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Electrical Resistivity of Some Zintl Phase and the Precursors

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Abstract

Electrical Resistivities of Some Zintl Compounds and Their Precursors

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Resistivity measurements have been performed for electronic characterization of the compounds Ba_5Sb_3 and $\text{Ba}_5\text{Sb}_3\text{Cl}$, both with the Mn_5Si_3 structure type, along with Ca_5Bi_3 and $\text{Ca}_5\text{Bi}_3\text{F}$, both with the $\beta\text{-Yb}_5\text{Sb}_3$ structure type. These measurements were taken as a function of temperature using the four probe method on pressed polycrystalline pellets of the compounds. A sealed apparatus was developed for containing these air-sensitive compounds throughout the experiments. By a simple electron count, one extra electron in both Ba_5Sb_3 and Ca_5Bi_3 should occupy a conduction band, giving these compounds a metallic character. In the cases of $\text{Ba}_5\text{Sb}_3\text{Cl}$ and $\text{Ca}_5\text{Bi}_3\text{F}$, the extra electron should bond to the halide, both filling the valence band and giving rise to semiconducting character. Ca_5Bi_3 , $\text{Ca}_5\text{Bi}_3\text{F}$, and $\text{Ba}_5\text{Sb}_3\text{Cl}$ were found to comply with

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the electron count prediction. Ba_5Sb_3 , however, was found to be a semiconductor ($E_g=0.30$ eV) with a larger band gap than its corresponding chloride ($E_g=0.09$ eV).

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ABSTRACT*

Resistivity measurements have been performed for electronic characterization of the compounds Ba_5Sb_3 and $\text{Ba}_5\text{Sb}_3\text{Cl}$, both with the Mn_5Si_3 structure type, along with Ca_5Bi_3 and $\text{Ca}_5\text{Bi}_3\text{F}$, both with the $\beta\text{-Yb}_5\text{Sb}_3$ structure type. These measurements were taken as a function of temperature using the four probe method on pressed polycrystalline pellets of the compounds. A sealed apparatus was developed for containing these air-sensitive compounds throughout the experiments. By a simple electron count, one extra electron in both Ba_5Sb_3 and Ca_5Bi_3 should occupy a conduction band, giving these compounds a metallic character. In the cases of $\text{Ba}_5\text{Sb}_3\text{Cl}$ and $\text{Ca}_5\text{Bi}_3\text{F}$, the extra electron should bond to the halide, both filling the valence band and giving rise to semiconducting character. Ca_5Bi_3 , $\text{Ca}_5\text{Bi}_3\text{F}$, and $\text{Ba}_5\text{Sb}_3\text{Cl}$ were found to comply with the electron count prediction. Ba_5Sb_3 , however, was found to be a semiconductor ($E_g=0.30$ eV) with a larger band gap than its corresponding chloride ($E_g=0.09$ eV).

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INTRODUCTION

Zintl Compounds

While Eduard Zintl was at Darmstadt, he published a wide variety of information on certain intermetallic compounds which would later be dubbed 'Zintl Phases'. These materials are made from electropositive metals compounded with relatively electronegative metametals (nonmetals). The metametals are the elements at that dividing line in the periodic table separating the metallic elements from the semimetallic - semiconducting elements. This line of metametals, however, is approximate to accommodate the fact that the definition of a metametal is not sharp; NaTl is, in fact, known as 'The Zintl Phase'. Figure 1 shows the boundary between metals and metametals defined by Zintl, as well as the boundary between metals and nonmetals suggested by Klemm (1).

Zintl phases are separated from other well known groups of compounds such as ordinary intermetallics. The following rules serve as a guideline for characterizing a compound as a Zintl phase using the Zintl-Klemm concept:

- 1) The relationship between the chemical structure of a Zintl compound and its electronic structure is well defined. The octet rule (2) is obeyed for all atoms. This is usually accomplished by making a simplistic electron transfer from the electropositive constituents to the electronegative ones. Many Zintl compounds form polyanionic networks to achieve this octet criterion.
- 2) Zintl phases are semiconductors.

							He
		B	C	N	O	F	Ne
		Al	Si	P	S	Cl	Ar
	Zn	Ga	Ge	As	Se	Br	Kr
	Cd	In	Sn	Sb	Te	I	Xe
	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 1. The main group elements showing the border of metals and metametals according to Zintl (double line), and the border of metals and nonmetals according to Klemm (1) (solid line). After Nesper (3).

3) Zintl phases are diamagnetic, but exceptions are permissible, such as that which occurs with O_2 (3). Zintl compounds usually do not show Pauli-paramagnetism.

One example of a Zintl phase is NaSi (3,4). To express the octet rule in this compound, the Si must be threefold bonded. This is accomplished by forming $[Si_4]^{-4}$ tetrahedra, similar to P_4 in white phosphorus and As_4 in yellow arsenic.

While some materials are easily classified as Zintl phases under these guidelines, many have not had conductivity studies performed on them to prove the semiconduction criterion. Still other compounds, which would qualify as Zintl compounds because of their constituent elements, are in limbo as to taxonomy owing to minor problems in their electronic structure - i.e., they have one electron too few or one electron too many. One such example of a system of this nature is given in the following section.

The A_5Pn_3 System

In the A_5Pn_3 binary systems, where A is an alkaline earth metal and Pn is a pnictogen, two structure types have been reported to date for $A=Ca, Sr, Ba$, and $Pn=Sb, Bi$ (5). The first structure type is a hexagonal Mn_5Si_3 type (6), while the second is an orthorhombic β - Yb_5Sb_3 type (7). Table 1 reports the structure type for each compound combination. Two of the compounds, Ca_5Sb_3 and Sr_5Bi_3 , are dimorphic, and two different comparisons between the two structure types are given by Wang et al. (8) and Hurng (9).

Recently, Hurng (9) and Hurng and Corbett (10) studied representative examples of the binaries to determine if they were true binaries or interstitially stabilized phases. This

Table 1. Structure types of A_5Pn_3 and A_5Pn_3X compounds.

