Anomalous Resistivity Peaks, Localization Transitions, and the Electronic Structure of Substoichiometric Lanthanum Trihydrides

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The resistivity $\rho(T)$ of LaH_x ($2.80 \le x \le 2.90$) was determined from Q-factor measurements at 100 K $< T <$ 700 K. Its temperature coefficient $\alpha > 0$ is small at $T \le 200$ K, and $\rho(T)$ peaks at some T between 220 and 260 K. The peak narrows with increasing x, and is extremely sharp for $x \ge 2.86$. At higher temperatures the behavior of $\rho(T)$ is consistent with variable-range hopping. It is suggested that a delocalized band of states at E_F, associated with the superlattice of octahedral vacancies, becomes localized and its mobility is quenched when the superlattice collapses above $\sim 240 \pm 20$ K.

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The electronic structure of substoichiometric LaH_x and CeH_x trihydrides, $2.70 < x < 3.00$, has evaded elucidation for many years.[1-13] Experimental[1-9] and computational[10-13] results show that the dihydrides are normal metals, with a resistivity ρ lower than that of the pure metals, and indicate that the trihydrides are narrow-gap semiconductors, with $E_g \sim 0.5$ eV for LaH_3.[7] In between these two stoichiometric limits, the fcc fluorite structure, in which La is at (0,0,0) and the tetrahedral H is at $\frac{1}{4}(1,1,1)$, continuously dissolves H at room temperature into random occupancy of the octahedral o sites at $\frac{1}{2}(1,1,1)$. For (essentially all) $x \ge 2.15$, the octahedral H (H_o) apparently forms a superlattice below a transition temperature around 250 K.[14-20] Although the structure of this superlattice has not been determined for any value of x, the structures of $\mathrm{CeD}_{2.25}$ and $\mathrm{CeD}_{2.5}$ have been established in the closely similar Ce-D system.[14,15,19] The indirect evidence for the existence of a superlattice in the La-H system is thus considerable.[14-20] In the range $2.60 \le x \le 2.86$, a slight tetragonal distortion of the metal sublattice occurs in LaH_x at temperatures similar to that of the H_o superlattice formation.[2,3,6,14-17,20] In $\mathrm{LaH}_{2.90}$, there is no detectable distortion, but a very broad anomalous minimum in the cubic lattice constant at $T \sim 250$ K has been reported.[16] For $2.80 \le x \le 2.90$, the temperature coefficient of the resistivity α, albeit small, is positive below these transitions. Above the transition, α is negative.[7] The behavior of CeH_x, $2.70 \le x \le 2.78$, is qualitatively similar.[2,3,7,8] This behavior is contrary to the "normal" metal-nonmetal transition, which leads from a high-T metallic phase to a low-T nonmetallic one. Thus, the nature of both the high-T state, whether gapless or not, and the low-T one, whether conducting as a normal metal or dominated by a defect band, has remained unanswered. This Letter suggests that the low-T state is indeed dominated by a defect band, probably due to electrons associated with the vacant o (V_o) sites of the H_o superlattice. It proposes that as T rises to the tetragonal-to-fcc and H_o-superlattice-to-disordered-lattice-gas transitions, these states become localized, and ρ consequently rises as their mobility is quenched. At higher T, ρ decreases in a manner consistent with a variable-range-hopping (VRH) mechanism.[21,22] This localization transition is accompanied by dramatic peaks of ρ, which are extremely sharp when $x \ge 2.86$. Small peaks in ρ are also observed in $\mathrm{La}_{2-y}\mathrm{Sr}_y\mathrm{Cu}_{1-x}\mathrm{Li}_x\mathrm{O}_{4-\delta}$, which also exhibits VRH,[23] but the magnitude of the peaks observed in LaH_x are, to the best of the authors' knowledge, unequaled in any other system.

The resistivity of coarse powder LaH_x samples was determined from indirect Q-factor measurements recently described in detail.[7] Because of various unknown geometrical factors, the absolute value of ρ could only be roughly estimated, with an uncertainty of a factor of 2 or 3. These geometric factors are, however, (almost) temperature independent, so the dependence of ρ on T can be determined with much greater accuracy. Since the samples were sealed in small evacuated quartz tubes, pressure buildup at high temperature limited hydride dissociation. Well established pressure-composition diagrams of LaH_x (Ref. 24) indicate that the decrease in x was less than ~ 0.001 below 700 K.

