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Proton spin-lattice relaxation mechanisms and the metal-insulator transition in cerium hydrides

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Nuclear-magnetic-resonance (NMR) experiments have been done on cerium hydride (CeH_x) samples to search for correlations between NMR properties and known electrical conductivity changes as a function of hydrogen concentration and temperature. Data are presented for the ^1H spin-lattice relaxation rate R_1 ($=1/T_1$) and some line shapes for $2.10 \leq x \leq 2.92$ for temperatures from about 100 to 375 K. Although two ^1H resonances are observed at some temperatures, proton spin-lattice relaxation is characterized by a single relaxation time at each x and T. To a good approximation $R_1 = A/T + R$, where A/T is attributed to direct dipolar coupling between protons and the electronic magnetic dipole moment of Ce^{3+}, and R is an essentially temperature-independent term attributed to indirect [Ruderman-Kittel-Kasuya-Yosida (RKKY)] coupling to the Ce^{3+} moment. The A/T term is so large that for most experiments the proton-proton dipolar and proton—conduction-electron couplings are negligible. The x dependence of the constant A is consistent with the dipolar coupling. The constant R decreases in a steep manner as x is increased above $x \approx 2.65$ just below the regime $2.75 < x < 2.85$, where the metal-semiconductor transition occurs in CeH_x. It is proposed that $R \propto N_d(E_F)$ and that the RKKY interaction includes coupling through the d-band density of states. The marked decreases in R_1 and in the electrical conductivity that are associated with the concentration-dependent transition are thus attributed to the vanishing electron density of states at the Fermi surface. No temperature-dependent transition in R_1 is found. Results are consistent with a Mott transition model in which the electron donors are hydrogen vacancies.

INTRODUCTION

In common with the hydrides of the other light rare-earth elements (i.e., La, Pr, and Nd), cerium forms nonstoichiometric homogeneous hydride and deuteride phases with an apparent range of composition from about $CeH_{1.9}$ to CeH_3.[1] The dihydrides all have the cubic fluorite structure, the hydrogen (deuterium) occupying predominantly the tetrahedral (T) interstitial sites. A further increase of the hydrogen concentration results in filling the octahedral (O) interstitial sites of this structure. The dihydrides CeH_2 exhibit metallic conductivity[2] due to the occurrence of overlapping energy bands,[3] but as the H to Ce ratio approaches 3 the bands are shifted considerably and semiconducting (or insulating) behavior is observed.[2]

As hydrogen is added to the dihydride its electrical conductivity at a given temperature (above 250 K) decreases continuously. The conductivity of $CeH_{2.75}$ is more than an order of magnitude smaller than that of $CeH_{2.0}$.[2] Between about $CeH_{2.75}$ and $CeH_{2.80}$ the conductivity decreases sharply by 2 orders of magnitude. In addition to this compositional transition a smaller temperature-dependent change in conductivity occurs near 250 K.[2] Through hyperfine interactions between the hydrogen nuclear-spin system and electrons of the conduction band, the spin-lattice relaxation time T_1 of the hydrogen spin system is expected to be changed by the metal-to-semiconductor transition. This interrelationship was one of the factors that motivated us to study experimentally the NMR of hydrogen in the cerium hydrides, CeH_x, $2.0 < x < 3.0$.

Despite the fact that nuclear magnetic resonance was among the first techniques utilized in studies of the cerium hydrides,[4,5] almost no further NMR investigations of this system have been reported. The early NMR measurements were concerned with the proton spin-lattice relaxation time T_1 in $CeH_{2.0}$ and in $CeH_{2.55}$,[5] and with the Knight shift and linewidth of the proton resonance in CeH_x, $2.0 < x < 2.85$.[4] The latter measurements dealt primarily with the low-temperature magnetic ordering (i.e., $T_N \approx 5$ K). The former, on the other hand, were concerned with the temperature dependence of the proton T_1 and found that $T_1 \propto T$ over the temperature range $77 \leq T \leq 300$ K. This behavior was interpreted in terms of an enhanced Korringa-type relaxation process, the dominant mechanism being the coupling of the proton moment to that of the rare-earth ion via the conduction electrons.

In the work reported here, we have studied both the temperature and composition dependence of the proton T_1 in CeH_x samples covering the range $2.1 \leq x \leq 2.92$. Wide-line measurements of the proton resonance were made over the same temperature range for many of the same samples. In addition, T_1 measurements were made on a series of lanthanum hydrides containing controlled low levels of cerium impurity. In brief, the results are consistent with a transition from metallic to nonmetallic behavior with increasing hydrogen content. However, no evidence of a temperature-dependent transition was found at any composition. The proportionality[5] of T_1 to T is confirmed and appears to be best understood in terms of direct dipolar coupling of the proton and cerium ion moments, a modified Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling making a much weaker, but composition-dependent, contribution to the total relaxation rate.

EXPERIMENTAL ASPECTS

Sample preparation

The cerium hydride samples studied were prepared both at Ames Laboratory and at Cornell University. Ames Laboratory cerium was used for all the samples prepared at Ames, and in addition several samples were prepared at Cornell from Ames Laboratory cerium. Other samples prepared at Cornell used Alpha-Ventron cerium metal (rare-earth oxide content less than 1000 ppm). Preparation of the hydrides at Ames followed procedures which have been described in detail for the yttrium hydrides.[6]

Sample preparation at Cornell consisted of first cutting, washing (with acetone), and weighing the sample in a dry helium atmosphere. The sample was then placed in a ceramic boat in a quartz tube and transferred to the vacuum system. After heating the cerium at 10^{-5} Torr and 420 °C it was exposed to hydrogen while the temperature was gradually decreased. H content was determined from (P,V,T) relations. The hydrided cerium was returned to the helium glove box for grinding (< 100-μm particle size) and loading into a Pyrex tube. The tube, containing the sample and helium exchange gas, was then sealed off.

NMR instrumentation

Proton T_1 measurements were made at Ames at a nominal resonance frequency of 40 MHz and at Cornell at 10 MHz. Both laboratories used home-built phase-coherent pulsed NMR spectrometers with digital pulse programming. Data from free-induction decays (FID) following $180°$-τ-$90°$ inversion recovery sequences were analyzed for T_1 using least-squares fitting programs. Temperatures in the range 100–400 K were achieved using nitrogen-gas-flow systems monitored by copper-Constantan thermocouples. At Cornell, signals were averaged with a Princeton Applied Research model CW-1 gated integrator.

