The possible role of van Hove singularities in the high $T_c$ of superconducting H$_3$S

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We observe that H$_3$S has a bcc structure and, with nearest neighbour hopping only, a strong singularity occurs at zero energy. This singularity is accompanied with a highly nested Fermi surface, which is not conducive to a stable superconducting instability. Introduction of next-nearest-neighbour hopping removes the singularity, but a robust peak remains in the electron density of states. Solution of the BCS equations shows an enhanced superconducting $T_c$ due to this peak. Furthermore, nesting is no longer present, so other instabilities will not compete effectively with superconductivity. We find high critical temperatures are possible, even with very modest coupling strengths. We also examine a limit of the $T = 0$ equations (in an Appendix) where an analytical solution is possible over the entire range of coupling strengths, and therefore the BCS-BEC crossover is fully covered.

I. INTRODUCTION

It has been essentially two years since a superconducting transition in the vicinity of 200 K was first reported in hydrogen sulfide. Since this time, however, experimental results concerning this system have been few, and to our knowledge, only one as-yet unpublished report has independently confirmed high temperature superconductivity via the Meissner effect. Nonetheless, the crystal structure has now been determined to be one of two variations of body-centred-cubic (BCC), and is associated with the stoichiometry H$_3$S. An optical spectroscopy study has also appeared, which claims to provide significant support for an electron-phonon-based mechanism for superconductivity. Much of the work to date on this compound has been on the theoretical side. Remarkably, even before the experimental discovery of superconducting H$_3$S, a Density Functional Theory (DFT) calculation predicted the correct high pressure structure, and a crude estimate based on the Allen-Dynes-McMillan formula suggested $T_c \approx 200$ K. Follow-up DFT calculations confirmed this work. Several of these authors further emphasized the electron-phonon interaction as the mechanism for superconductivity, primarily through the high frequency optical modes affiliated with the hydrogen atoms. These authors disagree, however, on the importance of anharmonicity, with Errea et al. and Papaconstantopoulos et al. finding evidence for large anharmonic effects, while Flores-Livas et al. do not.

In the meantime, Hirsch and one of the present authors have suggested that it is the conduction by holes through the sulfur ions that plays a primarily role in the superconductivity. The theoretical framework for the mechanism involved is expanded upon in earlier work, and will not be further discussed here.

The point we wish to make in this paper is that, somewhat independent of the mechanism, a large density of states near the Fermi level will enhance superconducting $T_c$. This point has been made repeatedly in the past, starting with the A15 compounds in the 1960’s and continuing with the cuprates over the past three decades. A survey of the effects of van Hove singularities in two and three dimensions on superconducting $T_c$ was published recently. Here we wish to emphasize that the three dimensional BCC structure, pertinent to superconducting H$_3$S, has a logarithmic (squared) singularity in the density of states when only nearest-neighbour hopping is taken into account, and this has a significant impact on superconducting properties. This was already recognized long ago by Jelitto. As already discussed in Ref. [15], a singularity also exists for the (face-centred-cubic) FCC structure, and in fact occurs at a filling where nesting effects (which favour other instabilities (e.g. charge density waves) are not present. We will focus on the BCC structure in this paper, and maintain a non-zero next-nearest neighbour hopping probability, as this seems to more accurately describe the actual situation in H$_3$S; it also serves to eliminate deleterious effects due to nesting, that would occur in the nearest-neighbour hopping only case for the BCC structure.

II. THE BCS FORMALISM

The BCS equations are

$$\Delta_k = -\frac{1}{N} \sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} [1 - 2f(E_{k'})],$$

where $\Delta_k$ is the superconducting gap, $V_{kk'}$ is the electron-phonon coupling, and $f(E)$ is the Fermi-Dirac distribution function.
and
\[
    n = \frac{1}{N} \sum_{k'} \left[ 1 - \frac{\epsilon_{k'} - \tilde{\mu}}{E_{k'}} (1 - 2f(E_{k'})) \right],
\]
with
\[
    E_k \equiv \sqrt{\left(\epsilon_{k'} - \tilde{\mu}\right)^2 + \Delta_{k'}^2}.
\]
Here, the wave vector summations cover the First Brillouin zone (FBZ), and we focus on a single band, whose characteristics are contained within $\epsilon_{k_i}$. Similarly the pairing potential, $V_{k,k'}$, is specified by the model under consideration, and the chemical potential, $\mu$, gives us the density of electrons, $n$. In practice, we ‘know’ the electron density, $n$, and therefore need to determine the chemical potential that leads to the desired electron density, for a particularly pairing potential and temperature (as included through the Fermi-Dirac distribution function, $f(x) = 1/[\exp(\beta x) + 1]$, where $\beta \equiv 1/[k_B T]$ is the inverse temperature, with $k_B$ the Boltzmann constant). In Eqs. (1-3), we use $\tilde{\mu}$, which is assumed to include corrections to $\mu$ associated with the normal state.

