Unconventional superconductivity in $\zeta$-phase of oxygen compressed to megabar pressure

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Abstract

Oxygen exhibits structural phase transformation from non-metallic $\varepsilon$-O$_2$ phase into metallic $\zeta$-O$_2$ phase at pressure of $P = 96$ GPa (Desgreniers et al 1990 J. Phys. Chem. 94 1117; Akahama et al 1995 Phys. Rev. Lett. 74 4690). Metallic $\zeta$-O$_2$ phase is a superconductor with transition temperature of $T_c = 0.6$ K at $P = 115$-$120$ GPa (Shimizu et al 1998 Nature 393 767). In this paper we have performed analysis of temperature dependent upper critical field, $B_{c2}(T)$, for $\zeta$-O$_2$ phase ($P = 115$ GPa) and show that this highly-compressed phase of gaseous molecular element is unconventional superconductor with the ratio of $T_c$ to the Fermi temperature, $T_F$, in the range of $0.009 \leq T_c/T_F \leq 0.108$. 
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I. Introduction

Jörg Wittig [1] heralded studies of pressure-induced superconductivity in non-superconductors by the discovery of superconducting transition in cerium with $T_c = 1.8$ K by applying isostatic pressure of $P = 5$ GPa. To date, the pressure-induced superconductivity has been detected in dozens of elements and compounds compressed at megabar pressures [2-18], including milestone experimental discoveries of near-room-temperature (NRT) superconducting hydrides [2-4,10-13].

Desgreniers et al [19] detected metallization of oxygen at pressures $P > 90$ GPa, and this phase transformation from non-metallic $\varepsilon$-O$_2$ phase into metallic $\zeta$-O$_2$ phase has been studied for three decades [20-23].

Shimizu et al [8] reported that $\zeta$-O$_2$ phase is a superconductor with transition temperature of $T_c = 0.6$ K at pressures in the range of $P = 115$-120 GPa. Shimizu et al [8] also reported temperature dependent upper critical field data, $B_{c2}(T)$, which we analyse herein with the purpose to classify superconductivity (i.e., conventional vs unconventional) in $\zeta$-O$_2$ phase.

Primary demand to perform this classification is based on our recent findings that all NRT highly-compressed superconductors are, surprisingly enough, unconventional superconductors [24-26], which exhibit the ratio of the superconducting transition temperature, $T_c$, to the Fermi temperature, $T_F$, in the range of $0.01 \leq \frac{T_c}{T_F} \leq 0.05$, which is the range for all known unconventional superconductors [27,28].

In result, we find that in all considered scenarios $\zeta$-O$_2$ phase ($P = 115$ GPa) has $T_c/T_F$ ratio in the range of $0.008 \leq \frac{T_c}{T_F} \leq 0.107$, and, thus, this highly-compressed phase of gaseous element should be classified as unconventional superconductor.
II. The upper critical field data analysis

Shimizu et al [8] in their Fig. 3 reported experimental $B_{c2}(T)$ data for $\zeta$-O$_2$ phase at pressure $P = 115$ GPa which we fit to two models:

1. The first model was proposed by Baumgartner et al [29]:

$$B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(0)} \left[ \left(1-\frac{T}{T_c}\right)^{-0.153 \left(1-\frac{T}{T_F}\right)^2 -0.152 \left(1-\frac{T}{T_c}\right)^4} \right]$$

where $\phi_0 = 2.068 \cdot 10^{-15}$ Wb is magnetic flux quantum, and $\xi(0)$ is the ground state coherence length. We will designate this model as B-WHH model, because Eq.1 is analytical approximation of general model proposed by Werthamer, Helfand, and Hohenberg [30].

2. The second used model was proposed by Gor'kov [31]:

$$B_{c2}(T) = \frac{\phi_0}{2\pi \xi^2(0)} \left[ \left(1.77-0.43 \left(\frac{T}{T_c}\right)^2 +0.07 \left(\frac{T}{T_c}\right)^4 \right) \cdot \left[1 - \left(\frac{T}{T_c}\right)^2 \right] \right]$$

It should be noted, that both models (Eqs. 1,2) are in wide use at the moment to analyse experimental $B_{c2}(T)$ data for whole variety of superconducting materials, ranging from atomically thin superconductors [32] and practical superconductors [29] to NRT superconductors [24-26].

