Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 12 Issue 3, March - 2025

Pressure Effects On Energy Of H_3S And LaH_{10} Superconductor Due To Collective Excitation Of Cooper Pairs

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***Abstract*—There are two categories of superconductors; s-wave superconductors that are isotropic and d-wave superconductors that are anisotropic. The microscopic theory of superconductivity by Bardeen, Schrieffer and Cooper (BCS theory) explains s-wave pairing of charges under ambient pressure but it fails to explain charge pairing under high pressure. Studies have shown that superconductivity in hydrides is due to electron-phonon mediation. Models have been developed to explain the pressure effect on Tc but so far, no unified model has been agreed upon to explain HTSC under pressure using the Bogoliubov-Valatin Transformation (BVT) formalism. The developed theory was used in this work to give more understanding of the superconducting process under pressure and carry on a comparison with other researchers. The systems energy, specific heats, entropy and Sommerfield coefficient were determined. Further, pressure effects on cell volume and energy were studied. The value of entropy for the two hydrides at their respective Tc is 0.15 meV/K^2 for H_3S and 0.13 meV/K^2 for LaH_{10}. The highest entropy for H_3S is 0.450 meV/K^2 and occurs at 900K while for LaH_{10} the highest entropy of 0.451 meV/K^2 occurs at 1000K. The two systems are found to have the lowest entropy at Tc. H_3S at a deformed volume of 158.4 a.u^3 has energy of -220.76 meV. At v=100a.u^3, E=0meV. Therefore, the cell volume of H_3S is found to be 100a.u^3. The bulk modulus for H_3S at 158.4a.u^3 is B=129.8 GPa Similarly LaH_{10} at a deformed volume of 81.5a.u^3 has energy of -86.16 meV. At v=45 a.u^3, E=0meV. Therefore, the cell volume is found to be 45a.u^3. From the study, the energy required to break the Cooper pairs in H_3S was found to be -220.76meV. The energy gap for the hydride at the stated pressure is 76mev. Twice this energy gives 152meV. A gap difference of 66.7meV is obtained and this is attributed to pressure increased that raises the energy required to break the Cooper pairs. However, this does not apply for the results of LaH_{10} with energy gap of 51meV and energy obtained of 86.16meV. These results will open room for more discoveries towards the room temperature hydride superconductors under ambient pressure for practical applications.**

Keywords—Hydrides, Pressure, Energy gap, Phonon, Collective excitation, BVT

Introduction

Room temperature superconductivity has been achieved under immense pressure. BCS theory accounts for excitation of Cooper pairs at ambient pressure. , Bardeen, *et al*, (1957) developed the microscopic theory of superconductivity based on electron pairing under phonon mediation. The theory explained all the accumulated experimental data on superconductivity. Bogoliubov (1958) showed that the BCS theory could be derived from electronic Hamiltonian. Similar results as those of the BCS theory are obtained when the Bogoliubov-Valatin Transformation (BVT) is used. Despite all the achievements, the BCS theory fails to explain the phenomenon at T_c>30K such as hydride superconductors.Ashcroft (2004) suggested that compounds with a high hydrogen content might be, in effect, chemically recompressed metallic hydrogen. In a recent development, superconductivity, highest T_c in carbonaceous Sulphur hydride under a pressure of about 2.6million atmospheres (267Gpa) has been achieved (Dias and Salamat, 2021) They used Diamond Anvil Cell (DAC) to achieve this pressure and the material super conducted at 288K (15°C). This development is the most significant breakthrough since the discovery of the high-Tc cuprates (Bednorz and Mueller, 1986). There is every reason to anticipate even higher values of Tc for other hydrides, which means that achieving superconductivity at room temperature now appears perfectly realistic. Determination of the structure of the new hydrides with synchrotron X-ray diffraction is overwhelming evidence of the conventional s-wave superconductivity in the hydrides at high pressures (Drozdov *et al*, 2015). Lanthanum superhydride has recently showed s-wave superconductivity under high pressure. (Sun *et al*, 2021). Purans *et al* (2021) motivated by the discovery of superconductivity above 250 K at high pressure in LaH_{-10} and the prediction of overcoming the room temperature threshold for superconductivity in YH_{10} and the urge for a better understanding of hydrogen interaction mechanisms used locally sensitive X-ray absorption fine structure spectroscopy (XAFS) to get insight into the nature of

phase transitions and the rearrangements of local electronic and crystal structure in YH_3 under pressure up to 180GPa. They provided evidence of strong effect of hydrogen on the density of yttrium states that increases with pressure and XAFS data showed evidence a strong anharmonicity.

