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STUDY OF SUPERCONDUCTIVITY IN ANTIMONY(Sb) UNDER PRESSURE

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STUDY OF SUPERCONDUCTIVITY IN ANTIMONY(Sb) UNDER PRESSURE

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Study of Superconductivity in Antimony(Sb) Under Pressure

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This work is dedicated to my wife, Tizita Gebeyehu

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Abstract

In this work, theoretical investigation on the superconductivity of Antimony under pressure has been made. Experimental and theoretical values of pressure dependent parameters like, electron-phonon coupling constant(λ), average phonon frequency($\langle\omega\rangle$) and the corrosponding Debye temperature(Θ_D) are used to calculate superconducting transition temperature(T_c) of the rhombohedral(A7), trigonal approximant(TA) and BCC phases of Antimony using the modified McMillan transition temperature equation. The calculated superconducting transition temperature(T_c) shows a characteristic dependence on pressure. At the phase transition from A7 to TA, a considerable increase in T_c is observed with increasing pressure. A large jump in T_c is found at the transition pressure from TA to BCC and reaches its turning point at T $\approx 9.79K$.

Chapter 1

General Introduction

1.1 The discovery of superconductivity

Superconductivity, one of the most interesting phenomena in condensed matter physics, was discovered in 1911 by H. Kamerlingh Onnes while he was investigating the electrical properties of metals in extremely cold temperatures [1]. Onnes passed current through a very pure mercury wire and measured its resistance as he steadily lowered the temperature. As in many other metals, the electrical resistance of mercury decreased steadily upon cooling. At 4.2K, however, its resistance suddenly dropped to zero as shown in figure(1.1). Current was flowing through the wire and nothing was stopping it. According to Onnes, "Mercury has passed into a new state called superconducting state" and he chose the name superconductivity for this newly discovered perfect conductor.

Following the first discovery of this remarkable phenomenon in mercury(Hg), many other elemental metals were found to exhibit zero resistance when their temperatures were lowered below a certain characteristic temperature called the critical temperature(T_c) [5]. In 1913, lead was found to superconduct at 7.2K and in 1930,

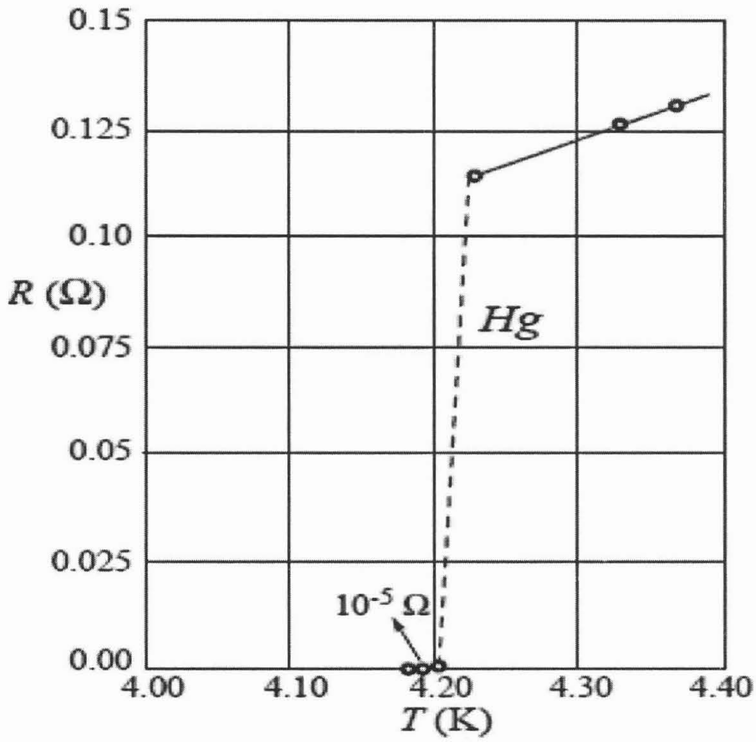

Figure 1.1: Abrupt change of resistivity of liquified mercury with temperature as observed by Onnes [1].

superconductivity was discovered in niobium, occurring at 9.2K and it has been the highest critical temperature amongst all elemental metals.

In 1950, Russian physicists V. L. Ginzburg and L. Landau developed a powerful phenomenological theory describing the transition between the superconducting and the normal phases that could explain superconductivity as a second order phase transition [3]. The Ginzburg-Landau theory was a macroscopic theory which was useful in understanding the unique electrodynamic properties of the superconductor. In the same year, Maxwell and Reynolds et al found that, the critical temperature of a superconductor depends on the isotopic mass of the constituent element. This important discovery was the first important motivation to study electron-phonon interaction as the microscopic mechanism responsible for superconductivity.

In 1962, the first commercial superconducting wire, a niobium-titanium alloy (NbTi), was developed by researchers at Westinghouse [2]. In the same year, Brian D. Josephson made an important theoretical prediction that, paired electrons could flow between two pieces of superconductors even when separated by a thin layer of insulator. This tunneling phenomenon, now called the "Josephson Effect", has been applied to electronic devices such as Superconducting Quantum Interference Devices (SQUID) which can detect even very weak magnetic fields [8].

An important development in physics that created much excitement in the scientific community was the discovery of high-temperature copper-oxide-based superconductors. The excitement was began in 1986 when Georg Bednorz and Alex Mueller [10] had discovered superconductivity in a lanthanum based cuprate perovskite material which had a transition temperature of 35K. Their discovery was remarkable since the critical temperature was significantly higher than those of any previously known superconductors. Barium yttrium cuprate ($Ba_2YCu_3O_7 - \delta$) (BYCO) was discovered in 1987 to be superconducting with a transition temperature (T_c) of 92K. It was the first material discovered to exhibit superconductivity above the boiling temperature of nitrogen (77K) [2].

1.2 The BCS theory

A microscopic theory of superconductivity was developed in 1957 by American physicists John Bardeen, Leon Cooper and J. Robert Schrieffer, which is nowadays known as the BCS theory [9]. From classical physics point of view, part of the resistivity of a metal is due to collisions between free electrons and part is due to scattering of electrons from impurities or defects in metals. Since electrons in a material always suffer from some collisions, resistivity can never be zero. Classical physics, therefore, could not explain the superconducting state [5].

Until the discovery of the BCS theory, no one could explain why electrons enter the superconducting state and why such electrons in a superconducting state are not scattered by impurities and lattice vibrations. In the BCS theory, superconductivity is resulted from condensation of electron pairs called Cooper pairs. A Cooper pair is the name given to the electrons that are bound together in a certain manner and first discovered by Leon Cooper [9]. Cooper showed that at sufficiently low temperatures, it is possible for two electrons interacting above a Fermi sea to form bound pairs as long as any attractive force between electrons existed. These pairs are phonon mediated and formed between electrons with opposite spin and momentum.

According to Cooper, an electron with spin$\uparrow$ and momentum ($\overrightarrow{k}$) moving through the crystal attracts the nearest ions as it moves through the lattice causing a small region of net positive charge which then attracts a second electron with spin$\downarrow$ and momentum (-$\overrightarrow{k}$). These two electrons, which are spatially separated by an average separation called the coherence length(ξ_0) have formed a pair in momentum-space.

The convenience of this phonon mediated process is that (ξ_0) is typically much larger than the lattice spacing, there by avoiding Coulomb repulsion between the two electrons.