Figure 1 shows the behavior of the normalized resistivity, $\rho_n(T) \equiv \rho(T)/\rho(295\ \mathrm{K})$, vs $10^3/T$, for $x = 2.80$, 2.81, 2.84, 2.86, 2.88, and 2.90. The approximate values of ρ(295 K) and ρ(150 K) are listed in Table I. As clearly seen in Fig. 1, for all x, $\rho_n(T)$ peaks at some 220 K $\le T \le$ 260 K. As x increases, the peak becomes more pronounced, and is extremely sharp for $x \ge 2.86$. The approximate values of ρ(295 K) rapidly increase with x, from $\sim 0.002\ \Omega$ cm in $x = 2.80$ to $\sim 0.1\ \Omega$ cm in $x = 2.90$ (see Table I). For all x, $\alpha > 0$ below 200 K, but small. ρ(150 K) also generally increases with x, but does not significantly exceed $\sim 5000\ \mu\Omega$ cm. At temperatures above the peak, α is negative, and the overall slope of $\ln\rho_n(T)$ vs $1/T$ increases with increasing x. In the normal metal-nonmetal transition, the high-T phase is metallic, with $\alpha > 0$, and the low-T phase is nonmetallic, with $\alpha < 0$. Since the sign of α is reversed relative to the

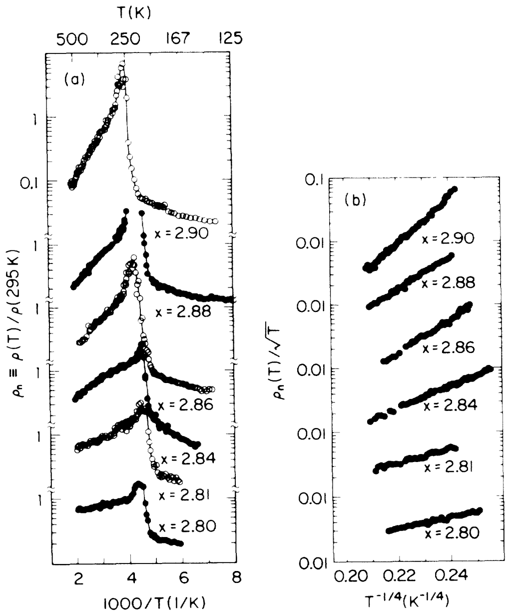

FIG. 1. (a) Normalized resistivity $\rho_n(T) \equiv \rho(T)/\rho(295\ \text{K})$ of LaH$_x$, $x = 2.80$, 2.81, 2.84, 2.86, 2.88, and 2.90, vs $1000/T$. Although the high-T branch appears to be thermally activated (see Table I), gapless behavior is suggested. Note that by definition, $\rho_n(295\ \text{K}) = 1$, which determines the numerical values on the ordinate. (b) $\rho_n(T)/\sqrt{T}$ vs $T^{-1/4}$ of the high-T branch of Fig. 1(a). Equation (2) (see text) shows that the straight lines are consistent with variable-range hopping. The resulting values of ρ_{02} and T_0 are summarized in Table I.

normal transition, there is a peak in $\rho(T)$ instead of the usual discontinuity. Although similar peaks are observed in $La_{2-y}Sr_yCu_{1-x}Li_xO_{4-\delta}$,[23] they are much weaker in that system. As mentioned above, the peaks shown in Fig. 1 are, to the best of the authors' knowledge, the most striking of their kind.

Stoichiometric LaH$_3$ and CeH$_3$ are apparently narrow-gap semiconductors.[2,7] The anomalous behavior of $\rho(T)$ described above might then be construed as resulting from a transition from a high-temperature semiconducting phase to a low-temperature metallic phase. The values of the activation energy E_a and prefactor ρ_{01} resulting from fitting the high-T measurements by an assumed thermally activated conductivity,

$$\rho(T) = \rho_{01}\exp(E_a/kT)\,, \tag{1}$$

approximately valid for a semiconductor of gap $E_g = 2E_a$,[25] are listed in Table I. As clearly seen, E_a rises strongly with x. Yet the Meyer-Neldel relation between ρ_{01} and E_a, so often observed in a wide variety of transport phenomena in disordered systems,[26-28] is apparently absent from this system. In addition, to the best of the authors' knowledge, a transition from a high-T semiconducting state to a low-T metallic one would be unprecedented.