At Ames, τ was incremented automatically and FID data were collected and digitized [8 bits (binary digits)] with a Biomation 610B waveform analyzer. At 40 MHz, the spectrometer recovered in 6 μs. The first few (e.g., eight) "channels" were summed in a Digital Equipment Corporation LSI-11/03 microcomputer. Next several (e.g., 128) baseline channels were summed in a region of the FID representing baseline level rather than initial signal. The weighted difference of these numbers, representing the initial amplitude of the FID relative to the baseline level, was then stored in memory. These data are insensitive to all sources of baseline drift slower than a few hundred microseconds. Typically, 100 data points were used for each T_1 determination. For the measurements at 40 MHz, a Varian Associates model V-4012 electromagnet provided a field of 0.9395 T. Although this field was stable within acceptable experimental limits, a deuteron magnetic-resonance-field stabilizer was used throughout the measurements to prevent any residual drift.

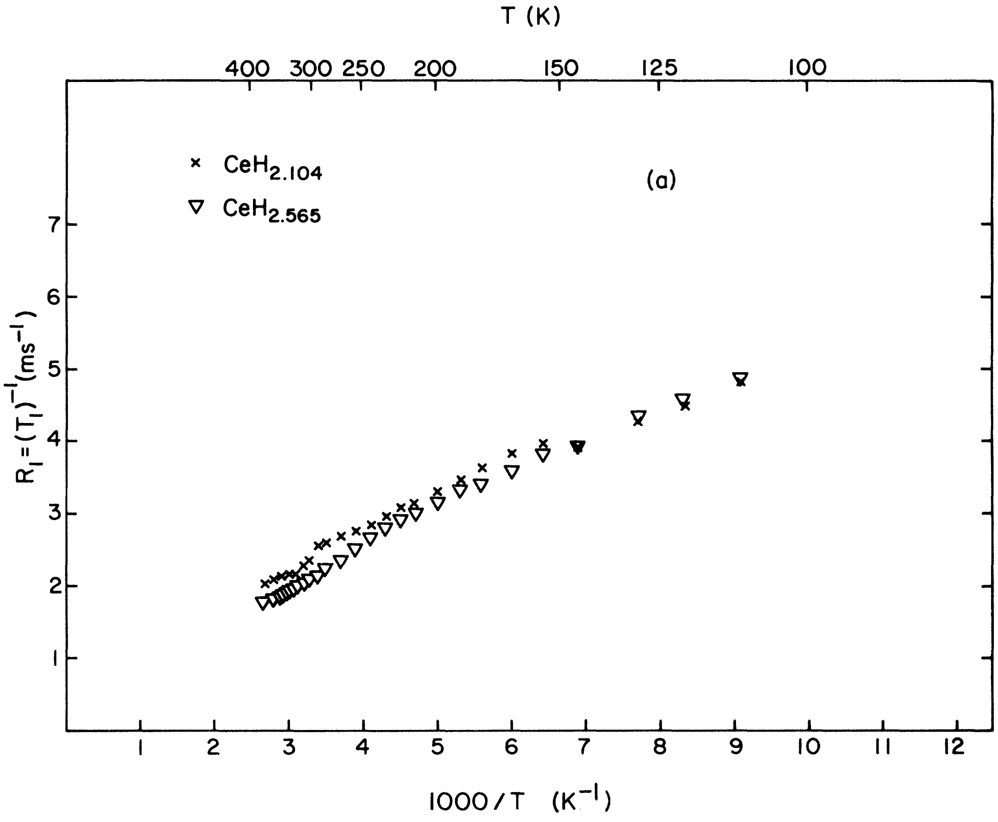
RESULTS

The measured proton spin-lattice relaxation times in CeH_x are very short in comparison to T_1 values in typical nonmagnetic hydrides. In particular, in LaH_x T_1 reaches values of several seconds at 100 K,[7,8] for example, whereas in all of the CeH_x compositions studied, T_1 falls within the range 100–1000 μs. Such short T_1 values were also found in the cases of UH_x and PuH_x which are also magnetically dense materials.[9,10] Typical examples of the temperature dependence of the spin-lattice relaxation rate R_1 are shown in Fig. 1. In all cases, R_1 varies linearly with reciprocal temperature, alternatively, T_1 is directly proportional to T.

The behavior of the rate R_1 as a function of hydrogen concentration at fixed temperature (295 K) is shown in Fig. 2(a) for a large number of sample compositions, made at both Ames Laboratory and Cornell University. The composition dependence of the conductivity (log conductivity) previously reported by Libowitz[2] is shown in Fig. 2(b). A similarity in behavior of the two properties (i.e., relaxation rate and conductivity) is observed.

In addition to these measurements on the cerium hydrides themselves, we have also investigated the proton T_1 in some lanthanum hydrides containing controlled levels of cerium, up to 1%. Figure 3 compares on a log-log plot the proton T_1 vs T in a sequence of samples ranging from $LaH_{2.92}$:500 ppm Ce to $CeH_{2.85}$. This comparison has several interesting features. First, the gradual vanishing of the dip in T_1 due to the proton-proton dipolar term is very evident. This contribution is still significant in the data for the 1% Ce-doped sample, whereas its presence in the data for $CeH_{2.85}$ is perhaps just discernible. On this plot it is seen that the temperature dependence of T_1 changes between cerium levels of 1000 and 2700 ppm, becoming steeper for the higher Ce concentrations ($T_1 \propto T$) and retaining that character up to $CeH_{2.85}$. Similarly, proton T_1 data were obtained for a series of $LaH_{2.25}$ samples containing cerium. In this case, the dependence of T_1 on T is roughly similar to $T^{0.5}$ at lower temperatures.

