# Trends of Superconducting Transition Temperatures in Ternary Alloys of Lead, Bismuth, and Group 3A Elements

### James E. Nicholson and Kerry G. Coffman*

*Department of Physics, Stephen F. Austin State University, Nacogdoches, Texas*

*The transition temperatures of lead–bismuth alloys doped with gallium or indium are measured using the inductance technique. The effects of varying the doping element, adjusting the amount of the doping element, and altering the $e/a$ ratio are studied.*

## 1. INTRODUCTION

The highest transition temperature (the temperature at which the material becomes superconducting) for an element is 9.3 K for niobium. This has been pushed up considerably for alloys. In fact, $Nb_3Ge$ has a transition temperature around 23 K.[1] While numerous people have attempted to explain the mechanism for high transition temperatures, no one to date has met with much, if any, success.

In 1955, Matthias published an empirical relation between the transition temperature of a material and its number of valence electrons per atom.[2] At that time the optimum $e/a$ ratios seemed to be 5 and 7. However, since then several studies have indicated optimum $e/a$ ratios of about 4.5 and 6.5.[3]

Our study concentrated on ternary alloys, since it appears the "only genuine hope of going to even higher temperatures lies in turning our attention to ternary systems."[4] Lead–bismuth mixtures doped with various amount of group 3A elements, especially gallium and indium, were used. Lead was chosen for this study because of its high transition temperature. Since this study wanted to examine systems with $e/a$ ratios around 4.5, a group 5A element was also selected. Bismuth was chosen since we also wanted the two major constituents to have comparable atomic sizes. The

*Present Address: Department of Physics, University of Texas, Austin, Texas.

group 3A elements were chosen as the doping agents in order to again have ternary alloys with $e/a$ ratios of approximately 4.5. We studied the effects of varying the doping element, adjusting the amount of the doping element, and altering the $e/a$ ratio.

## 2. THEORY

In a normal conductor, current is carried by what are called the "conduction electrons." If the conductor has perfect crystalline structure, then the electrons (due to their wavelike nature) are able to pass through the lattice without any loss of momentum. However, there are two effects which can spoil periodicity.[5] The first is thermal vibration. At any finite temperature the atoms of the lattice are vibrating about their equilibrium positions. Impurities prevent the lattice from exhibiting perfect regularity. Thus one can easily understand why the resistance decreases as the temperature is lowered.

However, this fails to explain the sudden loss of resistance at the transition temperature. The superconducting state is more than just a resistanceless state. One characteristic of a superconductor is the presence of perfect diamagnetism.[6] A perfect diamagnetic sample is one in which there is no net flux density when a magnetic field is applied.

Fritz London describes superconductivity as a "quantum state on a macroscopic scale."[7] Once a sample passes below its transition temperature, the conduction electrons tend to establish a type of coherency, and they behave as if they were part of an individual atom. By virtue of an interaction involving the lattice ions, electrons of opposite momentum and spin form pairs, which are called Cooper pairs. Surprisingly, this superconducting interaction is present in crystals of high imperfection.

Two elements with high transition temperatures are niobium, with a temperature of 9.3 K, and lead, with a temperature of 7.2 K. Empirically it is found that for most elements the following relationship for the transition temperature $T_c$ holds fairly well[8]:

$$T_c \sim r^{13}/M$$

where $r$ is the radius of the neutral atom and $M$ is the mass of the atom.

However, two general trends are found for the superconducting elements. For the non-transition elements it is found that[1]

$$T_c \propto 1/\sqrt{M}$$

The fact that the transition temperature is inversely proportional to the square root of the mass gives rise to the isotope effect. Originally H. Frölich

and John Bardeen assumed that the electron–phonon interaction was the universal cause of superconductivity.[1] Later the BCS theory expounded upon this. The above isotope shift was the first direct proof that an electron–lattice interaction occurred in the superconducting state.

While the isotope effect is evident for the non-transition elements, no such effect is found for the transition elements.[1] This implies that a different mechanism governs superconductivity for these elements. Since the high critical temperatures of the transition elements are always accompanied by an odd number of electrons, this tends to imply the influence of a net spin.[1] This in turn indicates a magnetic interaction. At the present time the theory tends to suggest a spin-exchange interaction mechanism for the superconductivity of transition elements.