An alternative picture accounting for the low-T behavior involves the one invoked to explain the n-type conductivity in this and the substoichiometric CeH$_x$ systems,[1-3] in which the low-T conductivity is dominated by donorlike electron states which peak about the V_O sites.[12] Since the H$_O$ and V_O sublattices are ordered as superlattices at low T,[14-20] at low x where the V_O-V_O distance is small, these states may overlap to yield a donor band around E_F. The structure of these superlattices, while not definitely established for any x, is probably similar to those of the Ce-D system.[14,15,19] For some values of x they may also be related to the vacancy-interstitial complexes identified in some pure or aliovalently doped superionic fluorites.[29]

The absence of an electron spin resonance (ESR) that can be associated with these donor states is also consistent with the foregoing alternative picture of a low-temperature (partially) delocalized defect band around E_F.[30] In addition, we note that when the error associted with the values of $\rho(150\ \text{K})$ (see Table I) is taken into account, these values do not exceed the Ioffe-Regel limit[31] of $\sim 3500\ \mu\Omega\,\text{cm}$ for $a = 3$ Å, again consistent with a defect band at E_F.

TABLE I. The resistivity at room temperature $\rho(295\ \text{K})$, at 150 K $\rho(150\ \text{K})$, the activation energy E_a and prefactor ρ_{01} [assuming a thermally activated conductivity; see Eq. (1)], characteristic temperature T_0, prefactor ρ_{02}, and correlation coefficient r resulting from fitting the high-T data by the variable-range-hopping transport, Eq. (2).

x in LaH$_x$	$\rho(295\ \text{K})$ (Ω cm)[a]	$\rho(150\ \text{K})$ ($\mu\Omega$ cm)[a]	E_a (meV)	ρ_{01} ($\mu\Omega$ cm)	T_0 (10^5 K)	ρ_{02} ($\mu\Omega$ cm)	r
2.80	0.002	350	18	860	1.38	360	0.987
2.81	0.011	1650	30	3520	3.87	970	0.981
2.84	0.014	980	49	1905	21.8	110	0.997
2.86	0.065	3300	90	2050	135	6.4	0.995
2.88	0.06	7800	90	1675	116	9.1	0.996
2.90	0.1	2500	140	370	497	0.05	0.997

[a] Because of unknown geometrical factors, the true value of ρ may be different from the listed value by a factor of 2 or 3. Since these factors are (essentially) temperature independent, $\rho_n(T) \equiv \rho(T)/\rho(295\ \text{K})$ is determined with much greater accuracy.

At ~250 K, when the H hopping rate exceeds $\sim 7\times 10^7$ sec^{-1},[4] the (mutually complementary) H_o and V_o superlattices collapse. At temperatures above this order-disorder transition, the H atoms and vacancies randomly occupy the o sites. It is thus expected that the electron states previously associated with the defect band at E_F should now become localized.[32,33] Their localization would then quench their mobility, and cause a sharp rise in ρ. Since the vacancies are randomly distributed among the o sites, the conductivity should follow VRH behavior. Thus, the high-T resistivity should depend on T in the following manner:[21–23]

$$\rho(T)=\rho_{02}(T/T_0)^{1/2}\exp[(T_0/T)^{1/4}]\,. \qquad (2)$$

Figure 1(b) displays the values of $\log_{10}[\rho_n(T)/T^{1/2}]$ vs $1/T^{1/4}$. Although the data agree excellently with Eq. (2) they exist only over a relatively narrow range in $1/T^{1/4}$. The suggestion that the electronic transport at high temperatures is governed by VRH is therefore frankly a speculation, albeit an expected and reasonable one. The parameters T_0 and ρ_{02} resulting from fitting the data by Eq. (2), as well as the quality of the agreement manifest in the correlation coefficient r, are listed in Table I.

The values of ρ(295 K) and T_0 (see Table I) are similar to those of the hole-type VRH in $La_{2-y}Sr_y$-Cu_{1-x}-$Li_xO_{4-\delta}$.[23] We thus tentatively assume that T_0 is related to $N(E_F)$ and the localization length ξ through the following relation:[22,23]

$$kT_0\simeq 16[N(E_F)\xi^3]^{-1}\,. \qquad (3)$$

Since ^{139}La Knight shift and proton Korringa spin-lattice relaxation rates are consistent with essentially free-electron-like behavior of $N(E_F)$ up to $x=2.80$,[34,35] we initially estimate $N(E_F)(x=2.80)$ assuming 0.2 free electron per La atom. $N(E_F)$ in a degenerate Fermi gas is given by[36]

$$N(E_F)=\frac{4m}{h^2}(3\pi^2 n)^{1/3}\,, \qquad (4)$$

where in this case n is the density of electrons associated with the vacancies. The fcc lattice constant $a_0(x=2.80)=5.61$ Å (Ref. 19) then yields

$$N(E_F)(x=2.80)\simeq 6.7\times 10^{21}\ \mathrm{cm^{-3}eV^{-1}}\,. \qquad (5)$$

