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ON THE INVERSE ISOTOPE EFFECT IN SUPERCONDUCTING (Zr-Hf) - (H,D) SYSTEMS

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Strongly enhanced superconducting transition temperatures T_c compared to the pure metal ones $T_c^{(0)} \lesssim 0.1 - 0.6$ K have been observed in recent H and D ion-implantation experiments on Ti, Zr, and Hf foils[1,2]. In addition to the T_c -enhancement in $ZrH_x(D_x)$ and $HfH_x(D_x)$ a remarkable inverse isotope effect (IIE) was found, i.e., $T_c^H = T_c(MH_x) < T_c^D = T_c(MD_x)$; M = Zr, Hf. Contrarily, no (zero) isotope effect (ZIE), i.e., $T_c^H \approx T_c^D$ for the maximal T_c-enhancement concentration range $x \approx 0.13$ and a slightly normal isotope effect (NIE), i.e., $T_c^H > T_c^D$ at lower concentrations, were found for the $TiH_x(D_x)$ system.

To our knowledge there is no satisfactory explanation for these effects at present. The standard mechanisms based on the essential influence of high frequency (H,D) optical phonons, which have been discussed in connection with the IIE for the well-known $PdH_x(D_x)$ system, (namely the mass dependences of the electron-optical phonon interaction[3,4,5] can be ruled out for the systems under consideration. The main reason for this is the weakness of the electron-optical phonon (H,D) interaction caused by the small value of the expected H,D-Hopfield parameter $\eta_{H,D} \ll \eta_{Zr}$. This is due to the Fermi energy falls probably in the region of d-bands, which leads to small partial densities of states with s and p symmetry compared with the d one (compare with the numerical results obtained for similar systems[8]). Furthermore, the number of available optical (H,D)-phonon modes $\approx 10^{-1}$ is also small and the optical force constants $f = M_{H,D}\langle\omega^2\rangle$ are very large. Hence, $\lambda^{H,D}_{opt} \ll \lambda^{H,D}_{opt}(PdH(D)) \sim 0.5$.

If one nevertheless assumes considerable strength of the electron-optical phonon interaction λ_{opt}, serious difficulties appear. In inelastic neutron scattering experiments for $ZrH_x(D_x)$ a "negative" anharmonicity $(M_H\langle\omega^2\rangle_H(1+\beta_A) = M_D\langle\omega^2\rangle_D$, $\beta_A \approx -0.08)$, which would lead to $\lambda^H_{opt} \approx (1. + 0.08)\lambda^D_{opt})$ was observed[9]. In the case of PdH(D) it can be shown that the other mechanisms which support the IIE like the appearance of the Debye-Waller factor in the matrix element of the electron-optical phonon interaction or the difference in the screening of the H,D potentials[10] are $3 \div 10$ times as less as $|\beta_A|$[7]. Therefore, they cannot cancel the effect caused by the anharmonicity of the force constants. Although the absence of any isotope effect for the pure Zr indicates strong electron-electron interaction, our attempts to describe the IIE on the basis of the Berk-Schrieffer equations at reasonable electron-electron pseudo-potentials fail; it was impossible to overcome the mentioned "negative" anharmonicity.

Thus, on the basis of two independent considerations any essential direct influence of high-frequency modes can be excluded. Therefore, we consider the influence of some hypothetical low-frequency local modes (of tunnelling or resonance types). For the metastable α- (hcp) systems under consideration it is known that the H(D) ions move in an anharmonic potential which in a particular case may take the form of a double (or many) well potential (compare[11]). Furthermore, rich tunnelling phenomena for H and D in various solids are reported (see, e.g., [12,13])

To get some insight into the influence of such a low-lying local mode on the superconductivity and especially the isotope effect for T_c, we consider a simple model. It describes the tunnelling of the H(D) ions between equivalent minima in the potential of the form

$$V(x) = \frac{1}{2} f(x \mp \ell) \qquad \text{for} \quad x \gtrless 0, \tag{1}$$

where the force constant $f = M\omega_0^2$ can be evaluated by the H(D) local vabration frequency: $\hbar\omega_0(ZrH_x) \approx 140$ meV. Thus, we get a two-level system (TLS) which has been used for the description of superconductors with structural unstable lattices[14,15] and superconducting metallic glasses[1,16]. In contrast with metallic glasses in the simplest approximation the tunnelling matrix elements are assumed to be identical for all tunnelling centers.