Therefore understanding the thermodynamic properties and pairing mechanisms of hydride compounds under pressure can help find a metastable form of hydrides for commercialization of the uses**.** A theory to explain the charge pairing mechanisms that pressure brings about is the limiting factor. There has been consistency between theoretical predictions and calculations and most importantly, the general theory of conventional superconductivity on superconductivity in hydrides and the experimental findings. However, some inconsistencies exist between the predictions and experiments, most prominent of all being the experimental electron–phonon coupling under high pressure. Exploring the thermodynamic properties of hydrides under pressure has been done in this research.

Methodology

In this research, the effective Hamiltonian of the system was diagonalized using the BVT (Bogoliubov-Valatin Transformation) formalism and used to further obtain energy of sulphur hydride (H_3S) and other thermodynamic properties. The general Hamiltonian of an electron-electron interaction is given by;

$$H = H_o + H_1 \tag{1.0}$$

H_o is the unperturbed Hamiltonian system and is sometimes called Bloch energy while H_1 is the interaction.

Which can be written as:

$$H = \sum_k \varepsilon_k n_k + \sum_{k'} \square_{k'} n_{k'} - \sum_{kk'} V_{kk'} n_k n_{k'} \tag{1.1}$$

In terms of electron creation and annihilation operators, equation (1.1) it can be written as;

$$H = \sum_k \mathfrak{E}_k c_{k\uparrow}^{\dagger} c_{-k\downarrow} + \sum_{k'} \mathfrak{E}_{k'} c_{k'\uparrow}^{\dagger} c_{-k'\downarrow} - \sum_{kk'} V_{kk'} c_{k'\uparrow}^{\dagger} c_{k\uparrow}^{\dagger} c_{-k\downarrow} c_{-k'\downarrow} \tag{1.2}$$

Where $n_k = c_{k\sigma}^{\dagger} c_{k\sigma}$ Is the electron number operator.

We now introduce quasiparticle creation and annihilation operators known as Bogoliubons where creation and annihilation operators are $\gamma^{\dagger}$ and γ respectively. The creation and annihilation operators of electrons and quasiparticles are related as.

$$c_{k\uparrow}^{\dagger} = u_k \gamma_{k\uparrow}^{\dagger} + v_k \gamma_{-k\downarrow}$$
$$c_{k\uparrow} = u_k \gamma_{k\uparrow} + v_k \gamma_{-k\downarrow}^{\dagger}$$
$$c_{-k\downarrow}^{\dagger} = u_k \gamma_{-k\downarrow}^{\dagger} - v_k \gamma_{k\uparrow}$$
$$c_{-k\downarrow} = u_k \gamma_{-k\downarrow} - v_k \gamma_{k\uparrow}^{\dagger} \tag{1.3}$$

Where the number operators are;

$$\gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} = m_k$$
$$\gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} = (1 - m_k) \tag{1.4}$$

We now substitute (1.3) and (1.4) in (1.2)

$$H = \left\{ \begin{array}{l} \sum_k \varepsilon_k (u_k \gamma_{k\uparrow}^{\dagger} + v_k \gamma_{-k\downarrow})(u_k \gamma_{-k\downarrow} - v_k \gamma_{k\uparrow}^{\dagger}) \\ + \sum_{k'} \varepsilon_{k'} (u_{k'} \gamma_{k'\uparrow}^{\dagger} + v_{k'} \gamma_{-k'\downarrow})(u_{k'} \gamma_{-k'\downarrow} - v_{k'} \gamma_{k'\uparrow}^{\dagger}) \\ - \sum_{kk'} V_{kk'} \begin{pmatrix} (u_{k'} \gamma_{k'\uparrow}^{\dagger} + v_{k'} \gamma_{-k'\downarrow})(u_k \gamma_{k\uparrow}^{\dagger} + v_k \gamma_{-k\downarrow}) \\ (u_k \gamma_{-k\downarrow} - v_k \gamma_{k\uparrow}^{\dagger})(u_{k'} \gamma_{-k'\downarrow} - v_{k'} \gamma_{k'\uparrow}^{\dagger}) \end{pmatrix} \end{array} \right\} \tag{1.5}$$

