Defecton Contribution to the High-Temperature Superconductivity of Hydrides

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Abstract—Formation of high-temperature superconducting phases of some hydrides requires high pressure (several hundred gigapascals), which causes lattice compression and, correspondingly, exponential increase in the probability of hydrogen-atom tunneling between equivalent interstitial sites. At low temperatures, vacancies in the hydrogen sublattice (occupied under stoichiometric conditions) and hydrogen atoms in the interstitial sublattice (absolutely vacant under stoichiometric conditions) are quantum defects (defectons). The defecton contribution to the superconductivity of hydrides has been estimated. It is shown that this contribution can be large both for free defectons and defectons clusterized with formation of two-level systems.

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1. INTRODUCTION

The experimental observation of high-temperature superconductivity in H₃S compound (with critical temperature $T_c$ exceeding 200 K [1]) at a pressure of 155 GPa induced great interest in superconductivity of hydrides. The existence of a number of high-temperature superconducting hydrides at pressures of several hundred GPa was predicted on the basis of computer simulation [2]. The electron–phonon mechanism underlay the theoretical description of the superconductivity of hydrides [3–6].

Hydrogen isotopes in a metal matrix are almost only (except for helium) atoms, the quantum tunneling of which between equivalent interstitial sites can be observed experimentally. From here on, these quantum defects are referred to as defectons.

Basic problems of quantum diffusion were addressed in the pioneering work [7], where it was noted that a quantum defect in an ideal crystal is delocalized at low temperatures and described by the Bloch wave function. Defectons in metals and their contribution to the superconductivity were considered for the first time in detail in [8].

The purpose of this study was to estimate the tunnel matrix element of a hydrogen atom in highly compressed high-temperature superconducting hydrides and the contribution from the electron–defecton interaction to the superconductivity.

2. DEFECTONS IN A METAL HYDRIDE

Let us consider a close-to-stoichiometry metal hydride MeHₓ. There are no quantum defects under the stoichiometric conditions and at zero temperature; however, Frenkel pairs of quantum defects (a vacancy in the hydrogen sublattice, which was completely occupied in the ground state, and a hydrogen atom in the interstitial sublattice, which was vacant in the ground state) occur upon heating. If the hydrogen concentration is higher (lower) than the stoichiometric, hydrogen atoms (vacancies) exist in the aforementioned sublattices even at zero temperature. Specifically this case (with the defecton concentration assumed to be temperature-independent) will be under consideration.

Since high pressure, which is necessary for the formation of high-temperature superconducting phases, shortens the interstitial spacing (on which tunnel matrix element $t$ of a defecton depends exponentially), a large $t$ value may be expected at high pressures. It can be estimated using the following simple algorithm.

Hereinafter, we assume that the hydrogen atom is at the ground vibrational level in a potential well, which is an interstitial site in the metal matrix (for hydrogen). This level generates a defecton band due to the atomic tunneling between equivalent interstitial sites. The value of the tunnel matrix element can be estimated as

$$t(a) = \frac{\text{Ry}}{\int_{-\infty}^{+\infty} \psi_0(x-a/2)\psi_0(x+a/2) dx},$$

where Ry is the Rydberg energy of 13.6 eV and $a$ is the dimensionless distance between the hydrogen-
atom equilibrium positions at neighboring interstitial sites,
\[ a = d \sqrt{\frac{m \Omega}{\hbar}}, \quad (2) \]
where \( d \) is the distance between the equilibrium positions, \( m \) is the hydrogen atomic mass, and \( \omega \) is the characteristic frequency of optical or local vibrations of this atom. The wave function \( \psi_{0}(x) \) of the harmonic-oscillator ground state can be written as
\[ \psi_{0}(x) = \frac{1}{\sqrt{\pi}} \exp\left( -\frac{x^2}{2} \right). \quad (3) \]
It can easily be seen that
\[ t(a) = \text{Ry} \exp\left( -\frac{a^2}{4} \right). \quad (4) \]
Using the value \( \hbar \omega = 160 \text{ meV} \) for \( \omega \) (which was chosen based on the phonon spectra calculated in [6]), we obtain the \( t \) values listed in Table 1.

The numerical simulation carried out for a number of high-temperature superconducting hydrides shows that \( d \lesssim 1 \AA \) in many superconducting phases [9–11] (e.g., 0.841 Å in SnH\(_4\) [11]).

It should be noted that the defecton bandwidth \( \varepsilon \) exceeds \( t \) by a factor of \( 2\varepsilon \) (\( \varepsilon \) is the number of the nearest equivalent interstitial sites).