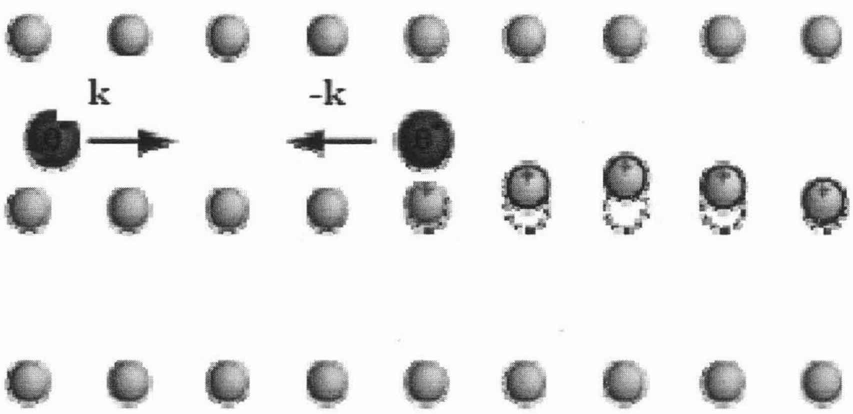

Figure 1.2: Diagram illustrating the formation of Cooper pair [12]

The BCS theory correctly predicts the energy required to break up a Cooper pair into two free electrons called the energy gap ($2\triangle$). To break one pair, we have to change energies of all other pairs unlike the normal metal in which the state of an electron can be changed by adding an arbitrary small amount of energy. The energy gap is highest at low temperatures but does not exist at temperatures higher than the critical temperature(T_c). This theory also expresses how the energy gap depends on the strength of attractive interaction, density of states, the temperature(T) and the critical temperature(T_c) but is independent of the material. BCS theory explored superconductivity at a temperature close to zero for elements and simple alloys (conventional) superconductors. However, at high temperature and with different superconducting system, the BCS theory has become insufficient to fully explain how superconductivity occurs.

The supercurrent(I_s) is not the movement of individual electrons as it is for normal conductivity rather it is the motion of the Cooper pairs' center of mass. Allowing Cooper pairs to be formed and move freely, there by giving superconductors their most well known feature (zero resistance), is not its defining feature.

1.3 The Meissner Effect

The first concept that comes to our mind when we hear the word superconductors is zero resistance. However, there is another equally significant aspect of superconductors called diamagnetism. The Meissner effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state. The German physicists Walther Meissner and Robert Ochsenfeld discovered the phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples [12]. The samples in the presence of an applied magnetic field were cooled below their transition temperature and the magnetic fields inside were expelled from the interior of the materials as shown in figure(1.3) provided the applied magnetic field is weak. The experiment demonstrated for the first time that superconductors were more than just perfect conductors and provided a uniquely defining property of the superconducting state.

In a weak applied field, a superconductor can produce electric currents near its surface. The magnetic field of these surface currents cancels the applied magnetic field within the bulk of the superconductor. As the field expulsion does not change with

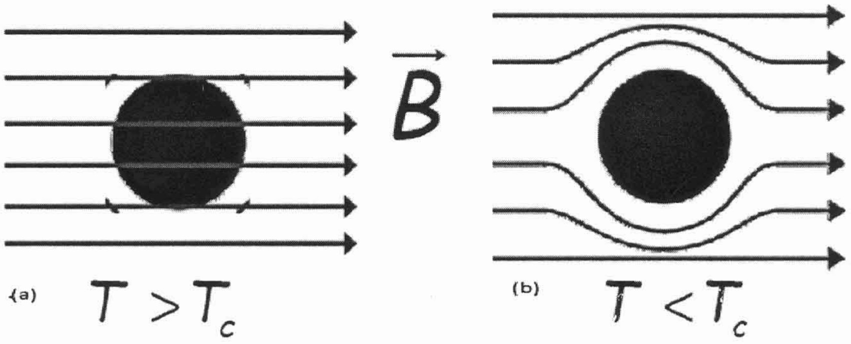

Figure 1.3: a) Magnetic filed penetrating a superconductor above the critical temperature $T > Tc$, b) Magnetic field expelled from superconductor below the critical temperature $T < Tc$ [6]

time, the currents producing this effect (called persistent currents) do not decay with time. Therefore, the conductivity can be thought as infinite resulting in a superconducting system. However, superconductors did not completely cancel the magnetic field near their surface and each superconducting material has its own characteristic penetration depth called the London penetration depth (λ_L) which characterizes the distance to which the magnetic field penetrates into a superconductor. Thus, we can define Meissner effect using London penetration depth. That is, when a superconductor is placed in a weak external magnetic field, the field penetrates for only a short distance (λ_L) called the penetration depth after which it decays rapidly to zero. This phenomenon is called the Meissner effect [12].

1.4 London theory

After the discovery of superconductivity, it took more than 20 years to develop the first phenomenological theory to describe the phenomenon. In 1935, F. and H. London [7] showed that, the Meissner effect was a consequence of the minimization of the electromagnetic free energy carried by superconducting current. To explain the Meissner effect, London proposed the London equation given by,

$$\nabla \times J + \frac{n_s e^2}{mc} B = constant \tag{1.4.1}$$

Since the magnetic field induction B in the bulk of a superconductor must be zero, London proposed that the constant had to be zero. The London equation implies that in stationary conditions, a superconductor can not sustain a magnetic field in its interior, but only with in a narrow layer. If we use the Maxwell equation

$$\nabla \times B = (\frac{4\pi}{c})J \tag{1.4.2}$$

implies

$$\nabla \times (\nabla \times B) = (\frac{4\pi}{c})\nabla \times J \tag{1.4.3}$$

Using equation (1.4.1) we have

$$\nabla \times J = (\frac{n_s e^2}{mc})B \tag{1.4.4}$$

Combining equations (1.4.3) and (1.4.4) we can get

$$\nabla \times (\nabla \times B) = -(\frac{4\pi n_s e^2}{mc^2})B \tag{1.4.5}$$

But we know that,

$$\nabla \times (\nabla \times B) = \nabla(\nabla \times B) - \nabla^2 B \tag{1.4.6}$$

Finally equations (1.4.4) and (1.4.5) gives us

$$\nabla^2 B = \frac{4\pi n_s e^2}{mc^2} B = \frac{1}{\lambda_L^2} B \tag{1.4.7}$$

where $\lambda_L^2 = mc^2/4\pi n_s e^2$ and is the London magnetic field penetration depth.

In one dimension the solution of equation (1.4.7) is

$$B(x) = B(0)\exp(-x/\lambda_L) \tag{1.4.8}$$

where, B(0) is the magnitude of magnetic field outside the superconductor applied parallel to the surface. This equation implies that, the applied magnetic field(B(0)) enters the superconducting sample and decreases exponentially over the London penetration depth(λ_L) as shown in figure(1.4). It is important to know that, the magni-

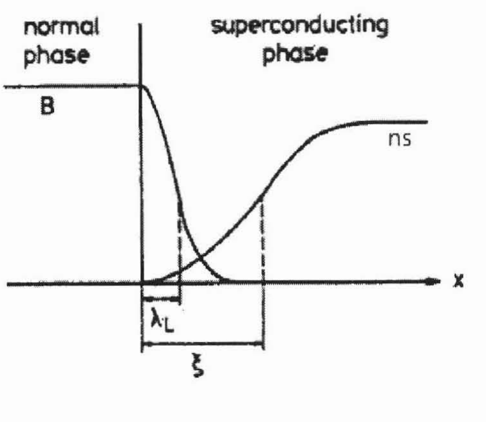

Figure 1.4: The exponential drop of the magnetic field and the rise of the Cooper-pair density at a boundary between a normal and a superconductor [11].

tude of the penetration depth is directly related to the Cooper pair density(n_s). As dependence of λ_L is given by the empirical formula

$$\lambda_L(T) = \frac{\lambda_L(0)}{[1 - (\frac{T}{T_c})^4]^{\frac{1}{2}}} \tag{1.4.9}$$

1.5 Types of superconductors

Strong magnetic field destroys superconductivity and restore the normal conducting state. Depending on the character of this transition, superconductors can be classified as type I and type II superconductors [1]. Even though their response to applied magnetic field is entirely different, both type I and type II superconductors have similar thermal properties at the superconductor- normal transition in zero magnetic fields. Moreover, there is no any difference in their mechanism of superconductivity. Their response to applied magnetic field can be explained depending on the Ginzburg Landau penetration depth(λ_{GL}) to the Ginzburg Landau coherence length(ξ_{GL}) ratio. i.e

$$\kappa = \frac{\lambda_{GL}}{\xi_{GL}}$$

where κ is Ginzburg Landau characteristic parameter.