Expanding equation (1.5)

$$\begin{aligned} H = \sum_k \varepsilon_k & \left(u_k^2 \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} + u_k v_k [\gamma_{-k\downarrow} \gamma_{-k\downarrow} - \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger}] \right. \\ & \left. - v_k^2 \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \right) \sum_k \square_k \left(u_k^2 \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} \right. \\ & \left. + u_k v_k [\gamma_{-k\downarrow} \gamma_{-k\downarrow} - \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger}] \right. \\ & \left. - v_k^2 \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \right) - \end{aligned}$$

$$\sum_{kk'} V_{kk'} \begin{pmatrix} u_k^4 \gamma_{k'\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{-k'\downarrow} - u_k^3 v_k \gamma_{k'\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{k'\uparrow}^{\dagger} \\ -u_k^3 v_k \gamma_{k'\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{-k'\downarrow} - u_k^2 v_k^2 \gamma_{k'\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{k'\uparrow}^{\dagger} \\ +u_k^3 v_k \gamma_{k'\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{-k\downarrow} \gamma_{-k'\downarrow} - u_k^2 v_k^2 \gamma_{k'\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{-k\downarrow} \gamma_{k'\uparrow}^{\dagger} \\ -u_k^2 v_k^2 \gamma_{k'\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{-k'\downarrow} + u_k v_k^3 \gamma_{k'\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{k'\uparrow}^{\dagger} \\ +u_k^3 v_k \gamma_{-k'\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{-k'\downarrow} - u_k^2 v_k^2 \gamma_{-k'\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{-k\downarrow} \gamma_{k'\uparrow}^{\dagger} \\ -u_k^2 v_k^2 \gamma_{-k'\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{-k'\downarrow} - u_k v_k^3 \gamma_{-k'\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \gamma_{k'\uparrow}^{\dagger} \\ +u_k^2 v_k^2 \gamma_{-k'\downarrow} \gamma_{-k\downarrow} \gamma_{-k\downarrow} \gamma_{-k'\downarrow} - u_k v_k^3 \gamma_{-k'\downarrow} \gamma_{-k\downarrow} \gamma_{-k\downarrow} \gamma_{k'\uparrow}^{\dagger} \\ -u_k v_k^3 \gamma_{-k'\downarrow} \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{-k'\downarrow} + v_k^4 \gamma_{-k'\downarrow} \gamma_{-k\downarrow} \gamma_{k\uparrow}^{\dagger} \gamma_{k'\uparrow}^{\dagger} \end{pmatrix} \tag{1.6}$$

Since we are interested in the pairing, all terms $\gamma\,\gamma\,\gamma\,\gamma$ will be ignored because they represent single unpaired particles. Then rearranged.

$$H = \left\{ \begin{array}{l} 2 \sum_k \varepsilon_k \begin{pmatrix} (u_k^2 + v_k^2) m_k + \\ u_k v_k [\gamma_{-k\downarrow} \gamma_{-k\downarrow} - \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger}] \\ - v_k^2 \end{pmatrix} \\ - \sum_{kk'} V_{kk'} \begin{pmatrix} u_k^4 m_k m_k' + v_k^4 (1 - m_k) \\ (1 - m_k') \\ -2 u_k v_k^3 \end{pmatrix} \begin{bmatrix} \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} \\ -\gamma_{-k\downarrow} \gamma_{-k\downarrow} \end{bmatrix} \\ - \sum_{kk'} V_{kk'} \begin{pmatrix} -u_k^2 v_k^2 m_k' (1 - m_k) - u_k^2 v_k^2 m_k \\ (1 - m_k') \\ +2 u_k^3 v_k m_k [\gamma_{-k\downarrow} \gamma_{-k\downarrow} - \gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger}] \\ +2 v_k^3 m_k' [\gamma_{k\uparrow}^{\dagger} \gamma_{k\uparrow}^{\dagger} - \gamma_{-k\downarrow} \gamma_{-k\downarrow}] \end{pmatrix} \end{array} \right\} \tag{1.7}$$

We determine the values of u_k and $v_k$used for the diagonalization. We equate the off-diagonal terms to zero and obtain:

$v_k = +1$ (1.8)

Since we are interested in the pairing, we impose bosonic probability condition,

$u_k^2 - v_k^2 = 1$ (1.9)

$u_k = \sqrt{2}$ (2.0)

We take positive values since u_k and v_k are real and positive. These values diagonalize the Hamiltonian

$$H_{Diag} = -2\sum_k \varepsilon_k v_k^2 - \sum_{kk'} V_{Kk'} v_k^4 \quad (2.1)$$

The magnitude of the ground state energy of the system is obtained as,

$|E_o| = 2\varepsilon_k + V_{Kk'}$ (2.2)

We express the energy of the system at any temperature as a function of temperature by multiplying the ground state energy by the thermal activation factor given by: $exp\left(-\frac{\Delta E}{k_B T}\right)$ where k_B is the Boltzmann's constant and ΔE is the superconducting energy gap. The energy of the quasi particles for superconductivity is very small quantity and is generally 1% of the minimum energy of the system (Ayodo, 2008). Therefore, at any temperature T, the energy of the system is given by:

$$E(T) = E_o exp\left(-\frac{2\varepsilon_k + V_o}{k_B T}\right) \quad (2.3)$$

For the two hydrides from table 1 and equation (2.1);

$E_o = 100meV\ or\ 0.10eV\ or\ 1.602\ x\ 10^{-20}J \quad for\ H_3S$

$E_o = 97.27meV\ or\ 0.09727eV\ or\ for\ LaH_{10}$

Table 1 *Experimental and computational values of pressure and* Tc *for* H_3S and LaH_{10}

Hydride	ε_k (MeV)	V_o (MeV)	ω_D (MeV)	Δ_o (Me V)	P (GPa)	T_c (k)	Reference
H_3S	25	50	160	76	150	200	Capitani *et al.*, 2017
LaH_{10}	24.3	48.6	113	51	210	237.9	Elatresh *et al.*, 2020

The values of ω_D, Δ_o, pressure and T_c are obtained from experimental results while values of ε_k *and* V_o are mathematically determined using the equation below.

$V_o = -2\varepsilon_k$ (2.4)

Where ε_k is a single particle energy

$\omega_D = 2\sqrt{{\varepsilon_k}^2 + |\Delta_o|^2}$ (2.5)

From the table, the energy of the system, using equation (2.3) can be given as;

$E(T) = 100exp\left(-\frac{11.59}{T}\right)$ For H_3S (2.6)

$E(T) = 97.2exp\left(-\frac{11.27}{T}\right)$ For LaH_{10} (2.7)

From these energy values, entropy is obtained. Moreover, the energy values are used to find a relationship between the energy of the systems and their cell volumes when pressure is applied.

Entropy (s)

It's the measure of disorder of a system. It's given as the integral of the specific heat capacity at constant volume with respect to temperature. It's given by;

$S = \int \frac{C_v}{T} dT$ (2.8)

Which simplifies to

$S(T) = 0.08628 + \frac{1127}{T}\left\{exp\left(-\frac{1127}{T}\right)\right\}$ (2.9)

Pressure effects

Birch-Murnaghan equation of state is used to determine the relation between pressure, volume and energy of the system. The equation of state relates to the high-pressure effect on matter at given volume. The equation is given by;

$$p(v) = \frac{3B_o}{2}\left[\left(\frac{v_o}{v}\right)^{\frac{7}{3}} - \left(\frac{v_o}{v}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(B_o' - 4)\left[\left(\frac{v_o}{v}\right)^{\frac{2}{3}} - 1\right]\right\} \quad (3.0)$$

Where p is the pressure, v_o is the reference volume at zero pressure, v is the deformed volume, B_o is the bulk modulus and B_o' is the derivative of the bulk modulus with respect to pressure. The bulk modulus and its derivative are usually obtained from experimental data.

In terms of energy, the Birch-Murnaghan equation written as.

$$E(v) = E_o + \frac{9v_o}{16}\left\{\left[\left(\frac{v_o}{v}\right)^{\frac{2}{3}} - 1\right]^3 B_o' + \left[\left(\frac{v_o}{v}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{v_o}{v}\right)^{\frac{2}{3}}\right]\right\} \quad (3.1)$$

We obtain the bulk modulus B by fitting E (Total energy of the system) versus v (volume) curve to the above equation. The smaller the B, the weaker the interaction between atoms and smaller forces constantly resulting in a lower frequency of phonons. (Huang *et al*, 2010)

For the hydrides under study, the following are experimental data from literature.

