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ENHANCEMENT OF SUPERCONDUCTING \( T_c \) IN Pd-H LIKE COMPOUNDS
BY OPTICAL PHONONS

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1. Introduction. — The high superconducting transition temperatures recently observed in Pd [1] and Th [2] hydrides raises the question of the relative importance of the acoustic and optical phonons in the determination of \( T_c \) in these systems and others such as Nb-N. Electron tunnelling [3] and normal state resistivity [4] clearly show that the optical phonons contribute in Pd-H, but the relative contribution of the two phonon branches is still somewhat controversial. Other puzzling aspects of this system are the inverse isotope effect when the hydrogen is replaced by deuterium, the further increase of \( T_c \) when some of the Pd atoms are substituted by monovalent atoms (Cu, Ag, Au) and the strong reduction of the electronic density of states in going from pure Pd to the hydride. While in principle the larger \( N(0) \) favours a higher \( T_c \), one must not forget that spin fluctuations or paramagnons set in for very large values of \( N(0) \), as one is approaching the magnetic instability condition. This gives a repulsive electron-electron interaction inhibiting superconductivity in pure Pd. As the density of states in Pd-H is rather similar [5] to what is observed in the noble metals, spin fluctuations are probably irrelevant. Although less information exists for thorium hydride, the density of states is not a decisive factor as it is slightly smaller [6] in the hydrides than in pure Th.

Based on the well-known McMillan formula [7],

\[
T_c \approx \langle \omega \rangle \exp \left( \frac{1}{(\lambda^2 - \mu^2)} \right)
\]

where

\[
\lambda = \frac{\lambda_e}{1 - \lambda_e} = \frac{\eta}{M} \langle \omega \rangle^2,
\]

it was believed until recently that in order to obtain a high \( T_c \) one had to soften the phonon spectrum, i.e. decrease \( \langle \omega^2 \rangle \). These ideas have been revised recently [8], as it has been demonstrated that McMillan’s formula is not valid for too large a value of \( \lambda \) and more exact calculations show that if phonons are added over a small energy range, \( T_c \) is always increased and that high energy phonons can increase \( T_c \) as effectively as low energy ones. This means that the

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high energy optical phonons may considerably enhance $T_c$.

Compounds like Pd-H and Th$_4$H$_{15}$ are particularly interesting in this respect because the great mass difference between the heavy ion (mass $M$) and the light ion (mass $m$, with $M/m \approx 100$) should give an optical branch well separated from the acoustical one. The optical branch is then dominated by the motion of the light ions and the acoustic branch by the motion of the heavy ones. Studies using D instead of H should also give sensitive tests of mass effects and anharmonic forces in the crystal lattice.

The object of this work is to show, using a simple model, how the relative contributions of the acoustic and optical phonons depend on the magnitude of the nearest and next nearest neighbour force constants in the crystal lattice. The model, an extension of that used by Rietschel [9], considers the conduction electrons as free and takes an isotropic phonon spectrum, whose dispersion curve is that for the longitudinal modes of a linear chain of alternate light and heavy atoms, with nearest and next nearest neighbour interactions. The lack of generality in the model is compensated for by the relative simplicity of the final formula so that the variation of $\lambda$ with the physical parameters can be easily followed. As we are primarily interested in the relative contributions of the optical and acoustic modes, the various amplitudes of the quantities leading to the McMillan $\lambda$ are calculated in arbitrary units but as a check a simple case was calculated to show that it gave a sensible answer.