Matthias found some empirical trends for superconductors, which are usually referred to as Matthias' rules.[9] Two of these rules are as follows:

1. The superconducting state is found only for metallic systems.

2. Superconductivity takes place when the ratio of the number of electrons to the number of atoms $e/a$ lies somewhere between two and eight. For metals and alloys of metals within the same period, $T_c$ varies with $e/a$. For non-transition elements $T_c$ increases as does $e/a$. Yet for transition elements, $T_c$ reaches maxima for $e/a = 4.7$ and $6.5$, with a minimum between these two values.

While Matthias' rules tend to give possible trends for maximum transition temperatures, there is no theoretical boundary to the range over which superconductors may exist. Likewise, it appears that no one mechanism governs superconductivity. However, theorists recently have argued that no compound can possibly superconduct when thermal conditions approach room temperature.[10,11] There are essentially two approaches one may take in searching for substances with high transition temperatures. The first is the development of theoretical models from first principles. Such models are based on an assumption about the type of interaction involved in superconductivity. Many such models indicate that superconductivity is possible at room temperature.[7] Nevertheless, not a single theory which depicts elevated transition temperatures has led to an experimental success.

The other approach is a more empirical one. Workers in this area have included Matthias and Geballe. This consists essentially in working with a variety of metallic compounds and alloys. For the elements and simple binary alloys the $e/a$ value predicts optimum transition temperatures in accordance with Matthias' rules. However, in 1973 Matthias and his co-workers reported more complicated criteria for multicomponent phases. Crystallographic instabilities now appear to be strongly associated with high-transition-temperature superconductors.[12]

For all alloys or solid solutions it is found that the valence electron per atom concentration varies between two and eight. The critical temperature for all superconducting elements may be altered by forming a solid solution. Matthias and his co-workers established a set of empirical rules which describe this effect.[1] An example of this would be the observation that the critical temperature of titanium is raised by adding to it any transition element that appears to its right in the periodic table.

The maximum $T_c$ for solid solutions (primarily binary solutions) as a function of the $e/a$ ratio varies with the crystal form. Also, the most perfect solid solutions are usually formed by neighboring elements. Due to the poor solid solubility between non-transition elements, very little work has been done on the solid solutions of these elements. On the other hand, considerable work has been done on the superconducting properties of solid solutions of transition elements.[7] In part this stems from the extensive range of solid solutions formed between the transition elements.

Extensive work has been done on binary alloys and Matthias' rules seem to adequately describe these systems. However, in the study of superconductivity, much like the work in ordinary metallurgy, alloys composed of several elements are usually better suited for applications than are the binary alloys.[9] Matthias himself felt that "the only genuine hope" of reaching higher critical temperatures lies in the study of ternary systems.

Although little work has been done of theoretical models for ternary systems, Miedema and Van Maaren developed a simple model which has met with relative success.[13] Miedema and Van Maaren were able to determine the ratio of the critical temperature to the Debye temperature $T_c/\theta_D$, or $\gamma$ values. These results were then compared to empirical results. On the basis of their model Miedema and Van Maaren expect to find no new high-temperature superconductors among the ternary solid solutions as compared to their binary alloys. However, this model only looks at solid solutions of transition elements and does not consider alloys consisting of both transition and non-transition elements.

## 3. EXPERIMENTAL APPARATUS

The cryostat, which houses the samples and several sensors, allows the study of several samples within a single run and under a wide spectrum of controllable conditions. The cryostat is submerged into a liquid helium bath contained within a set of glass dewars. In addition, an elaborate vacuum system and an assemblage of electronics are required for monitoring the experiment. Such monitoring includes the regulation of the temperature and the detection of a particular transition (critical) temperature. A block diagram of the equipment is given in Fig. 1.
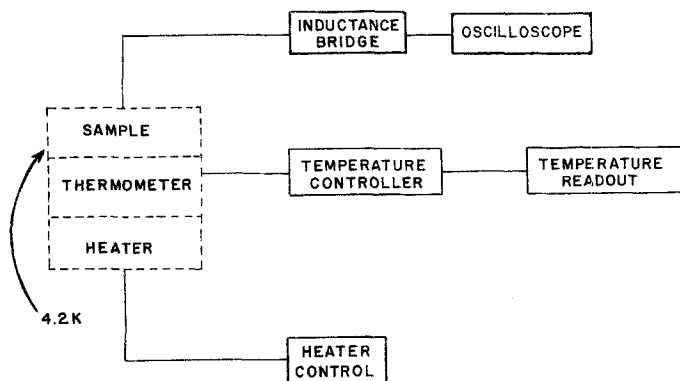
Fig. 1. Block diagram.