Table 2: Experimental and computational values of Bulk modulus and reference volume at zero pressure.

Hydride	E_o(meV)	B_o (GPa)	v_o($a.u^3$)	B_o'	References
Sulphur hydride	100	129.8	158.4	3.6	Durajeski *et al.*, 2017
Lanthanum hydride	97.2	31.1	81.5	4	Geballe *et al.*, 2018

From the above data, equation (3.0) becomes.

$$p(v) = 194.7\left[\left(\frac{158.4}{v}\right)^{\frac{7}{3}} - \left(\frac{158.4}{v}\right)^{\frac{5}{3}}\right]\left\{1 + 0.3\left[1 - \left(\frac{158.4}{v}\right)^{\frac{2}{3}}\right]\right\} \quad \text{For } H_3S \qquad (3.2)$$

$$p(v) = 46.65\left[\left(\frac{81.5}{v}\right)^{\frac{7}{3}} - \left(\frac{81.5}{v}\right)^{\frac{5}{3}}\right] \quad \text{For } LaH_{10} \qquad (3.3)$$

P-V graphs can be drawn to relate pressure on the two hydrides and volume on the structure.
From equation (3.1), in terms of energy, the Birch-Murnaghan equation for the two hydrides can be simplified to.

$$E(v) = 100 + 89.1\left\{\left[\left(\frac{158.4}{v}\right)^{\frac{2}{3}} - 1\right]^3 3.6 + \left[\left(\frac{158.4}{v}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{158.4}{v}\right)^{\frac{2}{3}}\right]\right\} \text{ For } H_3S \qquad (3.4)$$

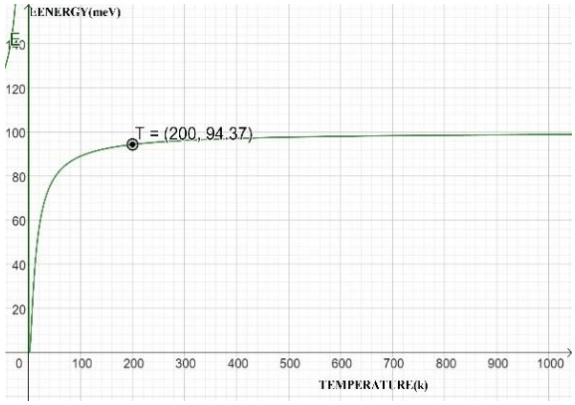
$$E(v) = 97.2 + 45.84\left\{\left[\left(\frac{81.5}{v}\right)^{\frac{2}{3}} - 1\right]^3 4 + \left[\left(\frac{81.5}{v}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{81.5}{v}\right)^{\frac{2}{3}}\right]\right\} \text{ For } LaH_{10} \qquad (3.5)$$

E(T)-V graphs can be drawn to relate energy of the two hydrides and volume under pressure.

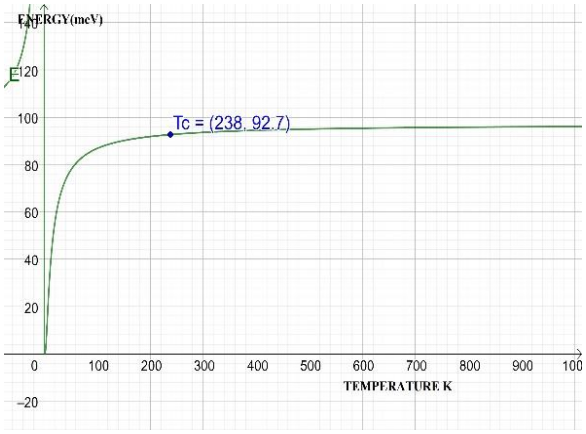
RESULTS AND DISCUSSION.

A. ENERGY OF THE SYSTEM.

The total energy of a system results from the interaction between the particles of the system. The energy due to interaction between the particles increases with an increase in the temperature of the system. At a temperature above the Tc the energy of the system is so high that the energy gap does not exist anymore due to the increased agitation of the particles. At this point the material changes from superconducting to normal state.