2. The phonon dispersion relations. — For a linear chain of alternate light ($m$) and heavy ($M$) ions spaced a distance $d$ apart with a nearest neighbour ($m-M$) force constant of $a_1$ and next nearest neighbour force constants of $a_2$ for the $m-m$ interaction and $a_3$ for the $M-M$ interaction, the dispersion relation is given by:

$$\omega_q^2 = [2 \alpha_1(m + M) + (2m\alpha_3 + 2 \alpha_2 M)(1 - \cos 2qd)]/2mM$$

where $A^2$ can be shown to be equal to:

$$A^2 = [2 \alpha_1(M - m) + 2(1 - \cos 2qd)(\alpha_2 M - \alpha_3 m)]^2 + 16 \alpha_3^2 mM \cos^2 qd.$$  (2)

Then the relative amplitudes of the two ionic vibrations are given by

$$A_M/A_m = 2 \alpha_1 \cos qd (-Mo\omega_q^2 + 2\alpha_1 + 2\alpha_3(1 - \cos 2qd))$$

$$= (-Mo \omega_q^2 + 2\alpha_1 + 2\alpha_3(1 - \cos 2qd))/2 \alpha_1 \cos qd.$$  (3)

The values of $\alpha_1$, $\alpha_2$ and $\alpha_3$ are chosen to be representative of those expected for Pd-H by using the results of Rowe et al. [10] for neutron diffraction in the [111] direction which is effectively a sequence of Pd and H planes, i.e. they are determined from the conditions that the maximum acoustic frequency $\theta_{ac}$ is 210 K and that the optical frequency starts at 600 K and becomes 1000 K at the zone boundary. This gives $\alpha_1/\alpha_3 = 0.18$ and $\alpha_2/\alpha_3 = 0.16$ (we always take $M/m = 100$). The results are easily particularised to nearest neighbour interactions by letting $\alpha_2$ and $\alpha_3$ go to zero. This is the case treated by Rietschel and perfect agreement with his formulae is obtained ($\alpha_1$ is then determined from the condition that $\theta_{ac} = 210$ K).

3. Calculation of $\lambda$. — Most superconductors with high $T_c$ are compounds with two (or more) different atoms per unit cell. The electron-phonon interaction must then take into account the interference scattering of an electron from the two (or more) ions. This was done for the first time in a consistent way by Rietschel [9]. The superconducting interaction parameter $\lambda$ takes then the following form

$$\lambda = 1 \frac{\int q^2 \omega_q^4 w_0^2 \frac{W(q)}{d} dq}{4 \pi^2 hV_F N}$$

where $w_0$ are the phonon frequencies of wave vector $q$, $U_M(q)$ and $U_m(q)$ the Fourier transforms of the respective ion potentials, $N$ the number of unit cells per unit volume, $V_F$ the Fermi velocity and $e_M$ and $e_m$ are normalized vibrational amplitudes such that

$$e_M^2 + e_m^2 = 1$$

$$\frac{e_M^2}{e_m^2} = \frac{MA_M^2}{MA_m^2}.$$  (4)

In further simplifying the problem, we only consider longitudinal phonons, neglect all umklapp processes and suppose that the $U(q)$ are $q$ independent. Although there restrictions may seriously affect $\lambda$, their influence on the ratio of the contributions of the two different modes is probably small. For want of better information, we are also finally forced to put $U_m = U_M$. For the numerical applications $\lambda$ can be calculated in two ways. Firstly, it can be put in the form

$$\lambda = \frac{1}{4 \pi^2 hV_F N} (a_M U_M^2 + a_m U_m^2 + 2 a_{Mm} U_M U_m).$$  (5)

One can show on general grounds [9] that the coefficients $a_M$, $a_m$, $a_{Mm}$ do not depend on the masses $M$ and $m$ but only on the force constants and that the same is true for $\lambda$. The values of $a_M$, $a_m$ and $a_{Mm}$ are given in appendix A for our case. One can see that they increase when $\alpha_1$, $\alpha_2$, $\alpha_3$ decrease : this is perfectly in line with the well known increase of $\lambda$ when the...
phonons get softer. For instance, the H-H interactions which broaden the optical phonons branch are unfavourable to superconductivity.