The temperature dependence of the steady-state (wide-line) proton resonance was also investigated in most of the



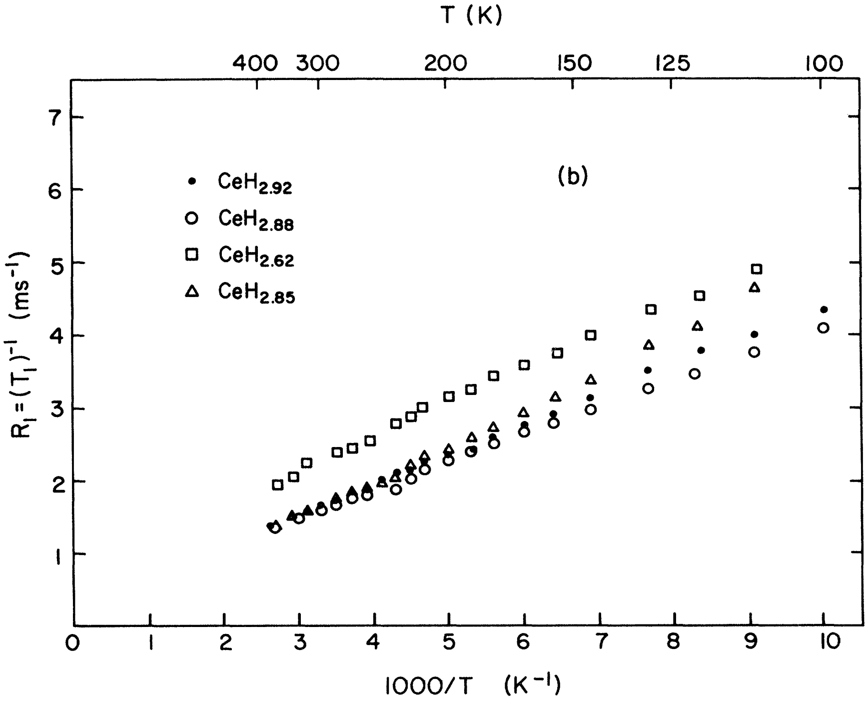


FIG. 1. (a) Comparison of dependences of R_1 upon reciprocal temperature for ^{1}H in CeH$_x$ for two values of x expected to be in the metallic regime. The crosses and inverted triangles are for $x=2.104$ and 2.565, respectively. (b) R_1 vs reciprocal temperature for ^{1}H in CeH$_x$. In the high-temperature regime, $1000/T<4.5$, $R_1(x)=A(x)/T+R(x)$ for each concentration in (a) and (b). Data for $x<2.65$ are clustered around $A\simeq4.9\times10^5$ s^{-1} K and $R\simeq650$ s^{-1}. For $x>2.65$, $A\simeq4.2\times10^5$ s^{-1} K and $R\simeq250$ s^{-1}. The transition from the metallic ($x<2.65$) to semiconducting ($x>2.65$) has a much greater effect on R than on A.

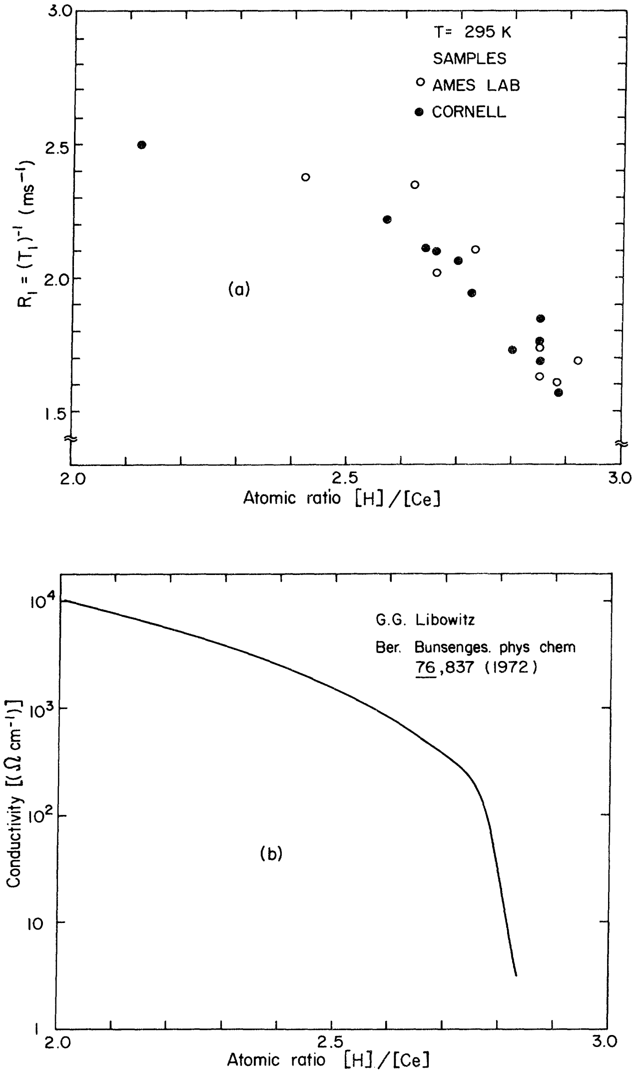


FIG. 2. (a) Concentration dependence of the spin-lattice relaxation rate of ^{1}H in CeH$_x$ for $T=295$ K. The open circles and the closed circles are for samples prepared at Ames Laboratory and at Cornell University, respectively. (b) Concentration dependence of conductivity of CeH$_x$ at 300 K, Ref. 20.