COMPOUND	STRUCTURE TYPES REPORTED		REFERENCES
	Mn_5Si_3	$\beta\text{-Yb}_5Sb_3$	
Ca_5Sb_3	X	X	11,12
Ca_5Bi_3		X	13
Sr_5Sb_3	X		14
Sr_5Bi_3	X	X	15,11
Ba_5Sb_3	X		15
Ba_5Bi_3	X		15
Ca_5Bi_3F		X	9,10
Ba_5Sb_3Cl	X		9,10

type of problem has occurred before, as typified with the A_2X system (16), where A is once again an alkaline earth metal and X is again a pnictogen. Using simple electron counting, and having known from previous, although incomplete, crystal structure studies that no X-X bonding exists, the compound A_2X should be metallic because of an extra electron. This compound, therefore, would not be a Zintl phase by definition because it would be metallic rather than semiconducting. However, using neutron powder diffraction and improved single crystal x-ray diffraction, the correct stoichiometry was found to be Ca_4Sb_2O (17). In the correct structure, which is an anti- K_2PtF_4 type, the oxygen atoms are interstitial to an octahedral arrangement of calcium atoms while the Sb^{-3} ions are surrounded by nine calcium atoms forming a monocapped distorted square antiprism. A simple electron count with these atoms in this structure is now consistent with a true valence compound.

It is therefore obvious that A_5Pn_3 , with an extra electron by a simple valence count, may bond an extra atom which can both interstitially stabilize the structure and create a valence compound. One such stabilization could occur with oxygen, forming a compound such as $A_{10}Pn_6O$ (18,19). In order to prove this one way or the other, Hurng studied by single crystal x-ray diffraction the compound Sr_5Bi_3 . Hurng's work concluded, down to a final difference Fourier map, that this Mn_5Si_3 phase is not interstitially stabilized. He also found that analogous ternary compounds A_5Pn_3X exist where X is a halide which takes the interstitial position. The identity and structure types

of the ternary compounds which will be discussed in this thesis are presented along with the binaries in Table 1.

The Problem

The problem which this thesis addresses is a simple but extremely important one. Namely, should A_5Pn_3 binary compounds, with an extra electron supposedly in an s-type (or d-type) conduction band, be classified as intermetallic or as Zintl phases? It will be shown later that there are no Pn-Pn interactions, for reason of long distances between like atoms. This holds true for examples of both the binary and ternary compounds in both structure types. And, assuming a high degree of ionicity which would be normal in compounds with elements of such high electronegativity differences, an electron count provides an excess of one electron. Obviously, before this question can be answered, the electronic transport properties of these materials must be measured, in terms of their resistivities versus temperature, to allow the compounds to be classified as semiconducting or metallic. If the binaries are proven to be metallic, as expected, will the corresponding ternary, interstitially-stabilized phases be semiconducting? Also, if the binaries are found to be semiconducting, are they to be considered Zintl phases? And if so, where did the extra electron go? It was the purpose of this thesis to address, partially, this question by measuring resistance as a function of temperature on the following compounds: Ba_5Sb_3 , Ba_5Sb_3Cl , Ca_5Bi_3 , and Ca_5Bi_3F . These compounds were chosen for two reasons: first, they have been synthesized successfully as pure phases. Second, each of the two structure types is represented here for both a binary compound and a ternary compound.

BACKGROUND

In order to justify the solution to any electronic problem, the crystal structure of the compound should be well understood. This is especially true for a problem where proof of structure is so important.

Structure of Ba_5Sb_3 and $\text{Ba}_5\text{Sb}_3\text{Cl}$

The structure of Ba_5Sb_3 and the corresponding chloride are described here after Eisenmann and Deller (15), and Hurng (9), respectively. Figure 2 shows a unit cell of Ba_5Sb_3 projected on the [001] plane. Also, one possible hexagonal network along the ab plane is demonstrated. The empty circles are Ba atoms, while the filled are Sb atoms. The dotted lines connect the Ba atoms at $z=1/4$, while the thinner solid lines are connecting Ba atoms at $z=3/4$. The thicker, hatched, solid lines connect Ba atoms from $z=1/4$ or $3/4$ to $z=0$ or $1/2$. The structure is made up of chains of Ba trigonal antiprisms running parallel to the c axis. Each Ba trigonal antiprism is surrounded by Sb atoms which form a trigonal antiprism of their own. There are also isolated Ba chains running parallel to the confacial trigonal antiprismatic chain. In the case of the chloride compound, the Cl atom is interstitial to the Ba trigonal antiprism. Figure 3 details the antiprismatic chain with a Cl atom inserted into the interstitial position.

Table 2 gives the literature value lattice constants for all of the compounds discussed within this thesis. Table 3 shows bond distances for Ba_5Sb_3 and $\text{Ba}_5\text{Sb}_3\text{Cl}$.

Figure 2. The unit cell of Ba_5Sb_3 (Mn_5Si_3 -type) projected on the $[001]$ plane, showing one possible hexagonal net, after Hurng (9). Empty circles are Ba atoms in the confacial antiprismatic chains. The hatched circles are Ba atoms in the isolated Ba chains. Filled atoms are Sb.

Figure 3. The antiprismatic chain expanding the c axis in $\text{Ba}_5\text{Sb}_3\text{Cl}$, after Hurng (9). Open ellipsoids are Ba, shaded ellipsoids are Sb, and crossed ellipsoids are Cl.

Table 2. Lattice Constants for AE_5Pn_3 and AE_5Pn_3X compounds

<u>Compound</u>	<u>a(A)</u>	<u>b(A)</u>	<u>c(A)</u>	<u>c/a</u>	<u>b/a</u>	<u>Reference</u>
Ba_5Sb_3	9.964(3)	9.964(3)	7.694(4)	.772		9
Ba_5Sb_3	9.97(1)	9.97(1)	7.73(2)	.775		15
Ba_5Sb_3Cl	10.062(4)	10.062(4)	7.770(6)	.772		9
Ca_5Bi_3	12.766(1)	9.706(2)	8.437(2)	.661	.760	9
Ca_5Bi_3	12.722(8)	9.666(6)	8.432(6)	.663	.750	13
Ca_5Bi_3F	12.602(2)	9.771(2)	8.501(2)	.675	.775	9

Table 3. Bonding distances in Ba_5Sb_3 (15) and $\text{Ba}_5\text{Sb}_3\text{Cl}$ (9).

<u>Atoms</u>	<u>Ba_5Sb_3 (Å)</u>	<u>$\text{Ba}_5\text{Sb}_3\text{Cl}$ (Å)</u>
Ba1-Ba1 (2X)	3.87	3.885(4)
Ba1-Ba2 (6X)	4.27	4.260(3)
Ba1-Sb (4X)	3.63	3.662(2)
Ba1-Sb (6X)	3.63	3.662(2)
Ba2-Ba1 (4X)	4.27	4.260(3)
Ba2-Ba2 (2X)	4.32	4.493(3)
Ba2-Ba2 (4X)	4.60	4.672(3)
Ba2-Sb (2X)	3.43	3.466(3)
Ba2-Sb (1X)	3.57	3.532(4)
Ba2-Sb (2X)	4.11	4.110(3)
Cl-Ba2 (6X)		3.241(2)
Cl-Cl (2X)		3.885(4)
Cl-Sb (6X)		4.389(3)
Sb-Sb (All)	>4.5	>4.5

These bond distances are very important, for they show that no Sb-Sb bonds exist within the structure. If one can then assume complete electron transfer (high ionicity), as would be expected for a Zintl-type Ba_5Sb_3 where Ba releases its electrons to Sb, one electron would remain in a higher-lying Ba 6s-type (or perhaps 5d-type) conduction band. This compound, therefore, should be metallic. In the case of $\text{Ba}_5\text{Sb}_3\text{Cl}$, this extra electron would serve to complete the octet of the chlorine atom.