In what follows we assume a featureless attractive interaction, denoted as $V_{k,k'} = -V$, with $V > 0$. This model constitutes the so-called attractive Hubbard model, as a constant in wave vector space implies an on-site attraction only. As discussed by Eagles,\textsuperscript{19} Leggett,\textsuperscript{20} and Nozières and Schmitt-Rink,\textsuperscript{21} these equations are valid for all pairing strengths (at $T = 0$); we discuss a particular limit in the Appendix where these equations can be solved exactly. Here in the main text, we introduce a cutoff for the pairing potential, so that attraction occurs only for states within an energy $\hbar \omega_D$ of the Fermi energy, i.e.
\[
    V_{kk'} = -V \theta [\hbar \omega_D - |\epsilon_k - \mu|] \theta [\hbar \omega_D - |\epsilon_{k'} - \mu|],
\]
where $\theta[x]$ is the Heaviside step function. Note that removal of this restriction reduces this model to the usual attractive Hubbard model; identification of $\omega_D$ with a phonon energy scale follows the original BCS treatment, though a more accurate procedure would be to use the Eliashberg equations\textsuperscript{22,23} where retardation effects are properly accounted for. We note that Sano et al.\textsuperscript{24} have already done for HgS.

The main purpose of this paper is to highlight the importance of electronic structure, through peaks in the electronic density of states (EDOS) for superconducting $T_c$. Both Quan and Pickett,\textsuperscript{25} and Sano et al.\textsuperscript{24} have included and highlighted this point, based on the results of DFT calculations. In our previous work\textsuperscript{15} we have focused on simple tight-binding descriptions, where, in our opinion, the origin of the peak in the density of states is more transparent.

We utilize the BCC, including both nearest and next-nearest neighbour hopping parameters results in the dispersion
\[
    \epsilon_k = -8t \left[ \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right] \quad \text{[bcc NNN]},
\]
with
\[
    -2t_2 \left[ \cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right],
\]
where $t$ and $t_2$ are the nearest and next-nearest neighbour hopping amplitudes, respectively. The only real impact on the BCS equations is most readily seen by rewriting them as follows (we also replace the pairing potential $V_{k,k'} = -V$ and linearize the equations so that they are valid only at $T = T_c$),
\[
    \frac{1}{V} = \int_{\mu_-}^{\mu_+} d\epsilon \frac{\tanh[\beta_\epsilon (\epsilon - \mu)/2]}{2(\epsilon - \mu)} \quad [T = T_c]
\]
and
\[
    n = 2 \int_{\epsilon_{\text{min}}}^{\epsilon_{\text{max}}} d\epsilon f(\epsilon - \mu), \quad [T = T_c]
\]
where only the EDOS, $g(\epsilon)$, contains information about the structure. Here $\beta_\epsilon = 1/[k_B T_c]$. The integration limits in Eq. (6) are normally $\mu_- = \mu - \hbar \omega_D$ and $\mu_+ = \mu + \hbar \omega_D$, but when $\mu$ is close to a band edge, then these limits are given by $\mu_- \equiv \max[\mu - \hbar \omega_D, \epsilon_{\text{min}}]$, and $\mu_+ \equiv \min[\mu + \hbar \omega_D, \epsilon_{\text{max}}]$, where $\epsilon_{\text{min}} (\epsilon_{\text{max}})$ is the energy of the bottom (top) of the band.