The most important aspect of the cryostat is the "can." By the special design of this, great flexibility is given to the cryostat. Added capabilities of the "can" include the ability to examine four samples without the need to remove the entire cryostat from the dewars, great ease in removing and changing a sample, added thermal stability of the samples, more stable and accurate determination of the temperature (in particular, the critical temperature), and ease in regulating the temperature. The "can" has an inner jacket which is either evacuated or pressurized via a stainless steel tube leading to the top of the cryostat.

The lid of the "can" is a brass disk with eight positions periodically spaced about the edge to allow the fastening of the lid to the "can" by brass screws. An indium O-ring ensures a vacuum fit.

Four stainless steel support rods are soldered to the bottom of the lid and symmetrically placed. These support rods are 8 cm in length and attach to the base of a 5-cm-diameter phenolic platform.

Symmetrically placed between the supports are four coils, each 2.5 cm in length. These are the pickup coils, one coil for each of the samples. The samples are placed in the center of these coils. Insertion of the samples occurs from the bottom of the phenolic base as depicted in Fig. 2. The samples are 2.5 cm long and 2 mm in diameter. The phenolic cylinder (which is wrapped to form the pickup coil) is perforated with small orifices to allow the sample to come into thermal equilibrium with its environment. As Fig. 2 indicates, a small copper strip within the cylinder maintains contact with the sample. Each cylinder contains such a strip, and each strip joins into a copper block within which a germanium thermometer is mounted with GE7031 varnish to ensure good thermal contact between thermometer and copper block. This arrangement minimizes sudden changes
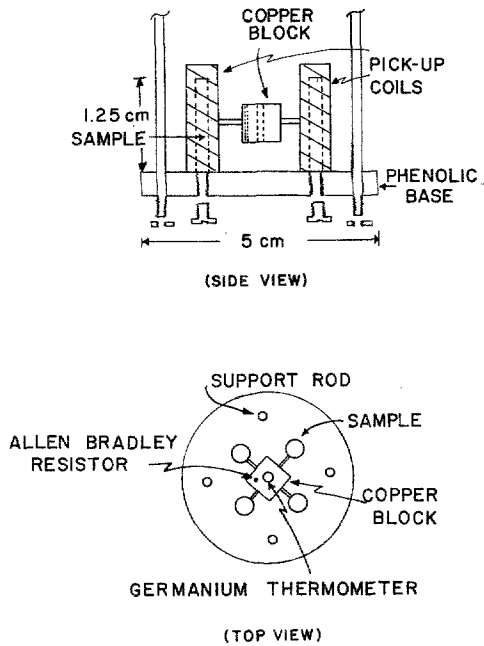
Fig. 2. The platform.

in temperature and tends to keep conditions rather uniform. An Allen-Bradley resistor placed on the base functions as a heater.

The germanium thermometer has a given temperature range of 0.3–100 K with a signal readout accuracy of ±0.002 K at 4.2 K. This particular thermometer employs the four-probe technique in its operation.[14]

The inductance method for determining the critical temperature centers on the fact that the self-inductance of a coil (with a specimen placed on it) will change dramatically when the sample changes to or from the superconducting state. The changing magnetic susceptibility of the sample is responsible for this effect.

An impedance bridge along with an oscilloscope and a differential preamp unit with a sensitivity of 1 mV/cm are used in the inductance method. The impedance bridge utilizes both Maxwell and Hays bridges, depending upon the unknown inductances.[15]

## 4. EXPERIMENTAL PROCEDURE

All starting materials are of 99.99+% purity. Materials are cleaned, carefully etched, and then scraped to assure minimum oxidation. The

appropriate amounts necessary for the proper $e/a$ ratio (in doping percentages) are measured on a Mettler analytical balance to ±0.0001 g. These materials are carefully placed in a sample holder and flushed several times ith argon.[14]

Once the sample is within the holder, it is attached to the pumping station to allow flushing and evacuation. The sample is evacuated to $10^{-3}$ Torr and flushed with argon. This is repeated several times to ensure an inert atmosphere. The holder is heated and gently agitated to allow the melted materials to flow into the lower portion of the sample holder while under a vacuum. After the material has stopped outgassing, the sample is sealed under a pressure of less than $10^{-4}$ Torr. At this point the sample may be remelted and adequately mixed to ensure a homogeneous alloy.

