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Electrical Csnductivity of Lanthanum Hydrides

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Abstract The conductivity of Lanthanum Hydrides compounds is computed by considering an approximate model Hamiltonian which takes into account the hybridization of the *d* and hydrogen-derived *s* bands. The model is used to discuss the role of hybridization on the electrical conductivity and the observed metal-semiconductor phase transition in LaH_x.

Interest in the unique conductivity properties of the rare earth hydrides began with the work of Stalinski[1] who studied a range of concentration of hydrogen in LaH_x using pressed powder samples. His work was supplemented by much more precise data on the CeH system by Heckman[2] and later by Libowitz[3] and his coworkers. So far many more experimental studies have been carried out on CeH than LaH_x. Further work on LaH_x has been presented by Misemer et *al*[4]. Their data are presented in fig. 1 indicating a nonvanishing conductivity (metallic behaviour) as $T \to 0$ for $x = 2.72$ and $x \simeq 1.98$, whereas for concentrations 2.90 and above, logarithmic increases in resistivity with decreasing temperature are observed, characteristic of semiconductors.

The metal-semiconductor transition in LaH_x has been interpreted in a previous work[6] as a consequence of the increasing hybrídization between the upper and lower hybrid bands. With increasing *H*-concentration the hybridization also increases and it was shown that an gap results between the hybrid bands, and consequently the system changes its phase from metallic state. Considering hybridization thus has provided valuable new insight into the mechanism ofthemetal-semiconductor transition in LaH_x.

The model Hamiltonian from ref. 6, which is recalled here is

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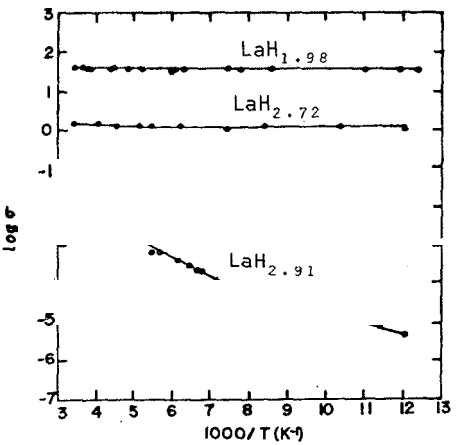

Fig.1 - Finnemore and Mazini's data[5] as presented by Mesemer *et al*[4] on the conductivity of LaH_x.

$$H = \sum_{k\sigma} E_{\vec{k}} n_{\vec{k}\sigma} + \sum_{ij\sigma} T_{ij} a^{+}_{i\sigma} a_{j\sigma} + U \sum_{i} n_{i\sigma} n_{i-\sigma}$$

$$+ \sum_{\vec{k}} \left(V_{\vec{k}d} e^{i\vec{k}.\vec{R}_i} a^{+}_{\vec{k}\sigma} a_{i\sigma} + V^{*}_{\vec{k}d} e^{-i\vec{k}.\vec{R}_i} a^{+}_{i\sigma} a_{\vec{k}\sigma} \right) \qquad (1)$$

The general form of the hybrid bands is shown in fig. 2. The cubic cell showing the positions of the f.c.c. lattice of La atoms as well as the tetrahedral and octahedral hydrogen sites and the electronic band structure and density of states of metallic LaH_2 and semiconductor LaH_3 are presented in ref.6.

Within this model the electrical conductivity can now be computed by

$$\sigma = - \int \frac{\partial f}{\partial E} \sigma(E) \, dE \qquad (2)$$

with

$$\sigma(E) = \frac{2\pi e^2 \hbar^3}{m^2} |D_E|^2_{av} |\sigma(E)|^2 \qquad (3)$$

where $\partial f/\partial E$ is the derivative of the Fermi-Dirõc distribution function, and the matrix element D_E is assumed to be a slow-varying function of the energy[8] and taken as D_{μ_F}.

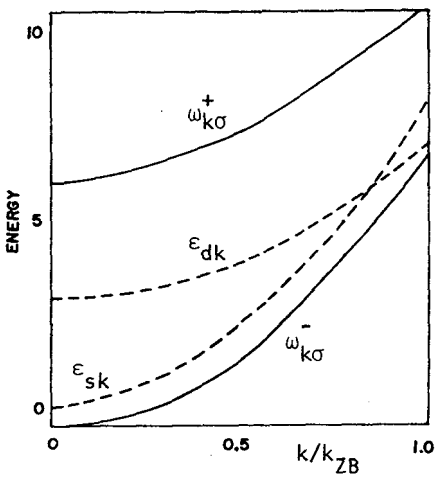

Fig.2 - General shape of hybrid bands in the Hartree-Fock approximation. k_{ZB} is the wave vector to the zone boundary.