Results of fit of $B_{c2}(T)$ data for $\zeta$-O$_2$ phase ($P = 115$ GPa) to Eqs. 1,2 are shown in Fig. 1 and deduced parameters are collected in Table 1.

| Model   | Deduced $T_c$ (K) | Deduced $\xi(0)$ (nm) | Assumed $m^*_e$ (in $m_e$) | Assumed $\frac{\Delta(0)}{k_B T_F}$ | $T_r$ (K) | $T_c/T_F$ |
|---------|-------------------|------------------------|-----------------------------|-----------------------------------|----------|-----------|
| B-WHH   | 0.635 ± 0.008     | 41.3 ± 0.4             | 0.49                        | 3.53                              | 5.86 ± 0.02 | 0.108 ± 0.003 |
|         |                   |                        |                             | 5.0                               | 11.8 ± 0.02 | 0.052 ± 0.002 |
|         |                   |                        |                             | 3.0                               | 35.9 ± 1.6   | 0.018 ± 0.001 |
|         |                   |                        |                             | 5.0                               | 72.0 ± 3.2   | **0.009 ± 0.001** |
| Gor’kov | 0.63 ± 0.01       | 42.0 ± 0.7             | 0.49                        | 3.53                              | 5.96 ± 0.40  | 0.106 ± 0.005 |
|         |                   |                        |                             | 5.0                               | 12.0 ± 0.02  | 0.053 ± 0.003 |
|         |                   |                        |                             | 3.0                               | 36.5 ± 2.5   | 0.017 ± 0.001 |
|         |                   |                        |                             | 5.0                               | 73.3 ± 4.8   | 0.009 ± 0.001 |

Table I. Deduced and calculated parameters for $\zeta$-O$_2$ phase compressed at pressure of $P = 115$ GPa. The smallest and the largest values for $\frac{T_r}{T_F}$ are marked in bold.
Figure 1. Superconducting upper critical field, $B_{c2}(T)$, data and fits to three models (Eqs. 1,2) for $\zeta$-O$_2$ phase compressed at pressure of $P = 115$ GPa (raw data is from Ref. 8). (a) fit to B-WHH model, $R = 0.9994$; (b) fit to Gor’kov model, $R = 0.998$. 95% confidence bars are shown.

III. $\zeta$-O$_2$ phase in Uemura plot

From known $\xi(0)$ and $T_c$ values, the Fermi temperature, $T_F$, can be calculated by an equation of the Bardeen-Cooper-Schrieffer (BCS) theory [33]:

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{\pi^2}{3} \cdot m_{eff}^* \cdot \xi^2(0) \cdot \left(\frac{\alpha \cdot k_B T_c}{\hbar}\right)^2,$$

where $\alpha = \frac{2 \Delta(0)}{k_B T_c}$, $\Delta(0)$ is the amplitude of the ground state energy gap, $\varepsilon_F$ is the Fermi energy, $\hbar = h/2\pi$ is reduced Planck constant, $k_B$ is the Boltzmann constant, $m_{eff}^*$ is the charge carrier effective mass.
As there are no available experimental \(\alpha = \frac{2\Delta(0)}{k_B T_c}\) and the effective charge carrier mass \(m_{\text{eff}}^*\) values for \(\zeta\text{-O}_2\) phase, to calculate \(T_F\) for \(\zeta\text{-O}_2\) phase we chose a reasonable lower and upper bounds for these values. For lower bound of \(m_{\text{eff}}^*\) we use the value for ambient pressure hydrogen-rich superconductor, PdH\(_x\) [34]:

\[
m_{\text{eff}}^* = 0.49 \cdot m_e
\]

(4)
despite a fact that the closest (by \(T_c\) and by the atomic mass) ambient pressure superconductor to \(\zeta\text{-O}_2\) is the aluminium [35] with

\[
m_{\text{eff}}^* = 1.0 \cdot m_e
\]

(5)

In this regard, in lower bound for \(m_{\text{eff}}^*\) (Eq. 4) is chosen as intendent underestimated value to cover some hypothetical case that \(m_{\text{eff}}^*\) might be reasonably low in \(\zeta\text{-O}_2\) phase. This lower bound for \(m_{\text{eff}}^*\) can be also supported by \(m_{\text{eff}}^* = (0.2 - 0.5) \cdot m_e\) reported by Medvedeva [36] for multicomponent conducting oxides.