Structure of Ca_5Bi_3 and $\text{Ca}_5\text{Bi}_3\text{F}$

The structures of Ca_5Bi_3 and $\text{Ca}_5\text{Bi}_3\text{F}$ are described here after Martinez-Ripoll et al. (13) and Hurng (9), respectively. Figure 4 shows a unit cell of $\text{Ca}_5\text{Bi}_3\text{F}$ ($\beta\text{-Yb}_5\text{Sb}_3$) projected on the [010] plane. This figure shows two different layers of Ca atoms which seem to be constituted of trigonal prisms sharing all edges along [010]. The dotted lines connect the Ca atoms at $y=1/4$, while the solid lines connect the Ca atoms at $y=3/4$. Each of the trigonal prisms is filled with an Sb atom. These condensed trigonal prisms create large hexagonal channels, diagrammed in Figure 5, which contain two additional Ca atoms at $y=0$, and $y=1/2$. The channels also contain two additional Sb atoms at $y=1/4$, and $y=3/4$. In the case of $\text{Ca}_5\text{Bi}_3\text{F}$, the F atoms occupy nearby tetrahedral sites surrounded by calcium at opposite ends of the large hexagonal channel. These fluorine atoms are indicated in Figure 5 with an 'F'.

Figure 4. The unit cell of $\text{Ca}_5\text{Bi}_3\text{F}$ ($\beta\text{-Yb}_5\text{Sb}_3$) projected on $[010]$. Ca atoms are open ellipsoids, shaded ellipsoids are Bi, crossed ellipsoids are F atoms. Dotted lines are at $y=1/4$, and solid lines are at $Y=3/4$. After Hurng (9).

Figure 5. The hexagonal network in the β -Yb₅Sb₃ structure along the b axis. After Hurng (9).

EXPERIMENTAL

Materials

All reactions considered in this work were between stoichiometric amounts of the elements in the case of binary compounds, or the elements and alkaline-earth metal salts in the case of ternary compounds. The elements used were: In (Aldrich, 99.99%), Ba (distilled, obtained from Ames Lab), Ca (distilled, obtained from Ames Lab), Sb (Aldrich, 99.99%, or Ames Lab, zone refined), and Bi (Oak Ridge, reactor grade). BaCl_2 (Baker Company) and CaF_2 (Fisher, reagent grade) were the alkaline-earth metal halides used. All of the metals used were shiny to the naked eye except for the barium, where a grey surface coating of oxide was often seen. This coating was scraped off the metal with a scalpel blade, in a glove-box, just prior to being loading into a reaction.

All of the reactions were run using chunks of either Ca or Ba and either Sb or Bi. In some cases, Ba was available either in arc-melted rod form or in dendritic crystalline form. Either form of Ba was scraped of its oxide layer and then cut using diagonal pliers. Indium was cut from a large flat piece using a scalpel blade. The alkaline-earth metal salts were used in vacuum-dried powder form.

Synthetic Techniques

All reactants and products used here, with the exception of indium antimonide, are highly air sensitive. Therefore, vacuum and glove-box manipulations were necessary at

all times to maintain compound composition and purity. For the former purpose, a glass vacuum line was employed with a dynamic vacuum pump and a glass-type mercury diffusion pump. Throughout the work the line was always maintained at a vacuum which would not support discharge of a Tesla coil. A Vacuum Atmospheres Corporation (VAC) DRI-LAB was also set up. The DRI-LAB was maintained with a He atmosphere since He is a superior conductor of heat, and it could be used as a heat carrier gas in later resistivity experiments. The DRI-LAB atmosphere was continuously circulated through a VAC DRI-TRAIN filled with both water-scavaging molecular sieves and oxygen-scavaging RIDOX. The moisture level in the dry-lab was continuously maintained at 1 ppm H_2O (v) or below (sometimes as low as 0.2 ppm) as indicated with a Panametrics system 3A hygrometer. Typically, a 25-watt light bulb without its globe would burn in the DRI-LAB for 30-40 hours before burn out.

Because of the extreme reactivity at high temperatures of the elements used, an inert crucible was required for synthesis, tantalum being an excellent choice. Sealed tantalum tubing was used for all of the reactions described, except for InSb, which was easily synthesized using fused silica as a reaction vessel. The Ta tubing (usually 4 cm long x 0.95 cm o.d.) was cleaned in a solution of 55% (v/v) concentrated H_2SO_4 , 25% (v/v) concentrated HNO_3 , and 20% (v/v) 48% HF for 3-5 minutes. The tubing was rinsed well with distilled water and dried at 100°C . One end of the tubing was welded shut under an inert He atmosphere using a tungsten - inert gas (TIG) procedure. In the glove-box, reactants were weighed out and placed into the Ta tube through the open end, which was

then crimped shut with Vice-Grips brand locking pliers. The loaded tube was placed into either a sealed mason jar or sample vial, carried back to the welder, and TIG welded closed. The sealed, loaded Ta tube was then sealed shut in an evacuated sealed fused-silica ampoule which had been previously cleaned with a 10% (v/v) HF solution for two hours or longer. The A_5Pn_3 synthesis conditions are the same as those described by Hurng and Corbett (10).

In the synthesis of InSb, stoichiometric amounts of indium and antimony were loaded into a fused silica ampoule in the glove-box. The ampoule was then evacuated to a pressure below Tesla coil discharge and sealed off using a natural gas - oxygen torch. The mixture was heated to 750°C , which is above the melting point of 1:1 InSb, for 15 hours. The molten compound was then allowed to cool at the cooling rate of the furnace in which it was run. The furnace used was a well-insulated Marshall type, and the natural cooling time period was approximately 5 hours to reach room temperature from 750°C .

Characterization

The only means of identification of both sample and impurity phases at this laboratory that is currently available is Guinier powder diffraction. Scanning electron microscopy (SEM) with an X-ray dispersive analyzer is available. However, no method exists for sample introduction into the SEM; therefore, the air-sensitivity of the studied compounds prevented the microscope's use. Since powder diffraction cannot generally detect

impurities of about 5% or less, all samples measured in this work were considered pure enough when their Guinier powder patterns showed single phase materials.

