Pressure effect on Hg-12$(n − 1)n$ superconductors and Casimir effect in nanometer scale

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Abstract
A description is presented for the T_c pressure-dependent behaviour of
Hg-12$(n-1)n$ superconductors that takes into account the Casimir effect by
considering the CuO_2 conducting layers to act as plasma sheets. The Casimir
energy arises from the parallel plasma sheets (Cu–O planes) whenever these are
separated by distances on the nanometer scale. The T_c pressure dependence in
Hg-12$(n-1)n$ superconductors can be described by a pressure-induced charge
transfer together with intrinsic terms that are associated with the Casimir energy.
For Hg-12$(n-1)n$ samples with optimum oxygen content, the charge transfer
term vanishes, leaving an explicit expression for the intrinsic term. By picking
up realistic parameters and inserting them in the expression for the T_c pressure
dependence, we have a good agreement with experimental intrinsic term data
observed in the mercury family Hg-12$(n-1)n$ superconductors.

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1. Introduction

High-T_c cuprate superconductors have been described since their discovery in 1986 [1] as
being composed of two major constituents in the unit cell; MBa_2O_{4-d} as a charge reservoir
block (M = Cu, Tl, Hg, Bi, C) together with conducting $nCuO_2$ layers (n = 2, 3, 4, 5, 6).
The charge reservoir layer supplies charged carriers to the conducting $nCuO_2$ layers and these
carriers in the CuO_2 planes are the source of superconductivity.

In 1993, Putilin *et al* [2] obtained a new family $HgBa_2Ca_{n-1}Cu_nO_y$ (n = 1, 2, 3, . . .),
which has provided the highest T_c (134 K) so far for n = 3. This Hg–cuprate system loses

its superconducting properties if there is CO_2 contamination. However, this matter has been overcome by partial substitution of mercury (Hg) by rhenium (Re) [3, 4]. With the rhenium substitution, it was possible for other research groups to study the physical properties of this family without problems of sample degradation and with precise control of oxygen content.

Our group has investigated $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ in its ceramic form (polycrystalline) since 1998 [5, 6]. This compound can be described as three CuO_2 conducting planes separated by layers of essentially insulating material, which is a feature that all high T_c cuprates have.

The mercury family $HgBa_2Ca_{n-1}Cu_nO_y$ ($n = 1, 2, 3, \ldots$) has a $nCuO_2$ conducting layers. This is a typical homologous series of superconducting cuprates, where the separation between the plates ($nCuO_2$ layers) is assumed large if compared to the spacing that separates individual layers inside the plate. Since there is no microscopic theory for high-T_c superconductivity, models have been proposed which correlate the superconductor properties with the coupling between CuO_2 layers within a unit cell (intralayer) and the coupling between adjacent outer layers (interlayers) [7, 8].

Taking into account the existence of these $nCuO_2$ conducting layers in cuprate superconductors, it was suggested in 2003 [9] that the Casimir effect [10] should occur between the parallel superconducting layers in high T_c superconductors. For ideal conducting layers separated by vacuum, the Casimir energy is found to be

$$E_c(d) = -\frac{\pi^2 \hbar c A}{720 d^3}, \tag{1}$$

where A is the area of the plate and is large with respect to the distance, d. This equation describes the Casimir energy for two parallel plasma sheets with large separation d.

Our previous study concerning $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ [11], with optimum oxygen content ($\delta = 8.79$ and $T_c^{max} = 133$ K), indicated that $dT_c/dP = 1.9(2)$ K GPa^{-1}. Considering that the optimum oxygen content represents the optimum condition for carrier transport in the Cu–O cluster formed by the $3CuO_2$ inner layers, we attributed the T_c increment with external pressure as a reduction of the distance, d, between the Cu–O clusters and the cluster compression. We pursue an investigation of the correlation distance (on a nanometer scale) between Cu–O clusters and the T_c variation from the point of view of the Casimir energy.

Our work is outlined according to the following organization. In section 2, we describe a recent proposed scenario in which the Casimir/van der Waals effect could be in large parts responsible for the condensation energy in Hg-12$(n-1)n$ superconductors, taking in account extensively published works [9, 13]. In section 3, we work out the pressure dependence of T_c within this scenario. In section 4, we correlate the pressure variation and the intrinsic term signal in order to provide corroborating evidence for the proposed scenario. In section 5 we present our concluding comments.