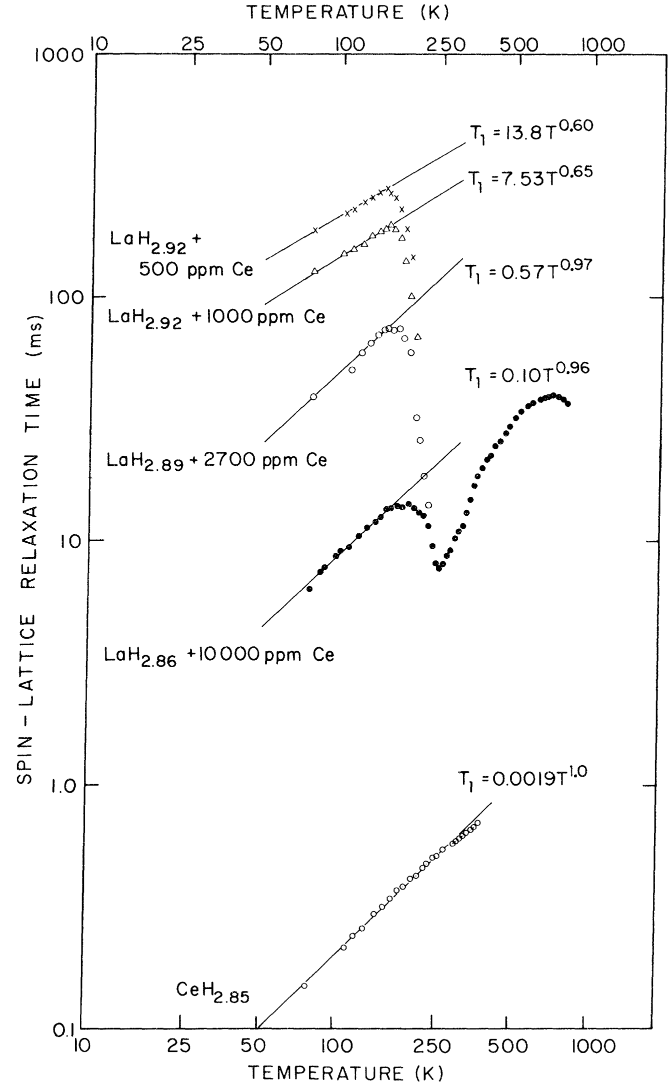


FIG. 3. Temperature dependence of the spin-lattice relaxation time of ^{1}H in MH$_x$ where M represents La with small amounts of substitutional Ce or, for the lowest curve, CeH$_{2.85}$. The nominal H concentration corresponds to $x=2.9$. Data are recorded at a Larmor frequency of 40 MHz.

Ames Laboratory samples. For $x>2.5$ two resonances are clearly distinguished within some temperature range below about 200 K. With decreasing temperature, the narrow proton resonance observed at 300 K broadens gradually. Beginning at about 200 K, a broad resonance appears superimposed on the narrow line, and both resonances remain observable for a further decrease of ~ 50 K after which the narrow line ceases to be discernible. Figure 4 shows an example of this behavior for CeH$_{2.85}$, at $T=183$, 173, and 163 K. It is also evident from the figure that the two resonances do not coincide exactly; the narrow resonance is not centered on the wide one. This fact is also very evident in the pulse measurements of T_1 in that, using phase-sensitive detection of the radio frequency signal, either the initial or final portion of induction decay (FID) can be put in exact resonance, but not both simultaneously. The Knight shifts of the two resonances are essentially at the limit of reliable measurement. For the resonances in Fig. 4, we find for the temperature range shown $K_{\text{av}}=+(0.023\pm0.003)\%$ for the wide line and $K_{\text{av}}=+(0.012\pm0.004)\%$ for the narrow line, without corrections for bulk susceptibility effects.

DISCUSSION

We consider the measured proton spin-lattice relaxation rate $R_1=(T_1)^{-1}$ to arise from four contributions,

$$R_1=(R_1)_{d,\text{Ce}}+(R_1)_{\text{RKKY}}+(R_1)_K+(R_1)_{dd}\ , \tag{1}$$

where $(R_1)_{d,\text{Ce}}$ results from the dipolar coupling to the electronic magnetic dipole moment of each Ce^{3+} ion; $(R_1)_{\text{RKKY}}$ results from the indirect coupling to the Ce^{3+} moments via the conduction electrons; $(R_1)_K$ represents the usual Korringa process coupling to the conduction-

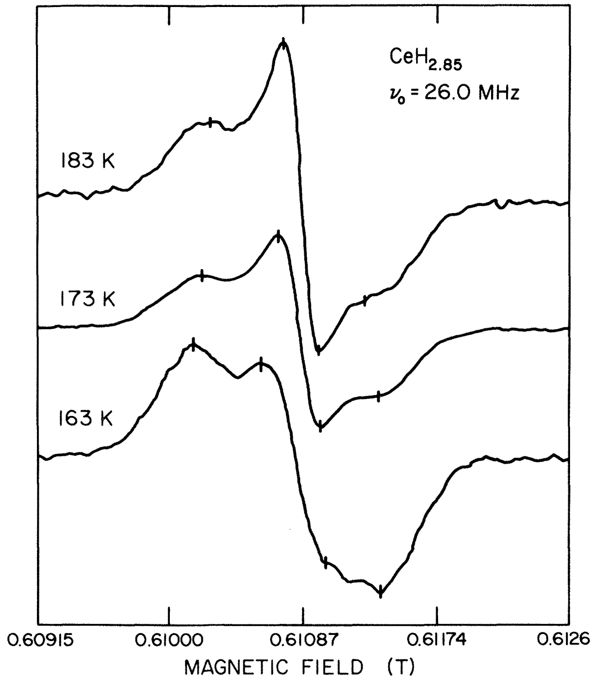


FIG. 4. First-derivative continuous-wave NMR spectra of ^{1}H in CeH$_{2.85}$ for three temperatures, 163, 173, 183 K. Data are recorded at a Larmor frequency of 26 MHz. Two lines, differing in width and shift, are observable at each temperature.

electron magnetization; $(R_1)_{dd}$ results from proton-proton dipolar coupling modulated by hydrogen diffusion. Within the context of the usual dipolar theory,[11] we expect that

$$(R_1)_{d,\mathrm{Ce}} \approx (\Delta\omega_{d,\mathrm{Ce}})^2 \frac{\tau_c}{1+\omega_I^2\tau_c^2} , \tag{2}$$

where ω_I is the proton angular resonance frequency, τ_c is a correlation time characteristic of fluctuations in the proton-moment—Ce^{3+}-ion-moment interaction, and $(\Delta\omega_{d,\mathrm{Ce}})^2$ is the mean-squared dipole-dipole interaction (frequency) for this relaxation process. The measurements reported here, as well as others for proton T_1 in yttrium hydrides containing controlled levels of cerium,[8] indicate that in the range of temperatures considered $\omega_I^2\tau_c^2 \ll 1$ holds at the resonance frequencies used. Measurements of the linewidth of the Ce^{3+} ESR in lanthanum intermetallic compounds[12] show that at temperatures $T<30$ K the spin-lattice relaxation time of the Ce^{3+} ion, τ_{e1}, follows Korringa-type behavior, $\tau_{e1} \propto T^{-1}$. And since, as will be shown, $\tau_c = \tau_{e1}$, we expect that $(R_1)_{d,\mathrm{Ce}} \propto T^{-1}$ and we write finally,

$$(R_1)_{d,\mathrm{Ce}} = A/T . \tag{3}$$

The conduction-electron contribution $(R_1)_K$ is given by the Korringa relation,[13]

$$(R_1)_K = BT , \tag{4}$$

where the parameter B depends on the density of states at the Fermi level and the hyperfine field. From the work of Fradin on paramagnetic impurities in metals,[14] we expect that the RKKY contribution has the form

$$(R_1)_{\mathrm{RKKY}} = RT/(T-\Theta) , \tag{5}$$

where Θ is the magnetic ordering temperature of the Ce moments.