1.5.1 Type I superconductors

For a Type I superconductor, loss of superconductivity occurs continuously through a first order phase transition at the critical field(H_c) [5]. Type I superconductors are characterized as the soft superconductors. They are usually elemental superconductors. In the superconducting state, type I superconductors are completely diamagnetic and $\kappa < \frac{1}{\sqrt{2}}$ [11], that is, when these superconductors are placed in a magnetic field, all the lines of induction are pushed out from the specimen. As magnetic field is increased, the material remains diamagnetic until the critical value H_c is reached. At

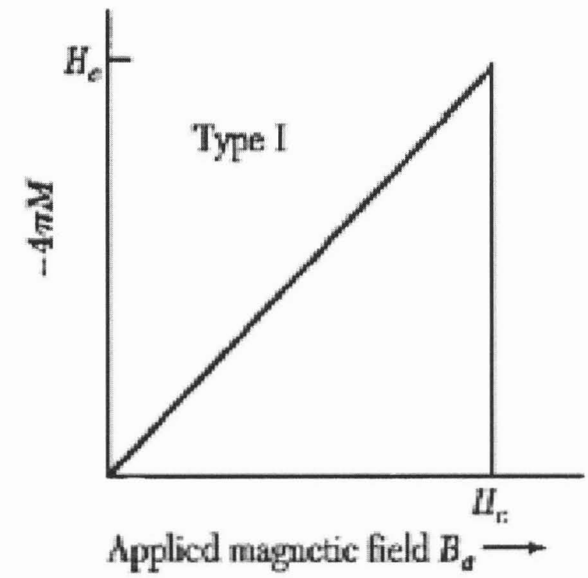

Figure 1.5: Magnetization versus applied magnetic field for a bulk superconductor exhibiting a complete Meissner effect [4]

this point the induced magnetic field exactly cancels the applied magnetic field until there is an abrupt change from the superconducting state to the normal state. From Fig.(1.5), it is clear that for Type I superconductors upto H_c, the magnetization of the material grows in proportion to the external magnetic field and then abruptly drops to zero at the transition to the normal conducting state. The strength of the applied magnetic field required to completely destroy the state of perfect diamagnetism in the interior of the superconducting specimen is called the thermodynamic critical field(H_c). The variation of this thermodynamic critical field(H_c) with temperature for type I superconductors is approximately parabolic and is expressed by,

$$H_c(T) \simeq H_c(0)[1 - (\frac{T}{T_c})^2] \tag{1.5.1}$$

where $H_c(0)$ is the value of the critical field at absolute zero.

1.5.2 Type II superconductors

In type II superconductors, the magnetic field behaves much different from type I superconductors. Type II or hard superconductors are those in which the ideal behavior is observed up to a lower critical field H_{c_1} above which the magnetization gradually changes and becomes zero at an upper critical field H_{c_2}. The Meissner effect is in-

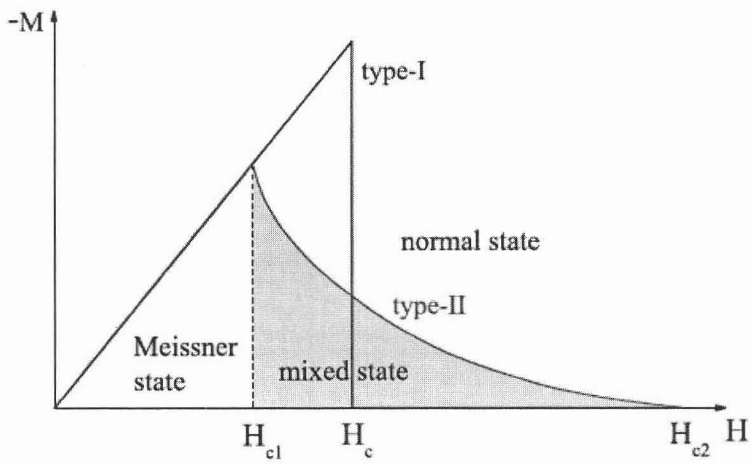

Figure 1.6: Superconducting magnetization curve of type II superconductor.The flux starts to penetrate the specimen at a field H_{c_1} lower than the thermodynamic critical field H_c. The specimen is in a vortex state H_{c_1} and H_{c_2} and it has superconducting electrical properties up to H_{c_2} [12].

complete in the region between H_{c_1} and H_{c_2} and the region is known as the vortex state as shown in fig(1.6). As the field is increased beyond H_{c_1}, the lines of induction penetrate gradually from the specimen and the penetration completes at H_{c_2} .The normal behavior of the specimen is observed only beyond H_{c_2}.

Type II superconductors are the most technologically useful because the second critical field can be quite high, enabling high field electromagnets to be made out of these superconducting wires. Type-II superconductors occur when the coherence length(ξ_{GL}) is shorter than the penetration depth λ_{GL} ($\kappa > \frac{1}{\sqrt{2}}$).

As can be seen in [4], the element Antimony shows stable superconductivity only in thin film form or under high pressures.

Li	Be 0.026 ...	Superconductivity parameters for elements Transition temperature in Kelvin Critical magnetic field in gauss (10^{-4} tesla)										B	C	N	O ... ...
Na	Mg	...										Al 1.140 105	Si* 7 ...	P* 5 ...	S* ... ...
K	Ca	Sc	Ti 0.39 100	V 5.38 1420	Cr*	Mn	Fe	Co	Ni	Cu	Zn 0.875 53	Ga 1.091 51	Ge* 5 ...	As* 0.5 ...	Se* 7 ...
Rb	Sr	Y*	Zr 0.546 47	Nb 9.50 1980	Mo 0.90 95	Tc 7.77 1410	Ru 0.51 70	Rh 0.0003 0.049	Pd	Ag	Cd 0.56 30	In 3.4035 293	Sn(w) 3.722 309	Sb* 3.5 ...	Te* 4 ...
Cs* 1.5 ...	Ba* 5 ...	La(fcc) 6.00 1100	Hf 0.12 ...	Ta 4.483 830	W 0.012 1.07	Re 1.4 198	Os 0.655 65	Ir 0.14 19	Pt	Au	Hg 4.153 412	Tl 2.39 171	Pb 7.193 803	Bi* 8 ...	Po ... ...