2. Casimir effect in Hg-12$(n-1)n$ superconductors

In homologous series Hg-12$(n-1)n$ superconductors, the role of the Casimir conducting planes can be attributed to the $nCuO_2$ layers, which initially form Cu–O non-superconducting charge carrier layers, and are able to form the superconductor layers below T_c. For the Kempf model [9], the superconducting condensation energy is of the same order of magnitude as the Casimir energy. As these superconducting Cu–O layers are separated by distances two orders of magnitude smaller than the London penetration depth, the Casimir effect is reduced by several orders of magnitude. For small d (nanometer scale), Bordag [12] has calculated, for a

transverse magnetic (TM) mode, a modification of the Casimir energy, as follows:

$$E_c(a) = -5.10^{-3} \, \hbar c A d^{-5/2} \sqrt{\frac{n^* q^2}{2m^* c^2 \epsilon_0}}. \tag{2}$$

In equation (2), A is the area of the sheet, d is the distance between the sheets and n^* represents the carrier density.

In the regime of small distances (nanometer scale) between the Cu–O layers, the Casimir effect becomes a van der Waals type effect dominated by contributions from TM surface plasmons propagating along the *ab* planes [9]. Taking into account the density of states for the case of a Fermi gas in two dimensions, the transition temperature T_c was predicted [9, 13] as

$$T_c = \frac{2^{3/4} \pi^{1/2} \hbar^{3/2} e^{1/2} n^{*1/4}}{10 \eta k_B m^{*3/4} \epsilon_0^{1/4} d^{5/4}}. \tag{3}$$

In equation (3), $m^* = 2 * \alpha * m_e$ stands for the carrier effective mass, n^* refers to the carrier CuO_2 layer density, $\eta = 1.76$ the BCS parameter, d is the distance between two $nCuO_2$ clusters of layers, while ϵ_0 is the electric permittivity of the vacuum.

The parameter α in $m^* = 2 * \alpha * m_e$ represents a factor associated with the effective mass of the conducting superconductor carrier, which comes from the convolution of the CuO_2 molecule symmetry (e.g., octahedral, pyramidal or plane) with the crystal symmetry. Based on the density functional theory (DFT) [14], it is possible to estimate the Fermi velocity (4), which is related to the conductivity tensor (5), n^* and m^* (6) as follows:

$$v_i = \nabla_i E(\vec{k}), \tag{4}$$

$$\sigma_{ij} \propto n^* \int v_i v_j \, dS, \tag{5}$$

$$\left[\frac{1}{m^*} \right]_{ij} = \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial k_i \partial k_j}. \tag{6}$$

The density functional theory is based on the notion that the total energy, E, of an electronic system is determined by the electron density, r, or $E(r)$. This notion was first suggested by Fermi (1930) and later on proven to be exact by Kohn in 1964 [15, 16]. Ever since, it has been widely used in condensed-matter physics, computational physics and computational chemistry [17–19]. The transport properties are sensitive to crystal symmetries and molecular structure variations on the atomic scale [20–23], so it is mandatory that we have a detailed knowledge of how the functional properties of molecules depend on structural features [24]. These structures can be predicted and calculated using DFT, as for example in GeO_2 molecule [25]. Molecular and solid-state conductivity can be evaluated by using the HOMO and LUMO orbital energy gap, once the conductivity is inversely proportional to this gap [26, 27]. These calculations can be performed with the help of the Gaussian 03 package with the most appropriated functional and basis sets [28].[4]

The main relationship revealed by equation (3) is that T_c is a function of $\alpha^{3/4}$, $n^{*1/4}$ and $d^{-5/4}$. In order to verify equation (3), we display a table (table 1) where we employed the Gaussian 03 package to estimate m^* and n^* based on realistic values found for d (in our laboratory and in the literature) [11, 29–32]. This mercury family $HgBa_2Ca_{n-1}Cu_nO_y$ ($n = 1, 2, 3, \ldots$) has the same crystal symmetry for different n (1, 2, 3, ...) and oxygen contents of the homologous series, which is a constrain that reduces the time of computational calculus of m^* and n^*.

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[4] See the site http://www.gaussian.com/; a package with a very big team of collaborators: M J Frisch *et al*.

Table 1. Critical temperature evaluated by Casimir energy T_c^{Cas}, T_c^{ref} obtained in the references and correlations.