In our case the concentration of the TLS c is assumed to be identical with the H,D-concentration. This value is then of an order of 10^{-2}-10^{-1}. Thus, c greatly exceeds the value usually accepted for glasses $c_{gl} \sim 10^{-5}$. Hence, the electron-TLS coupling constant λ_{TLS} can also greatly enhanced, that can easily explain the T_c-enhancement[17,18] and the observed IIE (see below).

In order to calculate the T_c-enhancement we need the Eliashberg function $S(\omega)$ which now consists of two terms, namely the convenient phonon spectral density $S_{ph}(\omega)$ and the spectral density of the TLS $S_{TLS}(\omega)$[15] which leads to

$$\lambda = \lambda_{ph} + \lambda_{TLS}\,, \tag{2}$$

where λ_{ph} is in our case given by the standard relation

$$\lambda_{ph} = \eta_{Zr}/(M_{Zr}\langle\omega^2\rangle_{Zr}) = N\,|\nabla U_{Zr}|^2/(M_{Zr}\langle\omega^2\rangle_{Zr}) \tag{3}$$

λ_{TLS} is determined by an analogous expression[15]:

$$\lambda_{TLS} = N_F\langle J_s^2\rangle\chi_s(0) = N_F|\nabla U_{H,D}|^2(2x_{sa})^2\, c\,\langle S_z\rangle/\Delta_0, \tag{4}$$

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where Δ_0, is the tunnelling energy which results from the overlap of the "left" state ψ_L into the "right" well and vice versa:

$$\Delta_0^{H,D} = \int_{-\infty}^{\infty} \psi_L \hat{H} \psi_R \, dx = \frac{\hbar\omega_0^{H,D}}{2} \exp\left[-\frac{M_{H,D}\,\omega_0^{H,D}\,\ell^2}{\hbar}\right] \qquad (5)$$

and $x_{sa} = \langle \psi_s | x | \psi_a \rangle \simeq \ell$ is the matrix element between the symmetrical ψ_s and antisymmetrical ψ_a states constructed by using the functions ψ_L and ψ_R. The mass dependence of the exponential function in (5) $\propto \sqrt{M}\,(2\ell)^2$ (2ℓ being the distance between the two potential minima) is quite general (compare, e.g., the expression used by Wipf and Neumaier /12/ for a sinusoidal potential). This strong inverse isotope dependence for the tunnelling energy $\Delta_0 \sim \exp(-\sqrt{M}\ \mathrm{const})$ leads to a very strong inverse isotope effect for the T_c enhancement provided that $\Delta_0 > 2\pi T_c^{(0)}$.

According to the experimental data for $ZrH_x(D_x)$ /9/ we take $\hbar\omega_0^H \approx 140$ meV and set approximately $\omega_0^D \simeq \omega_0^H/\sqrt{2}$. Then, from (1) and (5) one obtains, e.g., for $\ell = 0.3$ Å, $\Delta_0^H = 38$ K and $\Delta_0^D = 7.6$ K. Using (4) we have $\lambda_{TLS}^D \approx \lambda_{TLS}^H$ which indicates a strong IIE, provided λ_{TLS} is not too small compared with λ_{ph}. According to (3) and (4) the ratio $\lambda_{TLS}/\lambda_{ph}$ can be estimated by

$$\lambda_{TLS}/\lambda_{ph} \approx 2cM_{Zr} \langle\omega^2\rangle_{Zr}\, \ell^2 \eta_{opt} \tanh(\Delta_0/2T_c)/(\eta_{Zr}\,\Delta_0). \qquad (6)$$

Using $\langle\omega^2\rangle_{Zr} \approx 0.5\omega_{D,Zr}^2$, $\omega_{D,Zr} \approx 250$–$300$ L and as a crude estimate $\eta_{opt}/\eta_{Zr} \sim 10^{-2}$ (see e.g. $3.74 \cdot 10^{-2}$ for ZrH_2 one obtains $\lambda_{TLS}^D \sim (20 \div 40)\ c\ \lambda_{ph}^{Zr}$. The value of λ_{ph}^{Zr} is expected to be somewhat enhanced compared with that for the pure metal (≈ 0.34 – 0.41 due to the disorder resulting from the implantation process. Thus, taking $c \sim 10^{-1}$ we found the values $\lambda_{TLS}^D \sim 1 \div 2$ and $\lambda_{TLS}^H \sim 0.2 \div 0.4$ which can easily explain the observed T_c-enhancement and the IIE for $ZrH_x(D_x)$ ($T_c^D = 4.65$ K and $T_c^H = 3.14$ K).