The powder pattern samples were manipulated in the He-filled VAC dry-lab, and were first prepared by mixing with approximately 10% silicon (National Bureau of Standards) as an internal standard. The mixed powders were then placed between two layers of cellophane tape, and this tape was placed on the sample holder of the camera. The camera used was an Enraf-Nonius model (Delft), with an approximately 85° scan range in 2θ using Cu $K\alpha_1$. A silicon monochromator was employed to remove the $K\alpha_2$ line. The interior of the camera was kept under a dynamic vacuum for the duration of the sample's exposure. The powder patterns were measured with an Enraf-Nonius film reader. A computer program, GUIN (20), converted these measurements into 2θ values by obtaining a least-squares fit of the measurements of the five silicon lines to known NBS diffraction angles. The program LATT (21) was used to deduce the lattice constants of the products after the proper structure types and properly assigned reflection indices were considered.

Identification of the samples was made by comparing the experimental powder patterns obtained with a calculated powder pattern obtained by the program POWDER V5 (22,23).

Preparation of Pellets for Measurement

Because crystals of a large size are nearly impossible to obtain with these materials, a pressed pellet method was developed for conductivity studies. Of course, this denies all possibility of obtaining anisotropic measurements, and the results will be average resistivities. Another problem with this method is that one-dimensional conductors would neither be recognized, nor measured properly. However, from crystal structure data, and an optical inspection of the materials, one-dimensional conductivity can be safely ruled out in the case of the four materials studied. These materials vary in color from a shiny light gray to a duller dark gray, colors not close to the often seen dark black shiny color of a one dimensional conductor. The materials were not viewed under polarized light.

The pellets were pressed in a 7 mm radius die at approximately 34 tons/in^2 (2600 Kg/cm^2) for 10 minutes. Both the die set and the pellet press were manufactured by SPECAC, the press having been placed in the He-filled dry-box upon set up. Since all of the compounds here proved to be extremely brittle, two methods were considered to manufacture a pellet that was strong enough to stand up to pressure electrodes. The first method was annealing the pellets. Preliminary experiments, however, showed this to be an ineffective technique for three reasons: 1) The pellets broke easily upon being sealed into a Ta tube for annealing. Usually, one out of 5 pellets survived the trauma of being loaded into a Ta tube, sealed, and then placed into a fused silica ampoule. All manipulations were given the maximum amount of care which could be expected while

crimping shut Ta tubing, welding, and then rolling it around inside of a fused silica ampoule while sealing. 2) A pellet that was successfully annealed was often still too weak to hold up to electrodes, even though light pressure was used. This included annealing times of up to three weeks at 66% of the melting point of the compound. 3) The density of the annealed pellets varied as much as 20% from the theoretical density of the materials used. Density data were not taken on the pellets before annealing for fear of breakage.

The second method was therefore chosen for all experiments. This method consisted of using 5% (v/v) poly(tetrafluoroethylene) (PTFE, Aldrich Chemical Company) as a binder. A 5% (v) mixture or less of the PTFE binder was enough to make a sufficiently strong pellet. A pellet pressed with the PTFE had the same appearance, in both color and texture, as a pellet which was pressed without binder.

PTFE as a binder is a good choice, since its resistivity is greater than $10^{18} \Omega\text{-cm}$. Therefore, the conduction pathways which take part in the conduction are from the lower resistivity sample. A major problem, however, exists in the fact that the binder can possibly interrupt the geometry of the sample. This will affect any resistivity calculations, since the proper calculation of specific resistance in a sample heavily relies upon considering the geometry. However, since PTFE flows under pressure, it can be assumed that the resistivity calculated will approximate the resistivity found for unbound pellets, copying only the error associated with the experimental density being lower than

the theoretical density. This is because the flowing PTFE should assume the positions of the holes in the pellets while the pellet is being pressed.

An approximate resistivity is permissible, however, since the purpose of this thesis is two-fold: 1) to determine the thermal coefficient of resistivity, and 2) to determine a band gap for any semiconducting materials. Finding these properties does not rely on measuring an exact resistivity, but, rather, a resistance at a specific temperature normalized to room temperature. These resistance measurements are not dependent on the geometry of the sample or the sample density as long as the conduction pathways within the pellet contain only the sample which is being measured.

Resistivity Calculation

A method for calculating the specific resistivity of pressed pellets from resistance measurements was devised by Clem (24). The electrode configuration considered is shown in Figure 6, inset 'L', where 'I' indicates the voltage sensing electrodes, and 'J' indicates the current carrying electrodes. Assuming a two-dimensional current density (except very close to the contacts), and isotropic conductivity, the calculated resistivity is:

$$\sigma = \frac{I}{\pi V t} \ln \frac{(R+R_1)(R+R_r)}{(R-R_1)(R-R_r)} \quad \text{where} \quad \sigma = \frac{1}{\rho}$$

where σ is the specific conductivity, ρ is the specific resistivity, I is the current, V is the voltage, R is the radius of the sample (here, always 3.5 mm), R_1 is the distance from the

Figure 6. Conductivity cell and sample holder.
See text for description.

center of the pellet to the left voltage electrode (arbitrary), and R_r is the distance from the center of the pellet to the right voltage electrode (arbitrary).

Sample Holder for Measurement

Figure 6 shows a diagram of the sample holder built for conductivity measurements. 'A' shows a top view, while 'B' shows a side view with a cutaway. The sample holder, 'C', consists of a stainless steel '+' shaped unit produced by Varian, with a 3.5 cm i.d. and 5 inch length. Each side of the '+' is closed with an air-tight round copper-gasketed flange cover, 'D', and one side is capped with a Huntington model EV-705 vacuum valve, marked 'E'. A terminal strip is bolted to one of the flanges, marked 'F'. This terminal strip had been filed on the bottom until the nuts were exposed, and a piece of cigarette paper soaked with Apiezon N grease was sandwiched between the terminal strip and the flange. Because of this paper and grease, the sample holder was always outgassed overnight before using by either pumping it into the glove-box port or applying a vacuum through the Huntington valve. The grease soaked paper arrangement provides for good thermal conductivity with no electrical conductivity. All leads from the sample holder to the surroundings had been attached to this terminal strip so that thermal energy supplied through the leads would be heat-sinked.