After the transfer of liquid helium, the inductance bridge with a frequency of 20 kHz is balanced by minimizing the amplitude of the waveform on an oscilloscope. As the temperature is slowly swept upward, the imbalance of the bridge is noted on the oscilloscope. This point of imbalance is the beginning of the transition point. The bridge is continually balanced until a point is reached where it is no longer necessary to balance. This becomes the end of the transition point. The temperature is then reduced, noting the point at which the inductance bridge is out of balance.

## 5. DATA AND RESULTS

Type I superconductors tend to have a fairly sharp and well-defined transition point, while the type II materials tend to have a range over which the transition occurs. This range arises from the existence of the mixed state and from the alloy nature of the material. Thus, for the type I substances (essentially the elements) a rather sharp point is produced when the magnetization changes. Yet for the type II samples (essentially the alloys) the situation is quite different. Since a range exists over which the material goes back into either the normal or the superconducting state, there is a gradual change in the magnetization.

The oscillator driving the inductance bridge is set at a frequency of 20 kHz. This particular frequency allowed for maximum sensitivity, yet minimizes the ac skin effect on the sample.[16] It is well known that the inductance of a coil is a function of the applied frequency. This property, however, does not affect the measurement of critical temperature. This proved to be an extremely accurate and sensitive method for determining the transition temperature. As a check on this method, standards of lead–bismuth were prepared and critical temperatures were measured. Our measured $T_c$ is compared with those of Daams et al.[17] in Table I. There appears to be close agreement.

**TABLE I**

"Standard" Alloys

| Composition | $e/a$ | Reported $T_c$, K | Measured $T_c$, K |
|---|---|---|---|
| $Pb_{0.5}Bi_{0.5}$ | 4.5 | — | 9.14 |
| $Pb_{0.65}Bi_{0.35}$ | 4.35 | 8.95 | 8.75 |
| $Pb_{0.7}Bi_{0.3}$ | 4.3 | 8.45 | — |
| $Pb_{0.8}Bi_{0.2}$ | 4.2 | 7.95 | 7.82 |
| $Pb_{0.9}Bi_{0.1}$ | 4.1 | 7.65 | — |
| Pb | 4.0 | 7.19 | 7.36 |

Table II summarizes the critical temperatures determined for each of the respective samples. The percent composition of indium or gallium is selected, and various amounts of lead and bismuth are added to achieve the desired $e/a$ ratio. The maximum doping in most cases is 15%, since beyond this point a larger percentage will have the amount of the doping element more than the amount of lead or bismuth. These values are compared to the critical temperatures of the pure elements as given in Table III.

**TABLE II**

Critical Temperatures

| Sample | Composition | $e/a$ | $T_c$, K |
|---|---|---|---|
| 1 | 15% In | 4.5 | 8.64 |
| 2 | 10% In | 4.5 | 7.50 |
| 3 | 5% In | 4.5 | 9.11 |
| 4 | 2% In | 4.5 | 8.85 |
| 5 | 15% Ga | 4.5 | 9.61 |
| 6 | 10% Ga | 4.5 | 7.82 |
| 7 | 5% Ga | 4.5 | 10.40 |
| 8 | 2% Ga | 4.5 | 10.09 |
| 9 | 10% In | 4.1 | 8.65 |
| 10 | 10% In | 4.65 | 7.35 |
| 11 | 10% Ga | 4.1 | 10.84 |
| 12 | 10% Ga | 4.65 | 11.65 |
| 13 | 2% Ga | 4.65 | 9.42 |
| 14 | 5% Ga | 4.65 | 9.64 |
| 14a | 7.5% Ga | 4.65 | 8.78 |
| 15 | 2% Ga | 4.1 | 8.77 |
| 16 | 5% Ga | 4.1 | 11.52 |
| 17 | 15% Ga | 4.1 | 11.80 |
| 18 | 2% In | 4.1 | 7.51 |
| 19 | 5% In | 4.1 | 8.62 |
| 20 | 15% In | 4.1 | 8.10 |
| 21 | 5% In | 4.65 | 8.83 |