The appearance of the interference term \( M_{mm} \) which is due to the simultaneous motion of both ions in each mode, precludes at first sight the separation of the contributions due to the heavy and light ions. One can nevertheless decompose \( \lambda \) into contributions from the optical and acoustic modes and write:

\[
W(q) = W(q, \text{ac}) + W(q, \text{op})
\]

with

\[
\begin{align*}
W_{\text{ac}}(q) &= \frac{e_M^2(q, \text{ac})}{M_0\omega_0^2(\text{ac})} \left[ 1 + \frac{U_m A_m(q, \text{ac})}{U_M A_M(q, \text{ac})} \right]^2 q^3 \\
W_{\text{op}}(q) &= \frac{e_m^2(q, \text{op})}{m_0^2\omega_0^2(\text{op})} \left[ 1 + \frac{U_m A_m(q, \text{op})}{U_M A_M(q, \text{op})} \right]^2 q^3
\end{align*}
\]

\([M_0\omega_0^2(\text{ac})]^{-1} \text{ and } [m_0^2\omega_0^2(\text{op})]^{-1} \text{ depend on both masses (see equations (1) and (2)) as do also the other quantities appearing in equation (6) like } e_M, e_m \text{ and the ratio } A_M/A_m.\]

Although, as stressed by Rietschel, this does not allow a decomposition of \( \lambda \) into contributions by the heavy and light ions, numerical results show the decomposition is effectively made for \( M/m \sim 100 \) as \( \lambda_{\text{ac}} \) and \( \lambda_{\text{op}} \) then depend only on \( \alpha_1, \alpha_2, \alpha_3 \) to a very good precision. For instance, one finds \( \lambda_{\text{op}} \) (Deuterium) \( \approx 0.995 \lambda_{\text{op}} \) (Hydrogen). This is due to the fact that

\[
M_{\text{ef}}(\text{ac}) = M + m \quad \text{and } 1/M_{\text{ef}}(\text{op}) = 1/M + 1/m,
\]

while

\[
|A_M/A_m| < V/M
\]

for the optical mode and for the acoustic mode \( |A_M/A_M| \) varies between 1 and zero as \( q \) goes from zero to \( \pi/2d \), independently of the masses. This means that one can to a good approximation write

\[
\lambda_{\text{ac}} = \eta_{\text{ac}} M / \langle \omega_{\text{ac}}^2 \rangle \quad \text{and } \lambda_{\text{op}} = \eta_{\text{op}} m / \langle \omega_{\text{op}}^2 \rangle
\]

with \( M / \langle \omega_{\text{ac}}^2 \rangle \) and \( m / \langle \omega_{\text{op}}^2 \rangle \) independent of \( M \) and \( m \), while \( \eta \) specially \( \eta_{\text{ac}} \) contains an interference term depending on \( U_M/U_m \).

4. Results for nearest neighbour forces only. — For these results we let \( \alpha_2 \) and \( \alpha_3 \) go to zero in the expressions previously calculated and determined \( \alpha_1 \) from the condition \( \Omega_M = 210 \text{ K. } \)

Figure 1 shows the calculated values of \( W(q, \text{ac}) \) and \( W(q, \text{op}) \) taking \( U_M = U_m \). \( W^0(q, \text{ac}) \) is the value \( W(q, \text{ac}) \) would have if the light ion remains stationary, i.e. without the interference factor in eq. (6). Two things are immediately apparent, firstly that \( W(q, \text{ac}) \) is strongly enhanced by the interference term, in fact \( \lambda(\text{ac}) \approx 2 \lambda(\text{ac}) \) and secondly that, \( W(q, \text{op}) < W(q, \text{ac}) \), \( \lambda(\text{op}) \approx 0.4 \lambda(\text{ac}) \). It is a priori very surprising that the presence of the light ions affects \( \lambda \) more strongly through the acoustic than the optic mode but this is of course related to the in phase motion of the heavy and light ions for the acoustical modes.