Finally, the nuclear dipole-dipole rate $(R_1)_{dd}$ results from hydrogen diffusion. Although some of the measurements at 10 MHz suggest the possible presence of this contribution at temperatures above 300 K, there is no consistent evidence for its making a noticeable contribution in the cerium hydrides. On the other hand, as pointed out in the preceding section in regard to Fig. 3, the contribution from $(R_1)_{dd}$ is quite evident in the Ce-doped lanthanum hydrides, where the Ce concentration is never greater than 1%. We conclude therefore that the magnitude of $(R_1)_{dd}$ is always too small to noticeably influence the total R_1 in the cerium hydrides, and hereafter we neglect this contribution.

The net relaxation rate is then given by

$$R_1 = AT^{-1} + RT/(T-\Theta) + BT . \tag{6}$$

Now, since $\Theta < 6$ K for all CeH$_x$, $T/(T-\Theta) \approx 1$ for $T > 100$ K is a good approximation. The term BT is usually small for protons in hydrides, typical values for $B^{-1} = (T_1)_K\, T$ being on the order of 100—500 s K.[15] A value of $(T_1)_K T = 10$ s K in a hydride would be a strong Korringa contribution, indeed. Therefore, we expect that $(R_1)_K < T/10$ in the present cases. It follows that at 300 K we would have $(R_1)_K < 30$ s^{-1} which may be compared with the measured values of R_1 which are about 1600 s^{-1} for nonmetallic CeH$_x$ and 2300 s^{-1} for metallic CeH$_x$ ($x \lesssim 2.65$). Thus BT is very small, less than 2% of the measured R_1 at 300 K, and for preliminary discussion can be ignored.

From the temperature dependence of the measured R_1 values shown in Figs. 1—3, we draw the following conclusions: First, the dipolar term A/T in Eq. (6) is the dominant contribution to R_1. These rates are so unusually large for protons in metal hydrides that it is unlikely that any process other than direct dipolar coupling to the Ce^{3+} moments could be responsible. Second, at a typical temperature, e.g., 300 K, $A/T \simeq 1650$ s^{-1} for the metallic samples (i.e., $x < 2.65$) and $A/T \simeq 1400$ s^{-1} for the nonmetallic samples ($x > 2.65$). The corresponding measured R_1 values are 2300 and 1650 s^{-1}, respectively. This gives typical values of the RKKY interaction parameter R in Eq. (5) of

$$R_{\mathrm{metallic}} = 650 \pm 100 \text{ s}^{-1}$$

and

$$R_{\mathrm{nonmetallic}} \simeq 250 \text{ s}^{-1}$$

with a large uncertainty. Thus it appears that we have approximately $R_{\mathrm{metallic}} = 3R_{\mathrm{nonmetallic}}$. Third, although we do not have complete R_1 vs T data for all the samples, we have many points on the graph of R_1 vs x at 295 K (Fig. 2). These data show that the change in R_1 is continuous but strongly dependent on x for $x > 2.65$. In the following sections we consider each of these conclusions in greater detail.

Dipolar relaxation

The spin-lattice relaxation rate of a proton spin I coupled to the fluctuating electronic moment of the Ce^{3+} ion by a purely dipolar interaction is given by[11]

$$(R_1)_{d,\mathrm{Ce}}=\gamma_I^2\gamma_e^2\hbar^2 J(J+1)[\tfrac{1}{12}J^{(0)}(\omega_I+\omega_e)+\tfrac{3}{2}J^{(1)}(\omega_I)+\tfrac{3}{4}J^{(2)}(\omega_I-\omega_e)] , \qquad (7)$$

where γ_I and γ_e are the respective proton and ion gyromagnetic ratios, ω_I and ω_e are the respective Larmor frequencies, $\hbar$ is Planck's constant divided by 2π, J is the angular momentum of the Ce^{3+} ion, and the $J^q(\omega)$ are the spectral density functions of the fluctuating dipolar interaction. For the present purposes it suffices to take for the $J^{(q)}(\omega)$ the simple Lorentzian form, corresponding to exponential decay of the correlation functions of which the J's are the Fourier transforms. That is,

$$J^{(1)}(\omega)=\frac{2}{15}\frac{2\tau_c}{1+\omega^2\tau_c^2}\sum_i r_i^{-6} \qquad (8)$$

with $J^{(0)}:J^{(1)}:J^{(2)}=6:1:4$ for powder samples. The sum on r_i^{-6} runs over all Ce lattice sites, taking a hydrogen site at the origin. Since $\omega_e \gg \omega_I$, the latter may be neglected in comparison to the former in $J^{(0)}$ and $J^{(2)}$. Strictly speaking, the correlation time τ_c which appears in $J^{(1)}$ is the ion spin-lattice relaxation time τ_{e1}, whereas that which occurs in $J^{(0)}$ and $J^{(2)}$ is the transverse relaxation time of the ion, τ_{e2}. However, since it is apparent that these times are extremely short, especially τ_{e1}, we assume that the usual high-temperature limit $\tau_{e2}=\tau_{e1}$ holds. In addition, τ_c should include the effects of hydrogen motion via τ_D, the correlation time for diffusion. That is,

$$\tau_c^{-1}=\tau_{e1}^{-1}+\tau_D^{-1} . \qquad (9)$$

However, the extreme shortness of the measured proton T_1's indicates that $\tau_{e1} \ll \tau_D$ and therefore that $\tau_c=\tau_{e1}$. (Values of τ_D from NMR studies of the corresponding lanthanum hydrides[8] are much too long to be significant in the temperature range investigated here.)