Part 'G' of the figure shows the conductivity probe with a pellet mounted within it. The base was fashioned from a small block of Lexan brand plastic into which a 7 mm hole was bored for the pellet, as well as several 4-40 screw holes which could be used for fastening electrodes. When the sample pellet is placed into the 7 mm hole, it comes into

contact with an Omega ceramic resistance temperature detector (RTD) model number 1 PT 100K 4515, marked 'H'. The sample holder is cemented directly to the RTD so that the RTD (a ceramic rod) is holding the sample holder, sample, and electrodes about 2 inches above flange 'F'. The RTD, being in direct contact with the sample, allows sample temperature readings to be taken directly, avoiding the need to trust the temperature of the carrier gas in a localized spot.

There is one circuit board 'I', which contains electrodes made from gold pogo-type contacts which are used as point voltage contacts. This circuit board, as well as others used in the project, was cut from a large piece of copper stock printed circuit board, manufactured by UOP. The board was masked with a SHARPIE brand pen, using a pattern which would be suitable to the type of electrode being used. The remaining copper was etched out using a 30% (v/v) aqueous solution of ferric chloride. The etching usually took 20-30 minutes. The SHARPIE mask was then removed with acetone or ethyl acetate. Both the electrode and the lead were soldered onto the pattern using standard electrical quality rosin-core tin-lead solder. There were two more boards made, marked 'J', each containing one current carrying electrode. These current electrodes are positioned at opposing sides of the pellet.

Thus, the final electrode configuration places two voltage electrodes on one of the pellet faces, with two long, thin current carrying electrodes running the entire thickness of the pellet down opposing sides of the pellet. All of the electrodes are parallel and in one plane. Note that in an experiment, all electrodes are attached, while in the diagram only

one set or the other is shown attached for clarity. Inset 'L' shows the configuration of the electrodes on the pellet. All four electrode wires, as well as the RTD leads, are brought to the external world by plug 'K', the leads to which are brought in through holes in the top flange which are made air tight by the use of Torr Seal (Varian).

When a conductivity measurement is to be performed, the sample and the holder are pumped into the He-filled dry box, with flange 'F' removed from the cell. The pellet is then pressed, and loaded into sample probe 'G'. Circuit board 'I', and the two 'J' boards are screwed into place so that there is visually a good configuration of the electrodes. Flange 'F' is positioned as shown in 'B' and bolted in. The vacuum valve is closed, and the He-filled sample holder is removed from the glove-box ready for a conductivity measurement. The external plug 'K' is connected to the electronics discussed in the next section.

There are two advantages to this sample holder which should be mentioned. The first is that glove-box pure He is used throughout the transfer of sample to holder, and the same gas is used as carrier gas for temperature equilibration. This use of a single atmosphere reduces oxygen or water infiltration into the system. Also, the four flanges which surround the sample are made from very heavy 1/2 inch thick stainless steel. This helps the temperature inside the sample holder remain uniform as the temperature is being lowered. It also allows a very slow smooth warming curve when the sample holder is removed from its liquid nitrogen cooling bath.

Electronics

A block diagram of the electronic apparatus is shown in Figure 7. Current is supplied to the sample either by a Precision Current Source model CS-12 current source (up to 30V), or by a Hewlett Packard model 712A power supply (up to 500V). The temperature is read from the ceramic RTD with an Omega Engineering model 199B RTD temperature indicator, which was equipped with an analog output. This output was attached to the Y side of a Hewlett Packard model 7044A XY recorder. The X side of this recorder was tied directly to the sample voltage probes. For most of the sample measurements, the XY recorder was not employed, and the data were collected by hand. A Hewlett Packard 3465A digital multimeter kept track of the voltage, while a Keithley 169 multimeter read the amperage. A decade resistance box, manufactured by Leeds & Northrup, allowed the circuit resistance to be changed if necessary.

Temperature Control

The sample temperature was decreased by placing the sample holder into a well insulated styrofoam cooler and pouring in liquid nitrogen. The rate of temperature decrease was controlled by adjusting the flow rate of the liquid nitrogen. A typical time for cooling the sample from room temperature to -190°C was 20 minutes. The sample was warmed by pouring the liquid nitrogen out of the styrofoam container, but allowing the sample holder to remain inside the insulated container. Warming the sample from

Figure 7. Block diagram of the apparatus used for resistivity data collection.

-190 °C to room temperature in this configuration usually took 4 hours. When data were collected by hand, the sample holder was usually removed from the styrofoam container while warming. In this configuration, warm-up to room temperature usually took 0.5-1.0 hours.

Thermoelectric Tester

Thermoelectric effects may introduce serious errors in measurements, and therefore care must be executed to minimize the errors associated with these effects in the industrial creation of semiconductor components and devices. For semiconductors with high thermoelectric power, temperature gradients can introduce errors sufficient enough to throw off measured electromotive forces by 10% or more. Often, current reversal and AC electronic methods will correct for the smaller thermoelectric effects obtained.

However, on a small scale, thermoelectric effects can be useful in obtaining an indication of the types of carriers, and therefore impurities, contained within semiconductors. Since exact impurity measurement is not available in our lab, it was quite helpful to type the kind of semiconductor being measured, whether it be p-type or n-type.

A thermoelectric tester was created for this purpose and placed within the glove-box. It consists of a piece of copper sheet connected to the negative input on a galvanometer, and a soldering iron electrode connected to the positive side of the same galvanometer. The pelletized sample is placed on the copper sheet, and the hot soldering iron placed on

top of the sample (see Figure 9). In this configuration, the galvanometer will read positive for an n-type semiconductor and negative for a p-type semiconductor.

Figure 8. Illustration of the thermoelectric tester employed for estimating p or n type semiconducting materials.

RESULTS AND DISCUSSION

All compounds were synthesized as per the experimental section. Table 4 lists the lattice parameters obtained, an indication of the semiconductor type (measured thermoelectrically), and parameters of a pressed pellet of the compound used for determining resistivity. All lattice parameters agree with those listed in Table 2 within experimental error, and the samples were deemed suitable for conductivity measurements. Table 4 also lists specific resistivities at both 298 K and 273 K for each sample. All measurements shown in the following figures depict measurements which were performed in the sample holder described in the experimental section using the resistivity probe also described. All other measurements discussed were taken using sample holders which were being designed at the time of measurement (for example, a Pyrex sample holder rather than stainless steel) or differently configured electrodes such as Schnabel's configuration (25).