We think that the same feature holds in the case of Hf. In Ti, H and D probably occupy different interstitial positions (T- and O-sites) with different potentials too /9/. Thus, the case of $TiH_x(D_x)$ is more complicated and needs special investigations.

In order to check our estimates by treating $S_{TLS}(\omega)$ as a perturbation to $S_{ph}(\omega)$ by means of the functional derivative $\sigma(\omega) \equiv \delta T_c/\delta S_{ph}(\omega)$ /19/ we calculate the T_c-enhancement $\Delta T_c \equiv T_c - T_c^{(0)}$

$$\Delta T_c = \int_0^{\infty} \sigma(\omega) S_{TLS}(\omega)\, d\omega = \frac{\lambda_{TLS}\Delta_0}{2}\sigma(\Delta_0). \qquad (7)$$

It is well known that the shape of $\sigma(\omega/T_c^{(0)})$ is nearly an universal function and its magnitude is scaled by the factor $1/(1+\lambda)$ /21/. Therefore, one can use the curve obtained for Al($\lambda_{ph}^{Zr} \approx \lambda_{ph}^{Al} \approx 0.37$). Thus, we have $\Delta_0^D/T_c^{(0)} \approx 12.7$, $\Delta_0^H/T_c^{0} \approx 63.3$ and $\sigma^D \equiv \sigma(\Delta_0^D) \approx 0.6$ $\sigma^H \equiv \sigma(\Delta_0^H) \approx 0.35$. In the case of low concentration, one can rewrite formula (7)

$$\Delta T_c^{H,D} = \mathrm{const}\ c\ \sigma^{H,D}, \quad \sigma^D > \sigma^H \qquad (8)$$

in qualitative agreement with the experimental curves /21/ From those curves and (7-8) we extract $\lambda_{TLS}^D \approx 16.3$ c and $\lambda_{TLS}^H \approx 3.7$ c in good agreement with the estimates given above.

At higher concentration $c \gtrsim 0.1$–0.2 deviations from the linear c-low and finally a saturation (Zr) or a weak maximum were observed in the experiments. We think that these effects partially are due to the TLS-TLS interaction neglected so far in the expression for the tunnelling energy Δ_0. The latter should be shifted to higher values, $\Delta(c) > \Delta_0$ due to this interaction /15/.

In connection with the proposed mode experiments with tritium (T) would be of great interest. The tunnelling energy for T should be smaller compared with the deuterium one. Thus, Δ_0^T probably could be smaller than $2\pi T_c^{(0)}$, the optimal value for the T_c-enhancement. Then, for ZrT_x a normal or zero isotope effect compared to the D system is likely to occur. Furthermore, for these systems considerable strong-coupling deviations from the BCS theory for the thermodynamics properties should be expected.

To summarize, the IIE and T_c-enhancement of the systems under consideration can be qualitatively explained if a low-lying tunnelling mode is assumed. The presence of such a mode could be observed by excess specific heat at temperatures $\sim 0.5\ \Delta_0$ or by inelastic slow neutron scattering experiments.

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Дрекслер Ш.Л., Вуйчис Г.М., Плакида Н.М. E17-84-477
Об аномальном изотопическом эффекте в сверхпроводящих системах (Zr,Hf)-(H,D)

Дано качественное объяснение аномальному изотопическому эффекту и порядку величины повышения критической температуры T_c с возрастающей концентрацией H(D) в сверхпроводящих системах (Zr,Hf)-(H,D) на основе предположения о существовании в них низколежащих локальных возбуждений двухуровневого типа.

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Drechsler S.L., Vujičić G.M., Plakida N.M. E17-84-477
On the Inverse Isotope Effect in Superconducting (Zr-Hf) - (H,D) Systems

Asuuming the presence of low-lying local excitations of the two-level (TLS)-type in superconducting (Zr,Hf)-(H,D) systems, the inverse isotope effect for the critical temperature T_c and the amount of the T_c-enhancement with increasing H(D) concentrations is qualitatively explained.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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