### III. RESULTS

#### A. The BCC electronic density of states

The EDOS for the BCC structure with nearest-neighbour (nn) hopping only is given by\textsuperscript{15,16}
\[
    g_{\text{BCC}}(\epsilon) = \frac{2}{a^3} \frac{1}{2\pi a t} \int_{|x|}^{1} dx \frac{1}{\sqrt{1 - x^2 - \epsilon^2}} K \left[1 - x^2\right].
\]

where $\bar{\epsilon} \equiv \epsilon/(4t)$, and $K(z)$ is the complete elliptic integral of the first kind.\textsuperscript{26} This function diverges logarithmically at $z \to 0$, and results in
\[
    \lim_{\epsilon \to 0} g_{\text{BCC}}(\epsilon) \approx \ln^2 \left(\frac{1}{|\epsilon|}\right),
\]
which is a stronger divergence than occurs in two dimensions. When next-nearest-neighbour (nnn) hopping is included, then we use a limiting representation for the $\delta$-function and determine the EDOS through
\[
    g_{\delta}(\epsilon) = \frac{1}{2d a^3} \frac{1}{\sqrt{\pi a^2}} \int_{0}^{1} dx \int_{0}^{1} dy \int_{0}^{1} dz \ e^{-\frac{(x^2 + y^2 + z^2)}{d^2}},
\]
where we have substituted $x \equiv k_x a/\pi$ and similarly for $y$ and $z$, and $\delta$ is some small numerical smearing parameter (e.g. $\delta = 0.0005t$). In fig. 1 we show the BCC density of states for a variety of values of $t_2/t$. Note how the singularity evolves (and disappears) once $t_2/t$ departs from zero. Nonetheless, a highly peaked structure remains for modest values of $t_2/t$. 


Although not addressed here, it is also worth noting that the singularity for \( \epsilon = 0 \) disappears as \( t_2 \) becomes non-zero. Nonetheless a large peak, displaced from \( \epsilon = 0 \), remains in its place. Results are shown for negative \( t_2 \) since the results from DFT indicate a structure in the EDOS very similar to this one.\(^{25}\) Moreover, for positive values of \( \rho \) the results are symmetric (about \( \epsilon = 0 \)) to those shown. We used \( \delta = 0.001t \) to generate these results using Eq. (10) [the result for \( t_2 = 0 \) is indistinguishable from the more accurate result given by Eq. (8)].

\[ T_c \]

To determine \( T_c \) one must insert the EDOS from Eq. (8) or Eq. (10) into Eqs. (6,7), and perform the ensuing integrals numerically. Based on weak coupling, it is natural to examine dimensionless quantities, such as \( T_c/(\hbar\omega_D) \), vs. \( V/t, \hbar\omega_D/t, \) and \( n \). In Fig. 2 we show \( T_c/(\hbar\omega_D) \) as a function of electron density, \( n \), for various values of \( V \) as indicated. We use \( \omega_D = 0.01t \) for definiteness, although this ratio will vary with the specific mechanism that one has in mind. For these values of coupling strength the ratio \( T_c/(\hbar\omega_D) \) is fairly insensitive to \( \omega_D/t \), and so this figure can be used for other values of \( \omega_D \) to estimate \( T_c \) in real units. This is indicative of weak coupling, so in fact the shape of \( T_c \) vs \( \mu \) will resemble closely the density of states (as a comparison with the relevant curve in Fig. 1 indicates). Here there will be some distortion since \( T_c \) is plotted vs. \( n \) and not versus chemical potential.

\[ IV.\ \text{SUMMARY} \]

This study does not directly address the mechanism for superconductivity in H\(_3\)S. Instead, we have found, as have other DFT-based studies, that the BCC structure itself will tend to amplify pairing effects, due to the possibly very high electronic density of states at the Fermi level. More generally, the superconducting community should be more aware that singularities in the electronic densities of states can occur in three dimensions as well as lower dimensions, in all three types of cubic structures, simple, face-centred, and body-centred cubic. The existence of this possibility was first pointed out by Jelitto,\(^{16}\) and we elaborated on the nearest-neighbour models considered by him to those that include \( nnn \) hopping as well.\(^{15}\) Although not addressed here, it is also worth noting that the isotope effect is expected to display some peculiar characteristics, again due to the presence of van Hove singularities in the EDOS.\(^{15}\)

When \( nnn \) hopping is introduced, the singularity disappears in the EDOS.\(^{27}\) The peak that remains is in some ways more ‘robust’ — it (and therefore superconducting \( T_c \)) will withstand more readily the degradation that is inevitable due to impurities and imperfections. Note that the realization that the presence of a BCC structure in the material will lead to an enhanced \( T_c \) occurred also through DFT studies. Nonetheless, it is beneficial to have simplified tight-binding models like the one presented here to help identify important structure characteristics for enhancing \( T_c \). It is clear from characteristics of the EDOS, that doping with electrons (should that become
possible) will lead to a lower $T_c$, if this is all that mattered. Some mechanisms (e.g. the "hole" mechanism\textsuperscript{12}) predict a strong doping dependence independently of changes in the EDOS, and then the qualitative prediction of this model will depend on whether $H_2S$ lies on the electron- or hole-side of the maximum predicted in that model. The dependence of the effective interaction on doping is expected to overwhelm the dependence of the EDOS on doping in this particular model. It will be interesting to see if such experiments can be carried out.