Assuming a parabolic density of states, the conductivity can be computed as

$$\sigma = \sum_{p=+,-} c_p \left[- \frac{\omega_z^p}{1 + e^{\beta(\omega_z^p - \mu_F)}} + \frac{1}{\beta} \log \frac{e^{\beta(\omega_z^p - \mu_F)}}{1 + e^{\beta(\omega_z^p - \mu_F)}} + \frac{\omega^p}{1 + e^{\beta(\omega_n^p - \mu_F)}} - \frac{1}{\beta} \log \frac{e\beta(\omega_n^p - \mu_F)}{1 + e^{\beta(\omega_n^p - \mu_F)}} \right]$$

where c_p can be calculated by using eqs. (2) and (5); $\beta = 1/k_B T$; μ_F is the Fermi level energy; and $\omega_z^p = \omega^p_{k=k_{ZB}}$ and $\omega_0^p = \omega^p_{k=O}$ correspond to hybrid band dispersion energies $\omega^p_{k\tilde{o}}$, as shown in fig. 2, defined as

$$\omega_\sigma^{\pm} = \frac{1}{2} \left\{ E_{sk} + E_{dk} + U\langle n_{\bar{d}} \rangle/2 \pm \left[(E_{dk} + E_{sk} + U\langle n_{\bar{d}} \rangle/2)^2 + 4V^2 \right]^{1/2} \right\} \qquad (5)$$

The gap between the upper and lower hybrid bands can be expressed by[6]

$$g = \omega_0^{+} - \omega_z^{-} \qquad (6)$$

On figs. (3) and (4), the curves (a), (b) and (c) correspond to $g < 0$, $g \approx 0$ and $g > 0$, respectively, showing the conductivity versus ternperature, using the following values of the parameter V, where $V = |V_{kd}|$, related to hybridization: (a) V = 0.50; (b) V = 2.46 and (c) V = 4.00. For $g < 0$, $\omega_z^+ > \omega_z^- > \mu_F > \omega_0^+ > \omega_0^-$; for $g = 0$, $\omega_z^+ > \omega_z^- = \mu_F = \omega_0^+ > \omega_0^-$; and for $g > 0$, $\omega_z^+ > \omega_0^+ > \mu_F > \omega_z^- > \omega_0^-$.

In accordance with previous results, $g < 0$ corresponds to a metallic phase, $g \approx 0$ to a semiconductor phase and $g > 0$ representsthe phase transition.

So far the variation of conductivity in lanthanum hydrides has not been understood as resulting frorn an increase of hybridization between the upper and lower bands. It can be established again, as in ref. 6, that increase of hybridization, which occurs when the H-concentration is increased, is directly responsible for the phase transition frorn metal to semiconductor when $x = 2.8$.

The calculation presented here gives a qualitative explanation of the conductivity properties of LaH_x. As in ref.6, we have established the irnportance of taking into account the hybridization of the d and hydrogen-derived s bands to explain the metal-semiconductor transition in lanthanum hydrides.

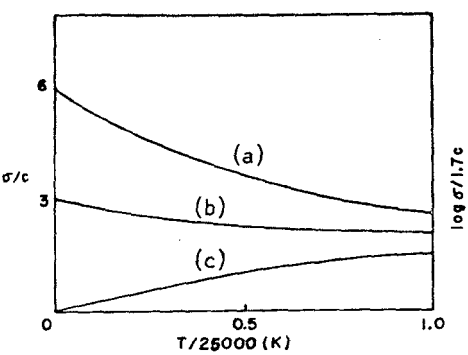

Fig.3 - Conductivity versus temperature for (a) V = 0.50; (b) V = 2.46; (c) V = 4.00.

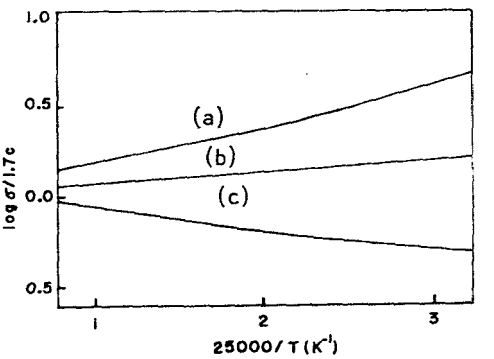

Fig.4 - Logarithmic behaviour of σ with inverse temperature for (a) V = 0.50; (b) V = 2.46 and (c) V = = 4.00.

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Resumo

A condutividade de Hidretos de Lantânio é calculada considerando-se um Hamiltoniano modelo aproximado que leva em conta a hibridização das bandas *d* e *s* derivada do hidrogênio. O modelo é usado para discutir o papel da hibridização na condutividade elétrica e na transição de fase metal-serniconductor observada em LaH .