**TABLE III**

Critical Temperatures for the Pure Elements

| Element | Lead | Bismuth | Gallium | Indium |
|---------|------|---------|---------|--------|
| $T_c$, K | 7.22 | <0.05 | 1.10 | 3.37 |

Figure 3 shows the critical temperatures for both the indium and gallium alloys with an $e/a$ ratio of 4.5. It is noted that the curves are intended only to indicate general trends and not to imply any type of true curve fit. This is the case for all included graphs. A limited number of data points are given, since a very small shift in number of atoms causes a large shift in percentages. The horizontal scale is thus exaggerated to an extent. Surprisingly, it can be seen that a minimum value of $T_c$ is reached for 10% doping for both the gallium and indium specimens. It is also quite obvious that both of these curves have the same striking appearance.

Figure 4 shows the plots for the gallium samples, with each $e/a$ set sketched, while Fig. 5 shows the same curves for the indium specimens. Again it is seen quite readily that the sets with $e/a$ ratios of 4.1 and 4.5 have the same characteristics as the indium 4.1 and 4.5 alloys. It is noted that while 15% is the maximum doping for the 4.5 samples, 10% is the maximum doping for an $e/a$ ratio of 4.65.

The indium samples ($e/a$ = 4.1 and 4.5) again have the same distinctive shape. Since only three points were established for the indium 4.65 samples, a trend cannot justifiably be established. Nevertheless, it can be seen that
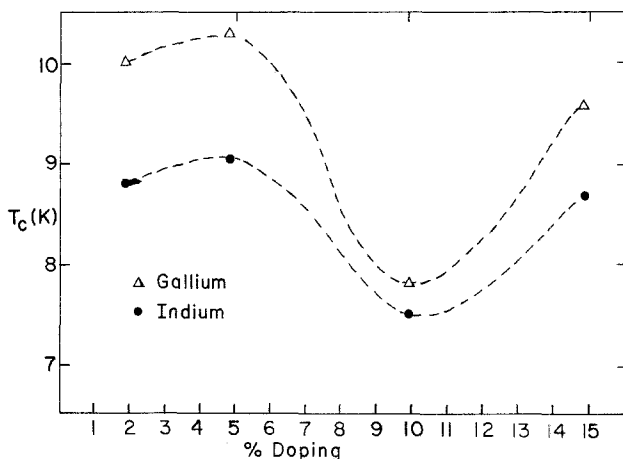


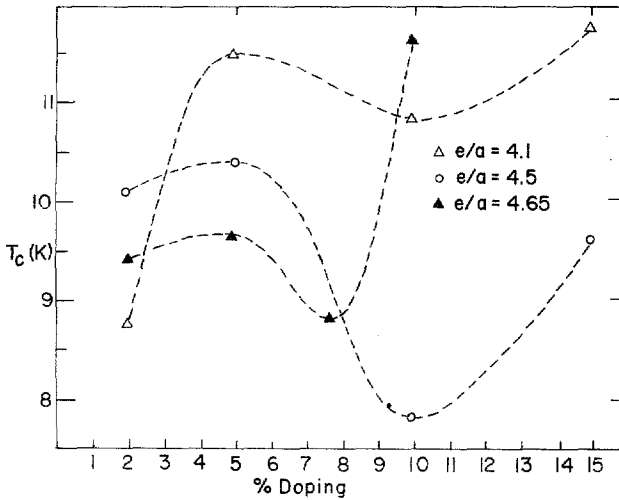Fig. 3. $T_c$ as a function of % doping; $e/a = 4.5$.

Fig. 4. $T_c$ as a function of % doping for gallium.

these points do fall in fairly well with the other corresponding indium samples.