5. Results for nearest neighbour and next nearest neighbour forces. — We use the values of \( \alpha_1, \alpha_2, \alpha_3 \) previously derived which fit the neutron results in the [111] direction. Figure 2 shows the values of \( W(q, \text{op}) \), \( W(q, \text{ac}) \) and \( W^0(q, \text{ac}) \) for this case; they are very different from the previous figure and give \( \lambda_0 \approx 2.5 \lambda_{\text{ac}} \) and \( \lambda_{\text{op}} \approx 1.5 \lambda_{\text{ac}} \). In figure 3 we put \( \alpha_2 = 0 \) maintaining the values of \( \alpha_1 \) and \( \alpha_3 \), i.e. we look for the influence of H-H interactions on \( \lambda \); one can see that \( \lambda_{\text{op}} \) is now considerably enhanced and that \( \lambda_{\text{op}} \approx 4.4 \lambda_{\text{ac}} \). The main result of both figures is that the optical contribution to \( \lambda \) dominates the acoustical one and this is probably the major reason for superconductivity in Pd-H. Another argument in this direction is the absence of superconductivity in pure Ag which is very similar to Pd-H concerning the nature and number of conduction electrons; it is tempting to account for the difference in superconducting \( T_c \) to the lack of an optical mode in Ag.

One must now realize that \( \lambda_{\text{op}} \) becomes higher than \( \lambda_{\text{ac}} \) only because of the exceedingly low value of \( \omega_{\text{op}} \) which satisfies the condition \( m \omega_{\text{op}}^2 \ll M \omega_{\text{ac}}^2 \) (in figure 1 one has \( m \omega_{\text{op}}^2 \approx M \omega_{\text{ac}}^2 \)); this in turn stems from the relations \( \alpha_1 \sim \alpha_2 \ll \alpha_3 \) which tells us that
Experimental results [4] on normal state resistivity show that $\lambda_{\text{op}} \approx 3 \lambda_{\text{ac}}$ for Pd-H in rough agreement with this model. More detailed calculations [11] arrive at similar conclusions.

Less experimental information is available for the thorium hydride but the fact that there are approximately four hydrogen atoms for each thorium atom may give $\lambda_{\text{op}} \sim \lambda_{\text{ac}}$ even if $m \sigma_{\text{ac}}(\text{op})$ is not smaller than $M \sigma_{\text{ac}}(\text{ac})$ [12].

6. Isotope effect. — It is observed [1] that $T_c$ for Pd-D is about 2 K higher than for Pd-H (a positive isotope effect) while no isotope effect is found for the thorium hydride. As $T_c$ should decrease with mass, the absence of an isotope effect can be taken as an indication of a positive one. To understand these effects, we need first an expression for $T_c$ including the acoustical and optical contributions to $\lambda$. We adapt to our situation an expression of $T_c$ derived in reference [13] for the case where two different attractive electron-electron interaction contribute to $T_c$. This gives us:

$$T_c = \theta_{\text{ac}} \exp \frac{1}{g}$$

$$g = \frac{\lambda_{\text{op}}^x - \mu_{\text{op}}^x}{1 - (\lambda_{\text{op}}^x - \mu_{\text{op}}^x) \ln \frac{\theta_{\text{op}}}{\theta_{\text{ac}}}}.$$  \hspace{1cm} (7)

This formula tends to the McMillan one in the limit $\lambda_{\text{op}} \to 0$ or $\lambda_{\text{ac}} \to 0$ and has probably the same domain of validity : all the $\lambda$'s for Pd-H and Th$_4$H$_{15}$ being smaller than one, we may apply it with some confidence.