Compound	d (nm)	$n^*(m^{-2})$	α	T_c^{Cas} (K)	T_c^{ref}	Cu–O symmetry	Crystal symmetry
Hg-1201 [30, 34]	0.95	1.2×10^{18}	13	96	98	Octahedral	Tetragonal
Hg-1212 [30, 34]	1.27	2.4×10^{18}	7	126	127	Pyramidal	Tetragonal
Hg-1223 [29, 30, 34]	1.58	3.1×10^{18}	5	135	134	Pyramidal	Tetragonal
(Hg, Re)-1223 [11]	1.56	3.2×10^{18}	5	134	133	Pyramidal	Tetragonal
Hg-1234 [31]	1.89	4.4×10^{18}	4.5	125	125	Pyramidal	Tetragonal
Hg-1245 [32]	2.21	5.5×10^{18}	4.5	108	108	Pyramidal	Tetragonal

The trend of α in table 1 is in agreement with Puzniak [33], who points out the decreasing of m^*/m_e as a function of n increment (n is the number of CuO_2 layers).

3. Effect of pressure on Hg-12$(n-1)n$

As a Hg-12$(n-1)n$ superconductor probe, the effect of hydrostatic pressure on $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ (denoted here as (Hg,Re)-1223) was investigated. First, to describe the effect of hydrostatic pressure, it was assumed that the volume compressibility of (Hg,Re)-1223 is the same that was determined for $Hg_1Ba_2Ca_2Cu_3O_{8+\delta}$ (denoted as Hg-1223), which is close to 1% GPa^{-1} [34]. For (Hg,Re)-1223, when the hydrostatic pressure is close to 0.9 GPa, the crystal unit cell volume is reduced by -0.8%. The variation of the hydrostatic pressure up to 1.2 GPa on (Hg,Re)-1223, with different δ, causes different T_c changes [11]. The reduction of the unit cell, under hydrostatic pressure, leads to a variation of T_c associated with the contraction of the *a, b and c*-axes. The different T_c-dependence induced by an external hydrostatic pressure is interpreted in the framework of the pressure-induced charge transfer model modified by Almasan *et al* [35]. The variation of T_c is described by Neumeier and Zimmermann's [36] equation:

$$\frac{dT_c}{dP} = \frac{\partial T_c^i}{\partial P} + \frac{\partial T_c}{\partial n^*}\frac{\partial n^*}{\partial P}, \tag{7}$$

where the first term is an intrinsic variation of T_c with pressure while the second is related to changes in T_c due to the variation of the carrier concentration in the $nCuO_2$ conducting layers, caused by the change of pressure. For the case of external hydrostatic pressure effects on samples with optimum oxygen content, such as $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ with ($\delta = 8.79$), the second term in equation (7) vanishes. From this, we have

$$\frac{dT_c}{dP} = \frac{\partial T_c^i}{\partial P}. \tag{8}$$

So, for this case, the T_c variation will be determined only by the intrinsic term. The non-negligible intrinsic term $\partial T_c^i/\partial P$ is correlated with an effective contribution of the lattice to the mechanism of Hg-12$(n-1)n$ superconductivity versus the role of carriers. $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8.79}$ has a value of $\partial T_c^i/\partial P = 1.9$ K GPa^{-1} [11].

The intrinsic term has been presented with a physical meaning, but no exact description has been provided, since its introduction in 1992 [35]. However, if T_c is associated with the temperature from the Casimir energy, as stated by equation (3), equation (7) can be rewritten as follows:

$$\frac{dT_c}{dP} = \frac{\partial T_c}{\partial d}\frac{\partial d}{\partial P} + \frac{\partial T_c}{\partial \alpha}\frac{\partial \alpha}{\partial P} + \frac{\partial T_c}{\partial n^*}\frac{\partial n^*}{\partial P}. \tag{9}$$

Table 2. Intrinsic term pressure dependence evaluated by Casimir energy.

Compound	K_c (10^{-3} GPa^{-1})	$\partial T_c^{exp}/\partial P$	$\partial T_c^i/\partial P$	$\frac{-5}{4}T_c\frac{1}{d}\frac{\partial d}{\partial P}$	$\frac{-3}{4}T_c\frac{1}{\alpha}\frac{\partial \alpha}{\partial P}$	$\frac{1}{\alpha}\frac{\partial \alpha}{\partial P}$ (10^{-3} GPa^{-1})
Hg-1201 [34]	5.8	1.7	1.7	0.7	1.0	−13.8
Hg-1212 [34]	6.0	1.7	1.7	0.9	0.8	−8.4
Hg-1223 [29, 34]	5.6	1.7	1.7	0.9	0.8	−7.9
(Hg,Re)-1223 [11]	5.6	1.9	1.9	0.8	1.1	−11.0
Hg-1234 [31]	5.8	1.2	1.2	0.8	0.4	−4.3