Figure 1.7: The elements shown by * form stable superconductivity only in the thin film form or under high pressure [4]

Chapter 2

LITERATURE REVIEW

2.1 Introduction

Both experimental and theoretical approaches in our search for superconductivity of Antimony under pressure are reviewed. Through our overview, the crystal structure, the high pressure phases and superconducting properties of Antimony are explained. The possible sources of data important for our investigation are mentioned. Finally, the effect of pressure on the superconductivity of Antimony will be discussed.

2.2 Crystal Structure of Antimony

Crystal structure is an arrangement of atoms or molecules in a crystalline liquid or solid composed of a set of atoms arranged in a particular way and a lattice exhibiting long-range order and symmetry. It plays great role in determining many of its physical properties such as cleavage, electronic band structure and optical transparency. At atmospheric pressure [13], Antimony is a semimetal whose crystal structure is based on the rhombohedral lattice of the A7 classification, with only slight distortion from simple cubic. It is commonly classified as a distortion of a cubic primitive atomic arrangement and forms layers of atoms stacked along the hexagonal axis. The distortion is resulted from rhombohedral elongation along one body diagonal and the rhombohedral shear of the unit cell.

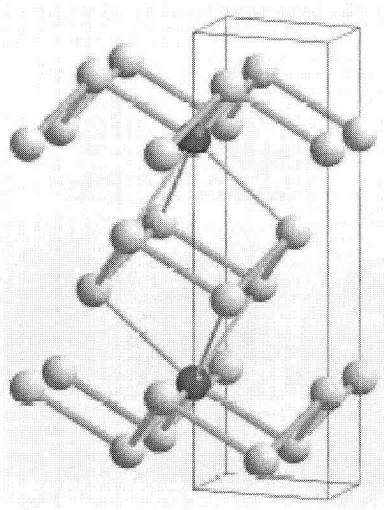

Figure 2.1: A rhombohedral(A7) structure of Antimony [15]

2.2.1 High Pressure Phases of Antimony

Structural changes of Antimony with pressure has been a topic of both experimental and theoretical interests for more than 60 years [14]. At a pressure of 8.5GPa, it undergoes a reversible transformation into the high-pressure modification Sb-II. This first transition takes place as a result of gradual removal of distortions in the initial 7A structure mentioned earlier. Further increase of pressure induces a transition into a body-centered cubic(BCC) arrangement of Antimony atoms at about 28GPa and it is stable in a wide pressure range [15].

2.2.2 Structure and Stability of the Modulated phase Sb-II

Regarding the crystal structure of the high-pressure phase Sb-II, a number of argumentative suggestions were forwarded by different scholars and has been reported to be hexagonal, monoclinic, or tetragonal [14]. Diffraction studies [16] show that, Sb-II adopt a tetragonal self-hosting structure with an incommensurate guest-host arrangement. Moreover, the occurrence of incommensurate modulations in Sb-II has been explained. The structural sequence for Sb under pressure is further complicated by the observation of another incommensurate phase, called Sb-IV, in a narrow pressure range from 8 to 9GPa intermediate between Sb-I and Sb-II. From high pressure Raman spectroscopy of Antimony, however, the Raman spectra above 7.2GPa shows the

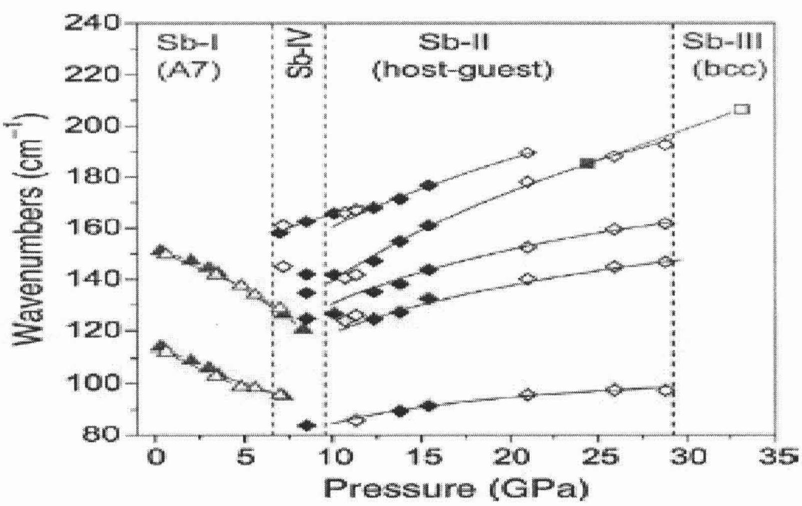

Figure 2.2: Pressure dependence of Raman frequencies of Sb.The open and closed symbols represent the compression and decomposition of Sb respectively [16]

appearance of additional lines, corresponding to the Sb-IV phase in a mixture with the Sb-I phase [16]. The pressure dependence of Raman frequencies of Antimony shown in fig.(2.2) can tell us the experimental pressure interval in which the incommensurate host-guest Antimony phases exist. Moreover, upon decreasing the applied pressure, the reversibility of the pressure shifts in the Raman bands is observed for all the three phases, Sb-I, II and III as can be seen in fig(2.2).

Even if Antimony showed a phase transition from rhombohedral to BCC structure through several intermediate structures, the first-principles electronic structure calculations for the Sb-II phase used an approximating approach to compromise the controversies mentioned above by reducing the order of structural transitions to $A7 \longrightarrow TrigonaApproximant(TA) \longrightarrow BCC$ [17].

2.3 Overview on the superconductivity of Antimony

Looking at the periodic table [4] we notice that, many elements, except those indicated by *, exhibit superconductivity at ambient pressure. From this, it can be deduced that ordinary Antimony with its rhombohedral lattice(Sb-I) is not a superconductor under such normal conditions. Crystalline modifications at very high pressure [17], however, induces superconductivty on it. The unique physical and chemical properties of Antimony has attracted both theoretical and experimental physicist. When Antimony undergoes structural phase transition with pressure, it possess different critical temperatures for its different phases [15]. As described in [18], Superconductivity of Sb has been observed in a metastable phase of unresolved structure which was prepared by releasing pressure in excess of 100kbar at 77K and the superconducting transition temperature was recorded between 2.6K and 2.7K. Qualitatively,

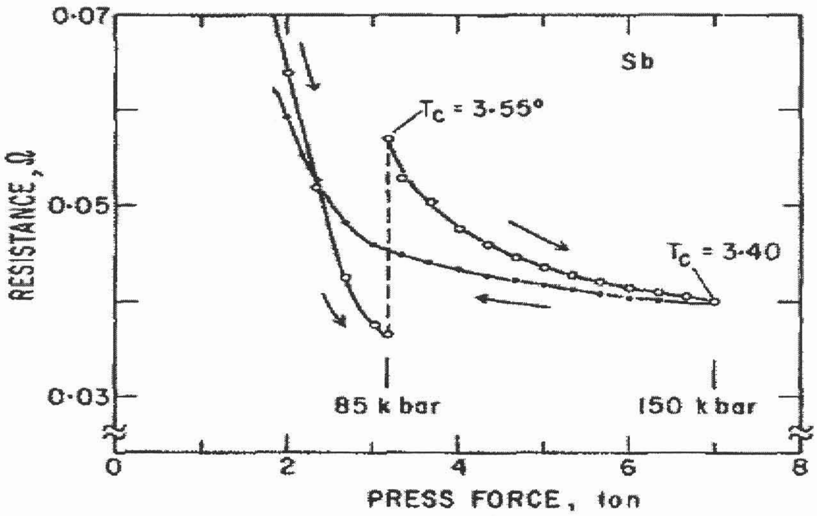

Figure 2.3: Room temperature resistance of Sb vs. press force. T_c for the specimen was measured at 85kbar, 150kbar and, for a two phase sample, again at 85 kbar [19].

the increase of T_c in the Sb-I phase can be understood to arise from strong phonon softening and an enhanced electron-phonon coupling. At the phase transition to Sb-II, the superconducting transition temperature(T_c) jumps to 3.7K and then it drops continuously to 2K at 25GPa [15]. According to [19], the high pressure phase of Antimony which is stable above 85kbar is superconducting with transition temperature of 3.55K and this transition temperature decreases very slightly with pressure as shown in fig.(2.4). From Witing's point of view on the other hand, the BCC phase Antimony is expected to show a higher superconducting transition temperature(T_c) [13]. Witing pointed out that for non transition elements in a group of the periodic table, the lighter element had the higher critical temperature(T_c). This empirical rule suggests that the BCC phase of Antimony shows a critical temperature in excess of 9K since the BCC phase Bismuth(Bi) shows a T_c of 8.4K [16].