InSb

InSb was chosen for the purpose of checking the conductivity cell. It is useful because it is easily synthesized, and it has a band gap which is near the band gaps of the other materials measured in this thesis. Figure 9 shows the results for two samples, A and B, which are two different pellets prepared from the same InSb reaction. Although the results are far from exactly reproducible, nevertheless, the differences are determined to

Table 4. Experimental Results

Sample	a	b	c	T ^a	t ^b	R _I ^c	R _T ^d	E _g ^e	ρ_{298}^f	ρ_{273}^f
InSb A	6.484(9)			n	3.0	1.75	2.0	0.17	0.528	0.718
InSb B	"			n	3.2	2.3	1.8	0.15	0.532	0.67
Ca ₅ Bi ₃	12.764(4)	9.710(8)	8.430(6)	-	2.8	2.3	1.9	—	251x10 ⁻⁶	237x10 ⁻⁶
Ca ₅ Bi ₃ F	12.617(7)	9.774(9)	8.494(8)	p	2.75	1.8	2.1	0.07	0.366	0.445
Ba ₅ Sb ₃	9.969(3)		7.733(6)	n ^h	2.95	1.85	1.92	0.30	0.488	0.883
Ba ₅ Sb ₃ Cl	10.062(5)		7.761(7)	p	3.30	2.30	1.83	0.09	0.271	0.314

^a T = Semiconductor type, p or n.^b t = Thickness of pellet used in measurement in mm.^c R_I = Distance between center of pellet and left voltage electrode in mm.^d R_T = Distance between center of pellet and right voltage electrode in mm.^e E_g = Band gap in electron volts.^f Resistivity units are Ω -cm. Temperature is degrees Kelvin.^g Actual temperatures for these two data are 287K and 274K, respectively.^h Very slight movement on galvanometer.

InSb Samples A and B

Conductivity vs. Temperature

Figure 9. Electrical conductivity of InSb samples A and B.

be within experimental error when considering different amounts of binder as well as slightly different electrode configurations. Figure 10 shows the results for sample A, in the form $\ln R_t/R_o$ vs. $1/kT$, from which the band gap can be extracted ($E_g = 2 * \text{slope}$). Figure 11 shows a similar plot for InSb sample B. The curves show the characteristic pattern of increasing resistance with decreasing temperature which is known with semiconducting materials. There is a large, noticeable change in both slopes, however, which occurs around 190 K and can be explained as follows:

Electronic properties, especially of semiconducting materials, are strongly dependent on the identities and concentrations of any impurities present within the crystal lattice. In many semiconducting materials, of which InSb is an excellent example, these impurities allow for a noticeable change of electronic property over three different temperature regions. These regions are:

- 1) The intrinsic region. In this region, the hole and electron carrier concentrations are nearly equal. These carriers are produced by thermal excitation across the band gap. This gives rise to a noticeable temperature dependence, as well as the ability to extract a band gap estimate from the slope of the resistivity vs. reciprocal temperature in this region.
- 2) The saturation region. Here, the concentration of one of the carrier types exceeds the concentration of the other. The band gap, therefore, is of less importance since the carrier concentration is mainly equal to the difference between fully ionized acceptors and donors. Since either holes or electrons will usually be in excess in this region, the temperature dependence of the conductivity is drastically reduced.

InSb Sample A

Figure 10. $\ln R_T/R_0$ vs. $1/kT$ of InSb Sample A. The short solid line predicts the slope of the intrinsic region. R_T = resistance at temperature T . R_0 = resistance at the lowest measured temperature.

InSb Sample B

$\ln \{R_T/R_0\}$ vs. $1/kT$

Figure 11. $\ln R_T/R_0$ vs. $1/kT$ of InSb Sample B. The short solid line predicts the slope of the intrinsic region. R_T = resistance at temperature T . R_0 = resistance at the lowest measured temperature.

3) The deionization region. Here, one type of carrier concentration still greatly exceeds the other, but the temperature dependence is increased as the concentration of carriers is decreased because of donor/acceptor atoms resuming their ground states at lower temperatures.

As a general rule (26), the onset temperatures for these three regions are usually as follows for InSb with an acceptor/donor concentration of approximately $3 \times 10^{14} \text{ cm}^{-3}$: the intrinsic region occurs above 230 K, while the saturation region usually occurs around 200 K for donors and 80 K for acceptors. The deionization region is around 50-20 K for acceptors, but it is not seen for donors except within an applied magnetic field of around 1000 Oe.

InSb samples A and B show an onset of the saturation region at around 190 K. This approximate temperature is expected for two reasons: 1) the aforementioned fact that the onset of the saturation region is around 200 K for donor type atoms, and 2) the thermoelectric test, being indicative of an n-type sample, indicates possible donor type impurities. The band gap was extrapolated using the slope of the line in the intrinsic region. It measures 0.17 eV for sample A, and 0.15 eV for sample B. In the literature, data for infra-red absorption coefficients near the absorption edge have yielded the most trustworthy values for the band gap in InSb (26). The data of Roberts and Quarrington (27) have been used to estimate the optical band gap at various temperatures. Here, E_g is shown to remain constant at 0.23 eV from 0 to 100 K. After 100 K, there is a linear decrease in the energy gap of $3 \times 10^{-4} \text{ eV K}^{-1}$. This calculates to a value of 0.16 eV

at 300 K. The Lincoln Laboratory group (28-32) has found $E_g=0.180\pm0.002$ eV at 298 K, $E_g=0.228$ eV at 80 K, and $E_g=0.2357\pm0.0005$ eV at 4 K. Electrical band gaps, extrapolated from a linear plot of resistivity data, cannot be as reliable since the band gap of a semiconductor increases with decreasing temperature. This effect is even nonlinear for InSb (26). Early electrical data from Weiss (33) resulted in an overestimated band gap of approximately 0.5 eV. However, Madelung and Weiss (34) have given an electrical E_g of 0.18 eV, very similar to that obtained for the room temperature optical values of E_g as stated above. Values of $E_g=0.17$ eV for InSb sample A and $E_g=0.15$ eV for InSb sample B can be considered good results when compared with the previously given values.

Good results, however, do not overshadow the fact that there is a problem with the resistivity values calculated. These calculated resistivities, which are $\rho_{287K}=0.521$ Ω -cm for InSb sample A and $\rho_{298K}=0.532$ Ω -cm for InSb sample B, are approximately 17 times higher than the highest found room temperature resistivity to date of 0.03 Ω -cm on a polycrystalline sample of unspecified shape (35). This problem is nearly impossible to explain. The best place for administering blame would be on the calculation rather than the sample itself. Clem's calculation assumed isotropic resistivity along a crystalline conducting button. All samples run in this thesis share the following three deviations from this assumption:

- 1) The pressed pellet samples are polycrystalline, allowing for many grain-boundaries.
- 2) The binder used to make the samples firm interrupts the pure internal cylindrical geometry by effectively shortening some of the conduction pathways across the pellet.