For samples with optimum oxygen content, the third term vanishes, as justified before. For this optimum condition, there is a direct correspondence between the intrinsic term (8) and the other two significant terms (9), as specified below:

$$\frac{\partial T_c^i}{\partial d} = \frac{\partial T_c}{\partial d}\frac{\partial d}{\partial P} + \frac{\partial T_c}{\partial \alpha}\frac{\partial \alpha}{\partial P}. \tag{10}$$

Substituting equation (3) into (10), we have an explicit expression for the intrinsic term:

$$\frac{\partial T_c^i}{\partial d} = \frac{-5}{4}T_c\frac{1}{d}\frac{\partial d}{\partial P} + \frac{-3}{4}T_c\frac{1}{\alpha}\frac{\partial \alpha}{\partial P}. \tag{11}$$

4. Discussion

The signs of both terms in equation (11) are negative. However, the intrinsic term is positive, when the pressure is increased. This behaviour can be justified by the negative sign of both the derivative terms,

$$\frac{\partial d}{\partial P} \rightarrow (P > 0) \rightarrow \frac{\partial d}{\partial P} < 0 \qquad \text{and} \qquad \frac{\partial \alpha}{\partial P} \rightarrow (P > 0) \rightarrow \frac{\partial \alpha}{\partial P} < 0. \tag{12}$$

The first derivative term represents the compression coefficient in the c-axis direction. The crystallographic c-axis is associated with the distance, d, between the two nCuO$_2$ clusters of layers, each located in different adjacent crystal cells. As a consequence, one can write the following expression:

$$K_c = -\frac{1}{c}\frac{\partial c}{\partial P} = -\frac{1}{d}\frac{\partial d}{\partial P}. \tag{13}$$

The other derivative term in (12) represents a variation of the effective carrier mass, which comes from the change in the dispersion relation whenever subject to pressure. X-ray diffraction and XANES analysis of (Hg,Re)-1223, with optimum oxygen content showed that the O–Cu–O bond angle is usually close to 180° [37]. The effect of the increase in the external pressure is to change this O–Cu–O bond angle closer to 180°, which changes the charge mobility. From our point of view, the α-coefficient is related to the convolution of the CuO$_2$ molecule symmetry and crystal symmetry by taking into account the density functional theory and by computing the σ_{ij}-tensor, which appears in the Gaussian 03 output file. As consequence, the α-value is reduced when one increases pressure:

$$(P > 0) \rightarrow \frac{\partial \alpha}{\partial P} < 0. \tag{14}$$

Therefore, the final sign of $\partial T_c^i/\partial P$ is positive, and the intrinsic term points to a positive response to the external pressure.

In order to test the agreement of equation (11) with the experimental results, we display table 2 by using realistic values found in the literature [29–32, 34] and in our laboratory for homologous series Hg-12$(n-1)n$ superconductors.

5. Conclusion

The Casimir energy has been related to the superconducting condensation energy [9, 13], by taking into account the density of states for a Fermi gas in two dimensions. As a consequence, the transition temperature T_c is predicted to be a function of $m^{*3/4}$, $n^{*1/4}$ and $d^{-5/4}$. With this model, the α-coefficient in $m^* = 2 * \alpha * m_e$ can be described as the effective carrier mass factor from the dispersion relation, by considering the convolution between the CuO_2 molecule symmetry (e.g., octahedral, pyramidal or plane) and the crystal symmetry. As shown in table 1, the trend of α evaluated by DFT reveals the decreasing of m^*/m_e as a function of n increment (n is the number of CuO_2 layers). The values found for the T_c expression are in agreement with the experimental values of T_c for $HgBa_2Ca_{n-1}Cu_nO_y$ ($n = 1, 2, 3, \ldots$) superconductors described in the literature and (Hg,Re)-1223 measured in our laboratory. The T_c behaviour under external hydrostatic pressure shows an intrinsic term, which is identified here with the variation of the Casimir energy. This pressure dependence of the intrinsic term provides an explicit expression proportional to the compressibility coefficient of the c-axis and the effective mass, m^*, of the carrier charge. To the best of our knowledge, an explicit expression for $\partial T_c^i / \partial P$ was not known before. Our proposal that associates a dependence of the intrinsic term on the pressure is in agreement with the values found in the literature and in our laboratory for homologous series Hg-12$(n - 1)n$ superconductors.

Acknowledgments

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