2.4 Previous studies on Antimony

Antimony(Sb) was discovered in 1450 by Basil Valentine of Germany [20]. Its name is derived from the Greek words "anti" and "monos" meaning not found alone. Though it is sometimes found free in nature, Antimony's main source is black stibnite (Sb_2S_3). It is also found as antimonides of the heavy metals and as oxides. The experimental and theoretical investigations of group V elements is highly limited due to the lower symmetry of the crystal structures known for these elements at moderate pressures. However, a number of theoretical and experimental physicists have been studied the structural, electronic and superconducting properties of Antimony. Some of the previous works include a work by U. Schwarz et al [17] who presented the structure and stability of the modulated phase Sb-II using angle-dispersive x-ray diffraction of synchrotron radiation.

The effects of pressure on the electronic structure, size of the lattice parameter, the volume and the bonding properties of Sb were modeled by two quantum-mechanical calculations, namely full-potential linear muffintin-orbital method (FP-LMTO) and full-potential local orbital method (FPLO) [14, 17]. According to O. Degtyareva et al, the three structural phases of Antimony have different compressibility as shown by the relative volume(V_0/V) versus pressure graph in fig.(2.4). The effect of pressure on the zone-center optical phonon modes of Antimony in the A7 structure has been

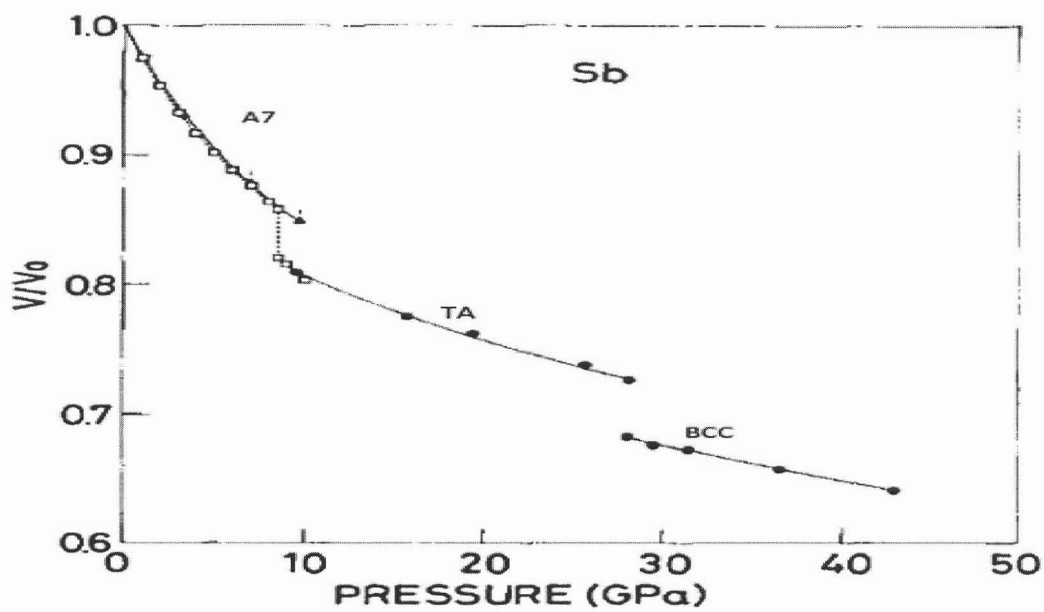

Figure 2.4: Relative volume versus pressure graph for different phases of Antimony[17]

investigated by Raman spectroscopy [15]. Phonon dispersion curves of Antimony was measured by [21] using neutral scattering techniques at room temperature. In this experimental investigation,

- The possibility of energy gap in the phonon spectrum was observed.
- The presence of large anisotropy has been detected from calculated phonon dispersion curves and the force constants of Antimony.

2.5 Available Data For The Study

Due to its strange properties, Antimony has led to a number of theoretical and experimental studies. Such investigations have offered basic inputs for further theoretical investigations on the element. Some of the theoretical studies include the self consistent linear muffin-tin orbital (LMTO) method, non-self consistent relativistic augment plane wave method, full potential linearized augmented plane wave method(LAPW). The papers and journals of the above experimental works along with the theoretical studies are used as available data for our study. Some parameters are taken from the calculations using equation of states and the Local Density Approximation(LDA) method. The most important parameters like average phonon frequencies($\langle\omega\rangle$) and the electron-phonon coupling constants(λ) of Antimony are found from calculations using full potential linearized muffin-tin orbital(FP-LMTO) method.

Chapter 3

Theory and Mathematical Methods

3.1 Theory

3.1.1 Electron-Phonon Interaction

A phonon is a collective vibration of atoms in a crystal [4]. A dispersion relation gives the angular frequency(ω) of the phonon as a function of the wave vector(k) of the phonon. Since most of the physical properties of solids like resistivity, supercoductivity, optical spectra etc depend on the lattice vibrations(phonons), the theory of lattice vibration is usually taken as one of the most interesting concepts in modern solid state physics. Calculation of phonon dispersion curves along high symmetry lines in terms of pressure is a way of determining the pressure dependence of phonon frequency which in turn affects the superconducting transition temperature and electron- phonon coupling constant.

Electron-phonon interaction [22] is another important process in solids affecting almost all physical properties. Superconductivity is the most dramatic manifestation of such interaction in materials. Theoretical and experimental studies of the superconducting transition temperature(T_c) is determined by the parameters: Debye temperature(Θ_D), mean phonon frequency($\langle\omega\rangle$), logarithmic frequency(ω_{log} = $\exp\langle\ln\omega\rangle$), electron-phonon coupling constant(λ), Coulomb electron-electron interaction described by the pseudopotential(μ^*), pairing potential(V), and electronic density of states($N(\varepsilon_F)$). The central part of this thesis is to investigate the pressure dependence of superconductivity of Antimony in terms of one or more of these parameters. The well known McMillan theory will be used as a method of investigating the problem raised [23].

3.1.2 Elemental Superconductors at High Pressures

Even if an element is not a metal at ambient pressure, its metallization may be induced at a certain pressure and the metalized element may possibly become a superconductor [24]. As explained earlier, Antimony is one of the 23 elements that have been found to become superconducting at high pressure. The effect of pressure on superconductivity can usually be understood by considering the McMillan expression for the electron-phonon coupling constant $\lambda = N(0)\langle I^2\rangle/M\langle\omega^2\rangle$. The mean square electron-phonon matrix element ($\langle I^2\rangle$) increases as the atoms come closer under pressure, while the electron bands broaden, resulting in a decrease in the electronic density of states(N(0)). However, the increase in ($\langle I^2\rangle$) is larger than the decrease in N(0) resulting in a higher value of the Hop-field parameter($\eta = N(0)/\langle I^2\rangle$). Phonon frequencies rise under pressure and often the higher value of $\langle\omega^2\rangle$ becomes the dominant factor in determining the pressure effect [25].