Although there do not appear to have been any studies of the Ce^{3+} electron spin resonance in hydrides, measurements of the temperature dependence of the Ce^{3+} ESR linewidth in lanthanum intermetallics, on the one hand,[12] and of the relaxation rate of isolated Ce^{3+} ions in liquid metals by means of time-differential perturbed γ-ray angular distribution (TDPAD),[16] on the other hand, indicate that τ_{e1} probably falls in the range 10^{-12}–10^{-13} s for $100<T<300$ K. Accordingly, $\omega_e^2\tau_{e1}^2 \ll 1$ and $\omega_I^2\tau_{e1}^2 \ll 1$ to an even greater degree so that Eq. (7) becomes

$$(R_1)_{d,\mathrm{Ce}}=\tfrac{4}{3}\gamma_I^2\gamma_e^2\hbar^2 J(J+1)\tau_{e1}\sum_i r_i^{-6} . \qquad (10)$$

Since hydrogen occupies sites on both the T and O interstitial sublattices in the fcc metal lattice, the measured relaxation rate is the weighted sum of the separate rates for the two sublattices. Designating the fractional occupancies of the O and T sublattices by α and β, respectively, so that $2\beta+\alpha=x=[\mathrm{H}]/[\mathrm{Ce}]$, we have for the net relaxation rate,

$$R_1=[2\beta(R_1)_T+\alpha(R_1)_O]x .$$

The lattice sums which enter $(R_1)_T$ and $(R_1)_O$ by way of Eq. (10) can be taken from the hydride NMR literature. For simplicity, we assume that $\beta=1$ in the range of compositions studied (all T sites occupied). Then $\alpha=x-2$, and we obtain as a final form for $(R_1)_{d,\mathrm{Ce}}$:

$$(R_1)_{d,\mathrm{CE}}=\tfrac{4}{3}\gamma_I^2\gamma_e^2\hbar^2 J(J+1)a_0^{-6}\tau_{e1}(422+477/x) , \qquad (11)$$

where $a_0=5.57$ Å is the lattice parameter of CeH_2 (the small composition-dependent change in a_0 is not significant here). This result shows that because the O sites are further from the Ce ions than the T sites, the filling of the O sites results in a small decrease (12%) in the dipolar relaxation rate as x increases from 2 to 3. This effect is evident in the experimental data as a decrease in the slope of R_1 vs $10^3/T$ with increasing hydrogen concentration (Fig. 1). Experimentally, however, the effect is greater than 12%. Comparing $(R_1)_{d,\mathrm{Ce}}$ values at 300 K, we find a decrease of about 22% as x increases from 2.10 to 2.92, and of 13% as x increases from 2.62 to 2.92 compared with 3% predicted by Eq. (11). The x dependence of the mean values of $(R_1)_{d,\mathrm{Ce}}$ at 300 K agrees well with Eq. (11) for $x \le 2.6$, but the decrease with x is stronger than that of Eq. (11) for $x>2.6$. Nevertheless, within the experimental uncertainties the x dependence is consistent with Eq. (11) and an assumption that the Ce^{3+} electronic magnetic dipole moment and its τ_{e1} are independent of x. Small changes in τ_{e1} or γ_e with increasing x could account for the observed deviations from Eq. (11).

Finally, we use the measured $(R_1)_{d,\mathrm{Ce}}$ values to infer values of the Ce^{3+} ion spin-lattice relaxation time τ_{e1}. To do this requires assigning values to γ_e and J of the Ce ion. This assignment is complicated by the crystalline electric field (CEF) level structure of this ion in the hydrides. Neutron CEF spectroscopy measurements made on single crystal $CeD_{2.12}$ found a single transition at 20 meV (235 K), consistent with cubic splitting of the Ce^{3+} $^2F_{5/2}$ ground-state multiplet into a Γ_7 doublet and a Γ_8 quartet.[17] The temperature dependence of the intensity of the transition favors the Γ_7 doublet as the ground state, but not definitely. Earlier specific-heat measurements on $CeH_{2.00}$ showed a Schottky anomaly which was interpreted as arising from a Γ_7-Γ_8 splitting of 156 K with the Γ_8 quartet lowest, and assigning an effective negative charge to the hydrogens (hydridic or anionic model).[18] Electron-spin-resonance measurements on Ce^{3+} in intermetallic compounds of the series LaP, LaAs, LaSb, and LaBi show unambiguously that the Γ_7 doublet is lowest in these.[12] This is consistent with the CEF arising from positive ions, whereas the reversed level order (Γ_8 lowest) is expected for negative ions. To the extent that all indications are that hydrogen in these hydrides is somewhat more negative than in the atomic case, it seems likely that the Γ_8 quartet is the ground level.

In contrast to these results for the dihydride, the low-temperature specific heat of $CeH_{2.70}$ yielded a Schottky anomaly consistent with a doublet ground state.[19] This was interpreted as arising from an axial CEF (tetragonal) level structure of three doublets. The two excited doublets were estimated to be 70 and 190 K, respectively, above the ground state. Such a CEF having tetragonal symmetry would be consistent with the reported tetragonal distortion of the metal lattice in $\mathrm{CeD}_{2.75}$ at temperatures below 240 K.[2] For a non-S-state ion such as Ce^{3+}, this change in CEF symmetry could itself suffice to account for the additional decrease in $(R_1)_{d,\mathrm{Ce}}$ with increasing x, discussed above, via changes in τ_{e1}.

Despite these complications, magnetic susceptibility measurements on $\mathrm{CeH}_{2.75}$ over the temperature range 77–300 K, using both vibrating sample and Faraday balance methods, yielded the effective moment, $g_J[J(J+1)]^{1/2}=2.43\pm0.03$, which differs by less than 5% from the free-ion value of 2.54.[20] More recently, TDPAD measurement of the hyperfine fields of isolated Ce ions in liquid and solid metals[16] showed these to be close to the free-ion value at all temperatures in the range 77–950 K. We therefore use the free-ion value in Eq. (11) in estimating τ_{e1} from the measured proton relaxation rates. In any case, we anticipate that at 300 K the free-ion values of g_J and J should be applicable. With these values, and the lattice parameter a_0, Eq. (11) becomes

$$(R_1)_{d,\mathrm{Ce}}=15.7\times10^{12}(422+477/x)\tau_{e1}\ . \tag{12}$$

From this we have at 300 K, for $\mathrm{CeH}_{2.1}$ that $\tau_{e1}=1.76\times10^{-13}$ s, and for $\mathrm{CeH}_{2.92}$, that $\tau_{e1}=1.5\times10^{-13}$ s. These values of τ_{e1} are in satisfactory agreement with expectations as noted above for the Ce^{3+} ion.