3) Although InSb is cubic, it cannot be guaranteed to have isotropic conductivity along every one of its possible crystal facets, all of which are statistically present within the sample.

One final point to mention about Figure 9 is the difference between conductivities upon increasing and decreasing temperature. Sample A's data at increasing temperature do not reproduce sample A's data with decreasing temperature. Analogously, InSb sample B's increasing temperature data do not reproduce sample B's decreasing temperature data. Rather, the increasing temperature data for sample A more closely reproduces the increasing temperature data for sample B. This is also true for the decreasing temperature data for InSb samples A and B. There are two possible reasons for this:

- 1) The electrodes shifted during cool down. Therefore, the resistances measured on cool down will be different than those measured on warm-up due to different electrode configurations.
- 2) Since the warm-up was usually much slower than cool-down, the electronics had more time to stabilize for each reading on warm-up. This is especially important for the RTD meter, since there can be a time delay between temperature readings. Since most data for this thesis were taken by hand, all data reported represent warm-up data.

In conclusion, it seems that while the sample holder may not be sufficient to measure specific resistivities well, it is adequate for measuring thermal coefficients of resistivities as well as finding well estimated band gaps.

Ca_5Bi_3 and $\text{Ca}_5\text{Bi}_3\text{F}$

Figure 12 shows resistivity vs. temperature for Ca_5Bi_3 . The preliminary null reading on the thermoelectric tester was the first clue of the metallic properties of this material, while the resistivity data prove it. The highest and lowest temperature resistivities are $\rho_{303\text{K}}=259 \mu\Omega\text{-cm}$ and $\rho_{103\text{K}}=120 \mu\Omega\text{-cm}$. The temperature coefficient is $0.715 \mu\Omega\text{-cm K}^{-1}$. A previous measurement performed on a different sample of this compound, but from the same synthesis, confirmed the metallic results with $\rho_{303\text{K}}=264 \mu\Omega\text{-cm}$ and a thermal coefficient of resistivity equal to $0.9 \mu\Omega\text{-cm (K}^{-1})$. This later result, however, is less reliable than the previous because of a large amount of noise. The compound is a rather poor metal with a resistivity similar to that of bismuth metal, $\rho_{273\text{K}}=106.8 \mu\Omega\text{-cm}$ (36).

This result agrees with the electron count, indicating an extra electron in an s-type or d-type conduction band. Therefore, this compound is not a Zintl compound.

Two studies were performed on $\text{Ca}_5\text{Bi}_3\text{F}$, the better being shown in Figure 13. This compound is obviously a semiconductor. The deviation from a pure logarithmic behavior is because the data for both an intrinsic region and saturation region are incorporated into the plot. Figure 14 plots $\ln R_\infty/R_0$ vs. $1/kT$, which shows a band gap of 0.07 eV. There is onset of a saturation region around 160 K. The thermoelectric test showed this to be a p-type semiconductor. As with Ca_5Bi_3 , the experimental result is in agreement with the predicted one; the extra electron in Ca_5Bi_3 completes the octet of the fluorine atom.

Figure 12. Electrical resistivity of Ca_5Bi_3 .

Figure 13. Electrical resistivity of $\text{Ca}_5\text{Bi}_3\text{F}$.

$\text{Ca}_5\text{Bi}_3\text{F}$

$E_g = 0.074 \text{ eV}$

Figure 14. $\ln R_T/R_0$ vs. $1/kT$ of $\text{Ca}_5\text{Bi}_3\text{F}$. The short solid line predicts the slope of the intrinsic region. R_T = resistance at temperature T . R_0 = resistance at the lowest measured temperature.

Magnetic studies and band structure calculations would help to confirm this.

In conclusion, Ca_5Bi_3 is shown to not be a Zintl phase due to its metallic properties. $\text{Ca}_5\text{Bi}_3\text{F}$ is a Zintl phase, ignoring the F atom which is a nonmetal.

Ba_5Sb_3 and $\text{Ba}_5\text{Sb}_3\text{Cl}$

The results of the Ba_5Sb_3 measurement are shown in Figure 15. The increasing resistivity with decreasing temperature indicates that this compound is a semiconductor. This result is extremely surprising considering the opposite result which was obtained with Ca_5Bi_3 . The figure shows the best run out of three. These different measurements involved both taking three different samples from two different reactions and using two different resistivity probe configurations, both Clem's configuration and Schnabel's. All results showed semiconduction. From data shown in Figure 16, the band gap is calculated to be around 0.30 eV. Thermoelectrically, this material was also shown to be a p-type semiconductor. For this sample, the resistivity is $\rho_{303\text{K}}=0.365 \text{ } \Omega\text{-cm}$ and $\rho_{113\text{K}}=101 \text{ } \Omega\text{-cm}$. This was the only sample of Ba_5Sb_3 measured which came from Guinier-pure sample. The other two measurements were made on samples which had one or two extra lines in their Guinier powder patterns which were approximately 10-20% of the intensity of the second most intense line in Ba_5Sb_3 . The conductivity measurements on the first were taken using Schnabel's method, and it will not be described here because resistivities could not be estimated. Two things should be noted, however. The thermal coefficient of resistivity had the same sign as all other Ba_5Sb_3 measurements which

Figure 15. Electrical resistivity of Ba_5Sb_3 .

Ba5Sb3

 $E_g = .30 \text{ eV}$

Figure 16. $\ln R_T/R_0$ vs. $1/kT$ of Ba_5Sb_3 . The short solid line predicts the slope of the intrinsic region. R_T = resistance at temperature T . R_0 = resistance at the lowest measured temperature.

indicated semiconduction. Also, this sample was an annealed pellet rather than a pellet pressed with binder, which proves that the binder had no effect of the sign of the temperature coefficient. Although the resistivities were not estimated, nevertheless, resistances found for this pellet were generally the same order of magnitude as the resistances found for the pellets with binder. On the second run, $\rho_{303K}=0.7 \text{ } \Omega\text{-cm}$ and $\rho_{113K}=112 \text{ } \Omega\text{-cm}$. These numbers are similar to those reported above for the first run. The band gap for this latter run is calculated to be around 0.02 eV. Once again, the results of the two Ba_5Sb_3 measurements can be considered to be within experimental error considering that the pellets were pressed with a binder and may have had two slightly different electrode configurations.

The results should be analyzed by looking at possibilities of both failure as well as why Ba_5Sb_3 might be semiconducting.