3.2 Mathematical Methods

3.2.1 The McMillan Strong Coupling Theory

According to the BCS theory of superconductivity [9], we have a relation amongst the superconducting transition temperature(T_c), the typical phonon energy($\langle\omega\rangle$) and the interaction strength($N(0)$V) and is given by

$$T_c = 1.14\langle\omega\rangle \exp[\frac{-1}{N(0)V}]$$

Since the BCS theory, much progress has been made in understanding the electron-phonon interaction in superconducting materials. One of the progresses is the strong coupling theory. The most extensive study of the relation between microscopic theory and transition temperature(T_c) for strong-coupling superconductors was made by McMillan [26]. The basis for this well known theory is Eliashberg's equation. Equations of the Eliashberg theory can be formulated in terms of both real and imaginary frequency axes. In the real axis formulation, the superconducting gap(Δ) is complex and defined for all frequencies(ω) while on the imaginary axis, the gap is real and defined only on the discrete set of imaginary Matsubara frequencies $\omega_n = \pi T(2n-1)$ [27], T being the temperature in energy units. Two of the central equations in the imaginary frequency formulation are coupled non-linear equations for the Matsubara gaps $\Delta(i\omega_n)$ and the renormalization factor $Z(i\omega_n)$. For anisotropic system, these two equations take the form of

$$Z(i\omega_n) = 1 + \frac{\pi T}{\omega_n}\sum \lambda(n-m)\frac{\omega_m}{\sqrt{\omega_m^2 + \Delta^2(i\omega_m)}} \tag{3.2.1}$$

$$Z(i\omega_n)\Delta(i\omega_n) = \pi T \sum_{m}^{|\omega_n| \ll \omega_c} [\lambda(n-m) - \mu^*(\omega_c)] \frac{\Delta(i\omega_m)}{\sqrt{\omega_m^2 + \Delta^2(i\omega_m)}} \tag{3.2.2}$$

where $\mu^*(\omega_c)$ is the Coulomb pseudopotential, ω_c is the cut-off frequency and it is very important for the summation to converge. The electron-phonon contribution is contained in,

$$\lambda(n-m) = \int_0^\infty \frac{d\omega^2 \alpha^2(\omega) F(\omega)}{\sqrt{(\omega_n - \omega_m)^2 + \omega^2}} \tag{3.2.3}$$

where $\alpha^2(\omega)F(\omega)$ is the Eliashberg spectral function which is the key quantity in equation(3.2.3) and is defined as

$$\alpha^2(\omega)F(\omega) = \frac{1}{N(0)} \sum_{k,k',ij,\nu} |g_{k,k'}^{ij,\nu}|^2 \delta(\varepsilon_k^i)\delta(\varepsilon_{k'}^j)\delta(\omega - \omega_{k-k'}^\nu) \tag{3.2.4}$$

where $g_{k,k'}^{ij,\nu}$ is the electron-phonon matrix element, with ν being the phonon polarization index and k, k' representing electron wave vector with band indices i and j respectively, ε_k^i denotes the band energy of an electron of wave vector k in the i^{th} band measured with respect to the Fermi energy(E_F). If the Eliashberg function is known, then a simple integration gives the total electron-phonon coupling constant by

$$\lambda = 2\int_0^\infty \frac{d\omega}{\omega} \alpha^2(\omega)F(\omega) \tag{3.2.5}$$

The expression $\alpha^2(\omega)F(\omega)$ is a function of electron-phonon interactions and of the phonon energy distributions($F(\omega)$). Here, the ultimate goal of the Eliashberg theory of superconductivity is to calculate the critical temperature without any experimental investigation for a given material. However, the Eliashberg theory contains one unknown parameter, the so-called Coulomb pseudopotential(μ^*). The screened Coulomb repulsion between the two electrons attracted to each other via emission and absorption of virtual phonons is represented by a dimensionless quantity:

$$\mu = \langle N(0)V_c^{kk'}\rangle FS \tag{3.2.6}$$

where $V_c^{kk'}$ is the screened coulomb interaction between the electrons in states (i,k) and (j,k'). Due to retardation and other factors, the effective Coulomb interaction is significantly weakened and μ is renormalized to a lower value μ^* approximated by,

$$\mu^*(\omega_c) = \frac{\mu}{1+\mu\ln(\frac{E}{\omega_c})} \tag{3.2.7}$$

where E is a characteristic electron energy typically of the order of the plasma frequency(ω). The more simple and important result of the Eliashberg theory is the prediction of T_c. According to this theory, T_c is the lower temperature for which $\Delta(i\omega_n) = 0$ for n values. Systematic expressions for T_c in terms of the electron-phonon coupling constant(λ) and the Coulomb pseudopotential(μ^*) can be obtained from Eliashberg equations (3.2.1 and 3.2.2) under some approximations.

McMillan [26] considered the integral equations for the normal and pairing self-energies in the real frequency formulation of the Eliashberg theory, involving the complex gap function $\Delta(\omega)$ by considering the trial gap function,

$$\Delta_t(\omega) = \begin{cases} \Delta_0 & 0 < \omega < \omega_0 \\ \Delta_\infty & \omega_0 < \omega \end{cases}$$

where ω_0 is the maximum phonon frequency. Eliashberg was able to show the approximate solutions for the critical temperature to be,

$$T_c = \omega_0 \exp\left\{-\frac{1+\lambda}{\lambda - \mu^*(1+(\frac{\langle\omega\rangle}{\omega_0})\lambda)}\right\} \tag{3.2.8}$$

with $\langle\omega\rangle$ being the average phonon frequency, defined by

$$\langle\omega\rangle = \frac{\int_0^{\omega_0} \alpha^2(\omega')F(\omega')d\omega'}{\int_0^{\omega_0} \frac{d\omega'}{\omega'}F(\omega')} \tag{3.2.9}$$

By extensive numerical solutions of the integral equations, McMillan [26] was able to show that, in most cases T_c could be expressed as

$$T_c = \frac{\Theta_D}{1.45}\exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\} \tag{3.2.10}$$

where Θ_D, is the Debye temperature.

McMillan also showed that the electron-phonon coupling constant λ given by equation(3.2.5) can be written in the form of $\lambda = N(0)\langle I^2\rangle/M\langle\omega^2\rangle$ where $\langle I^2\rangle$ is a mean square electron-phonon matrix element and $\langle\omega^2\rangle$ is the mean square average phonon frequency, with M$\langle\omega^2\rangle$ acting as an effective spring constant.