We can look for the terms which depend on the light mass $m$ in formula (7). We know that $\lambda = \lambda_{\text{ac}} + \lambda_{\text{op}}$ does not depend on $m$ but $\lambda_{\text{op}}$ and $\lambda_{\text{ac}}$ separately may do so : this dependence has been found to be very small, i.e. $\lambda_{\text{op}}(\text{H}) \approx 0.995 \lambda_{\text{op}}(\text{D})$ and cannot explain the observed $\Delta T_c$ (the same is true also for $\theta_{\text{ac}}$). The only terms which depend directly on $m$ or $\omega_{\text{op}}$ are:

$$\mu_{\text{op}} = \frac{\mu}{1 + \mu \ln \frac{E_F}{\hbar \omega_{\text{op}}}}$$

and the logarithm in the expression of $g$.

Differentiating equation (7) with respect to $\omega_{\text{op}}$, we obtain (see also reference [14]):

$$\frac{\Delta T_c}{T_c} = \left(\frac{\Delta \omega_{\text{op}}}{\omega_{\text{op}}}ight) \left(\frac{\mu_{\text{op}}}{\lambda_{\text{op}}^x} - 2 \frac{\lambda_{\text{op}}^x}{\lambda_{\text{op}}^x - \mu_{\text{op}}^x} \Delta \omega_{\text{op}} \right).$$

Here

$$\Delta T_c = T_c(D) - T_c(H), \quad \Delta \omega_{\text{op}} = \omega_{\text{op}}(D) - \omega_{\text{op}}(H).$$
\[ \Delta T_c/T_c \text{ will be positive only if } \lambda_{\text{op}}^x < 2 \mu_{\text{op}}^x \text{ (because } \Delta \omega_{\text{op}}/\omega_{\text{op}} < 0) \text{ and its maximum value is} \]
\[ \left[ \frac{\mu_{\text{op}}^x}{g} \right]^2 \frac{\Delta \omega_{\text{op}}}{\omega_{\text{op}}} \text{ when } \lambda_{\text{op}}^x = \mu_{\text{op}}^x. \]

If we take \( \theta_{\text{ac}} \sim 210 \text{ K}, g = 0.324 \) (for \( T_c \approx 9.6 \text{ K} \)) we get
\[ \Delta T_c \approx 0.3 \text{ K for } \lambda_{\text{op}}^x = \mu_{\text{op}}^x = 0.1. \]

This increase of \( T_c \) is much too small and one must take \( \mu^x > 0.2 \), an unusually high value, to fit the experimental \( \Delta T_c \). All these values imply that \( \lambda_{\text{op}} < \lambda_{\text{ac}} \) while some experiments [4] and the present model (see also reference [11]) give \( \lambda_{\text{op}} > \lambda_{\text{ac}} \). But, if we take \( \lambda_{\text{op}} \approx 2-3 \) times \( \lambda_{\text{ac}} \), one obtains a negative value of \( \Delta T_c/T_c \) in direct contradiction with experiment. This contradiction may be solved if we look for another source of isotope effect not contained in formula (7). Anharmonicity for instance may be involved: the H ion has a higher zero point motion, its larger vibration amplitude means it will sense any anharmonic force more strongly than the D ion and this can lead to different values of \( \alpha \) for H and D. This hypothesis first proposed in reference [14] has some experimental basis [10, 15].

The following change in \( T_c \) can then be calculated:

\[ \left( \frac{\Delta T_c}{T_c} \right)_2 = \left[ g - \frac{\lambda_{\text{op}}^x}{g} \right] \frac{\lambda_{\text{op}}^x (1 - \lambda_{\text{ac}}^x)}{(\lambda_{\text{op}}^x - \mu_{\text{op}}^x)^2} |\Delta f/|f| \text{ (9)} \]

\( f = m \langle \omega_{\text{op}}^x \rangle \approx \alpha_x \).