Had an experimental error occurred, it would have been one of three:

- 1) Oxidation of the sample. This material had the tendency to decompose quickly, even within the glove-box. It is doubtful that this should have caused inaccurate results, however, because of the time frame involved. A small portion of Ba_5Sb_3 powder left in a mortar exposed to glove-box atmosphere would turn black after one hour. This is a much faster noticeable decomposition than that which occurred with Ca_5Bi_3 powder which would turn just slightly darker after two hours exposure to glove-box atmosphere. The powder pattern sample was always prepared first, leaving chunks of the sample intact allowing only a small amount of surface decomposition. To press a pellet, the chunks

were first mixed with the appropriate amount of PTFE, ground, loaded into the pellet die, and pressed. Time between unloading the sample from the Ta tube and finishing preparation of the powder X-ray diffraction sample was usually 3-5 minutes. Then, the time between grinding the chunks of remaining sample with PTFE and loading into a pellet press and pressing was usually no more than two minutes. This short time involved, as well as grinding with PTFE which could possibly protect the sample, should have prevented a large amount of decomposition from destroying the majority of the sample. Also, the pressing should break up any surface layers.

2) Surface effects. Conductivity effects due to current travelling on the surface of the pellet could lead to erroneous results. Fortunately, however, this problem was circumvented, too. Direct current was always used, and a pure dc signal is less likely to transverse the surface rather than the bulk. Because of the tricky operation of loading the pellet into the resistivity probe within the glove-box and fastening all of the electrodes down, there was usually a 20-30 minute period of sample exposure to the glove-box atmosphere, allowing some time for an oxidized surface layer to form with a higher resistance than the bulk. But in this case, any error due to a high contact potential is removed by using the four-probe method, just as the four-probe method eliminates the problem of high contact potential due to the formation of a semiconductor depletion layer. Also, not only should further surface oxidation be minimal under the pressure electrodes, but the pressure electrodes may break any surface oxidation which would have possibly occurred. Since a thick black layer was never seen on the pellet upon

completion of the measurements, a dc capacitance effect due to a conductor-dielectric-conductor layer can be ruled out.

The results obtained are possible for three reasons:

1) Band splitting. As noted before, this structure type contains two crystallographically distinct Ba positions. It might be possible because of the two different coordinations of the Ba and, therefore, different crystal field effects for a narrow band to split off below the Ba (6s or 5d) conduction band.

Although there is one extra electron per formula unit (Ba_5Sb_3), it is important to realize that in this structure $Z=2$, leaving two extra electrons in the electronic Brillouin zone ($\text{Ba}_{10}\text{Sb}_6$). These two extra electrons could pair up and fill a narrow split-off band. This hypothesis would need to be proven with both accurate band structure calculations and magnetic studies showing diamagnetism.

2) Hurng's work did not check a single crystal of Ba_5Sb_3 . Rather, his synthesized Ba_5Sb_3 matched a Guinier powder pattern which was calculated using known parameters (37). These parameters were assumed to be correct, for they were in line with the single crystal parameters determined on the Mn_5Si_3 -type compound Sr_5Sb_3 . This material may be an unrecognized interstitially stabilized one. Or, crystallographically, there may be an unseen superstructure condition such as a doubling of the c axis that might lead to a semiconducting arrangement (38). Mn_5Si_3 -type superstructures have been seen before (38); however, no superstructure reflections were seen on either Hurng's powder patterns or the powder patterns of Ba_5Sb_3 taken during this research. Further crystallographic

work should be employed to rule out all of these possibilities, especially single crystal work on Ba_5Sb_3 using Weissenberg or precession methods to rule out a superstructure.

Figures 17 and 18 give the results for $\text{Ba}_5\text{Sb}_3\text{Cl}$. This compound shows semiconducting properties as expected, with $\rho_{298\text{K}}=0.271 \text{ } \Omega\text{-cm}$ and $\rho_{273\text{K}}=0.314 \text{ } \Omega\text{-cm}$. The band gap is 0.092 eV. This was the only $\text{Ba}_5\text{Sb}_3\text{Cl}$ sample measured using Clem's geometry. An earlier experiment using Schnabel's method yielded resistance data with a similar negative thermal coefficient of resistivity indicating a semiconductor. The band gap calculation for this earlier measurement yielded a value of approximately 0.091 eV.

In conclusion, it can be seen that $\text{Ba}_5\text{Sb}_3\text{Cl}$ can be considered a Zintl phase, accepting the fact that Cl would be an unusual Zintl element. Ba_5Sb_3 , on the other hand, needs to wait for classification until such a time as the cause of its semiconduction can be better determined. If the band splitting phenomenon is correct to explain this semiconduction, then the compound meets all of the criteria for being considered a Zintl phase.

Ba₅Sb₃Cl

Resistivity vs. Temperature

Figure 17. Electrical resistivity of Ba₅Sb₃Cl.

Ba₅Sb₃Cl $E_g = 0.092$

Figure 18. $\ln R_T/R_0$ vs. $1/kT$ of Ba₅Sb₃Cl. The solid line predicts the slope of the intrinsic region. R_T = resistance at temperature T . R_0 = resistance at the lowest measured temperature.

SUMMARY AND FUTURE WORK

The present study shows mostly results consistent with theory; namely, $\text{Ca}_5\text{Bi}_3\text{F}$ and $\text{Ba}_5\text{Sb}_3\text{Cl}$ are semiconductors, while Ca_5Bi_3 is a metal. Unexpectedly, Ba_5Sb_3 was found to be a semiconductor with a band gap of 0.3 eV.

Obviously, many more efforts are needed to understand why Ba_5Sb_3 should be semiconducting as well as why it should have a larger band gap than $\text{Ba}_5\text{Sb}_3\text{Cl}$. As a result of this thesis, the crystallography of Ba_5Sb_3 is questionable and needs some further study. Also, magnetic measurements would be valuable, and band structure calculations would be extremely important.

Extended Hückel type calculations were started in this laboratory; however, good parameters for alkaline-earth metals are nearly nonexistent because of a lack of good literature values. A charge iteration from calculated valence shell ionization potentials and Slater-type zeta values was considered, but charge iteration parameters are also absent from the literature and would be untrustworthy, anyway, because of the large and very diffuse valence orbitals associated with the alkaline-earth metals. One chance for a good calculation would be to use a first approximation linear combination of atomic orbitals method.

Resistance data from all compounds in Table I need to be studied to establish consistency or periodicity in the A_5Pn_3 compounds of these structure types. Also, single

crystal methods need to be developed in this laboratory for these extremely air sensitive materials. Single crystal measurements would allow for determination of a more exact resistivity as well as anisotropic properties.

Finally, for an overall picture, other transport properties should be measured, such as Hall coefficients. This would allow an estimation of carrier density as well as a confirmation of carrier type. Reflectance spectroscopy would be a worthwhile tool for determining or confirming band gap energies.

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- END -

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