3.2.2 Transition Temperature from Allen and Cohen point of view

The principal content of the McMillan's theory [26] is to determine the superconducting transition temperature(T_c) for various conditions. McMillan's method of finding T_c was later revised by Allen and Cohen [27, 28]. According to Allen and Dynes, T_c is described by the parameters ω_{log}, λ which characterizes the phonon spectrum and by the pseudopotential(μ^*) as,

$$T_c = \frac{\omega_{log}}{1.20}\exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\} \tag{3.2.11}$$

where λ as we have seen earlier is given by,

$$\lambda = 2\int_0^{\infty}\frac{d\omega\alpha^2(\omega)F(\omega)}{\omega} = \frac{N(\epsilon_F)\langle I^2\rangle}{M\langle\omega^2\rangle} = \frac{\eta}{M\langle\omega^2\rangle}$$

$$\lambda = \frac{\eta}{M\langle\omega^2\rangle} \tag{3.2.12}$$

where $F(\omega)$ is the phonon density of states, M is the atomic mass, $\eta = \frac{N(\epsilon_F)}{\langle I^2\rangle}$ is called the Hopfield parameter. The logarithmically averaged characteristic phonon frequency ω_{log} in the Allen-Dynes formula is obtained from,

$$\omega_{log} = \exp\left(\frac{2}{\lambda}\int_0^\infty \frac{d\omega}{\omega}\alpha^2 F(\omega)\langle\ln\omega\rangle\right) \tag{3.2.13}$$

The phonon frequency(ω) averaged over the phonon spectrum is given by

$$\langle\omega^2\rangle = \frac{2}{\lambda}\int_0^\infty d\omega\alpha^2 F(\omega)\omega \tag{3.2.14}$$

and the square of the electron-phonon interaction matrix element averaged over the Fermi surface is given by,

$$\langle I^2\rangle = \frac{\sum_{q\nu}\sum_{kjj'}|g^{q\nu}_{k+qj',kj}|^2\delta(\varepsilon_{kj}-\varepsilon_F)\delta(\varepsilon k+kj'-\varepsilon_F)}{\sum_{q\nu}\sum_{kjj'}\delta(\varepsilon kj-\varepsilon_F)\delta(\varepsilon_{k+qj'})} \tag{3.2.15}$$

where $g^{q\nu}_{k+qj',kj}$ is conventionally written as,

$$g^{q\nu}_{k+qj',kj} = \langle k+qj'|\delta^{q\nu}V_{eff}|kj\rangle \tag{3.2.16}$$

equations (3.2.11-3.2.15) follow from the dependence of the superconducting transition temperature on material properties(λ, μ^*, phonon spectrum) as explained in Eliashberg theory [27]. Within the pseudopotential model, McMillan has derived $\langle I^2\rangle$ as,

$$\langle I^2\rangle = \frac{8}{9}k_F^2 E_F^2\langle\upsilon_q^2\rangle \tag{3.2.17}$$

Here, E_F and k_F are the Fermi energy and the wave vector respectively and $\langle\upsilon_q^2\rangle$ is the average of the pseudopotential $V(q)$ squared and is given by,

$$\langle\upsilon_q^2\rangle = \frac{\int_0^{k_r} V^2(q)q^3dq}{\int_0^{k_r} V^2(0)q^3dq} \tag{3.2.18}$$

For a free electron gas, the density of states of one spin per atom according to [28] is given by,

$$N(0) = \frac{3Z}{4E_F} \tag{3.2.19}$$

where Z is the atomic number of the atom.

After writing the the average phonon frequency in units of the ionic plasma frequency, as

$$\Omega_p^2 = \frac{4\pi N Z^2 e^2}{M} \tag{3.2.20}$$

and according to McMillan [26], the coupling constant is given by

$$\lambda = \frac{N(0)\langle I^2\rangle}{M\langle\omega^2\rangle} = \frac{1}{2}\pi\frac{E_F\langle\upsilon_q^2\rangle}{k_F e^2(\langle\omega^2\rangle/\Omega_p^2)}$$

implies

$$\lambda = \frac{1}{2}\pi\frac{E_F\langle\upsilon_q^2\rangle}{k_F e^2\langle\frac{\omega^2}{\Omega_p^2}\rangle} \tag{3.2.21}$$

But $E_F/k_F e^2 = 0.96r_s$ [26] where, r_s is the radius in atomic units of a sphere with one electron in it. Thus, λ can be simplified as

$$\lambda = \frac{1.51\langle\upsilon_q^2\rangle}{r_s(\langle\omega^2\rangle/\Omega_p^2)} \tag{3.2.22}$$

According to McMillan [26], the observed phonon frequencies are extremely sensitive to small changes in pseudopotntial and the important dependence of the coupling constant (λ) upon the pseudopotential arises from the $\langle\omega^2\rangle$ term in the denominator of eq.(3.2.22), rather than from the $\langle\upsilon_q^2\rangle$ in the numerator. For elemental superconductors, the pseudopotential theory infers that, the coupling constant varies inversely with the phonon frequency squared. Thus eq.(3.2.22) can be re-written as,

$$\lambda \cong \frac{C}{(\langle\omega^2\rangle/\Omega_p^2)} \tag{3.2.23}$$

where $C = (1.51\langle v_q^2\rangle)/r_s$.

More approximately, using eq.(3.2.20) in eq.(3.2.23), we get

$$\lambda \approx \frac{C'}{M\langle\omega^2\rangle} \tag{3.2.24}$$

where $C' = 4\pi CNZ^2e^2$

3.2.3 The Modification of the McMillan Theory

From McMillan's point of view, the mathematical formulation to find T_c involves parameters like the electron-phonon coupling constant(λ), the Coulomb pseudopotential(μ^*), and the phonon spectrum. This transition temperature(T_c) calculation was later marked by some complexities and therefore tends to have less general use. Two of the complexities for example are:

- Understanding the electron-phonon spectral function($\alpha^2(\omega)F(\omega)$) and the pseudopotential(
- Calculating T_c as a function of $\alpha^2F(\omega)$ and μ^*.

Following Allen-Dynes and Rowell [28], however, a simplified way of calculating the transition temperature(T_c) in terms of electron-phonon coupling strength(λ) and the Debye temperature(Θ_D) has been proposed and is given by

$$T_c = \left(\frac{\Theta_D}{20}\right)(\lambda - 0.25) \tag{3.2.25}$$

Here, finding the exact value of the Debye temperature(Θ_D) was another difficulty before the empirical relations between the average phonon frequency($\langle\omega\rangle$) and the Debye temperature(Θ_D) was given by [31],

$$\langle\omega\rangle \simeq 0.69\Theta_D \tag{3.2.26}$$

3.3 Murnaghan's Equation of State

The fundamental quantity that is varied in a high pressure experiment is the relative volume of the material. Many condensed matter properties can be understood on the basis of the average distance between the atoms, which can be derived directly from the equation of state. An equation of state tells us how pressure(P), temperature(T), and density($\rho = N/V$) can be related in condensed matter. For a fixed number of particles(N), confined in a varying volume(V) and in thermal equilibrium at temperature of absolute zero, Murnaghan's equation of state is given by [30],

$$P(V) = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \tag{3.3.1}$$

where, B_0 is the equilibrium bulk modulus, B_0' is the first derivative of the bulk modulus with respect to pressure, V_0 is the equilibrium unit cell volume.

Chapter 4

Results and Discussion

This chapter focuses on the analysis of the relationship that exists between pressure and atomic volume, superconducting transition temperature(T_c) and the electron-phonon coupling constant(λ). The effect of pressure on superconducting transition temperature(T_c) on Antimony is analyzed using the equations obtained in chapter three. Moreover, theoretical argument and empirical evidences are presented using graphs and numerical values.

4.1 The Effect of Pressure on Atomic Volume

To explain the pressure dependence of the atomic volume of Antimony, we took the experimental data from one of the data sources mentioned.

Table 4.1: Bulk Modules and its first derivative for the three phases of Antimony[17].