A positive \( \Delta T_c \) can be obtained only if \( \Delta f/|f| < 0 \); this may result from an even order anharmonicity in the nearest neighbour Pd-H ion-ion interaction potential, the H ion vibrating to a first approximation in the symmetric potential of its neighbouring Pd atoms. Numerically, if we take \( \mu^x = 0.1, \lambda_{\text{op}}^x = 0.38, \lambda_{\text{ac}}^x = 0.13 \) (this gives again \( g = 0.324 \)), we get a total \( \Delta T_c = (\Delta T_c)_1 + (\Delta T_c)_2 \approx + 1.8 \text{ K for } |\Delta f/|f| = 0.1. \text{ This is not an unreasonable value in our mind, meaning a } 5\% \text{ shift i.e.} \]

\[ \omega_{\text{op}}(D) = \frac{0.95}{\sqrt{2}} \omega_{\text{op}}(H) \]

in the optical mode D compared to H. Let us remark also at this stage that \( \Delta T_c \) is smaller in the Pd-Ag-H(D) alloys, which have a higher [1] \( T_c \) : the more asymmetric neighbourhood of the H ions may here decrease \( \Delta f/|f| \) through odd order anharmonicity. Another explanation can also be proposed as is indicated on figure 4: the total \( \Delta T_c \) depends strongly on \( \lambda_{\text{op}}^x \) and a change of sign for \( \Delta T_c \) is expected for higher \( \lambda_{\text{op}}^x \) (\( (\Delta T_c)_1 \)) finally dominating over (\( (\Delta T_c)_2 \)). This can be true only if part of the increase of \( T_c \) in the alloys comes from an increase in \( \lambda_{\text{op}}^x \). It is difficult without further knowledge of the changes with alloying of the various electronic and atomic parameters involved in \( T_c \) to pinpoint the decisive factors leading to this increase of \( T_c \). Several properties [16, 17] of the palladium + hydrogen system (i.e. binding energy of the hydrogen atoms, position of the \( \alpha \rightarrow \beta \) phase diagram) change with alloying indicating that variation of \( \alpha_x \) and \( \alpha_2 \) may be involved but for reliable quantitative estimation to be done one needs more results concerning the phonon dispersion curve of the alloys [18].

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Appendix A.—The calculation of \( \lambda \) needs the determination of the quantity \[ \left[ \frac{e_m U_M + e_m U_m}{\sqrt{M}} \right]^2. \]
We consider only the case \( U_m = U_M \). The coefficient \( a_m \) is then given by

\[ \int \frac{1}{M} \left( \frac{e_m^2(\text{ac})}{\omega_m^2(\text{ac})} + \frac{e_m^2(\text{op})}{\omega_m^2(\text{op})} \right) q^3 dq. \]
This can be evaluated using relations (1), (2) and (3). The results are:

\[ a_M = \frac{a_1 + \alpha_2 (1 - \cos 2qd)}{\alpha_2^2 (1 - \cos 2qd) F(\alpha_1, \alpha_2, \alpha_3)} \cdot q^3 dq \]

\[ a_m = \frac{a_1 + \alpha_2 (1 - \cos 2qd)}{\alpha_2^2 (1 - \cos 2qd) F(\alpha_1, \alpha_2, \alpha_3)} \cdot q^3 dq \]

\[ a_{mM} = \int_0^{\pi/2} \frac{x_1 \cos qd}{\alpha_2^2 (1 - \cos 2qd) F(\alpha_1, \alpha_2, \alpha_3)} \cdot q^3 dq \]

\[ F(\alpha_1, \alpha_2, \alpha_3) = 1 + \frac{2(\alpha_2 + \alpha_3)}{\alpha_1} + \frac{2 \alpha_2 \alpha_3}{\alpha_1^2} (1 - \cos 2qd) \]

All these coefficients \(a_M\), \(a_m\) and \(a_{mM}\) do not depend on the masses \(m\) and \(M\).

References

[15] A recent work (to be published) by Skold, K., Rahman, A., Pelezzi, C., Sinka, S., Flatow, H., shows indeed large anharmonicity effects in the phonon spectrum of Pd-H0.63 compared to Pd-D0.63.