The foregoing analysis of the proton spin-lattice relaxation rate also indicates that, over the range of temperatures investigated, the Ce-ion relaxation time τ_{e1} varies according to an effective Korringa relation, i.e., $\tau_{e1}T=\mathrm{const}$. This is in fact the case. The measurements of Sugawara and Huang of the EPR linewidth of Ce^{3+} in Ce-doped LaP, LaAs, etc., could be represented by[12]

$$\Delta H=aT+b\Delta/[\exp(\Delta/T)-1]\ , \tag{13}$$

where the residual ($T=0$) linewidth has been subtracted. The first term represents the Korringa relaxation rate within the CEF ground-state levels due to the localized-moment conduction-electron exchange coupling. The second term results from the combination of the Hirst[21] and Orbach[22] mechanisms, which involve relaxation via higher CEF levels induced by conduction-electron exchange coupling or by host phonons, respectively. Such behavior has also been found to apply to other non-S-state ions in intermetallic compounds, and in particular to the case of Er^{3+} in YH_2.[23] At temperatures on the order of the CEF splitting parameter Δ or higher, the second term in Eq. (13) approaches bT yielding an effective overall Korringa-type relation between ΔH (or τ_{e1}^{-1}) and T.

The TDPAD measurements of the Ce-ion relaxation rate in liquid metals already referred to[16] also indicate that an approximately linear relation holds between τ_{e1}^{-1} and T in such systems, although the interpretation advanced differs somewhat from that outlined above. Nonetheless, the experimental measurements in all cases are consistent with appropriate Korringa-type behavior, as we have also observed. The conclusion that the major contribution to the proton spin-lattice relaxation rate arises from the dipolar coupling to the fluctuating spin of the Ce^{3+} ion is thus appropriate.

RKKY interaction

The relaxation-rate contribution which we have ascribed to indirect coupling of the proton and Ce-ion moments via the conduction electrons (the RKKY interaction) is represented by Eq. (5). The data show that the interaction parameter $R\simeq650\ \mathrm{s}^{-1}$ in the range of metallic compositions and $R\simeq250\ \mathrm{s}^{-1}$ in the range of nonmetallic composition. Fradin[14] has shown that $(R_1)_{\mathrm{RKKY}}$ can be expressed as

$$(R_1)_{\mathrm{RKKY}}=\frac{4N_s(E_F)(g_J-1)^2J(J+1)\,|J_{s\text{-}f}|^2}{3k_B(T-\Theta)(T_1)_K}\ , \tag{14}$$

where $N_s(E_F)$ is the s density of states at the Fermi level, $J_{s\text{-}f}$ is the s-f exchange interaction parameter, Θ is the ordering temperature, k_B is Boltzmann's constant, and $(T_1)_K$ is the conduction-electron contribution to the proton spin-lattice relaxation time T_1 in the absence of localized moments [$(T_1)_K^{-1}=(R_1)_K=BT$; see Eq. (4)]. As noted already, for the cerium hydrides, Θ does not exceed 6 K and can be neglected at the temperatures of interest here. Replacing $(T_1)_K^{-1}$ with BT, Eq. (14) becomes

$$R\simeq\frac{4N_s(E_F)(g_J-1)^2J(J+1)\,|J_{s\text{-}f}|^2B}{3k_B}\ . \tag{15}$$

To compare the measured R values with the expectations based on Eq. (15), we take for the Korringa parameter B its value in the corresponding lanthanum hydrides. In that case, $(T_1)_KT\simeq400$ s K, so that $B\simeq2.5\times10^{-3}$ $(\mathrm{s\,K})^{-1}$. $J_{s\text{-}f}$ for rare-earth ions is expected to be of the order of 0.1 eV.[24] Recent band-structure calculations[3,25] for cerium and lanthanum hydrides have found values of $N_s(E_F)$ which are very small, certainly less than 2 states/Ry spin unit cell [thus $N_s(E_F)\simeq1.5\times10^{-2}$ states/eV atom spin]. With these values, and $g_J=\frac{6}{7}$, we find from Eq. (15),

$$R\simeq10^{-3}$$

(measured in s^{-1}). This result is clearly incompatible with the experimental findings, being too small by orders of magnitude.

Equation (14) applies to an indirect interaction between the Ce electronic magnetic moment and the H nuclear magnetic moment via the hydrogenlike s-electron states at the Fermi energy. We see that this mechanism is too weak to account for the magnitude of our temperature-independent term, R.

It is believed that hydrogen bonding is primarily covalent in the hydrides. The host metal d bands participate in the covalent bonding and, through an exchange coupling, can produce a resultant contact hyperfine interaction between the hydrogen nucleus and its *s* core electrons. This core polarization is an effective proton spin-relaxation mechanism in nonmagnetic transition-metal hydrides which have high *d*-band densities of states at the Fermi energy.

We suggest that the same mechanism can be incorporated in the RKKY formalism. That is, the *f*-electron magnetic moment can polarize the *d*-band states at the Fermi energy. The *d*-band states couple to the hydrogen nuclear spins through core polarization of *s* hydrogenlike states. The high *d*-band density of states could provide the increase in magnitude needed for this mechanism over the *f*-*s* mechanism originally considered by Fradin in formulating Eq. (14). This *f*-*d*-*s* RKKY coupling could account for the term R in Eq. (6).

Metal-semiconductor transition

The relationship between the spin-lattice relaxation rate and electronic structure is contained in the description of the RKKY interaction between the protons and the Ce^{3+} electronic magnetic dipole moment. With the assumptions previously argued, Eq. (6) becomes

$$R_1=\frac{A}{T}+R \ . \tag{16}$$

The dependence of R_1 upon concentration is controlled by the RKKY term, R. For the *f*-*d*-*s* RKKY coupling it is expected that $R \propto N_d(E_F)$. Band-structure calculations by Fujimori and Tsuda[26] show a sharp decrease in the density of states between $\mathrm{CeH}_{2.7}$ and $\mathrm{CeH}_{3.0}$ and the formation of the gap in the density of states. The vanishing of $N_d(E_F)$ would mean $R \rightarrow 0$, and $R_1 \approx A/T$ in the semiconducting regime. We observe a nonzero value of R in the nonmetallic regime, however, to within experimental uncertainties, $R_{\text{semiconducting}} \ll R_{\text{metallic}}$, which is consistent with a sharp decrease in $N_d(E_F)$.

The striking similarity of the concentration dependences of the electrical conductivity and the relaxation-rate data indicates that both are related to the same phenomenon. The decrease of the relaxation rate at $\mathrm{CeH}_{2.7}$ supports the results of band-structure calculation of a sharp decrease in the density of states at hydrogen concentration above $\mathrm{CeH}_{2.75}$. A model which explains the conductivity data should be able to explain the T_1 behavior.