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Appendix A: Exact results (within $T = 0$ BCS) for any filling and coupling strength for a constant density of states

We start with Eqs. (1-2), and illustrate that for the attractive Hubbard model,

$$V_{k,k'} = -|U|,$$

(A1)
an exact solution exists\textsuperscript{28} at $T = 0$, if we adopt a constant density of states model, $g(\epsilon) = 1/W$, where $W$ is the electronic bandwidth, and the band extends from $-W/2$ to $W/2$. With these assumptions, Eqs. (1-2) become

$$\frac{2W}{|U|} = \int_{-W/2}^{+W/2} d\epsilon \frac{1}{\sqrt{(\epsilon - \tilde{\mu})^2 + \Delta^2}}$$

(A2)

$$W(1 - n) = \int_{-W/2}^{+W/2} d\epsilon \frac{e - \tilde{\mu}}{\sqrt{(e - \tilde{\mu})^2 + \Delta^2}},$$

(A3)

where $\tilde{\mu} = \mu + |U|n/2$ is the bare chemical potential with the Hartree correction. As remarked in Ref. [21], these equations amount to a change of variables from $(\Delta, \mu)$ to $(|U|, n)$. These equations retain their validity for all coupling strengths, from weak to strong coupling, and describe pairing from the Cooper pair limit to the Bose Condensed pair limit. To our knowledge, they have never been inverted analytically over the entire range of parameters until now.

To proceed, one performs both (elementary) integrals. Successive squaring of the result from Eq. (A3) results in an explicit determination of $\tilde{\mu}$ in terms of $\Delta$:

$$\tilde{\mu} = -\frac{W}{2}(1 - n) \left\{ 1 + \left( \frac{\Delta}{W/2} \right)^2 \frac{1}{n(2 - n)} \right\}.$$  \hspace{1cm} (A4)

Proceeding with Eq. (A2), defining variables $Y \equiv \exp(2W/|U|)$ and $x \equiv \tilde{\mu} + W/2$, successive squaring of this equation results in yet another explicit determination of $\tilde{\mu}$:

$$\tilde{\mu}^2 = \left( \frac{W}{2} \right)^2 \left( \frac{Y + 1}{Y - 1} \right)^2 \left\{ 1 - \left( \frac{\Delta}{W} \right)^2 \frac{(Y - 1)^2}{Y} \right\}.$$  \hspace{1cm} (A5)

Equating Eq. (A5) with the square of Eq. (A4) then allows us to solve for $\Delta$; back-substituting this result into Eq. (A4) then gives us an explicit result for $\mu$. The final results are

$$\mu = -\frac{|U|}{2}n - \frac{W}{2}(1 - n)\coth \left( \frac{W}{|U|} \right),$$  \hspace{1cm} (A6)

and

$$\Delta = \frac{W}{2} \sqrt{\frac{n(2 - n)}{1 - (1 - n)\tanh^2 \left( \frac{W}{|U|} \right)}} \text{csch} \left( \frac{W}{|U|} \right).$$  \hspace{1cm} (A7)

From Eq. (A6) one immediately obtains

$$n = \frac{\mu + \frac{W}{2}\coth \left( \frac{W}{|U|} \right) - \frac{W}{|U|}}{\frac{W}{2}\coth \left( \frac{W}{|U|} \right) - \frac{W}{|U|}},$$  \hspace{1cm} (A8)

this result includes both Hartree and pairing contributions. One can readily verify that the weak and strong coupling limits are achieved correctly with these equations.

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28 Again we emphasize that this statement is true within BCS theory for a finite band with a constant density of states. To our knowledge even with these caveats, this solution has not been noticed before in the literature. A truly exact solution is available by way of the Bethe Ansatz only in one dimension,29 and comparisons have been made with BCS theory in Ref. [30].

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