 (1987).

[20] F. Jaggy, W. Kieninger, and R. Kirchheim, Z. Phys. Chem. **163**, 431 (1989).

[21] *Hydrogen in Intermetallic Compounds I: Electronic, Thermodynamic, and Crystallographic Properties, Preparation*, edited by L. Schapbach (Springer-Verlag, Berlin, 1992), Chap. 7.

[22] A. Stern, A. Resnik, and D. Shaltiel, J. Less-Common Met. **88**, 431 (1982).

[23] A. Stern, S. R. Kreitzman, A. Resnik, D. Shaltiel, and V. Zevin, Solid State Commun. **40**, 837 (1981).

[24] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

[25] E. R. Andrew, A. Bradbury, and R. B. Eades, Nature **182**, 1659 (1958); **183**, 1802 (1959).

[26] I. Lowe, Phys. Rev. Lett. **2**, 301 (1959).

[27] M. Mehring, in *High-Resolution NMR in Solids*, edited by P. Diehl, E. Fluck, and R. Kosfeld, NMR: Basic Principles and Progress Vol. 11 (Springer, New York 1976).

[28] A. N. Garroway, J. Magn. Reson. **49**, 168 (1982).

[29] V. N. Fedeyev, Russ. Metall. **5**, 148 (1972).

[30] B. J. Beaudry and F. H. Spedding, Metall. Trans. **6B**, 419 (1975).

[31] D. L. Anderson, R. G. Barnes, S. O. Nelson, and D. R. Torgeson, Phys. Lett. **75A**, 427 (1979).

[32] G. M. Begun, J. F. Land, and J. T. Bell, J. Chem. Phys. **72**, 2959 (1980).

[33] J. E. Bonnet, C. Juckum, and A. Lucasson, J. Phys. F **12**, 699 (1982).

[34] J. N. Daou and P. Vajda, Phys. Rev. B **45**, 10 907 (1992).

[35] J. A. Goldstone, J. Eckert, P. M. Richards, and E. L. Venturini, Solid State Commun. **49**, 475 (1984).

[36] J. T. Markert, Ph.D. thesis, Cornell University, 1987.

[37] D. L. Anderson, R. G. Barnes, D. T. Peterson, and D. R. Torgeson, Phys. Rev. B **21**, 2625 (1980).

[38] D. Khatamian, W. A. Kamitakahara, R. G. Barnes, and D. R. Torgeson, Phys. Rev. B **21**, 2622 (1980).

[39] J. N. Daou, A. Lucasson, P. Vajda, and J. P. Burger, J. Phys. F **14**, 2983 (1984).

[40] J. T. Markert and R. M. Cotts, Phys. Rev. B **36**, 6993 (1987).

[41] J. S. Frye and G. E. Maciel, J. Magn. Reson. **48**, 125 (1982).

[42] I. D. Gay, J. Magn. Reson. **58**, 413 (1984).

[43] K. W. Zilm, R. A. Merrill, M. M. Greenberg, and J. A. Berson, J. Am. Chem. Soc. **109**, 1567 (1987).

[44] P. J. Allen, F. Creuzet, H. J. M. de Groot, and R. G. Griffin, J. Magn. Reson. **92**, 614 (1991).

[45] W. T. Dixon, J. Chem. Phys. **77**, 1800 (1982).

[46] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill, New York, 1959), Chap. 10.

[47] B. Stalinski, C. K. Coogan, and H. S. Gutowsky, J. Chem. Phys. **34**, 1191 (1961).

[48] R. E. Taylor, T. Taki, and B. C. Gerstein, Phys. Rev. B **23**, 5729 (1981).

[49] R. C. Bowman, Jr., W. L. Johnson, A. J. Maeland, and W.-K. Rhim, Phys. Lett. **94A**, 181 (1983).

[50] D. R. Torgeson, R. J. Schoenberger, and R. G. Barnes, J. Magn. Reson. **68**, 85 (1986).

[51] T. Ueda, S. Hayashi, and K. Hayamizu, Solid State Commun. **87**, 429 (1993).

[52] J. B. Lambert, R. J. Nienhuis, and J. W. Keepers, Angew. Chem. Int. Ed. Engl. **20**, 487 (1981).

[53] T. Gullion and M. S. Conradi, Phys. Rev. B **32**, 7076 (1985).

[54] O. Kanert, H. Kolem, and B. Gunther, in *Advances in Magnetic Resonance*, edited by W. S. Warren (Academic, New York, 1989), Vol. 13, pp. 161–181.

[55] M. M. Maricq and J. S. Waugh, J. Chem. Phys. **70**, 3300 (1979).

[56] D. Suwelack, W. P. Rothwell, and J. S. Waugh, J. Chem. Phys. **73**, 2559 (1980).

[57] G. Majer, W. Renz, and R. G. Barnes, J. Phys. Condens. Matter **6**, 2935 (1994).

[58] U. Stuhr, D. Steinbinder, H. Wipf, and B. Frick, Europhys. Lett. **20**, 117 (1992).

[59] P. Vajda, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, New York, 1995), Vol. 20, Chap. 137, p. 207.

[60] T. J. Udovic and Q. Huang (unpublished results).

[61] T. J. Udovic, J. J. Rush, and I. S. Anderson, Phys. Rev. B **50**, 15 739 (1994).