$T_0\simeq 1.4\times 10^5$ K (see Table I) then yields $\xi\simeq 5.8$ Å. Yet this is precisely the V_o-V_o distance d_V at $x=2.80$. Since d_V increases to ~8.6 Å at $x=2.90$,[12,37] a constant value of $\xi\simeq 5.8$ Å would result in striking effects on the x dependence of ρ.

If ξ indeed remains essentially unchanged for $2.80\le x\le 2.90$, then the values of T_0 (Table I) and Eq. (3) yield an $N(E_F)$ which decreases to 1.9×10^{19} cm^{-3}eV^{-1} at $x=2.90$. The total number of electrons, however, only decreases from 0.2 to ~0.1 per La atom over this range. This suggests that as x increases, the V_o-induced band shifts downward from E_F. Indeed, Q-factor measurements on $LaH_{2.93}$ indicate that this composition is semiconducting, with a gap $E_g\simeq 0.48$ eV, although a "remnant" kink is observable at the (apparent) localization transition at 237 K.[7] Yet as $N(E_F)$ presumably decreases by a factor of 350 from $x=2.80$ to 2.90, the change in ρ(150 K), from ~400 μΩ cm in $LaH_{2.80}$ to ~3000 μΩ cm in $LaH_{2.90}$ (see Table I), is only eightfold. It thus appears that $N(E_F)$ cannot decrease by a factor of 350 over this range, and that ξ must also change as x changes. If ξ decreases by a factor of ~3.5 and $N(E_F)$ by a factor of 8 only, then the behavior of ρ(150 K) and T_0 remain mutually consistent. This ~3.5-fold decrease in ξ is actually expected from the relation

$$\xi=\xi_0/[1-(3-x)/(3-x_c)]\,, \qquad (6)$$

where $x_c=2.77$ is the critical content for the onset of the localization transition. This relation is expected if LaH_x ($2.80\le x\le 2.90$) is regarded as a "heavily n-doped" degenerate semiconductor.[38]

The sharp rise in ρ towards a peak value may now be understood to result from the localization transition induced by the order-disorder transition of the H_o. This transition quenches the mobility of the electrons associated with the V_o sites. Thus, the only part of ρ that remains unaccounted for is the sharp drop at temperatures immediately above the peak, which is particularly dramatic in $x\ge 2.86$. At present we can only speculate about the nature of this behavior: The total hopping rate of the V_o electrons is the sum of two contributions, that of VRH in a quasistatic "frozen" H_o configuration, and that mediated by the hopping of the H_o. Since the range of the latter hopping process is not variable, its T dependence should not be that of VRH. Rather, it should equal that of the H_o hopping rate ν_H, about 7×10^7 sec^{-1} at 250 K,[4,34,35] multiplied by the inverse ratio of their concentrations. Their contribution should therefore be, and indeed is, comparable to that of fast ion conductors.[29,39]

In summary, the Q-factor resistivity measurements on the substoichiometric lanthanum trihydride system LaH_x, $2.80\le x\le 2.90$, were described and discussed. The resistivity exhibits weakly metalliclike behavior below 200 K apparently due to a donorlike defect band associated with the superlattice of vacancies of the octahedral sites. This defect band is believed to undergo a localization transition at ~250 K, when the superlattice is disrupted by a sufficiently rapid H motion. The transition quenches the mobility of these electrons, resulting in an extremely sharp peak in the resistivity ρ in $x\ge 2.86$. It is speculated that at temperatures immediately above this peak, the motion of these electrons is governed by the octahedral H motion. At higher temperatures, the behavior of ρ is consistent with variable-range hopping. The comparison between the characteristic temperature T_0 and the low-temperature values of ρ suggests that the localization length ξ decreases by a factor of ~ 3.5 and $N(E_F)$ by a factor of ~ 8 as x increases from 2.80 to 2.90.

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