For the upper bound of \(m_{\text{eff}}^*\) we use the highest value reported for highly compressed hydrides, \(m_{\text{eff}}^* = 3.0 \cdot m_e\) [37]. The possibility for heavy effective charge carrier mass in \(\zeta\text{-O}_2\), i.e. \(m_{\text{eff}}^* > 3.0 \cdot m_e\), cannot be of course rejected a priori, but large effective masses, as a rule, always associated with strong interaction between spin and \(d\)- or \(f\)-orbitals, and the latter does not exist in such light elements, like oxygen. Thus, we do not consider a possibility that the effective mass can exceed mentioned above value of \(m_{\text{eff}}^* = 3.0 \cdot m_e\).

The lowest value for \(\frac{2\Delta(0)}{k_B T_c}\) is weak-coupling limit of 3.53 [33], and for all known \(s\)-wave superconductors [38-40] \(\alpha\) is limited by the upper bound of \(\frac{2\Delta(0)}{k_B T_c} \leq 5.0\) [38]. Thus, \(T_F\) is calculated (Table 1 and Fig. 2) in the assumption that \(\alpha\) is varying within a range of \(3.53 \leq \frac{2\Delta(0)}{k_B T_c} \leq 5.0\) (it should be noted, that this range is cover most highly-compressed hydrogen-rich superconductors [24,37-42]).
As the result, $\zeta$-O$_2$ phase ($P = 115$ GPa) in all considered scenarios (Table 1) has $0.009 \leq T_c/T_F \leq 0.108$ and falls in unconventional superconductors band of the Uemura plot [27,28] (Fig. 2).

![Figure 2](image_url)

**Figure 2.** A plot of $T_c$ versus $T_F$ where $\zeta$-O$_2$ phase compressed at pressure of $P = 115$ GPa is shown together with the most representative superconducting families. Raw data is taken from [24-28]. Characteristic lines for the Bose-Einstein condensate (BEC), the Bardeen-Cooper-Schrieffer (BCS) superconductors and for $T_c/T_F = 1.0, 0.05, 0.01$ are shown for clarity.

It should be stressed that primary physical reason, that $\zeta$-O$_2$ phase is classified as unconventional superconductor is belong solid experimental result, that this superconductor exhibits relatively high ground state upper critical field, $B_{c2}(0)$, and relatively low superconducting transition temperature, $T_c$. Truly, if $\zeta$-O$_2$ phase will be conventional superconductor similar to Al (which exhibits $T_c/T_F = 8.4 \cdot 10^{-6}$), than in accordance with the expression [25] based on BCS theory [33]:

$$B_{c2} \left( \frac{T}{T_c} = 0 \right) = \frac{\pi \cdot \phi_0 k_B}{16 \hbar^2} \cdot m_{eff}^* \cdot \alpha^2 \cdot \left( \frac{T_c}{T_F} \right) \cdot T_c = 2.7 mT$$

(6)
where for the simplicity we assumed that \( m_{eff}^* = 1.0 \cdot m_e \) and \( \alpha = \frac{2 \Delta(0)}{k_B T_c} = 3.53 \) are identical to ones for aluminium. We note, that experimental value for \( \zeta\)-O\(_2\) phase [8] is:

\[
B_{c2} \left( \frac{T}{T_c} = 0.08 \right) = 190 \text{ mT}, \tag{7}
\]

which is about two orders of magnitude larger than hypothetical value for a conventional superconductor.

V. Conclusions

In summary, in this paper we analyse experimental \( B_{c2}(T) \) data for superconducting \( \zeta\)-O\(_2\) phase of highly-compressed oxygen \((P = 115 \text{ GPa})\), reported by Shimizu et al [8], and find that in all considered scenarios this highly-compressed \( \zeta\)-O\(_2\) phase is unconventional superconductor.

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