H_3S (Fig 1(a)): Energy versus Temperature

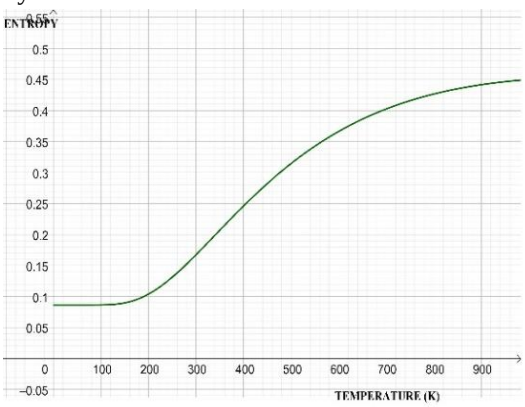


LaH_{10} (Fig 1(b)) Energy versus Temperature

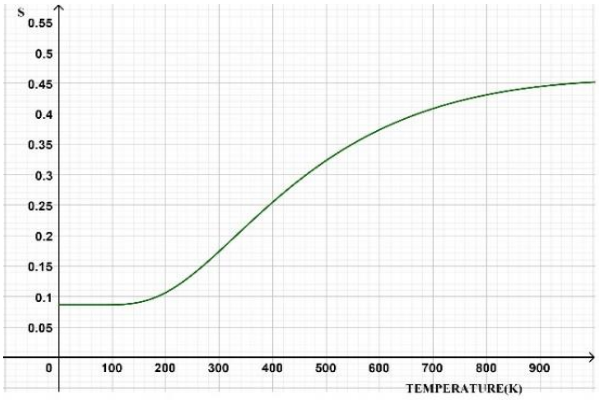
The system in the ground state has the lowest energy as clearly illustrated by the figure 1(a) and 1(b). The electrons are non-interacting at this zero temperature hence coupling energy is zero. The lower states are filled up and above superconducting gap states are empty. As temperature increases, an increase in energy is noted and approaches plateau. Kibe (2015) and Odhiambo (2016) observed sigmoid curves when at different time related energy of a system to temperature. However, the curve observed in this study for the hydrides are not sigmoid but show a sharp increase in energy with temperature.
Under ambient pressure (1atmos), H_3S and LaH_{10} do not superconduct. As pressure increases for LaH_{10}, electrons can be transferred from filled S-orbitals to d-orbitals due to small energy difference between the orbitals when pressure is exerted. The Cooper pairs are collectively excited to cause an exponential increase in energy. There is an increase in density of states at the Fermi level. The maximum energy of the cooper pairs at T_C=200K (Capitani, *et al*, 2017) for H_3S is observed from the curve fig 1(a`) to be $94.37meV$ *or* $0.09437eV$ at 150GPa while LaH_{10} with a T_C=237.9K at 210GPa (Elatresh *et al*, 2020) has been observed to be $92.7meV$ *or* $0.0927eV$. E=0meV when T=0k.

B. Entropy

The entropy versus temperature curves for the two hydrides are shown below.



H_3S (2a): Entropy versus Temperature



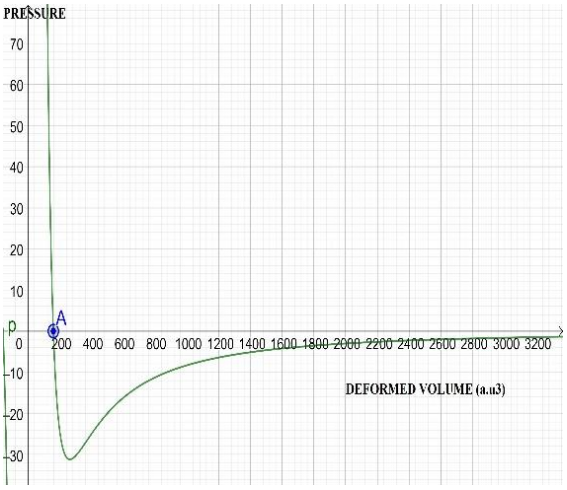
LaH_{10} (2b): Entropy versus Temperature