Upon examination of the critical temperature as a function of $e/a$ for each corresponding amount of doping element one can observe that in every case (for the same percent doping) the gallium specimen possesses a higher transition temperature than the corresponding indium sample.
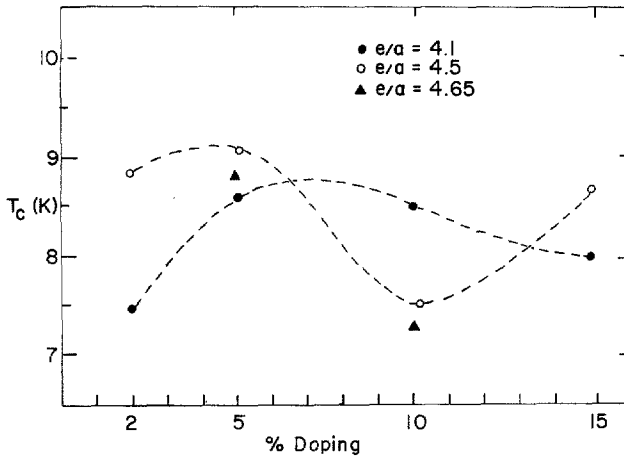


Fig. 5. $T_c$ as a function of % doping for indium.

## 6. CONCLUSIONS AND DISCUSSION

A summary of the basic findings of this study include the following:

1. The possibility of using ternary systems with aluminum as the doping element was ruled out. This stems from the low solubility of aluminum in both lead and bismuth.

2. In all the samples studied, the corresponding gallium specimens consistently had higher $T_c$ values than the indium counterparts.

3. A characteristic form for the critical temperature as a function of the amount of doping element was found. This shape usually indicated a local minimum at a concentration of doping element near 10%.

4. No clear or discernible pattern appeared evident as one examined the variation of the $e/a$ ratio.

5. A definite temperature range over which the sample went supercon-ducting was observed.

6. Although the measured $T_c$ values were not extremely high, several of these values were moderately high. The maximum values found were slightly above 11 K.

In the measurements which determined these corresponding transition temperatures, several uncertainties were present. Most of these, however, were reduced to a minimum. It is noted that $T_c$ was determined as the temperature was being raised and then again as the temperature was being lowered. This procedure was repeated for each sample to ensure con-sistency. However, it is noted that "better" values were obtained during the downward sweep. By "better" it is meant that the actual point at which the ac bridge went out of balance was much more discernible. Also, the temperature could be lowered quite steadily and at a more gradual rate than the upward sweep. Thus the resistance of the germanium thermometer could be ascertained with a certainty of about $\pm 0.5\ \Omega$. In the temperature range examined, this usually corresponded to about 0.03 K. Since the temperature could be regulated much more carefully while the temperature was being lowered, this minimized the temperature lag between the ther-mometer and the sample. This was verified by comparing the results of various rapid sweeps in both directions. The rapid sweeps in the upward direction yielded lower temperature readings than the consistent findings of the slow sweeps. Likewise, rapid downward sweeps resulted in higher temperature readings. Both of these results were expected.

Also, the purity and homogeneity of the samples were somewhat in doubt. Although the samples were carefully made to ensure a homogeneous nature, several factors could affect this. By far the most significant one is the settling or migrating of the doping element. This has been reported in the literature.[18] A nonhomogeneous sample would manifest itself by

possessing a slightly broadened transition point. The rather small transition ranges found in this study would tend to support the idea that the samples were fairly homogeneous.

In addition, it has been found that a small amount of the gallium often tends to "go into the glass structure" of the sample holder.[19] This phenomena would tend to lower the actual concentration of the doping gallium. For the samples used in this study, this would imply that the $e/a$ values for the gallium runs were slightly higher than the reported values, and the gallium curves would also be slightly shifted. However, the amount of gallium which had previously been reported to permeate the glass was usually very small and virtually negligible.

The fact that the gallium atoms are smaller than the indium atoms is undoubtedly a paramount factor in explaining the higher critical temperatures of the gallium alloys, especially since gallium superconducts at a lower temperature than does indium, (1.10 K contrasted to 3.37 K). This effect is probably due to the gallium and indium specimens having different structures. It Matthias' new criterion is valid, then the gallium samples probably have more crystallographic instabilities than the analogous indium samples. It would be both interesting and beneficial to examine the crystal structures (or lack thereof) of these samples in great detail.

## ACKNOWLEDGMENTS

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