Structure	B_0	B_0'
A7	37.1	5.1
TA	75	4
BCC	123	2.8

From equation(3.3.1), we have,

$$P(V) = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \tag{4.1.1}$$

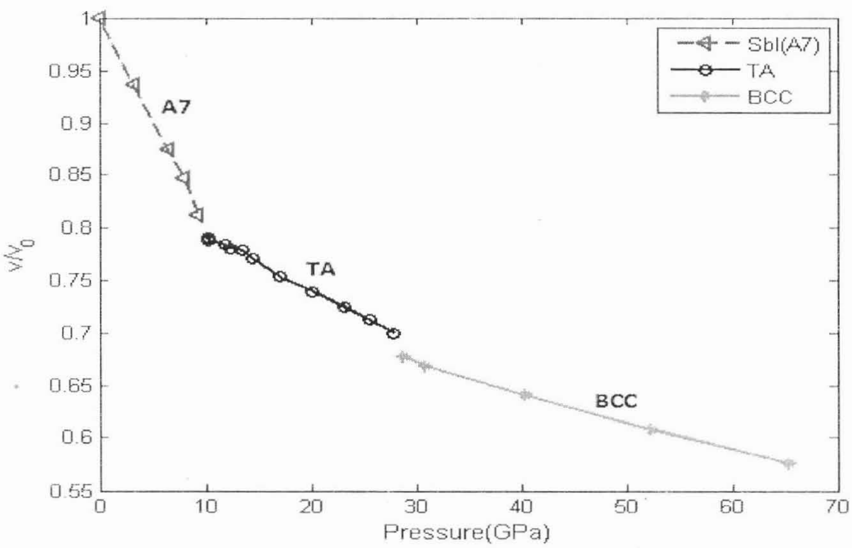

Figure 4.1: The pressure dependence of atomic volume for the three phases of Antimony.

The equilibrium unit cell volume(V_0) of Antimony is $30.20\mathring{A}^3$. From figure(4.1), we see that rhombohedral(A7) Antimony is the most compressible of all the three phases and our graphical interpretation of the phenomenon is in good agreement with the previous experimental investigations [17].

4.2 Superconductivity

To explore how T_c behaves under pressure, we took the pressure dependent average phonon frequency($\langle\omega\rangle$) calculated at different pressure values by FP-LMTO method [17] using equation (3.2.14) so that the corresponding electron-phonon coupling constant(λ) can be calculated from equation (3.2.24). The calculated values of $\langle\omega\rangle$ and λ are summarized in table (4.2).

Table 4.2: Average phonon frequency($\langle\omega\rangle$) and electron-phonon coupling constant(λ) of Antimony under pressure (FP-LMTO method [17]).

Structure	P(GPa)	$\langle\omega\rangle(10^{10}Hz)$	λ
A7	5.1	366	-
A7	7	348	0.64
AT	8.5	321	0.76
BCC	28	303	1.58
BCC	35	312	0.83
BCC	42	323	0.58

From equations (3.2.26) and (3.2.25), we have,

$$\langle\omega\rangle \simeq 0.69\Theta_D \tag{4.2.1}$$

$$T_c = \frac{\Theta_D}{20}(\lambda - 0.25) \tag{4.2.2}$$

Once the pressure dependent average phonon frequency($\langle\omega\rangle$) is known, the corresponding Debye temperature values can be calculated using equation(4.2.1). The critical temperatures($T_c s$) for the three phases of Antimony are calculated using equation(4.2.2) and all the values are summarized in table(4.3).

Since the superconducting transition temperature(T_c) of Antimony is calculated using pressure dependent parameters, (i.e the Debye temperature and the electron-phonon

Table 4.3: Calculated Debye temperature(Θ_D), Transition temperature(T_c) of Antimony under pressure using equations (4.2.1) and (4.2.2).

Structure	P(GPa)	$\Theta_D(K)$	$T_c(K)$
A7	5.1	177.92	-
A7	7	151.67	2.96
AT	8.5	156.67	3.98
BCC	28	147.29	9.79
BCC	35	151.67	4.40
BCC	42	151.67	2.54

coupling constant), the characteristic dependence of T_c on pressure for the element can be interpreted graphically as shown in fig.(4.2).

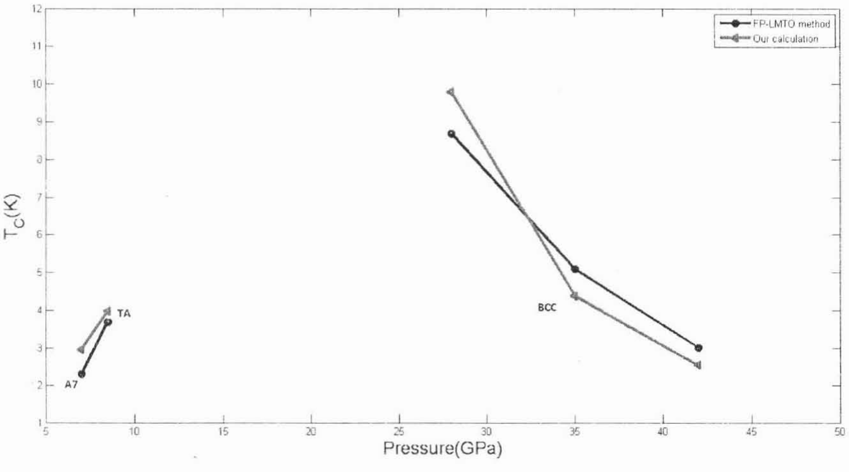

Figure 4.2: The value of T_c calculated for A7, TA and BCC phases of Antimony as a function of pressure.

When pressure increases to 8.5GPa, superconducting A7 Antimony transforms to the tetragonal approximant(TA) phase and the critical temperature increases. As can be seen from figure(4.2), there is a sudden jump in T_c (3.98K to 9.79K) at the transition from TA to BCC phase. This sudden jump in T_c is occurred when the average phonon frequency($\langle\omega\rangle$) becomes least. Thus, as Antimony shifts from TA to BCC phase, the increase in T_c can be understood in view of the strong phonon softening and an enhanced electron-phonon coupling.

The gap observed between 8.5GPa and 28GPa in figure(4.2) corresponds to the phase SbII which has challenged many theoretical physicists due to its complex crystal structure and the behavior of its superconducting transition temperature has not yet understood well.

Chapter 5

Conclusions and Recommendations

In conclusion, we have examined in detail the superconductivity of Antimony where its superconducting state arise only under pressure. To show the pressure dependence of superconducting transition temperature(T_c), previously studied experimental results and theoretically investigated parameters under pressure have been used.

From our calculations, an increase in the superconducting transition temperature(T_c) is observed as A7 is changed to TA phase of Antimony. A large drift of T_c is observed at the transition from TA to BCC phase due to strong phonon softening and an enhanced electron-phonon coupling. From our theoretical observations, we have shown that the modified transition temperature equation is a better way of calculating the critical temperature(T_c) of superconductors than the complex McMillan equation. Moreover, we can conclude from our investigation that, the superconducting transition temperature(T_c) of Antimony is highly dependent on the pressure at which it undergoes structural phase transition.

Finally, we recommend that, since the present experimental and theoretical knowledge about the pressure induced superconductivity of trigonal approximant Antimony is limited and the data were not conclusive enough to be interpreted in terms of enhanced electron-phonon coupling, further intensive studies could be conducted to fully explain the behavior of its superconducting transition temperature for the pressure interval of $8.5GPa < P < 28GPa$.

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Declaration

I, hereby declare that the thesis is my original work and has not been presented for a degree in any other university, and that all sources of materials have been duly acknowledged.

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This thesis has been submitted for examination with my approval as University advisor.

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Date: 13/01/2006 EC