In a normal metal, the main contribution to the damping of defectons is from their scattering from electrons [8], while the phonon contribution to the damping of defectons is from their scattering from heavy interstitial impurities to \( 10^{-2} \text{ eV} \) for two hydrogen atoms in metal [20].

The characteristic time of defecton scattering from electrons \( \tau_{\varepsilon} \) is [8]
\[ \tau_{\varepsilon}^{-1} = \frac{4\pi g T}{\hbar} \left[ 1 + \exp\left( \frac{\Delta}{T} \right) \right], \quad (5) \]
where \( \Delta \) is the superconducting gap in the electronic excitation spectrum. In the normal phase,
\[ \tau_{\varepsilon}^{-1} = 2\pi g T/\hbar. \quad (6) \]
Parameter \( g \) equals to
\[ g = 2 \int \frac{d^2k}{(2\pi)^2} |V_{0}(k-k')|^2 \left| \nabla E(k)/\nabla E(k') \right|^2. \quad (7) \]
the integration is over the Fermi electron surface, \( E(k) \) is the electron dispersion relation, and \( V_{0}(q) \) is the seed amplitude of the electron scattering from a defect. Expressions (5) and (6) are valid at \( \max(\Delta, T) \gg \varepsilon \). In the normal phase at \( T < \varepsilon \), an additional factor \( T/\varepsilon \) arises in the right-hand side of expression (6) [12].

The above considerations were carried out on the assumption that the defecton motion exhibits a band character, which is valid if its energy is much higher than the \( \hbar \tau_{\varepsilon}^{-1} \) value. Upon heating, the defecton motion becomes hopping and cannot be consistently described.

When studying the electron–defecton interaction, one cannot restrict oneself to the Born approximation, because, as was observed by Kondo [13], the presence of a sharp edge of the electron Fermi occupation induces IR divergences. By analogy with the calculation of X-ray absorption and emission anomalies in metals [14–16], IR renormalizations of the defecton parameters were successively taken into account (the results were reported in [17]). However, the description of defectons runs into some other problems.

3. CLUSTERIZATION OF QUANTUM DEFECTS

The description of defectons is hindered by the fact that mobile defects in metal are clusterized with a decrease in temperature [18]. The clusterization is caused by the alternating character of the long-range interaction between point defects in metal. It is composed of elastic interaction \( W_{\text{elas}} \) and interaction through Friedel electron-density oscillations \( W_{\text{el}} \):
\[ W(R) = W_{\text{elas}}(R) + W_{\text{el}}(R), \quad (8) \]
where \( R \) is the radius vector connecting the defects.

The elastic interaction is determined as follows [19]:
\[ W_{\text{elas}}(R) = W_{f}(n) \frac{\Omega}{R^2}, \quad (9) \]
where \( \Omega \) is the unit-cell volume, \( n = R/R \), and \( W_{f}(n) \) takes positive or negative values, depending on the orientation of vector \( n \) with respect to the crystallographic axes. The \( W_{f}(n) \) value varies from 1 eV for heavy interstitial impurities to \( 10^{-2} \text{ eV} \) for two hydrogen atoms in metal [20].

The interaction through Friedel electron-density oscillations can be written for a spherical Fermi surface with radius \( k_{F} \) as follows [21]:
\[ W_{\text{el}}(R) = W_{2} \frac{\Omega}{R^2} \cos(2k_{F}R), \quad (10) \]
where \( W_{2} = \text{const} \sim 10^{-2} \text{ eV} \). It is as important as the elastic interaction and similarly decreases with an increase in the distance between defects.
The alternating character of $W(R)$ induces a number of bound states of two defectons or a defecton and a heavy “frozen” impurity. The highest binding energy $W_0$ corresponds to the case $R \sim d$. The short-range component of interaction between the defects can change the interaction-energy sign only for several of the smallest $R$ values. Therefore, all mobile point defects in metal (and neutral impurities in insulator) are clustered with a decrease in temperature [18, 22]. The characteristic clusterization temperature at low defecton concentrations $x \ll 1$ has the following order of magnitude:

$$T_{cl} \approx W_0 / [\ln x].$$

Clusterization often induces a metastable state with clusters of a finite number of particles instead of a large-scale stratification into phases with high and low hydrogen concentrations.

Clusters of light and heavy impurities arise in a crystal, in which the concentration of heavy “frozen” impurities is comparable with that of defectons. In some cases, the hydrogen atom occupies one of two equivalent (with respect to the binding energy with the heavy impurity) equilibrium positions at two neighboring interstitial sites. Due to its tunneling between them, a two-level system (TLS) arises. An example of TLS occurrence is the hydrogen capture by heavy impurities of oxygen, nitrogen, or carbon in niobium. The experimental value of the tunnel matrix element ($t \sim 90 \mu eV$ [23]) is only several times larger than the estimate $t \sim 27 \mu eV$ obtained from formula (4).