The curves indicate that entropy is nearly zero (0.0882) when temperature T=0K. The system with a large energy gap absorbs low energy. The system energy absorption is suppressed; the system is more ordered hence low entropy. At Tc, the systems have lowest entropy but rises exponentially as temperature rises. The system becomes more disordered as more energy is absorbed beyond Tc. Higher pressure speeds up closing of the gaps. It plateaus as temperature rises because pressure cannot sustain the increased disorder anymore. The value of entropy for the two hydrides is 0.15meV/K^2 for H_3S and 0.13meV/K^2 for LaH_{10} at Tc. The highest entropy for H_3S is 0.450meV/K^2 and occurs at 900K while for LaH_{10} highest entropy of 0.451meV/K^2 occurs at 1000K. This suggests LaH_{10} could be more ordered at a higher temperature than H_3S and could be better candidate for room temperature superconductor. The entropy at Tc is much lower. The free energy of the normal state is much higher than the free energy of the superconducting state at temperatures below the critical temperature value and this therefore makes the superconducting phase appear below T_C. A decrease in internal energy of the system is observed with the diminishing or reduction of the state of the disorder and so this implies that increase in temperature provides more kinetic energy causing increase in thermal entropy (Mumali *et al*, 2016)

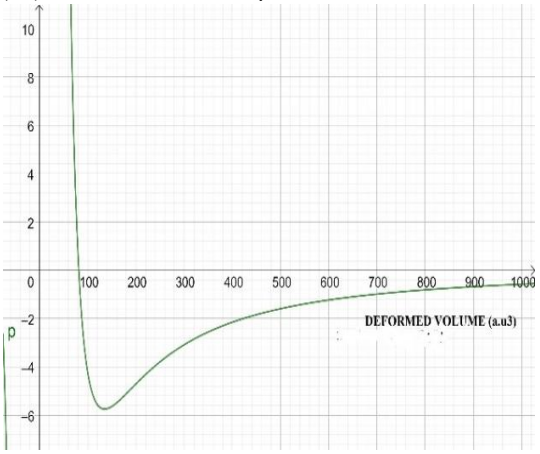
From the curves, state of disorder in normal state is generally higher than that of superconducting state at all temperatures below the Tc (200k for H_3S and 237.9K for LaH_{10}) showing that superconducting state is more ordered. These results agree with those of other theoretical studies involving s-wave pairing mechanisms like in heavy fermions (Kibe *et al*, 2015 and Waswa *et al*, 2017).

C. Pressure and deformed volume

The pressure verses deformed volume for the two hydrides are as shown below;



H_3S (3a) Pressure versus Deformed volume



LaH_{10} (3b) Pressure versus Deformed volume

Both graphs *H_3S (aa) and LaH_{10} (3b)* are a convex hull just like those obtained experimentally by Zhou, D *et al* (2020) while studying praseodymium super hydrides (Pr-H system). Kruglov *et al* (2020) obtained similar curves while studying stability of LaH_{10} and LaH_{10} polyhydrides under pressure. Li, Z. *et al*. (2022) found that most of elemental metals on the boundary of s and d blocks in the elemental periodic table such as La in LaH_{10} and Y in YH_9 their electrons can be transferred from filled s orbital to d orbital under high pressure due to the small energy difference between these orbitals, which usually increases the structural instability and enhances the electron-phonon coupling strength and thus leads to possible high Tc as well. And therefore under high pressure, incoherent Cooper pairs first preform aboveTc, causing the opening of a pseudogap, and then, at Tc, condense into the phase-coherent superconducting state. Such a two-step scenario implies the existence of a new energy scale, Δc, driving the collective superconducting transition of the preformed pairs just as suggested by Dubouchet, *et al* (2019). Therefore, high pressure alters the lattice of the materials, causing a two-step superconducting state that causes collective excitation of Cooper pairs.

From the two curves, at a larger volume, pressure is almost equal to zero. As pressure increases, cell volume reduces and more attractive potential between Cooper pairs is

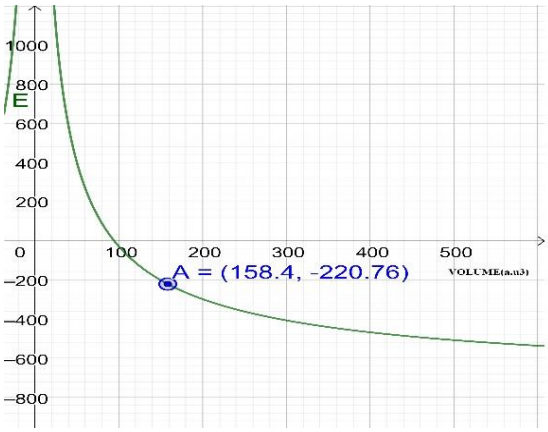
favored until a reference equilibrium volume is attained. Beyond this, pressure results to a repulsive effect as the curve shifts upwards to the positive. This study therefore suggests that pressure reduces coherence length of the Cooper pairs causing a possible increase in the energy gap. Coherence length ξ_o is inversely proportional to energy gap Δ