The model proposed assumes that in cerium trihydride hydrogen vacancies act as donors. Thus CeH_x is "doped" with hydrogen vacancies having a concentration proportional to $3-x$. For zero vacancy concentration, stoichiometric CeH_3 is an insulator. For small values of $3-x$, CeH_x is a semiconductor. At a critical concentration of vacancies there is a Mott transition to the metallic state from a state which behaves as a heavily doped semiconductor.

Such a system would be expected to fit Mott's relation

$$N_c^{1/3}a_{\mathrm{H}}=0.25 \ , \tag{17}$$

where N_c is the critical density of donors and a_{H} is the first Bohr radius of an isolated center. For $\mathrm{CeH}_{2.8}$ the density of hydrogen vacancies is $N_c=2.35\times10^{22}\ \mathrm{cm}^{-3}$, and using Mott's relation, $a_{\mathrm{H}} \approx 1.5\times10^{-8}$ cm. This value falls in the range found in many other doped semiconductors.[27]

Coexistence of two resonances and comparison with LaH_x

The present results display both similarities and dissimilarities with respect to the corresponding lanthanum hydrides. Thus, in both systems, two proton resonances are observed to coexist over some temperature interval in the vicinity of 150—170 K for hydrogen concentrations $x>2.5$. In the case of LaH_x it has been found that the two resonances have different spin-lattice relaxation times, consistent with the presence of two phases. No evidence for cross relaxation between the two resonances was found.[28] In the present CeH_x measurements resolution of two values of T_1 was not achieved. Two resonances might arise from coexistence of the metal and semiconductor phases if there is a temperature-dependent transition. However, the present measurements fail to establish the occurrence of such a transition. Alternatively, the two phases might be ordered (low-temperature) and disordered (high-temperature) hydrogen sublattice arrangements that might coexist over a small temperature range due to lattice imperfections and internal strain. In such a case the difference in T_1 values would most likely correspond to a difference in hydrogen diffusion rates in the two phases. Such differences occur in some hydride systems. Accordingly, since the proton relaxation rate in CeH_x is overwhelmingly dominated by the Ce^{3+} dipolar contribution, a small difference in $(R_1)_{dd}$ would probably not be detectable. Thus the possibility cannot be ruled out.

Another possibility is that the two resonances arise from hydrogen in the tetrahedral and octahedral interstitial sites if these have different diffusion rates and if there is a low probability of hopping from one type of site to the other. The occurrence of two proton resonances has also been observed in PuH_x, which has the same structure. In PuH_x the resonances are well resolved apparently as a consequence of different shifts of the proton resonance frequency.[10] It was concluded[10] that the two resonances could be associated with the tetrahedral and octahedral sites, the *O*-site hydrogen having the higher diffusion rate. Because of the interpenetration of the octahedral site and tetrahedral site sublattices, the two spin systems would, by magnetic dipolar coupling, reach a common spin temperature and relax with a single, common relaxation rate.

CONCLUSIONS

The temperature and concentration dependences of the NMR spin-lattice relaxation rate R_1 of protons in CeH_x have been presented along with some observations of the resonance line shape over a limited temperature range. The dominant relaxation mechanism is shown to be the direct magnetic dipolar coupling between the proton spin system and the electronic magnetic moment of the Ce^{3+}

ions. The power spectrum of this interaction is controlled by the spin-lattice relaxation rate of the Ce^{3+} electronic magnetic dipole moment system. It was argued that the Ce^{3+} relaxation rate would be proportional to the temperature in the high-temperature regime of the data reported here. This temperature dependence follows from application of the Hirst[21] and Orbach[22] mechanisms with CEF splittings, Δ, less than $k_B T$. The magnitude of Δ assumed for this inequality was shown to be consistent with what is known from the literature about Δ for Ce^{3+}. Thus it follows that the dominant proton spin-lattice relaxation mechanism is inversely proportional to temperature over a large range of temperature.

As further support for the application of the proton-Ce^{+3} dipolar relaxation mechanism, it was shown that this term decreases with hydrogen concentration across the entire range from the dihydride to the trihydride in a manner consistent with our data. Because of the unusually large strength of the proton-Ce^{3+} dipolar interaction, the proton-proton dipolar coupling and the proton—conduction-electron Korringa mechanisms are shown to be negligible. However, at very low Larmor precession frequencies the diffusion-induced maximum in the proton-proton mechanism would be observable.

The secondary, but nevertheless important, proton spin-lattice relaxation mechanism was ascribed to the indirect RKKY coupling between the protons and the Ce^{3+} dipole moments. Because of the low temperature for magnetic ordering in the CeH_x system, the RKKY mechanism is essentially independent of temperature. The size of the temperature-independent term in our data is too large to be explained by an RKKY interaction based on an f-s exchange interaction because of the very low $N_s(E_F)$ in CeH_x. Instead, it has been proposed that the Ce^{3+} f-electron magnetic moment polarizes the d-band states at the Fermi energy which couple to the hydrogen nuclei by core polarization. The large $N_d(E_F)$ in CeH_x for $x<2.6$ would be sufficient to account for the RKKY terms. Therefore, the RKKY term decreases sharply along with the density of states at the Fermi surface as hydrogen concentration is increased beyond $x=2.7$ into the semiconducting regime. The proton spin-system relaxation rate is thus affected by changes in the electronic structure associated with changes in hydrogen concentration.

A percolation model for the metal-semiconductor transition would predict two values of proton T_1 at concentrations near the transition region on the semiconducting side. Since there is no evidence of a two-component relaxation, associated with protons within and outside clusters, our NMR data do not support a percolation model. It is suggested that the concentration-dependent transition in electric conductivity of CeH_x near $x=2.75$ is a Mott transition. In the low-conductivity regime, hydrogen vacancies are counted as donors in the cerium trihydride host. Above a critical vacancy concentration given by $N_c=(0.25/a_\mathrm{H})^3$ where $a_\mathrm{H}=1.5\times10^{-8}$ cm, the sample becomes metallic. No temperature-dependent transition is observed in the NMR data. The conductivity data[2] show a relatively small change with temperature at $T=240$ K for $x=2.81$. This temperature-dependent change is probably associated with an order-disorder transition in hydrogen site occupancy[26] and is not, we believe, a metal-semiconducting transition.

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