The mutual influence of TLSs violates the equivalence of two minima of the TLS potential relief and induces the Lorentzian distribution of the energy difference between these minima with width

$$\delta = \epsilon W_0$$

[24], where $c$ is the TLS concentration.

As the interaction with free defectons, the interaction of electrons with TLSs leads to the Cooper pairing and contributes to the superconductivity [25, 26].

4. CONTRIBUTION OF FREE DEFECTONS TO THE SUPERCONDUCTIVITY

The contribution of defectons (both free and TLSs) to the superconductivity was consistently described in [27] taking into account the IR renormalizations. This contribution is due to the inelastic scattering of electrons from defectons. The corresponding diagrams for the normal and anomalous self-energy parts of the electron Green’s function are shown in Fig. 1. If the superconducting gap is the same at all Fermi-surface points (we restrict ourselves to this case), the elastic scattering from defects does not affect the superconductivity. The general form of the Eliashberg equations [28] in the presence of electron–defecton interaction was given in [27].

On the assumption that the electron–defecton interaction makes the main contribution to the superconductivity and the critical temperature is $T_c \gg T_{cl}$ (this case was not considered in [27]), we have (by analogy with the considered case of TLS within the weak-coupling approximation ($\lambda_d \ll 1$)) the following expression:

$$T_c = \epsilon \exp \left( -\frac{1 + \lambda_d}{\lambda_d} \right),$$

(12)

where

$$\lambda_d \approx \frac{xe E_0}{\epsilon}$$

(13)

and $E_0$ is the characteristic width of the electron conduction band.

At the applicability limit, estimate (12) yields the maximum attainable (based on the defecton superconductivity mechanism) value of $T_c \sim \epsilon$. Specifically, this fact makes the defecton superconductivity mechanism significant in the high-pressure phases.

If the main contribution to the superconductivity is from the electron–phonon mechanism, at $T_{cl} \ll T \ll T_c$, small additive $\Delta_1$ caused by the electron–defecton interaction to the superconducting gap $\Delta_0$ in the electron-excitation spectrum equals to

$$\Delta_1 = \frac{xge E_0}{\Delta_0}$$

(14)
and may reach appreciable values. The defecton correction is about 6% at \( x \sim 0.01, g \sim 0.1, \Delta_0 \sim 200 \text{ K}, E_0 \sim 5 \times 10^4 \text{ K}, \) and \( \varepsilon \sim 50 \text{ K} \).

5. CONTRIBUTION OF TWO-LEVEL SYSTEMS TO THE SUPERCONDUCTIVITY

If TLSs make the main contribution to the superconducting pairing, the critical temperature of the superconducting transition (according to [27]) is determined by the following formula:

\[
T_c = t \exp \left( -\frac{1 + \lambda_d}{\lambda_d} \right), \tag{15}
\]

where

\[
\lambda_d = \frac{c g E_0}{\max(t, \delta)} \tag{16}
\]

At \( c > c_0 \approx t/W_0 \), a further increase in the TLS concentration does not increase \( \lambda_d \) and \( T_c \).

In the case where the TLS contribution supplements the electron–phonon superconductivity, we have at \( c < c_0 \) and \( T \ll T_c \)

\[
\Delta = \frac{c g t E_0}{\Delta_0} \tag{17}
\]

The defecton correction is about 1% at \( x \sim 0.01, g \sim 0.1, \Delta_0 \sim 200 \text{ K}, E_0 \sim 5 \times 10^4 \text{ K}, \) and \( t \sim 10 \text{ K} \).

6. CONCLUSIONS

(i) The use of pressures of several hundred gigapascals for the formation of high-temperature superconducting hydrides leads to the lattice compression and exponential increase in the matrix element that describes the hydrogen-atom tunneling between neighboring interstitial sites.

(ii) The band motion of quantum defects (defectons) may occur at low temperatures. Defectons are vacancies in the hydrogen sublattice (absolutely occupied at zero temperature under stoichiometric conditions) and hydrogen atoms in the interstitial sublattice (absolutely vacant under the same conditions).

(iii) Defectons are inevitably clusterized with a decrease in temperature. In some cases, this is accompanied by the formation of TLSs.

(iv) Both free defectons and TLSs contribute to the Cooper pairing of electrons, which may become a determining mechanism at wide defecton bands (large values of the tunnel matrix element of a TLS).

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