$\xi_o = \frac{2\hbar v_F}{\pi\Delta}$ (Drozdov *et al*. 2016). v_F -electron velocity near Fermi level and Δ - superconducting energy gap

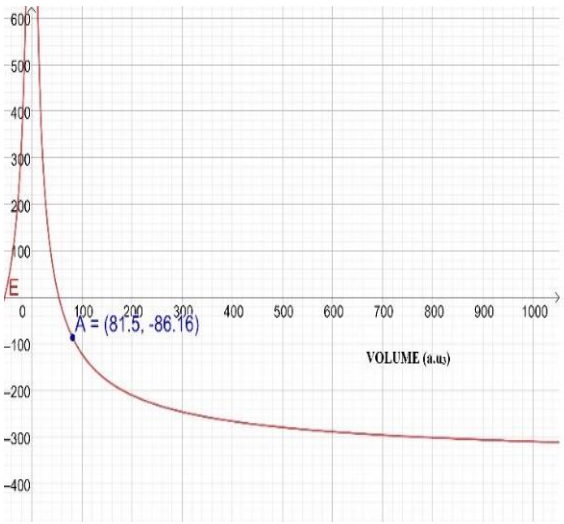
Energy gap is directly proportional to Tc, giving rise to high Tc when pressure is increased.

D. Energy of system under pressure and deformed volume

The energy verses deformed volume for the two hydrides are as shown below;



H_3S (4a): Energy of the system versus deformed volume



LaH_{10}(4b): Energy of the system versus deformed volume.

Both graphs *H_3S (4a) and LaH_{10} (4b)* are a convex hull just like those obtained experimentally by Zhou, D *et al* (2020) while studying praseodymium super hydrides (Pr-H system). Kruglov *et al* (2020) obtained similar curves while studying stability of LaH_{10} and LaH_{10} polyhydrides under high pressure. At larger cell volumes, the coherence length of Cooper pairs is longer. A decrease in the cell volume decreases coherence length, increasing energy gap until an equilibrium volume beyond which the attractive potential between Cooper pairs decreases and favors Coulombic forces. From the graphs, H_3S at a deformed volume of 158.4 $a.u^3$ has attractive potential energy of -220.76meV. At v=100$a.u^3$, E=0meV. Therefore, the cell volume of H_3S is found to be 100$a.u^3$. The bulk modulus for H_3S at 158.4$a.u^3$ is B=129.8GPa (Durajski, & Szczęśniak, 2017)).

Similarly, LaH_{10} at a deformed cell volume of 81.5$a.u^3$ has an attractive potential energy of -86.16meV. At v=45 $a.u^3$, E=0meV. Therefore, the cell volume is found to be 45$a.u^3$. Bulk modulus at deformed volume of 81.5 $a.u^3$ is B=31.1GPa (Geballe *et al*., 2018).

The smaller the B, the weaker interactions between atoms and the smaller the force constants resulting in a lower phonon frequency (Huang et al., 2010). Therefore, H_3S has higher energy at the stated volume and due to its higher B, there are stronger interactions and hence higher phonon frequencies than LaH_{10}.

Energy required to break a Cooper pair is twice the superconducting energy gap of the system (Pan, X *et al*. 2022). From the curves, the energy required to break the Cooper pairs in H_3S was found to be -220.76meV. The energy gap for the hydride at the stated pressure is 76mev. Twice this energy gives 152meV. A gap difference of 66.7meV is obtained and this is attributed to pressure increased that raises the energy required to break the Cooper pairs. However this does not apply for the results of LaH_{10} with energy gap of 51meV and energy obtained of 86.16meV from the curve 5.7(b).

ACKNOWLEDGEMENT

The authors would like to express their gratitude to Kibabii University and Bomet University College for the opportunity and enabling environment to conduct this research.

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